SHS 2011

XI International Symposium of Self-Propagating High Temperature Synthesis

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SHS 2011

5 - 9 September 2011
Anavyssos, Attica, Greece
EDEN BEACH Resort Hotel
shs2011@ims.demokritos.gr

DEMOKRITOS
National Centre for Scientific Research
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Institute of Structural Macrokinetics and Materials Science
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BOOK OF ABSTRACTS

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Science of the Russian Academy of Sciences,
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Organised by:
Institute of Materials Science, NCSR Demokritos, Greece
Institute of Structural Macrokinetics and Materials Science of RAS, Russia

Supported by:
World Academy of Ceramics (WAC)
International Association on Self-Propagating High Temperature Synthesis (SHS-AS)
Russian Foundation for Basic Research (RFBR)

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Agia Paraskevi Attikis, 15310, GREECE
Tel: +30 210 6503348, 6503322, Fax: +30 210 6503377
Email: shs2011@ims.demokritos.gr
web.ims.demokritos.gr/SHS2011

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B: Structural Macrokinetics of SHS processes

C: Chemistry and Technology of SHS processes

D: SHS of advanced materials: nanomaterials, metals, ceramics, intermetallics, composites, etc.

E: Non–conventional SHS processes: New methods and applications

F: Industrialization of SHS

POSTERS

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ABSTRACTS

PLENARY TALKS

P1

RE-DISCOVERING ANCIENT GREEK TECHNOLOGY - FROM DAILY LIFE'S CRAFTS TO HIGH TECHNOLOGY ACHIEVEMENTS

Thomas Katsaros

Byzantine Museum, 22 Vas. Sofias Ave., 106 75, Athens, Greece
tkatsaros@rhodes.aegean.gr

Until a few decades ago we believed that ancient Greeks had built a theoretical civilization. Their knowledge in Mathematics and Astronomy completed the space of their technological achievements. Since then, the development of new analytical methods has uncovered an amazing world of technological wealth associated with Ancient Greece. It is this "new world" that is the subject of this talk.

At first, even in Greek Mythology we see gods and goddesses of Technology, such as the god Hephaestus and Athena. But we also find Titans such as Prometheus and Heroes such as Hercules all involved in various Technological activities.

From the era of Homer and his Epics already we receive much information about arms and armouring, medicines, metallurgy, engineering, complex wooden constructions (Trojan horse), paints and pigments (such as "Miltos") and many other which were being continuously perfected throughout the ancient Greek period.

The talk will start the re-discovery of such technological achievements by looking at the ancient mining area of Lavrion at the Southeastern tip of Attica which was active even at the earliest periods. Already in the 4th century BC, Xenophon notes that: "..nobody knows about the beginning of the metal extraction and mining activity in the region of Laurion, because it is disappearing in the past.. ".

The ancient use of magnifying lenses in the production of fine jewellery, certainly leaves no room for rejection of the proposal that lenses were also used for wider scientific endevours, such as astronomy. The results of Prof. Sakelarakis excavation in Minoan Crete (c. 15th c. B.C.) of quartz lenses found in situ in a Minoan craftsman room, certainly leave no question about the knowledge of prehistoric inhabitants of the wider Hellenic region on optics. With this fresh point of view we must re-interpret the notes of Theophratsus of Eressos in his book "On Stones" about the use of beryl crystals on making optic lenses.

But the ancients were also cunning in the business use of technological achievements. The use of pills in medicine is mentioned by many ancient Greek writers. The importance of these reports is that they stressed the value of the "label" on the pills in an effort at avoiding forgeries. The earliest conception of "brand-name" for a product was made in the Northern Aegean island of Lemnos for the use of "Lemnian Sphraghis" or "Lemnian Earth" pill. Theophrastus also mentions in his treatise "On Stones" about the production of some artificial pigments such as "Verdigris" and "Lead-White". It is very important to highlight here that the term "Verdigris" comes from a medieval etymology for "green" of the Greeks, leading to "Verdun" in Latin. So this is another case of use of a brand name, i.e. the establishment of this specific name until now, which arrives from antiquity.

Many technological novelties come from this hitherto unknown space of ancient Greek Technology and maybe this is the challenge for all of us to re-discover them.

P2

CHARACTERIZATION OF ADVANCED THERMAL PROTECTION SYSTEMS FOR SPACECRAFT USING PLASMA FACILITIES: FACILITIES OVERVIEW AND CRITICAL ISSUES AND CHALLENGES

Jean-Marie Muylaert

von Karman Institute, 72 Ch. de Waterloo, 1640 Rhode St Genese, Belgium
muylaert@vki.ac.be

The purpose of this presentation is to review the present and future ESA missions requiring Thermal Protection System developments. Missions such as those associated with future International Space Station - manned and unmanned re-entry as well as those for planetary entry exploration and subsequent sample return will be addressed.

The European ground based facility capabilities will be reviewed.\

The performance envelops of the 4 major European Plasmafacilities :

- the SCIROCCO from CIRA at Capua Naples Italy,
- the L3 K from DLR at Koln Germany,
- the SIMOUN from EADS ASTRIUM at Bordeaux France as well as
- the Plasmatron facility from VKI at Rhode Saint Genese Brussels Belgium

will be discussed and typical examples shown.

Of particular interest are the 2 ESA missions EXPERT and IXV respectively planned for flight in 2012 and 2013. Both projects extensively use the European plasma facilities for Thermal Protection System (TPS) qualification.
EXPERT, being a suborbital class 3 -In Flight Research- ballistic blunt vehicle, for gathering flight data on critical Aerothermodynamic and TPS gas surface interactions and IXV, being an orbital class 2 – system flight demonstrator- lifting body configuration for mastering full orbital re-entry capability.

Emphasis will be put on "Uncertainty Quantification" (UQ) as they are essential in the definition of the margins for a robust design. Examples will be given for TPS characterization in a Plasmatron; uncertainties related to nozzle flow quality, embedded instrumentation, gas surface interaction modelling and flight extrapolation will be addressed.

P3

THE EFFECT OF DOPING ON THE COMBUSTION AND REACTION KINETICS OF SILICON REACTIVES

Steven F. Son

School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907-2088, USA
sson@purdue.edu

The modern concept of burn rate modification was born in parallel with the science of modern rocket propellants. With the discovery of composite propellants, the ability to fine-tune their output to meet mission criteria and performance specifications was an immediate need. The propellant burning rate is a property that directly impacts performance and can be easily tuned. Historically, burnrate modification centered on the physical addition of particles such as transition metal oxides or aluminum.1 Morphological properties of additives are also known to affect burning rate modi- fication. Novel burning rate tailoring techniques are continuously being sought after that exhibit greater effects with less intrusion, e.g., techniques that affect the burning rate without decreasing the specific impulse. This paper highlights the dis- covery of semiconductor doping as one such novel method.

Doping is any process that introduces impurities into an otherwise pure material. In the semiconductor industry, doping is used to tailor the electrical properties of intrinsic semiconductors. Common silicon dopant elements are boron, phosphorous, arsenic, and antimony. When a single group V dopant (n-type dopant), which has five valence electrons, replaces a silicon atom in the lattice, which has four valence electrons, the extra electron is no longer tightly bound to the dopant atom, as depicted in Fig. 1. Group III atoms (p-type dopants) only have three valence electrons, and so each dopant atom creates an electron hole. The addition of an electron or hole to the silicon lattice takes place as a 1:1 ratio of electron/hole:dopant atom. Because the extra electrons and electron holes act as charge carriers, the electrical conductivity/resistivity of doped wafers can be tailored by varying the type and concentration of dopant atoms. The role of doping in semiconductor properties and processing is well-understood and documented; however, the role of doping in combustion reactions is not understood.

The effect of low levels of doping in silicon on the reaction kinetics and combustion of silicon reactives was investigated and will be presented. Doped silicon powders were manufactured from doped silicon wafers and characterized. Energetic composites consisting of silicon and polytetrafluoroethylene (PTFE) powder were produced and characterized by thermal analysis and combustion rate measurements. The apparent activation energy was seen to decrease from 130 to 110 kJ/mol as dopant concentration was increased, and burning rates increased from 2 mm/s to 3 mm/s (see Figs. 1&2). In systems where nano boron particles were added to intrinsic powders, a change in burning rate was not observed. The ability to modify combustion behavior through low levels of doping represents an important discovery, with implications in general burn rate modification and tuning, and the emerging study of integrated nanoenergetics.

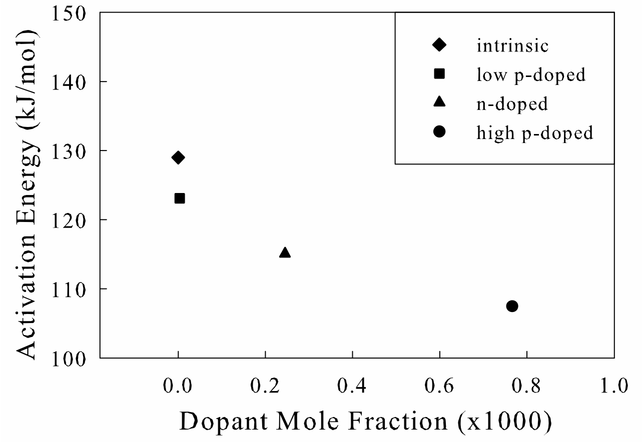


Fig. 1 Activation energies of the doped Si/PTFE mixtures.

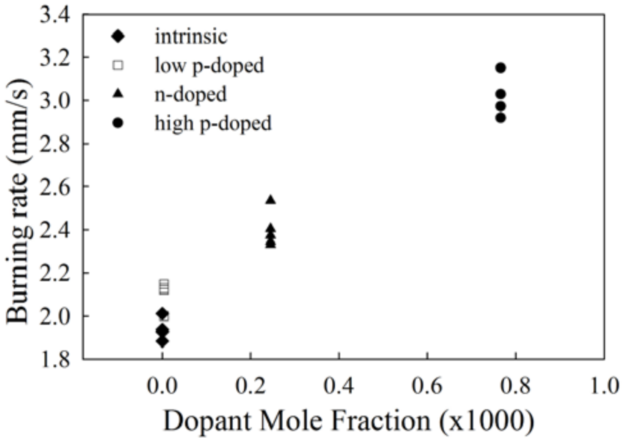


Fig. 2 Burning rates of 26/74 wt% doped Si/PTFE pellets are shown here.

P4

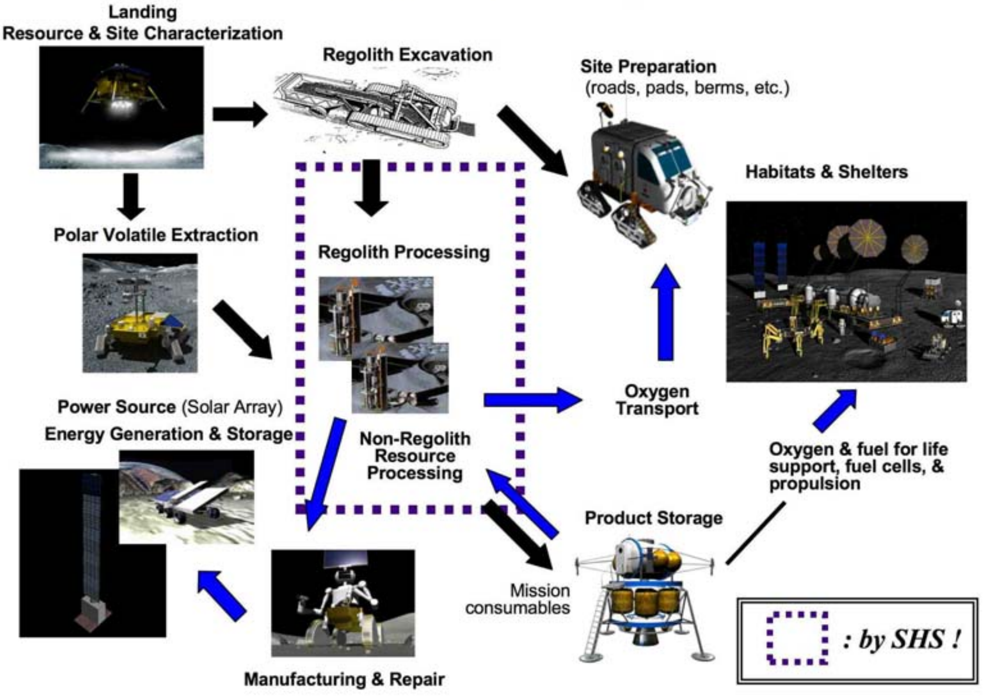
SHS RESEARCH AND INTERNATIONAL COLLABORATION ON *IN-SITU* RESOURCE UTILIZATION BEYOND LOW-EARTH ORBIT

Osamu Odawara

Tokyo Institute of Technology, J2-48, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8502 Japan
odawara.o.aa@m.titech.ac.jp

Space technology has been developed for frontier exploration not only in low-earth orbit (LEO) environment but also beyond LEO to the Moon, Mars and others. For performing such explorations, none would be enough to develop technologies with resources only from the earth; it should be required to utilize resources on other places with different nature of the earth, i.e., *in-situ* resource utilizations (ISRU). The resources such as metal oxides that exist on planets or satellites could be refined, and utilized as a supply of heat energy, where self-propagating high-temperature synthesis (SHS) can stand as a hopeful technology for such requirements; the SHS technology is a rapid, versatile and near net shaping one that can operate under various conditions such as centrifugal-force, low-gravity and high vacuum. When a sustainable settlement would be established beyond LEO, energy could mainly be supplied by solar cells on its surface and some fabrication scenario with thin film deposition in moon-based ultra-high vacuum should be designed as an ISRU. For Lunar ISRU [1], the resources on the Moon have been identified and characterized, especially the polar region, and some activities have already been performed as early demonstrations of ISRU on the Moon in preparation for human exploration of Mars and to develop and evolved about Lunar ISRU capabilities supporting sustainable human space transportation and presence on the Moon as shown in Figure. These concepts, technologies, and hardware would be applicable to both the Moon and Mars, and these capabilities might achieve the maximum benefits of ISRU with the aid of SHS technology applications.

Fig. Lunar *ISRU* Activity Design



Over the years, the Japan-US Science, Technology and Space Applications Program (JUSTSAP) has formed networks between government, private sector and university-based capabilities and resources in both Japan and the United States to facilitate innovative and cost-effective earth orbiting missions and both robotic and manned exploration of the moon and Mars. It also has facilitated several collaborative ventures between Japan and the United States, including the development and demonstration of the first trans-Pacific high data rate (155 mbps) seamless satellite-fiber optic communications bridge between Japan and the United States; microgravity experiments aboard the U.S. Space Shuttle to test the efficiency of manufacturing new products in a zero-G environment; innovative data-base networking to support collaborative disaster management protocols throughout the Asia-Pacific Region; and the establishment of an annual University Space Systems Symposium to provide innovative mentorship opportunities for the next generation of space scientists and entrepreneurs. At the 20th anniversary meeting of JUSTSAP, held in November 14-18, 2010, a decision was made to broaden the organization beyond its founders, Japan and the US, and to include other space-faring nations around the world, emphasizing those on the Pacific Rim. The activities of the new JUSTSAP which is named as the Pacific International Space Alliance (PISA) has mainly focused on the establishment of the International Lunar Research Park (ILRP) for migrating to the Moon in the next decade and eventually preparing the way for a permanent human settlement on the Moon.

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P5

NEW PERSPECTIVES OF TIME-RESOLVED INVESTIGATIONS OF SHS AT NEW SYNCHROTRON RADIATION SOURCES

Boris Tolochko.[1]*, Sharafutdinov M.R[1], Rogachev A.S.[2]

1-Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia
2-Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Russia
* tolochko@inp.nsk.su

The synchrotron radiation (SR) is a powerful instrument for study of SHS. At the last decade progress in this area was determined by progress in development of new specialized generator of synchrotron radiations - wigglers and undulators, installed at 3-th generation storage rings [1] and helped to reach the grate parameters:

- High brightness and high intensity, many orders of magnitude more than with X-rays produced in conventional X-ray tubes;
- High level of polarization (linear or elliptical);
- High collimation, i.e. small angular divergence of the beam;
- Low emittance, i.e. the product of source cross section and solid angle of emission is small;
- Wide tunability in energy/wavelength by monochromatization (sub-electronvolt up to megaelectronvolt range) i.e. hard X-ray range is available now (Figure 1);
- High brilliance, exceeding other natural and artificial light sources by many orders of magnitude: 3rd generation sources typically have a brilliance larger than 10^{23}photons/s/mm^2/mrad^2/0.1%BW,where 0.1%BW denotes a bandwidth $10^{-3}w$ centered around the frequency w and will reach 10^{35} (photons/sec/mm^2/mrad^2 in 0.1% bandwidth) in the nearest future;
- Pulsed light emission (pulse durations at or below one nanosecond or a billionth of a second).

High brilliance allows to realize the high time resolved diffraction experiment with millisecond time resolution now [2] and nano/femto- second time resolution in the nearest future. There are no chance to realize such experiments with using commercial X-ray devices. High time resolved diffraction experiment needs high count rate area detectors, which developed in last decade with big progress in Budker Institute of Nuclear Physics SB RAS.

Using of this method for SHS allows to receive new, inaccessible earlier information - about phase transformation in chemical reaction zone, about formation of an intermediate phases, about behavior of the reagents crystalline lattice before reactions, and about relaxation process after reaction. At present time was reached following parameters of diffraction experiment for SHS: locality - 5 micrometers, time resolution - 1 ms, number of the frames - 1000. The same systems was investigated in mode of SHS, and under slow heating up to the high temperature. It is found that in different case of the reactions was realized on different mechanism.

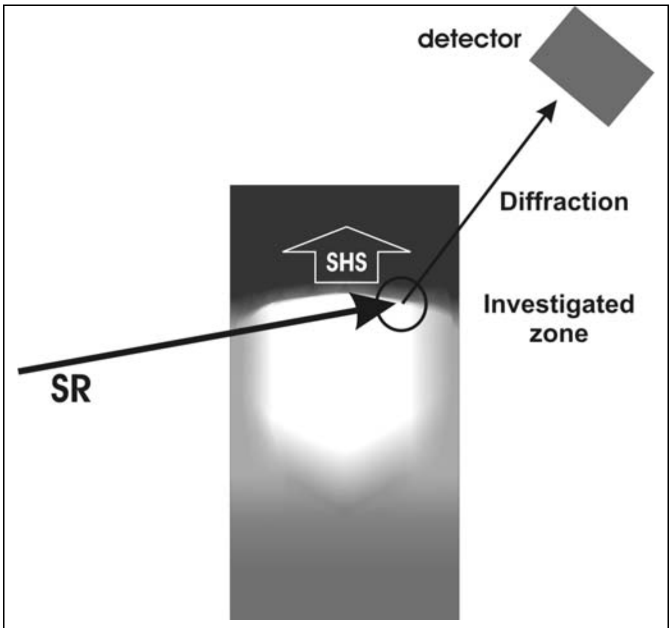

Figure 1. The hard SR X-ray can penetrate inside sample during SHS and give information about structural changes in local investigated zone with microsecond time resolution.

The progress in generations of SR opens the new possibilities for use of SR for study SHS: locality - 100 nm, time resolution - 1 microsecond/femtoseconds, depth of the penetration of the radiation - 1 sm.

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P6

MEDICAL IMPLANT MATERIALS WITH DESIGNED MICROSTRUCTURE AND CONTROLLED BIOLOGICAL AND MECHANICAL PROPERTIES

Irena Gotman

Faculty of Materials Engineering, Technion, Haifa 32000, Israel
gotman@tx.technion.ac.il

Medical implants and materials they are made of have had a major impact on the practice of contemporary medicine in both saving and improving the quality of lives of tens of millions of people. Nowadays, the field of biomaterials is becoming one of the most intellectually exciting and challenging areas of materials science and engineering that not only targets human body repair but also science and technology in general. The main objective in biomaterials research has become the design of materials that can interact specifically with the biological environment for a given purpose. This includes the so-called tissue regeneration approach: biomaterials are used as templates on which specific types of cells can elaborate three-dimensional tissues. To help biology regenerate the missing or dysfunctional body parts, specially designed biomaterials are being explored as delivery vehicles for biologically active molecules and proteins. Great advances in understanding the biological response elicited by biomaterials that have occurred over the past few years are becoming increasingly useful in implant design. In particular, manipulating the chemical, mechanical and surface properties of biomaterials to control cell behaviors such as growth, adhesion and migration is of great interest. These new trends in the biomaterials field require novel design approaches based on vision and nontraditional thinking.

In this talk, we'll mainly concentrate on biomaterials for hard tissue replacements, such as joint prostheses and artificial bone graft substitutes. In these orthopaedic applications, materials with a wide range of properties are required, from mechanically and biologically inert bulk materials to porous 3-D structures and tissue-reactive coatings. Several state-of-the-art implant materials as well as novel approaches to biomaterials synthesis and surface modification will be discussed.

P7

COMBUSTION SYNTHESIS OF MATERIALS ADDRESSES CURRENT AND FUTURE INDUSTRIAL CHALLENGES

Galina Xanthopoulou

Institute of Materials Science “Demokritos” National Center for Scientific Research, Aghia Paraskevi,
15310 Athens, Greece
gxantho@ims.demokritos.gr

Combustion synthesis, including SHS, offers almost unlimited capability for addressing many of the current and future industrial materials challenges. This review talk will briefly highlight the most important of these, but many others exist as well.

Highly active **catalysts** and carriers have been developed by SHS or solution combustion for many processes: production of industrial gases and liquids, oxidation of CO, NO, H_2, hydrocarbons, aldehides, alcohols and methane to synthesis gas, dehydrodimerization of methane, pyrolysis of diesel, petrol and naphtha, dehydrogenation of hydrocarbons, steam reforming of kerosene, carbon combustion, hydrogenation, hydrodesulphurization reactions, ammonia synthesis, etc. Very important generic development was the “impregnated support combustion” method which involves impregnation of reaction solution inside the porous structure of the inert solid support, followed by reaction initiation because it permits synthesis of supported catalyst with extremely high surface areas (up to $200m^2$ g^{-1}). Impregnation of incombustible paper or sponge ceramic material followed by solution combustion is also a very interesting approach for preparation of block catalysts. Crucially, according to various sources we could run out of cheap oil in a few decades, which has meant that much emphasis has been put to natural gas conversion catalysts. The European Catalytic Society considers methane conversion to valuable products (olefins, aldehides, ketones, alcohols, hydrogen-rich fuels, synthesis gas for polymer production, acids etc) to be high priority studies.

A relatively new area for combustion synthesis is in **space technologies.** Some examples in-situ resource utilization (ISRU) for making shaped blocks from lunar or Mars regolith by SHS in vacuum, processes for manufacture of solar reflectors using lunar materials etc. A related area is the use of SHS for making the porous sub-structure of a hybrid **Thermal Protection Systems** for spacecraft entering an atmosphere at high speeds.

SHS is also being developed as a **Joining technology** for difficult-to-join systems, such as SiC-SiC, ceramic-metal and intermetallic and some metal-metal systems, in particular Al-Ti, Al-Ni, Al-Ni-O, Al-Fe-O, Al-Cr-O, Al-Co-O, Ti -C –Ni, Al-Ni, Al-Fe etc.. In particular bonding of SiC/SiC with a metal substructure is very important for development of fusion reactors. Prospective developments in joint technology are multi-compound formation and wet ability control.

Metal aerogels are valuable materials because they combine the unique properties of metals with those of aerogels and are being produced by SHS. These are high specific surface areas (100-500 m^2/g) and electrical conductivity and this combination makes them valuable for applications such as supercapacitors, efficient fuel cells, safer hydrogen storage, batteries, water desalination, antimicrobial scaffolds, irregularly-shaped magnetic media and X-Ray Optics. Nanosized particles of metals can be made by SHS and can exhibit enhanced catalytic activity over bulk forms of the same metal.

SHS and solution combustion are also used to produce inorganic **Pigments.** Almost any color and hue can be made and the pigments have very good color and chemical stability at elevated temperatures, good dispersity and low production cost. They have been made on the basis of various ores and even solid wastes. They have been applied industrially in plastics, cosmetic, paints, ceramic, metal and porcelain glazes, paper and glass. Lately, solution combustion synthesis of pigments shows strong promise for synthesis of **nano-size powders** with greater applicability. Notable examples are gold - purple nitrides/non-stoichiometric pigments for cosmetic. Related are **luminescent** materials prepared by solution combustion for **i**maging, inorganic light emitting diode materials and devices, conversion materials and thin-film electroluminescent phosphor materials and devices.

A very interesting new area is the production of coatings by **in-flight SHS during Thermal or Plasma Spraying.** Intermetallic have already been produced and, no-doubt, the area will expand rapidly. Another recently active area is **Biotechnology**. Oxides, glass ceramics and organic biomaterials have been prepared by SHS for dental and hard tissue replacements, such as joint prostheses and artificial bone graft substitutes. In such orthopaedic applications, materials with a wide range of properties are required, from mechanically and biologically inert bulk materials to porous 3-D structures and tissue-reactive coatings.

Significantly, combustion synthesis is being used extensively for **Environmental** cleaning and remediation**.** These include highly active catalysts for exhaust emission control and methane conversion and various methods of neutralising or recycling industrial inorganic wastes and absorbing oil from polluted water. Room-temperature SHS has been developed for encapsulating and vitrifying toxic or radioactive materials but also for covering large contaminated areas by creating in situ large-scale protective vitrified coatings. Watste utilization has been mentioned above for catalysts and also includes SIALON synthesis, multi thermite reactions. For **Energy** applications, SHS has also been used for making solar cells and similar functional materials.

Much other technically important research is also under way covering areas such as centrifugal SHS for pipe linings, continuous SHS-based production, orientation-controlled materials, 1-D synthesis and propagation control, 3-D processing: stereo-fabric and boundary control, thin layer compounds with interface control, chemical oven/propagation control, geo magma-water reaction/hydrogen generation, fiber synthesis and continuous processing of fibers, composite layer formation -C-T process, quantum spin glass composite synthesis, electrical controlled SHS, functional graded materials and layer-controlled SHS, wide band-gap nitride compound synthesis for ultra-violet protection and porous materials synthesis by SHS.

P8

STRATEGY DEVELOPMENT FOR THE TRANSFER OF NEW TECHNOLOGIES TO INDUSTRY: CONVERTING A CLEVER INVENTION TO A VALUABLE INNOVATION

George Vekinis

Institute of Materials Science "Demokritos" National Center for Scientific Research, Aghia Paraskevi,
15310 Athens, Greece
gvekinis@ims.demokritos.gr

What makes a clever invention successful in industry or the market? There are as many detailed answers to this question as technology transfer consultants, but the underlying common denominator is "good organisation, hard work and perseverance". The truth is that no honest entrepreneur ever became successful by chance or by taking a "back-seat". In all cases, they had to study the market, plan everything carefully and work, work, work towards their goal.

The talk will offer a very brief framework for developing a strategy for transferring a clever novel technology or idea to industry or the market and is based on similar workshops offered by the European Commission to various consortia funded by the EC. It covers the 'organisational" part of the strategy. The perseverance and hard work are your responsibility!

At the start, we'll consider the crucial difference between an "invention" (a clever novel "idea" for a service or product) and an "innovation" (something that people want or demand or need which is thus valuable). This will be followed by a discussion on valorisation ("what makes a technology valuable?") and how to enhance the value of your technology, be it a material, a device or a service.

After that we'll discuss the various formal and not-so formal steps that need to be taken for technology transfer with emphasis on the need for developing trust between the two parties (the "Provider" who is the inventor and the "Adopter" who wants to use the technology) and the crucial role that an objective technology broker plays. Some of the aspects we'll consider include various ways of finding adopters and methods of evaluting them.

An interesting theme we'll look at is the "art" of negotiating successfully and what we need to keep in mind during all types of business (and non-business) negotiations.

Finally we'll look at how to carry out an objective SWOT ("Strengths-Weaknesses-Opportunities-Threats") analysis for our technology (and also our markets) and how to improve areas that may be an obstacle to success. This will lead us to the Business Plan and aspects related to it.

Many people consider Technology Transfer as a "dark art" or an "indeterminate science" because of its many unknown factors and the many parameters that are often unknown. In reality, by accepting the principle of "90% Perspiration + 10% Inspiration", it is possible to win!

ORAL PRESENTATIONS

A: Combustion theory and modelling

2A-K – KEYNOTE TALK

LAYER AND SURFACE MODES OF FILTRATION COMBUSTION: THEORY AND EXPERIMENT

Grachev V.V.*, Linde A.V.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432, Russia
* vlad@ism.ac.ru

The first experiments on combustion of compacted metal powder samples in a gaseous nitrogen atmosphere exhibited two qualitatively different combustion modes: a layer mode and a surface mode [1]. In the layer mode, the combustion front is flat and extends over all the cross section of the sample. In the surface mode, the combustion front is strongly curved, and the leading edge of the reaction front propagates within the surface regions of the sample, whereas the reaction in the core part of the sample either occurs far from the leading edge of the front or is absent. The external patterns of combustion in both modes are identical; therefore, a conclusion on the combustion mode is made based on visual observation of cross sections of burnt samples (the formed nitride and the initial metal powder differ in color) and on chemical analysis of samples taken from the burnt samples.

The combustion mode was proposed to quantitatively characterize by quantity m, which is determined by chemical analysis and is the ratio of the conversion in the core part of a sample to the average conversion throughout the sample [1]. On the one hand, a theoretical analysis of a two-dimensional model of filtration combustion showed that m is essentially dependent on the sample length [2]. On the other, a general theory [3] states that a steady combustion wave is an intermediate asymptotics and its characteristics are independent of the sample length. From this standpoint, m is not fully adequate characteristic of the combustion mode for comparing theoretical forecasts and experimental data.

In this work, for the first time, we proposed to judge the combustion mode not from indirect data of chemical analysis of combustion products, but from direct determination of the front shape during combustion. The front shape was found from the recordings of two thermocouples installed in the same cross section of the sample: one of which was placed on the sample surface and the other was introduced along the sample axis through the lower base of the sample to a depth of 15 mm. These thermocouples measured the difference Δt in time between the moments of front propagation through this cross section on the surface and the axis of the sample. Δt characterizes the front curvature and, hence, the combustion mode. If Δt is large, then there is a pronounced surface combustion mode; otherwise (in the limit $\Delta t \to 0$), the front is flat and there is a layer combustion mode.

Modes of combustion of porous niobium powder samples in a gaseous nitrogen atmosphere within the pressure range 0.12–10 MPa were studied. Thermocouple measurements determined the time difference Δt between the moments of combustion front propagation through a given cross section of the sample on the surface and at the core part of the sample, which allowed us to evaluate the combustion front curvature over the cross section and make a conclusion on the combustion mode. It was experimentally determined that, within the pressure range 0.12–1 MPa, there is a surface combustion mode, and within the range 1–10 MPa, there is a layer combustion mode. The velocities of front propagation on the surface and in the core part of the sample were experimentally found. X-ray diffraction and chemical analyses revealed nonuniformity of the composition of the combustion products over a cross section of the sample burnt in the surface mode. Values of the criterion SL [2, 4] were calculated from experimental data. This criterion theoretically determines the combustion mode: the surface mode at SL > 1 and the layer mode at SL < 1. Comparison of experimental observations with calculated SL values suggested agreement between the theoretical forecasts and experimental data.

Acknowledgments

This work was supported by the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (grant no. NSh - 6497.2010.3).

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2A-1

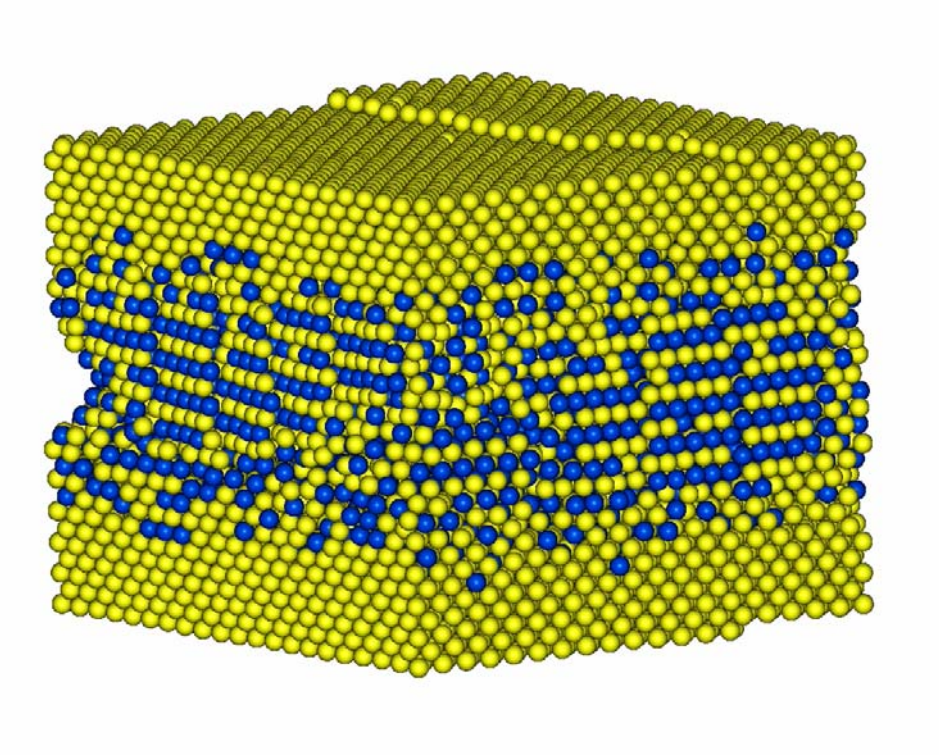
STUDY OF THE REACTIVITY OF NANOMETRIC Ni-Al MULTILAYERS BY MOLECULAR DYNAMICS SIMULATIONS

Baras F.*[1], Linde A.V.[1,2] and Politano O.[1]

[1] Laboratoire ICB, UMR 5209 CNRS Université de Bourgogne, Dijon, France
[2] ISMAN, Chernogolovska, Moscow Region, Russia
*mailto:fbaras@u-bourgogne.fr

To understand the extreme reactivity of nanometric metallic multilayers (N2M), it is necessary to study the dynamics of phase and structural transformations associated with heterogeneous reactions at nanoscale. Since these nano-objects are essentially made of interfaces, it raises many questions about the role of huge concentration gradients in the nucleation process, the limiting role of diffusion on the reaction, the presence of defects due to the misfit in the lattice parameters, the real possibility of crystallization in nanosytems, … Besides the very powerful experimental techniques which are now available to study N2M such as time-resolved X-ray diffraction (TRXRD) using synchrotron radiation or differential scanning calorimetry (DSC) [1], it is interesting to develop an appropriate modeling of these nanosystems. Molecular dynamics seems to be a promising tool [2] to study N2M since the typical length scales (a few nanometers) precisely correspond to the ones accessible by the simulation. Moreover, a great effort has been made to develop effective potentials for binary metallic systems and their compounds [3]. By means of this atomistic approach, we are able to detect the very first steps of the spontaneous dynamics at nanoscale.

We have developed the molecular dynamics study of a layered Ni-Al-Ni system using a specific geometry designed to model a Ni-Al N2M. The system made of an *fcc*-Al slice embedded in *fcc*-Ni, is initially thermalized at the fixed temperature of 600 K. The system then evolves in a microcanonical ensemble. We first observe the interdiffusion of Ni and Al at interfaces which is followed by the spontaneous phase formation of NiAl (*B2*) in the middle layer. The solid-state reaction is associated with a rapid system's heating which further enhances the diffusion processes. NiAl phase is organized in small regions separated by linear two-dimensional defects. Such crystallites are larger in the direction parallel to the interface than in the perpendicular one. The figure shows a snapshot of the system after 6 ns: we clearly see the formation of small domains of NiAl phase characterized by alternating lines of Ni and Al atoms (Ni in yellow and Al in blue) . For longer times, the temperature has reached a notably higher value (> 1000 K) and the system may partly lose its *B2*-NiAl microstructure in favor of the formation of Ni_3Al in *L12* configuration. A layer by layer development of the Ni_3Al is observed. This work shows the spontaneous development of a real exothermic solid-state reaction in metallic multilayered thin films mostly constituted by interfaces. It allows to explain the extreme reactivity of such systems and gives the basic mechanisms at its origin.



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2A-2

GASDYNAMIC ASPECTS OF CCSO AS A SMOLDERING COMBUSTION WAVE

Markov A.[1], Filimonov I.A.[2] and Martirosyan K.S.[3]

[1]Institute for Problems in Mechanics of the Russian Academy of Sciences, 101Vernadskogo ave, B. 1, Moscow, 119526, Russia
a_a_markov@yahoo.com
[2]Institute of Structural Macrokinetics and Material Science of the Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia Chernogolovka, Moscow Region
fil_limonov@hotmail.com
[3]University of Texas at Brownsville, Department of Physics and Astronomy, 80 Fort Brown, Brownsville, TX, USA, 78520
karen.martirosyan@utb.edu

An increasing number of studies of the synthesis of nanostructured complex oxides have recently been conducted to support their growing array of emerging technological applications. A few prominent examples are nanoenergetic materials, advanced nanoelectronics, memory devices, digital pigments, biomedical imaging contrast agents, drug delivery and bio-nano-sensors. Nanoparticles generally have unique novel properties different from those of bulk materials. Due to their active surface area they are becoming a core component of advanced materials that have many practical applications. The rapidly growing market demand for nanostructured complex oxides particulates calls for cost-effective and environmentally friendly technologies for their large-scale production. Recently, Martirosyan and Luss developed a new, simple, economical and energy efficient synthesis of submicron and nanostructured complex oxides from inexpensive reactant mixtures [1-6]. In this process, referred to as Carbon Combustion Synthesis of Oxides (CCSO), the exothermic oxidation of carbon $C+O_2=CO_2$ $\Delta H_{CO_2}^{298}$ = -393.5 kJ/mol generates a self-sustained thermal reaction wave (temperature gradient of up to 1000 °C/cm) that propagates at a velocity of 0.1-3 mm/s through the solid reactant mixture (oxides, carbonates or nitrates) converting it to the desired oxide product by the reaction:

$$\sum_{i=1}^{n} \mu_i X_i^{(s)} + \alpha C^{(s)} + \beta O_2^{(g)} = \sum_{j=1}^{m} P_j^{(s)} + \delta CO_2^{(g)} + (-\Delta H)$$

Such gradients and velocities are certainly the bottom values for the combustion synthesis (CS) using not only oxides but also metals in green mixtures (while the wave temperatures are about twice lower than those in the CS and SHS using metals fuel. Usually in Eq. (1) we have: $\beta \neq \delta$ Therefore we believe that there is some gas accumulation and release during CCSO. We observe experimentally carbon oxide release at $\beta < \delta$, and oxygen absorption at $\beta > \delta$ We see carbon oxide release or oxygen consumption dependent on the wave combustion zone and the synthesis stage. In our opinion there is oxygen consumption in the CCSO preheated layer and carbon oxide release in the post combustion zone. Thus, the gasdynamic structure of CCSO isn't so simple but rather complex. Two opposite countercurrent flows of oxygen and carbon oxide take place inside the reacting sample. In some places these flows penetrate each other (preferably near the reactor walls) or they are self-organized in some vortex-like motion (along the center core region). We consider that we have the coflow filtration of carbon oxide and counterflow filtration of oxygen.

In this report we present the computational technique developed in order to provide the scale capturing as well as the stable algorithm for numerical simulation of the combustion front motion during the Carbon Combustion Synthesis of Oxides (CCSO). In CCSO the exothermic oxidation of carbon nanoparticles generates a steep thermal reaction wave that propagates through the solid reactant mixture converting it to the desired complex oxide product. The combusted carbon is emitted from sample as carbon dioxide and its high rate of release increases the porosity and the friability of the product. Based on the model kinetics scheme and the previous investigations of it, the temperature distribution, mass fractions, and particle size are presented for the various values of similarity parameters of the problem. The recent experiments in heterogeneous combustion revealed that almost all the gasless thermal waves which appear to be macroscopically (reacting sample scale) continuous and smooth are actually descret on the microscopic level (single particle scale) [7, 8]. Due to the different reasons, such as: formation of cracks, defects and thermal non-uniformity the microscopic behavior strongly differs from the macroscopic. Macroscopically stable and steady-state combustion maybe accompanied by autooscillations, scintillations or spin spot front motions. Thus, we may call these deviations as *structurally induced microscopic* instability. Nevertheless, when gas is intensively produced by reaction, it is difficult to separate *structural* changes caused by reaction from those induced by complex gas movement in the highly porous sample (*gasdynamic instability*). The thermal front distribution and morphology of the condensed product as well as the rate of the oxidation and phase transition are predicted using the numerical simulation based on micro and macro scale technique developed by Markov [9].

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2A-3

THERMAL MODES OF SYNTHESIS IN NON-ISOTHERMAL DIFFUSION PROCESSES CONSIDERING THE CRYSTALLIZATION KINETICS OF THE PRODUCT PHASE

Filimonov V.Yu.*[1], Koshelev K.B.[2]

[1]Altay Technical State University, Barnaul, Lenina str.46, 656038, Russia
[2]Institute for Water and Environmental Problems SB RAS, Barnaul , Molodyoznaya str.1, 656038, , Russia
*vyfilimonov@rambler.ru

At present, mathematical modeling of the phase formation in heterogeneous binary systems is a well-developed direction in the theory of combustion of condensed matter. The methods of the theory have been known since 1980-s [1,2] and successfully used up to the present day. Noteworthy is the fact that in most studies the rate-limiting role of the diffusion processes in the forming product layers is quite common. This virtually corresponds to an asymptotic representation $\omega = t_d / t_r \to \infty$, where t_d – characteristic time of diffusion, t_r – characteristic time of reaction. However, any heterogeneous process of phase formation has its own macroscopic kinetics, and the interface growth kinetics of a new phase can be characterized by non-diffusion transformations [3] related to a thermodynamically non-equilibrium state of the forming phase.

In the present work, mathematical modeling of the phase formation kinetics was performed considering finite values of the parameter ω, and the size of the reaction cell. Critical conditions of ignition were studied showing that the ignition can occur as a result of a transition from a kinetic to a diffusion mode or in a kinetic mode of the product crystallization.

Fig.1 shows how that the critical parameter δ (the rate of heat dissipation to the rate of heat release ratio) depends on the parameter ω for different values of $\sigma = E_{cr} / E_d$ (the activation energy of the crystallization reaction to the activation energy of diffusion ratio).

It can be seen that the critical conditions for ignition do not depend on the true kinetics of the reaction only in the diffusion mode, when $\omega \to \infty$ and under a given σ. Therefore, with finite values of the parameter ω, the reaction kinetics will differ from the diffusion kinetics. The conditions $\sigma = 1$, $\omega \to \infty$ correspond to a particular case of traditionally analyzed ignition conditions in a strictly diffusion mode [1,2].

We have found that depending on the content of a component in the reaction cell, the ignition can proceed either in a kinetic or in a diffusion mode. In the former case, the critical conditions are defined by the Semenov criterion (curves in Fig.1 become linear), in the latter case – by a possibility of self-heating in a diffusion mode. The conditions of the kinetic mode of the reaction have been determined.

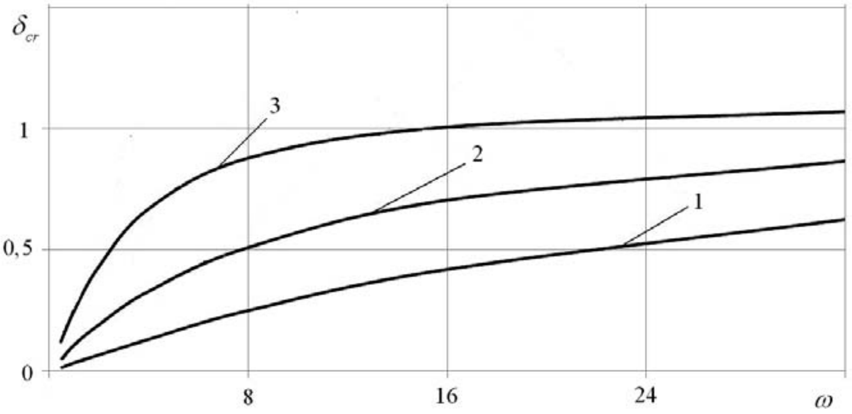

Fig.1. Diagram of the critical conditions of ignition $\delta_{cr}(\omega)$ for different values of the parameter σ : 1- $\sigma = 0,5$; 2 - $\sigma = 1$; 3 - $\sigma = 1,5$.

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2A-4

SIMULATION OF SOLID-PHASE REACTION SYNTHESIS UNDER SHOCK WAVE LOADING

Ivanova O.V.*, Zelepugin S.A.

Department for Structural Macrokinetics of the Tomsk Scientific Center of Siberian Branch of the Russian Academy of Science, Tomsk, 10/3 Akademichesky ave., 634021, Russia
* bliz3@yandex.ru

The most interesting direction in explosive processing is shock wave loading of materials and mixtures capable of chemical and phase transformations. The material behaviour differs essentially under shock wave and statical loading. The density of materials after shock wave loading reaches almost 100 %. However, such transformations are studied mostly experimentally, and their mathematical models are virtually unavailable. It is natural because chemical transformations are difficult to study under explosive loading and reliable data on the dynamics of these phenomena are not always easy to obtain from experimental results. Meanwhile, novel promising materials are more and more often produced and used in fast processes at high strain rates, pressures, and temperatures. At the same time, the effect of shock waves on solid-phase reactions is still insufficiently studied and, by the present time, has not yet reached a technology level because of the lack of experimental data and also mathematical models that could take into account the coupling of mechanical and physicochemical processes, including their combined action, and the effect of each factor.

The purpose of this work was to numerically study the dynamics of development of aluminum sulfide synthesis under explosive loading on the basis of a multicomponent medium model [1].

It was numerically solved an axisymmetric problem of explosive loading of a cylindrical steel ampoule containing a porous Al–S mixture. A synthesis reaction in a reacting porous multicomponent mixture was described using a phenomenological model of chemical transformations with zero-order kinetics without reverse transformations [2].

The analysis of the theoretical results suggested the following dynamics of development of chemical transformations in the Al–S mixture in the cylindrical ampoule under explosive loading. In the top and central parts of the ampoule, the reaction is initiated by a shock-assisted mechanism, by which the reaction is initiated in the shock wave and continues and is completed behind the shock wave front. In this case, the amplitude and duration of the shock wave are insufficient for full completion of the chemical transformation within the shock wave action time. In the bottom part of the ampoule, within the action time of the transmitted shock wave, neither of the reaction initiation criteria is valid. The pattern of the process radically changes after the reflection of the transmitted shock wave from the bottom cap of the ampoule as a compression wave: a shock-induced mechanism of forced chemical transformations takes place, by which the chemical reaction is initiated, continues, and is fully completed within the shock wave at high pressures.

Thus, based on a phenomenological model of chemical transformations, the numerical study into the dynamics of development of aluminum sulfide synthesis under explosive loading of a cylindrical ampoule has established a transition from partial to complete conversion in the synthesis reaction in the shock front after reflection of the shock wave from the bottom cap of the ampoule. The high heat release rate during the chemical reaction in the bottom part of the ampoule causes the formation of a gas phase, which, in turn, leads to an increase in the pressure in this area. It was established that, once the reaction in the shock wave is fully completed, the ampoule is broken down because of the formation of a gas phase and an increase in pressure, with the breakdown being initiated in the bottom part of the ampoule.

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2A-5

MICROWAVE IGNITED COMBUSTION SYNTHESIS AS A JOINING TECHNIQUE FOR DISSIMILAR MATERIALS: MODELLING AND EXPERIMENTAL RESULTS

Colombini E.*, Rosa R., Veronesi P., Leonelli C., Poli P.

University of Modena and Reggio Emilia, Via Vignolese 905/A, 41125 Modena
* elena.colombini@unimore.it

All Combustion Synthesis (CS) reactions ignited by conventional heating techniques usually show an inversion of the heat flow before and after the synthesis: initially heat is transferred from the ambient to the colder reactants; after ignition, the usually extremely high temperatures of the newly formed products cause the reversal of the heat flow (from products to the ambient). For this reason, as soon as the reaction occurs, it is no longer possible to continue to transfer heat by conventional heating from the external heating source to the reaction zone. The use of microwaves heating selectivity, instead, is expected to lead not only to a more rapid temperature increase of the whole reaction zone, but also to a continuous energy transfer to the reactants and products during and after the ignition, with consequent heat generation.

Traditional fusion welding is difficultly applicable to joining processes involving dissimilar materials, due to the mismatch in the base materials properties [1]. Nevertheless, welding of dissimilar materials is increasingly attracting more attention in industry because it can reduce the material costs and improve the design flexibility [2]. The goals of hybrid structures which combine dissimilar materials metal/ceramic or metal/intermetallic are numerous: achievement of special properties or properties combination, maximization of structural efficiency and/or minimisation of weight, conservation of limited materials resources, minimization of fabrication and operating costs, and environmental compatibility [3]. The major advantages of powder metallurgy techniques is the ability to adapt the size and composition of the brazing material, so that it can be exploited to join different materials at a relative low cost. The disadvantages are that the properties of the formed products are greatly influenced by processing conditions and residual porosity, which therefore require careful control. [4].

In this study, microwaves are used to activate self-propagating reactions. The selectivity by which microwave are absorbed by the reactive powder mixtures avoids the exposition to high temperatures of the entire materials to be joined, minimizing the extents of heat affected zones. After ignition, the reaction front travels along the entire contact surface between the substrates, promoting, depending on the combustion temperature, wetting and possible reactions in the joining couple. This simple and energy-saving technique, when applied to systems presenting the formation of eutectics with the brazing materials, allows exposing to high temperature only a thin layer of the substrates to be joined, leading to peculiar microstructures at the interface, which enhance the adhesion.

Among the brazing materials for high temperature and lightweight applications, intermetallics are regarded as extremely promising for improving the performance of engines, pumps, heat exchangers, furnace components, tool and die parts [5]. These properties make them suitable for high temperature structural and coating applications, despite a relative intrinsic brittleness [6]. Among intermetallic compounds, aluminides, are promising candidates for the next generation of high temperature, high performance structural and coating materials. In particular, NiAl is one of the most attractive, having a high melting point (1638 °C), a low density (5.91 $g \cdot cm^{-3}$), an excellent oxidation resistance and a good thermal conductivity (75 $W \cdot m^{-1} \cdot K^{-1}$), [7] so it represents a good compromise between a relatively low density and the capability to withstand high temperatures.

The aim of the present work is to experimentally study and to numerically simulate the microwave ignited combustion synthesis of intermetallic materials to rapidly join different kinds of metallic and ceramic substrates. Numerical simulation of the process led to overcome the difficulties in experimental temperature measurements, allowing to estimate the heating and cooling rates of the reactants and products, as well as of the surrounding substrates.

A simplified model of the microwave-assisted combustion synthesis of Ni and Al metal powders to form the NiAl intermetallic phase between metals will be showed. The simulation couples an electro-thermal model with a chemical model, necessary to study the exothermic reaction between powders. Numerical results are validated by experimental measurements, showing a good agreement in terms of joint temperature and microstructural effects related to microwave exposure after CS completion. They show the capability of microwaves to convey energy, so that they can be used to alter the temperature profiles during and after the CS and hence the resulting microstructure. Moreover, microwave-heating selectivity allows maintaining the reflective metallic substrate or the low loss one at a much lower temperature, compared to conventionally ignited CS process.

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2A-6

OXIDATION KINETICS AND MATHEMATICAL MODELING OF SELF-PROPAGATING REACTION IN AN INERT SUBSTRATE FILLED WITH PYROPHORIC IRON NANOPARTICLES

Doorenbos Z.[1], Kapoor D.[2], Haines C.[2] and Puszynski J.A.[3]

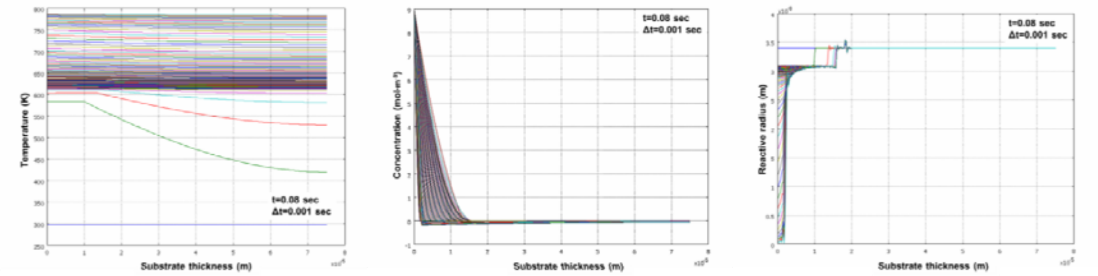
[1]Innovative Materials and Processes, LLC, Rapid City, SD 57702
[2]Armament Research, Development, and Engineering Center, Picatinny Arsenal, NJ 07806
[3]Chemical and Biological Engineering Department, South Dakota School of Mines and Technology, Rapid City, SD 57701
Jan.Puszynski@sdsmt.edu

The oxidation of different metals has been investigated for many years, however, less attention has been paid to a behavior of metallic nanoparticles, which are pyrophoric in nature when exposed to air. This work investigates the oxidation kinetics of iron nanoparticles and mathematical modeling of combustion wave propagation in inert substrates filled with alpha-iron pyrophoric nanoparticles. While there are many methods available for the formation of iron nanoparticles this work focused on alpha-iron nanoparticle formed by the hydrogen reduction of iron oxide nanoparticles [1-2].

While the oxidation of iron in the bulk form has been well described over the years [3], there is only scattered information on the oxidation of nanoscale iron in air. In 2005 Grosvenor et al. presented activation energies for the oxidation of iron thin films under low partial pressures of oxygen at room temperature [4]. A mathematical model for the oxidation of highly porous iron films has been proposed by Wilharm [5]. This model presents a one-dimensional (1D) heat and mass transfer for the prediction of the combustion temperature of the porous iron thin films. Due to the lack of reliable experimental data, Wilharm assumed the first order reaction kinetics and adjusted the reaction constant to achieve combustion temperatures so they matched experimental results.

This presentation will focus on measurements of oxidation kinetics of partially passivated iron nanoparticles under atmospheric conditions using simultaneous differential scanning calorimetery/thermal gravimetric analysis (DSC/TGA) at heating rates of 1, 5, 10, 15 and 20K/min up to 1073K. Using the data collected from the controlled oxidation experiments and an assumption that the oxidation of iron follows Arrhenius reaction kinetics, similar to the oxidation of nickel nanoparticles [10], the activation energy and pre-exponential factor of partially passivated iron nanoparticles in air were determined as: 168 $kJ \cdot mol^{-1}$ and $4.67 \cdot 10^{-13}$ s^{-1}, respectively.

This presentation will also on 1-D and 2-D mathematical modeling of self-propagating combustion wave in porous inert structures filled with pyrophoric nanoparticles. The transient temperature profile for the combustion of alpha-iron nanoparticles when exposed to air can be predicted using the derived heat and mass transfer equations along with the assumption listed above. These equations were solved using the Comsol software. Temperature, oxygen concentration and reactive particle radius profiles for the combustion of 68 nm alpha-iron nanoparticles are shown in Figure 1.



a b c

Figure 1: Transient temperature (a), oxygen concentration (b) and reactive particle radius (c) profiles at time = 0.08 seconds and Δt=0.001 seconds.

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3A-K – KEYNOTE TALK

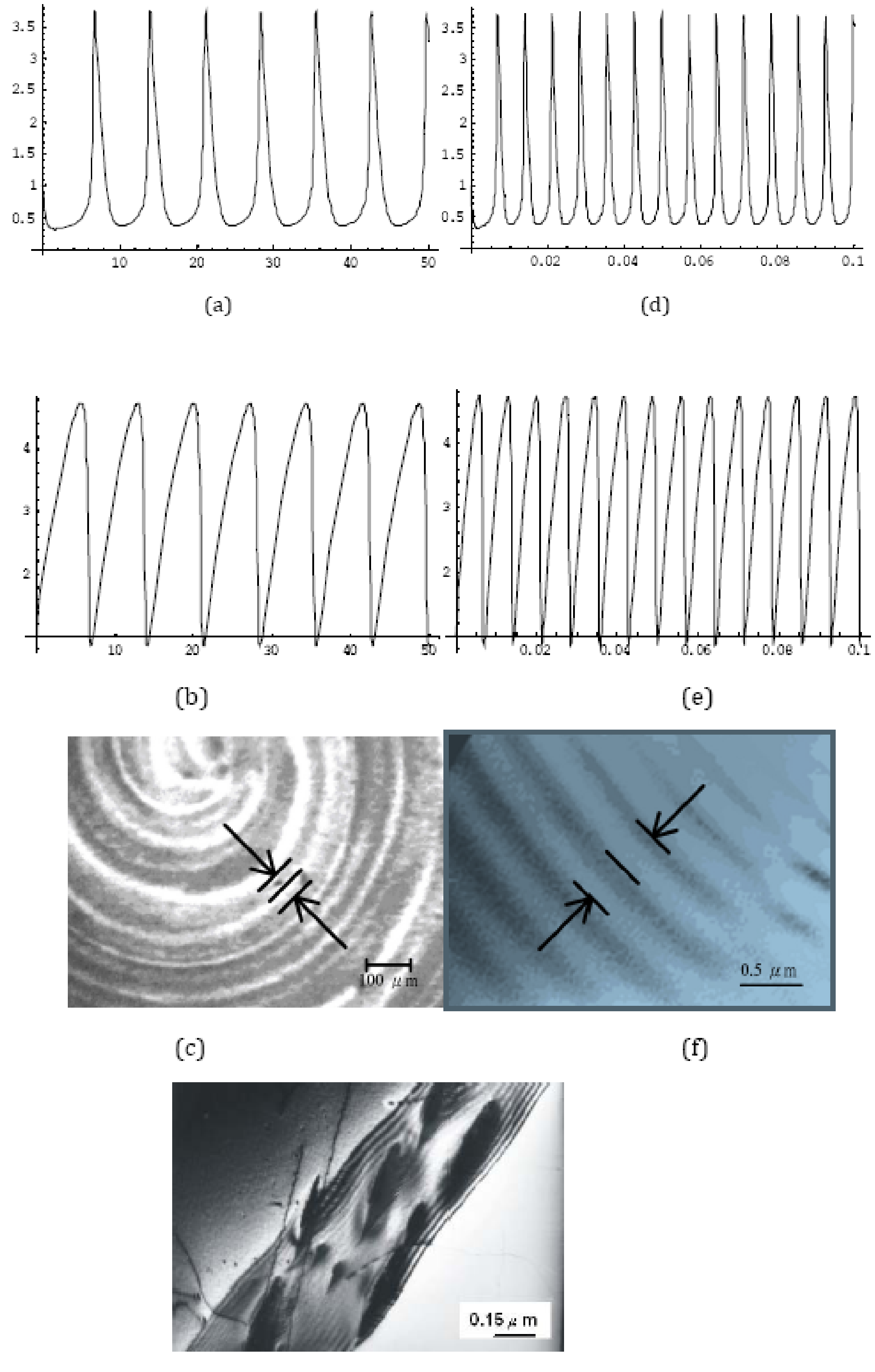
RELATING ENTROPY RATE MODELS TO COMBUSTION KINETIC MODELS FOR NANO-FEATURE FORMATION ESPECIALLY FOR STRUCTURAL AND ONCOLOGICAL USE

Sekhar J.A.[a,] Li H.-P.[b], Weber G.[a], Dey G.K.[c] and Bensah Y.[a]

[a] University of Cincinnati, Cincinnati, OH 45221-0012, USA
[b] Jinwen University of Science and Technology, Hsintien, Taipei County 23154, Taiwan
[c] Homi Bhabha National Institute, Trombay, Mumbai 400 085, India

The manipulation of the rate of entropy generation during a chemical reaction is possible by changing the initial conditions of the same chemical product-forming reaction. These represent different pathways, sometimes yielding nano-features or nano-crystals. Such pathway differences (Sekhar, Li, Dey; Acta Mat, Volume 58, 2010; Sekhar and Weber; Nano- Insights, Issue 3, 2010) are becoming important for the development of nano-metal combinations for use in bulk structural materials or antineoplastic drugs. However, the modeling of such a pathway selection approach has been absent in the small molecule, rapid-reaction-kinetics literature. We will discuss recently developed results for pathway recognitions in inorganic compounds and nanostructured compounds that allow for the manipulation of the size and morphology in micropyretically synthesized objects.

Micropyretic reactions (also called SHS or combustion synthesis reactions) are employed for the synthesis of important refractory materials. We have previously reported on micropyretic synthesis as a possible method useful for near-net-shaped synthesis of intermetallics and composites, sometimes with banded, rapidly-solidified microstructures. The possible synthesis methods for making ceramic armor materials such as Titanium Boride or Boron Nitride and high temperature intermetallic materials such as NiAl, all with embedded nanofeatures are discussed in this presentation. In this presentation, we will discuss example pathways that are available for the novel manufacturing of bulk alloys containing unique nano-features. Such nano-features, when present in bulk alloys are clearly very valuable. This is particularly true for new engineering alloy formulations that are currently under early-stage consideration in application areas that span electronics, medical applications to aerospace, especially because alternate materials processing methods that employ nanopowders or small size starting materials for the manufacture of large objects are fraught with very high energy penalties and potentially dangerous handling concerns along with product-uniformity concerns. Consequently, there is a considerable worldwide ongoing effort to identify and develop novel processing methods that overcome the energy penalty and for handling the potential nano-toxicity. In a recent set of articles (International Journal of SHS, 2010; and Acta Materiala, 2009, 2010) we were able to identify high temperature rapid oscillatory Belousov-Zhabotinsky (BZ) reactions that lead to nanostructure formation in near-net-shaped bulk objects. Depending on the initial conditions chosen, including the initial alloy chemistry, the sub-reactions may display BZ type oscillations. Such oscillations lead to the dispersion of nanoparticles and nano-size banded-faults in a bulk (meter scale) alloy. Some uncommon 100 nm nanobands and nanoparticles in NiAl alloys formed by such rapid reactions are shown in Figure EA1 and compared to equivalent micro-size features and oscillation frequencies from slower BZ reactions. In order for supporting the hypothesis for oscillatory reactions and the paradoxical far-from equilibrium formation conditions that maximize the rate of entropy production via rapid kinetics, several supporting thermal, microstructural, and time resolved synchronous X-ray diffraction reports are also presented. All results point to the possibility of the oscillatory BZ and possibilities of other entropically variable pathways. The BZ is modeled as a simple Brusellator which yields the necessary information on the frequency and length scale of the product microstructure by coupling the macro and microkinetics of formation. The nanoscale features are supported by reaction constants exceeding 10^3 s^{-1}.



Such high reaction constants that are now recognizable in the high temperature micropyretic reactions offer the possibility for obtaining alloys containing nanofeatures, through net-shape *bulk-processing* routes (such as micropyretic routes) and have advantages that have not been explored previously for most materials, except steels. Soft bands and nano-particles in steels have been proposed for making improved ductile steels, but processing limitations have prevented wide scale use. Controlled micropyretic synthesis offers a similar property control possibility for NiAl and possibly for other compounds. A comparison is made for all microstructural and reported property measurements with and without invoking BZ reactions for NiAl. For this presentation, we also discuss our more recent results, on energy efficient pathways, which differ considerably in entropy generation rates during synthesis in the framework of the Prigogine approach of minimum entropy production. The selection of synthesis pathways chosen with entropy production as the key variable is proposed as a unique synthesis differentiator for obtaining the nanostructural features in several important intermetallic alloys for a wide range of medical and structural applications.

Figure 1. The intermediates formed during chemical oscillations establish the length scales for various internal structures whether on a microscale or a nanoscale. There are several sub-reactions typically identified with many reactant to product forming reactions. Oscillations of intermediate concentrations of X and Y are shown in figures a, b, d and e for the Brusselator Model of a four reaction sequence where k_f is the forward reaction constant; the vertical and horizontal axes in (a), (b), (d) and (e) are the dimensionless concentrations of intermediates and time(s) respectively. (a) k_{if}=1.0, intermediate=X, (b) k_{if}=1.0, intermediate=Y, (d) k_{if}=1000., intermediate=X, (e) k_{if}=1000., intermediate=Y. The corresponding micron level and nano level bands are shown in (c) and (f) respectively, [figure (c) from Köehler JM. & Müeller SC., Frozen Chemical Waves in the Belousov-Zhabotinsky Reaction, J. Phys. Chem., **99**, 980-983, 1995 and figure (f) G. K. Dey and J. A. Sekhar, Metallurgical and Materials Transactions B, Volume 28, Number 5, 905-918, DOI: 10.1007].

Figure (g) is a bright-field electron micrograph showing V_2NiAl nano-particles at the low angle fault boundaries in a $Ni_{50}Al_{48.5}$Cr0.5$Fe_{0.5}V_{0.5}$ alloy.

3A-1

KINETICS MODEL OF SHOCK SYNTHESIS PROCESSES

Leitsin V.N.*, Dmitrieva M.A.

I.Kant Baltic Federal University, Kaliningrad, 236041, Russia
* leitsin@mail.ru

The modeling of physical and chemical processes in the reactive medium is based on the concept of physical modeling, taking into account complex features of the initial structure of the real system and the possible physical mechanisms of heat and mass transfer, phase transitions, stress relaxation, etc., providing the evolution of structural-phase state of the system and its reactivity in all stages of synthesis [1]. Exothermic chemical reactions in powder mixtures under shock compression is considered. The macroscopic structure of concentration inhomogeneity of components and specific pore volume formed during the preparation of the mixture and pre-compaction is taken into account. Element of the macroscopic structure is considered as a representative volume of the reacting medium - the reactive cell. Reactive system is represented by heterogeneous system of components with defined structural parameters, physical and chemical characteristics. Material of separate component is homogeneous and isotropic with specified physical properties. The change in the parameters of macrokinetics of chemical transformations due to the dynamic compaction of the mixture, determined by the processes of plastic deformation, destruction of surface layers and the reducing of the reacting components is taken into account. Taking into account the existence of an incubation time of fracture, instant and current damage level of the material particles of the powder mixture, lets sufficiently simulate the process of shock modification on the front of the shock pulse. To take into account the kinetics of the development of powder component damageability, the model of powder medium is adjusted by the introduction of the structure-temporal criterion formulated by Yu. Petrov [2]. The instant component of damage level on the front of the shock pulse and damage level of the material accumulated during the incubation time are separated. This approach allows us to consider the "starting" and the current levels of shock activation of reactive powder components.

The possibility of phase transitions and changes in the aggregative state of heterogeneous components is allowed To simulate the process of achievement of thermal balance during the endothermic phase transition it is assumed that the sink of energy is initiated when the temperature reaches the threshold of phase transformations and is equilibrated by the heat source of mechanical and chemical nature up to the full completion of phase transitions work - the exhaustion of the phase transition in each microvolume of reacting material. It is believed that the processes of phase transitions are characterized by a certain incubation period. We introduce a function that characterizes the part of material transfer from one phase state to another.

This model provided the basis for the development of a computer simulation of coupled processes of mechanical modification of powder mixture in the shock loading process, the macrokinetics of chemical transformations, heat balance, and liquid phase filtering in view of the kinetics of mechanical damageability and phase transitions. All simulation parameters are specified at each temporal step. The simulation takes into account the concentration of components, porosity, and phase composition. We also introduced into the simulation the statistical parameters of dynamic compaction processes in local microvolumes of powder medium.

Product mechanochemical transformations is a composite material composed of the structural elements of the initial mixture components and the reaction product. Linear dimension of the structural elements of the product of chemical reactions depends on the size of the mechanically activated zones of the particles of the reacting components.

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3A-2

MODELLING OF COMBUSTION OF LAYERED GASLESS COMPOSITIONS

Prokofyev V.*[1], Smolyakov V.[2]

[1] Tomsk State University, 36, Lenina ave., Tomsk, 634050, Russia
2 Department for Structural Macrokinetics, Tomsk Scientific Center of SB RAS, 10/3 Academichesky ave., Tomsk, 634021,Russia
*pvg@ftf.tsu.ru

Synthesis of layered compositions is one of the prospective directions of SHS use. To do this one should form starting layered structure from mixtures with various reaction ability and initiate the propagation of combustion wave in the direction, being parallel to the plane of conjugation of layers [1]. Proceeding of melting, crystallization, and capillary spreading processes are possible apart from thermal and chemical interaction between composition layers. In the work following variants of the sample formation in the form of three-layered composition:

I – model of «chemical furnace» – weak exothermal layer is placed between high calorie layers of the sample;
II – model of SHS welding – inner layer, consisting from easy melting inert material, is in contact with outer strong exothermal layers;
III – model of SHS impregnation: inner layer melts and `leaks into porous skeleton from external active layers - donors.

The combination of strong and weak exothermal layers is used to conduct synthesis with the method of «chemical furnace» (variant I). The calorific value of the composition of auxiliary external layer substantially exceeds analogous characteristics of main internal layer that provides the rise in temperature of internal layer. Three main combustion conditions of layered packet were established in dependence on relation of reaction among reaction velocities of layers [2]: control, break-off and induction mode.

For strongly exothermal inner layer coalescence is possible, when a linear velocity of combustion of layers coincides.

One of the SHS method is welding i.e. placement of the object, being welded, between layers of the charge, able to reaction. Isolation from external media and thermal contact with reaction mixture lead to high heating velocity of the material, being welded.

Various conditions of melting of inner layer: contact, full and combined melting was revealed for the sample with inert melting inner layer, bordering with active non-porous layers (variant II). Realization of conditions depends on relation of sizes of inert and active layers, adiabatic combustion temperature, thermal physical characteristics of materials, parameters of phase transition and conditions of heat exchange with external media. Propagation of combustion wave along the substance, able to reaction, which in contact with inert media, depends on conditions of conjugated teat exchange. Propagation of combustion wave is impossible with intensive heat removal from the combustion zone, for example, with decrease in the size of reacting layer. Conditions of transition of reacting system from stable combustion to extinction determine critical diameter.

Melting of inner layer and leakage, under the action of capillary forces, of metal melting into skeleton pores from external layers , lie in the base of obtaining of composite material with gradient structure with SHS method (variant III). The depth of melt leakage, which determines composite structure, depends on size of pores, surface stress, parameters of phase transition and temperature distribution. One can obtain necessary structure of the product, being synthesized, and changing relations between layers of the composition.

The paper is supported by the Russian Foundation for Basic Research (project number is 11-03-00136-á)

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3A-3

3D SIMULATION OF DISCRETE COMBUSTION WAVES: FROM MICROSTRUCTURE TO COMBUSTION

Rashkovskiy S.A.

Institute for Problems in Mechanics, 101/1, Vernadskogo Ave., Moscow, 119526, Russia,
rash@ipmnet.ru

The real SHS systems are the solid powder mixtures with random heterogeneous structure. Combustion of such system cannot be described by homogeneous combustion models because these models do not take into account the heterogeneous structure of the system and connected with them the mechanisms of heat transfer and chemical transformations. The models of discrete combustion waves [1-5] were suggested for simulation of combustion of solid powder mixtures.

A comparative analysis of two kinds of one-dimensional models of discrete combustion waves [1-3] are carried out. The exact solutions for both models that describe the steady-state propagation of combustion wave in periodic systems are obtained. It is shown that both models give practically similar results. Because the real systems have a random structure the discrete combustion model in one-dimensional disordered system [4] was considered. The analysis of discrete combustion wave in such a system is carried out. It is shown that at certain conditions a clearly defined nonuniformity in the burnt front propagation is observed: the combustion occurs in a regime of strong pulsations. In this regime a burnt front moves by jumps: the segments of relatively uniform propagation of the front with approximately constant burn rate are changed into the long periods of front stopping. This fact fully corresponds to experimental observations for combustion of actual heterogeneous systems [2] where the steady-state and pulsating regimes are observed as well and these regimes are changed into each other at changing of the parameters of the system. A behavior of the burn front is similar to Devil's staircase, which appears in researches of fractals. This one allows assuming that the system under consideration has the fractal properties, which usually appears in transitions from deterministic behavior to chaos.

It is established, that burning rate of disordered systems is many times lesser than the burning rate of periodic system at identical average parameters. This means that combustion models of periodic systems can not be used for simulation of discrete combustion waves in real 3D systems with random structure.

To describe combustion in 3D powder mixture the method of numerical simulation of the structure and temporal evolution of burnt zone is developed. The method under consideration falls into three stages. On the first stage, a simulation of solid powder mixture structure [6,7] is performed. On the second stage, the thermal conductivity of powder mixture is calculated. It is shown that a filling of pores between the particles by gas increases the thermal conductivity of the powder mixture many times. On the third stage of simulation the thermal, chemical and mechanical evolution of the particles is considered. The full model includes detailed calculation of (i) heat exchange between contacting particles, (ii) melting and merging of the particles, (ii) ignition, and (iv) combustion of the particles.

For illustration of the method a DNS of combustion of mechanically activated SHS system is carried out in detail. For this purpose the simplification of the model above was made. The particles are considered as unchanged and characterized by ignition temperature. The results of simulations are analyzed and compared with exact solution for one-dimensional discrete combustion wave in periodic and disordered systems. Results of 3D simulations are represented both in the graphical form and as the movies. The results of calculations are compared with experimental data on combustion of mechanically activated systems.

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3A-4

SIMULATION OF COATING STRUCTURE FORMATION ON THE BASE OF CYLINDRICAL FORM

Sorokova S.N., Knyazeva A.G.

Tomsk Polytechnic University, Tomsk, 634050, Russia
ssorokova@tpu.ru

The joining formation between the coating and base or the transitive zone between materials may happen rarely during the synthesis process on the base [1]. To form the transition zone additional heat treatment is required. Moreover under such conditions its not always possible to organize steady self-sustaining process. However the substrate that removes heat from the heating zone may considerably influence on the reaction regimes initiation and layer-by-layer propagation in the solid phase, similar to the effect of inert inclusions, inert rods, or the joined materials on the transformation regimes in such systems.

In this work the two-dimensional model of the coating solid-phase synthesis on base of cylindrical form in conditions of the adjustable heating take into account the kinetic and thermal phenomena is suggested and investigated [2]. As a model system the mix of the titan and aluminum is chosen. The base is steel. The system of chemical reactions is written according to the phase diagram of Ti-Ni [3]. It is considered in the model that chemical reactions are decelerated by the product layer. In macrokinetics for reactions of such type (heterogeneous reactions) special deceleration parameters are introduced [4]. The thermodynamic and physical properties are known from the experimental date or are calculated by special shape. The numerical decision of the problem on each step of time is run two stages. The first stage consists of the solution of the problem of heat conductivity by the method of splitting onto coordinates with the use of linear screw die. The second stage consists of the solution of the kinetic problem by Euler's implicit method. Distributions of temperature and concentration of elements and connections in different time moments for different conditions of synthesis are defined.

In case of technological process when diameter of pressing is less than diameter of basis and the external source heats up only surface of pressing. In initial stage of process the substrate has the most temperature. In the exposed portions it cools down only due to radiation and in the field of the closed pressing due to heat conductivity. In this case it is possible to allocate three stages of synthesis process: 1. - slow increase of products concentration and decrease of reagents concentration (or the induction period); 2. - the reaction acceleration, rapid products accumulation accompaniment merging of reactionary zones; 3. - deceleration and termination of reactions consequently of heat losses and reagent exhaust.

Different synthesis mode of is observed if the pressing surface heats up the source of constant intensity with characteristic radius smaller pressing radius. In this case the heterogeneous field of temperature is formed. Analysis show that at such organization of synthesis process all phases are distributed in coating non-uniformly and there is the semimajor area of not reacted pressing (in consequence of heat losses by radiation). It is unacceptable for practical use. In this case it is possible to allocate following stages of synthesis process: 1. - increase of the product concentration (decrease of the reagent concentration) in the region of external heating; 2. - delay of reaction as result of partial exhaustion of reagents in the region of external heating; 3. - reactions acceleration in consequence of the reactions beginnings from the substrate; 4. -

reactions inhibition accompanied merge of reactionary zones; 5. - deceleration and termination of reactions consequently of heat losses and reagent exhaust.

The third variant of coating synthesis is carried out under conditions when diameter of pressing is equal to diameter of the basis and the pressing surface heats up the invariable source of smaller size. In this case synthesis is initially observed in the region of external heating. For the given technological process it is possible to allocate three stages of synthesis process, it is similar to the first case of processing. The increase in initial temperature of the substrate leads to more total synthesis process. In contrast to the first regime the induction stage appears less that is connected with rapid formation of heating zones sufficient for reaction acceleration. Long appears the final stage on which synthesis completed without external heating due to the heat storage generated at the previous stages and an additional thermal emission in reactions. As a result of synthesis in such conditions heterogeneity of coating structure is not great. So this variant of the process organization can be comprehensible.

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ORAL PRESENTATIONS

B: Structural Macrokinetics of SHS processes

2B-K – KEYNOTE TALK

MACROKINETICS OF FAST REACTIONS IN CONDENSED ENERGETIC MATERIALS

Shteinberg A.S.[1,3], Berlin A. A.[1], Denisaev A. A.[1], Mukasyan A.S.[2]

[1]Semenov Institute of Chemical Physics, RAS, Moscow, Russia
[2]University of Notre Dame, Notre Dame, IN, USA
[3]ALOFT, Berkeley, CA, USA

The most important stage of SHS is reaction between the components taking place in the “solid flame” front. This process is characterized by high temperatures and therefore high rates of conversion of reagents into intermediate and final SHS products. As was shown by Merzhanov and his school, classical isothermic methods of chemical kinetics are absolutely unsuitable for measurement of parameters of fast reactions in condensed energetic materials (EM) including all SHS reagent mixtures. Recently a complex of new non-isothermic methods allowing one to obtain qualitative and quantitative data on kinetics and macrokinetics of fast and super-fast reactions at high temperatures (under static conditions) and at relatively moderate temperatures (under dynamic conditions including low-speed and high-speed impacts) has been developed.

Some specialty methods (including novel ones) are described. Some kinetic and macrokinetic data for high-temperature gasless SHS reactions are given. For the first time, experimental data on kinetics of high-temperature reactions in thermit systems containing micro- and nano-particles are presented. The effect of mechanical pretreatment (mechanoactivation) of the reagents on the reaction kinetics is discussed. In the conclusion, some relevant results on macrokinetics and initiation of combustion and explosion of EM (including SHS-systems) under dynamic conditions are analyzed. Some new results as well as new aspects of the role of mechanochemical processes in impact-induced explosion initiation in such systems are discussed. Some aspects of gasless detonation are considered.

2B-1

MYSTERY OF BORON CARBIDE STRUCTURE

Kovalev I.D., Ponomarev V.I., Vershinnikov V.I., Konovalikhin S.V.

Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Russia
i2212@yandex.ru

Due to unique physicochemical properties boron carbide is widely applied in science and industry. Since 1940 more than 40 publications have been devoted to its structure investigation but the composition of both icosahedron B12 and linear C–B–C group from the point of substitution boron atoms by carbon are not still clear.

In this work we studied structure modifications of SHS boron carbide with various carbon contents by XRD. For the first time boron carbide was synthesized from green mixture with 5-30 at. % C in SHS mode and interval of significant cell parameter changes (7–22%) was determined where additional zone division was observed (Fig. 1).

All the differences between data of cell parameter in literature [1,2] can be explained from the point of structure positions (admixtures, production conditions, ordering, etc). Variety in ways of substitution boron atoms by carbon is one of them (Fig. 2).

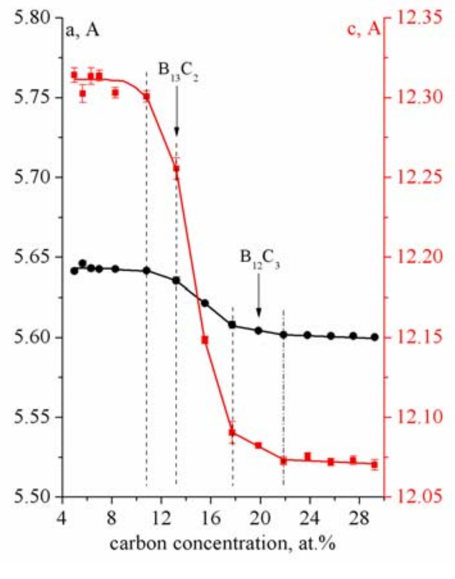

Fig. 1. Cell parameters *a* and *c* as a function of carbon concentration.

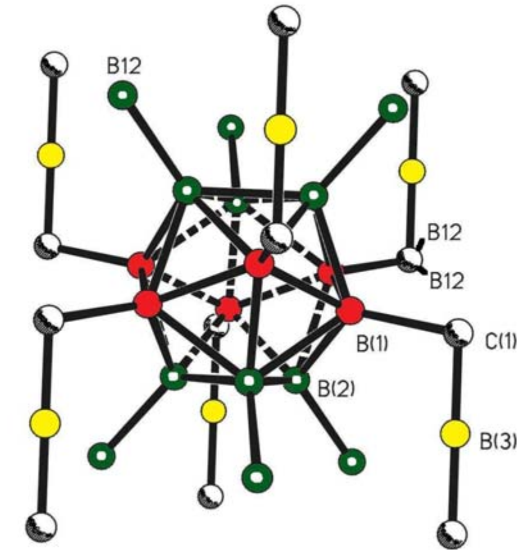

Fig. 2. Fragment of boron carbide structure.

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2B-2

ADIABACITY OF SHS WAVE UNDER THE CONDITIONS OF ROTATION AND CHARACTERISTIC CONCENTRATION LIMITS OF COMBUSTION ON THE EXAMPLE OF OXIDE SYSTEMS

Ksandopulo G.I.

Institute of combustion problems, 172 Bogenbaibatir str., Almaty, Kazahstan.
ksand@inbox.ru

Furnace out combustion of oxide systems, or SHS process, has been used in industry for a long time to produce doped ferroalloys. The characteristic problems are especially noticeable in production of noble ferroalloys – molybdenum, tungsten, vanadium, niobium, tantalum and other with high prices for concentrated raw materials. The main of them are significant losses when depositing metal melt under the conditions of slag viscosity and comparatively high the lower level of the metal content in the raw material concentrate. In this connection, the search for directions eliminating, at least partially, the mentioned drawbacks are actual.

Additional decomposition of smaller particles can be achieved using centrifugal force the value of which may be regulated. The degree of domination of centrifugal force over gravitational one can be stated by division factor $f = \frac{F}{P} \approx 4Rn^2$, where $F = \frac{mU^2}{R}$ and P = mg,

R is radius and n is the number of rotations per minute $U = 2\pi Rn$ is the rotation velocity.

For example, at $n = 8{,}3\ s^{-1}$ domination over the force of gravitational deposition at R = 0,3 m makes up ≈ 80 times. However, conductance of SHS-process with such or more division factor causes characteristic macro kinetic processes in the front of combustion wave.

The characteristic peculiarity of SHS under the conditions of the centrifugal force action is giving back part of the burning mixture enthalpy to the propagating combustion wave in the forn of energy of melted metal particles – one of the reaction products. The metal having a higher density in relation to the melt, under pressure developed by centrifugal force penetrates into the porous space of the fresh reaction mixture and with every rotation widens the reaction zone of the combustion wave accelerating its heat propagation of the combustion wave there arises the situation similar to that described by O.M. Todes when the reaction gets an adiabatic regime which forms in the course of the reaction provided the heat removal becomes negligible small in comparison with the rate of heat generation.

In the considered case it is an accelerated process of combustion. Hence, complete enthalpy of the sample, i.e. sizes, compactness and concentration, of the metal become important. In this connection, without carrying out experiments the following was shown:

1. The existence of characteristic concentration limits at the designed frequency of rotation.
2. The characteristic limiting value of rotation velocity n for the lower concentration limit of combustion under the conditions of SHS.

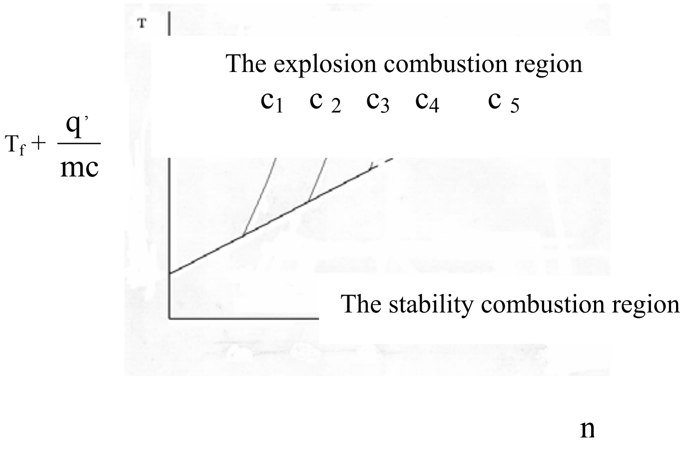
In a whole, the quantitative estimation of stationary combustion boundaries is difficult owing to uncertainty of instantaneous viscosity of the melt and kinematics of filling the porous space. Besides, there is also uncertainty due to the fact that the inhibiting or diluting effect on the reaction of the mass m of the reaction product penetrating into the porous space is neglected. The article states characteristic regularities of the process of centrifugal combustion.

The transition to adiabatic combustion at some limiting concentrations of the metal in the initial burning mixture is shown in the modified Arrenius equation:

$$W = K_0 C_A C_B \exp\left({}^{-E}\!/_{R\left(T_f + \frac{q}{mc}\right)} \right)$$

T_f – the temperature of the flames wave; q – enthalpy of liquid metal and m – his masse had centrifuged to flame wave; c – head capacity.

The decrease in the lower concentration limit of combustion of oxide system under the conditions of rotation is shown. The expected diagram of stable region of combustion is presented figure:



The flame stability region on rotating combustion oxides system ($c_1 > c_2 > c_n$)

2B-3

KINETICS OF THERMITE REACTIONS: Ti/Fe_2O_3 SYSTEM

Lin Y.-C.[1], McGinn P.J.[1], Shteinberg A.S.[2], Mukasyan A.S.*[1]

[1]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA
[2]ALOFT Corporation, 61 Fairlawn Dr., Berkeley, California 94708, USA.
* amoukasi@nd.edu

The kinetics of reduction reactions in Fe_2O_3-Ti heterogeneous system with different grades (micron- and nano-) of Fe_2O_3 powders was investigated by, so-called the electro−thermal explosion (ETE) method [1, 2]. Electro-thermal analysis is the only technique that allows studying kinetics of a rapid heterogeneous gasless reaction at temperatures above the melting points of the precursors. Methodological aspects of the ETE are thoroughly analyzed in our recent publication [3].

The rapid Joule preheating ($>10^4$ K/s) allows thermal explosion taking (TE) place in extremely short time (msec), therefore the reaction can be considered as an adiabatic TE. The ETE process was monitored by the high-speed infrared thermal imaging system, a unique device recording simultaneously the temperature−time profiles as well as depicting precisely the area where thermal explosion occurred (see Figure 1).

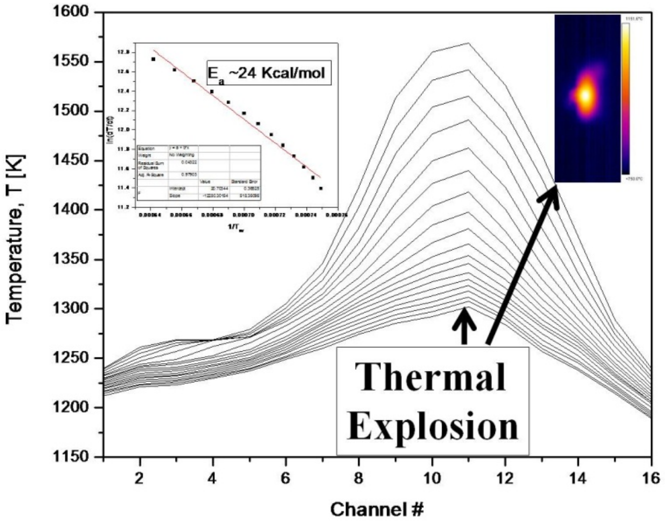


Figure 1: Temperature profiles during TE time span between each profile 0.1 ms; left upper corner: IR image; right upper corner: Arrhenius plot.

Conventional differential thermal analysis (DTA) in the temperature range of 500−1300 K with different heating rates (10−50 K/min) followed by Kissinger method analysis was also conducted to compare high and low temperature kinetics. SEM microstructural characteristics on different precursor morphologies as well as results of EDS and XRD analyses are also discussed. For example, it was shown that reaction systems possess different apparent activation energies for ETA (see upper right corner insert in Figure 1) and DTA conditions (E_a = 24 and 44 Kcal/mol respectively). Comparison of these data with those reported in the literatures is also made. Mechanism for Ti/Fe_2O_3 thermite reaction is proposed.

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2B-4

SYNTHESIS OF TITANIUM-BASED CEMENTED CARBIDES AND BONDING TO STEEL

Matsuura K.*[1], Yu J.[1], Ziemnicka M.[1], Ohno M.[1], Kata D.[2] and Lis J.[2]

[1] Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[2]AGH University of Science and Technology, 30-059 Krakow, Poland
* matsuura@eng.hokudai.ac.jp

Titanium-based cemented carbides such as TiC-Fe, TiC-SS (Stainless Steel), TiB_2-Fe, TiB_2-FeAl, and TiC-TiB_2-Ni were combustion-synthesized from elemental powders under pseudo isostatic pressure in vacuum using an equipment shown in Fig. 1. The synthesized hard particles were homogeneously dispersed in the metal binder phase, as shown in Fig. 2. The thermal energy of the exothermic reactions was used for bonding the reaction products to steel substrate. The size of the hard particles decreased with the increase in the metal binder phase and the increases in the preheating temperature and time before the ignition of the combustion synthesis reaction. The particle size also decreased in the vicinity of the bonding interface because of the heat sink effect of the steel substrate, as shown in Fig. 3. The curved interface between the steel substrate and the synthesized cemented carbide indicates melting of the substrate surface due to the exothermic combustion or SHS reaction. The Vickers hardness number and compressive strength of the cemented carbides varied in ranges from 1000 to 2000 and from 1000 to 3000 MPa, respectively, depending on the composition of the cemented carbide. The bending fracture of the bonded samples always occurred in the cemented carbide area close to the bonding interface showing high fracture strength.

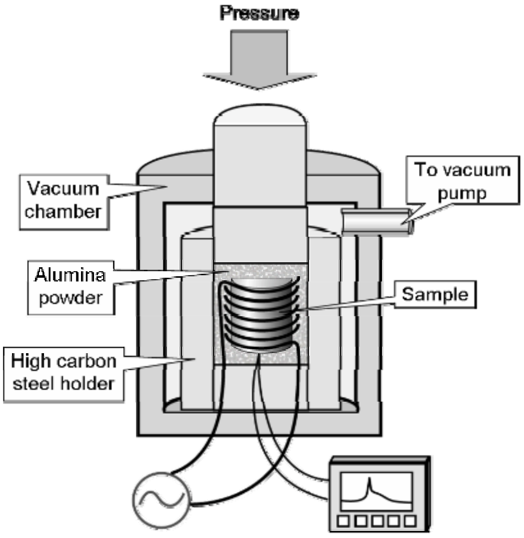

Fig. 1 Schematic illustration of Pseudo-HIP/SHS equipment

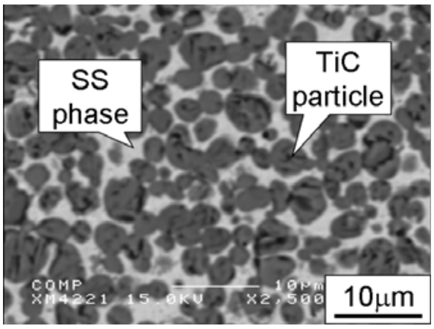

Fig. 2 Microstructure of TiC-30%SS alloy.

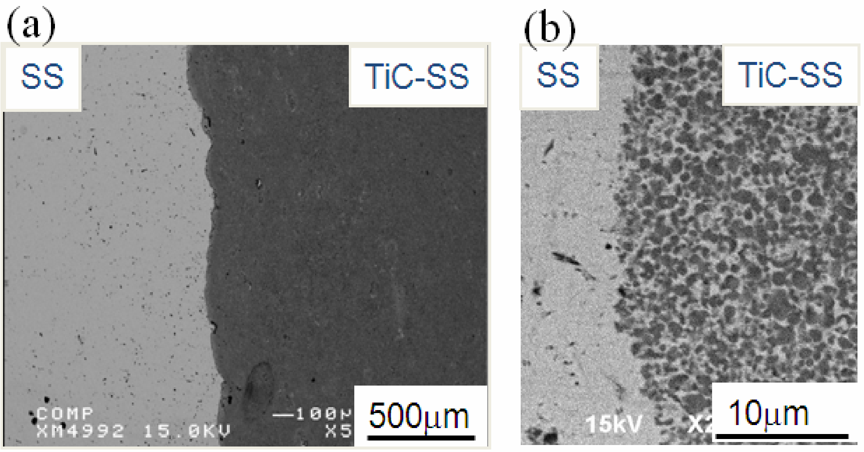

Fig. 3 Interface between SS/TiC-SS joint samples shown at (a) low and (b) high magnifications.

2B-5

SINGLE CRYSTALLINE SILICON NITRIDE NANOWIRES PREPARED WITH SELF-PROPAGATING HIGH TEMPERATURE-SYNTHESIS

Xia M.[1], Ge C.[1,2]*, Hongyan G.[1]

Institute of Powder Metallurgy and Advanced Ceramics, Southwest Jiaotong University, Chengdu 610031, China.
And Institute of Special Ceramics and Powder Metallurgy, University of Science & Technology Beijing,
Beijing 10083, China.
xmdsg@126.com

Defects free single-crystalline silicon nitride nanowires (Si_3N_4 NWs) with high aspect ratio were synthesized through a vapor-solid (VS) mechanism using tungsten as catalyst, with self-propagating high temperature synthesis (SHS) process. In the process, the nanowires were fabricated directly by the reaction between silicon powders and other additives, without using silicon NWs as template nor carbon nanotubes react with silica at high temperature. The as-synthesized Si_3N_4 NWs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED). The as-synthesized Si_3N_4 NWs typically had diameters of ~100nm with a length of several hundred micrometers, and exhibited a smooth and straight surface (figure1). HRTEM images revealed that the NWs is almost transparent, the copper grid can even be seen through the whisker (figure2). Defects such as built-in screw dislocations and stacking faults were not detected, showing a perfect single-crystalline structure, the preferential growth direction was [101] (figure 3). Si_3N_4 NWs with controlled diameter reported in this paper is catalyst by tungsten through a vapor-solid (VS) mechanism, which is quite different from the reported Si_3N_4 NWs. Possible growth mechanism of Si_3N_4 NWs was studied. Results revealed that tungsten plays a significant effect on the growth of Si_3N_4 NWs.

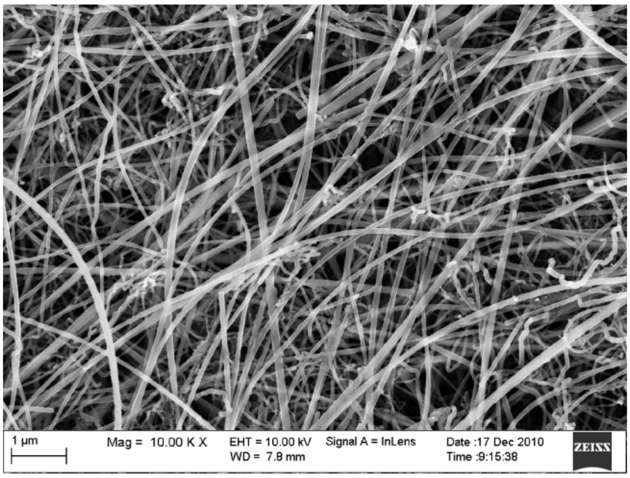

Figure 1. SEM image of as-synthesized Si_3N_4 NWs.

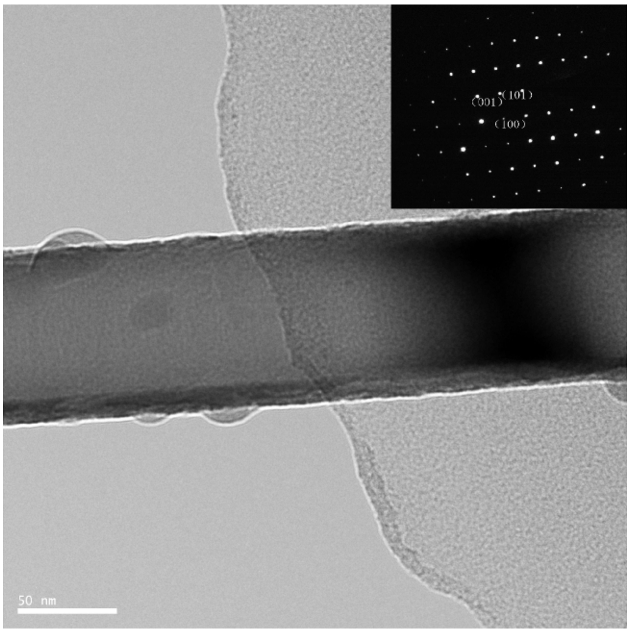

Figure 2 : HRTEM images of the as-synthesized Si_3N_4 NWs. an individual Si_3N_4 NWs, with a smooth and straight surface, no defects are detected. SAED image (inset figure2)also demonstrate a perfect single-crystalline structure.

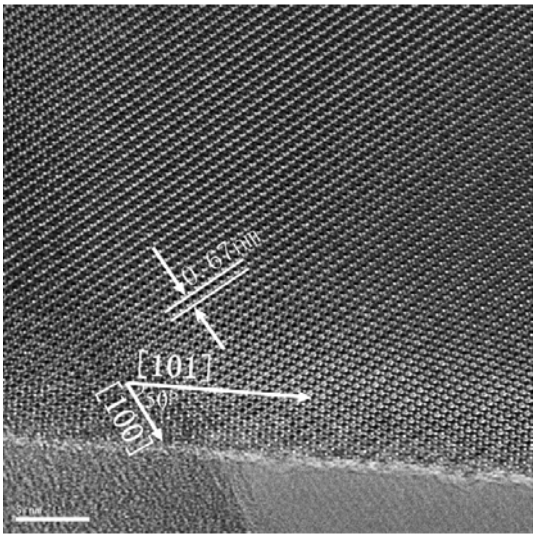

Figure 3 : High-magnification image shows Si_3N_4 NWs grown with the [101] direction.

2B-6

THE COMBUSTION AND STRUCTURE FORMATION IN THE MECHANOACTIVATED TI–CR–B MIXTURE

Patsera E.I., Levashov E.A., Kurbatkina V.V., Rogachev A.S., Kochetov N.A.

National University of Science and Technology «MISIS»
119049, Moscow, Leninsky prospect, 4, 164
patsera_yevgeniy@mail.ru

Investigation of structure formation in the combustion wave mixtures Cr-B, Ti-Cr-B, as well as the composition of the synthesis products was carried out for both pre-mechanically activated (MA) charge, and for not activated.

MA of powders was activated in a planetary ball mill AIR-0,015 with centripetal acceleration - 250 m/s^2 and mass ratio of balls to the mass of the charge - 10: 1. Heat of reaction formation of borides was determined by high-speed calorimeter BKS-4. The effect of initial temperature T_0 on the combustion temperature T_c was detected using a W–Re thermocouple. The burning velocity Uc was inferred from video records.

In the MA mixtures is possible to implement SHS at T_0 = 300 K; in the Cr–29.4%B with τ_{MA} = 1 min sample, this is possible only at T_0 = 525 K; and in the nonactivated Ti-10%Cr-12,6B, Ti-20%Cr-11,2%B, Ti–30%Cr–9.8%B and Ti–40%Cr–8.4%B mixture, it is possible only at T_0 = 393, 494, 523 and 653 K, respectively. For all MA compositions at T0 > 530–540 K, the combustion sources are formed throughout the sample volume (combustion is similar to explosion) and their motion is directed chaotically. For the activated Cr–B and Ti–Cr–B charges, the combustion rate is higher at the same initial temperature than nonactivated charges. For example, for the Cr–29.8% B mixture at T_0 = 525 K, after activation for 1 min, U_c = 1.8 mm/s, while it is 8.7 mm/s for τ_{MA} = 21 min.

For all compositions the relation of burning velocity of the initial temperature has a linear function, as well as the fact that in a certain range then the MA mixture combustion temperature T_c depends very little. For all samples, except for Ti-10'% Cr-12,%B combustion temperature below the melting temperature of the components. Investigation of possible reactions showed that the combustion process goes through the gas phase with the formation of volatile B_2O_2, and transfer it to the surface of metal particles, where the interaction of B_2O_2 with Me formation the boride and B_2O_3.[1, 2] Since the transfer of gas transport is weakly activated process, the dependence of T_c is very weak.

By the SHS method were obtained experimental samples. In the systems Ti-Cr-B established the formation of previously unknown ternary compounds of Cr_4Ti_9B and Ti_2CrB_2.

According to the results of our investigations, were synthesized samples 125 mm in diameter. Proceedings of Ti-Cr-B have a lower residual porosity in comparison with Cr-B (Table 1). The samples have high hardness HV up to 16.1 GPa, and thermal stability up to T = 1273 K and τ = 60 h was for the MA Ti -40% Cr-B, which can also be caused by low porosity (2.2%) and high chromium content. Oxidation follows the parabolic law, when the growth of the oxide film is limited by the diffusion of oxygen through the oxide layer.

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3B-K – KEYNOTE TALK

EXOTHERMIC REACTIONS IN NANO-HETEROGENEOUS SYSTEMS AS NOVEL ROUTES OF SHS

Rogachev A.S.

[1] Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences (ISMAN),
Chernogolovka Moscow region, 142432 Russia
rogachev@ism.ac.ru

Several new classes of SHS-systems have been developed and reported recently. General property of these classes is use of nano-sized solid reactants, which results in extraordinary reactivity of the well-known SHS-systems. Two types of such systems are overviewed in the present work: multilayer reaction nano-foils and mechanically structured lamellar ribbons.

Reaction nano-foils, commonly produced with layer-by-layer magnetron sputtering, consist of relatively flat altering layers, e.g., Ni/Al, Ti/Al, Nb/Si, etc., with thickness 5 - 100 nm and number of the layers up to several thousand [1,2]. Mechanically structured ribbons can be obtained by mechanical activation of reaction powder mixtures followed by cold rolling [3,4]. They possess irregular structure with randomly intermixed layers of reactants, while thickness of individual layer varies in the range of 50 – 1000 nm. Analysis of newest experimental results, as well as data published in the literature, leads to conclusion that foil and ribbon both may have similar high reactivity, elevated sensitivity and low self-ignition temperature, as compared to the powder mixtures of the same composition. Understanding mechanism of the unusual but similar properties appearance of such different objects represents intriguing puzzle.

Mechanisms of reaction in multilayer nano-foils have been studied at various conditions (slow heating vs. combustion wave) by meats of different complementary methods, including quenching of the reaction wave, high-speed video and thermography, time-resolved XRD and Synchrotron – ray diffraction analysis. It is shown that reaction route strongly depends on the layer thickness and temperature-time profile of the process. When heating rate increases (combustion front) and layer thickness decreases, reaction occurs in one, very fast stage. Most probable mechanism of the stage is direct reactive dissolution of refractory reactant (e.g., Ni or Ti) into the melt of second reactant (Al, etc.), without formation of solid products interlayers. Final product precipitates from the melt as rounded nano-sized grains. Fast grain coarsening takes place immediately after precipitation, resulting into formation of polycrystalline material.
Nature of mechanical activation of the SHS mixtures is not clear yet. Experimentally, the process of structure transformations during mechanical treatment has been studied at all structural levels^ macroscopic (direct observation of the process inside the activator drum), microscopic (evolution of particle sizes and inner microstructure of composite particles), and atomic (crystal structure, defects). These transformations are considered in relation with the reaction properties of mixtures, self-ignition temperature, and combustion wave propagation velocity. It is shown that high reactivity of the activated mixture correlates with the presence of active composite particles (even small fracture of such particles can initiate reaction in the whole mixture). High sensitivity of the composite lamellar particles can be explained, in turn, by presence of nano-sized active sites on the boundary between reactants inside the particle. This sites appeared due to slicing and friction of one reactant on the surface of another reactant.

Thus, formation of active nano-sites can be considered as a possible cause of the extraordinary reactivity both for the magnetron-sputtered foils and mechanically structured ribbons.

This work is supported by RFBR grant 10-03-00217.

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3B-1

MODIFICATION OF SHS PARAMETERS VIA A MECHANICAL ACTIVATION IN VARIOUS INTERMETALLICS

Gallet I., Baras F., Bernard F.[1].

[1] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS / Université de Bourgogne – 9 ave.
A.Savary BP47870 - 21078 Dijon cedex, France
fbernard@u-bourgogne.fr

A mechanical activation on reactant powder mixtures as a precursor stage to self-propagating High-temperature Synthesis (SHS) leads to the formation of nanostructured porous materials [1]. In particular, nanostructured agglomerates (agglomerate with a micrometric size composed of a nanocristallites mixture) which are formed during the high energy ball milling process may be considered as nano-SHS reactors [2]. In fact, the mechanical activation step was found necessary (i) to modify the thermal parameters of the combustion front (i.e. combustion front velocity, thermal heating rate,...) in the case of various intermetallics [3] and (ii) to initiate a combustion front in the case of systems having a low exothermicity [4].

In this paper, some examples from intermetallic systems (Ti/2B/Al, Ni/Al and thermites) will be investigated in order to illustrate the influence of the mechanical activation on thermal and kinetics aspects of SHS reaction. Moreover, the nature and the microstructure of SHS end-products will be also reported.

However, the control of the mechanical activated mixture features and, the understanding of the mechanical activation role on SHS parameters are essential for producing SHS end-products with expected microstructure [5].

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3B-2

RESEACH IN THE NONLINEAR SELF-CONSISTENT SYSTEM “MECHANO-ACTIVATED POWDER MIXTURE OF TI-NI – EXPLOSION WAVE – SYNTHESIZED PRODUCT”

Shkoda O.A., Raskolenko L.G.

Department for Structural Macrokinetics of the Tomsk Scientific Center of Siberian Branch of the Russian Academy of Science, Tomsk, 10/3 Akademichesky ave., 634021, Russia
caryll@english.tsc.ru

The work represents the holistic and system approaches to process experimental data for the processes taking place in the self-consistent system “mixture of Ti-Ni mechano-activated powders – explosion wave – synthesized product». There are three subsystems united for one purpose. It is the formation of an explosion wave accompanied by the formation of TI-Ni alloys, compounds, and solid solutions. Subsystem characteristics influences on the behavior of a separate and combined system. For an example, the typical peaks of a fragile fraction in the frequency distribution curves stimulate the similar peaks in the temperature characteristic curves of an explosion wave due to the change in mechanical activation time. The temperature characteristics are the maximum temperature of thermal explosion (T^o_{max}), critical temperature (T^o_{crit}), and temperature of an initial reaction (T^o_{init}). The initial temperature is chosen by the system when the mechano-activated mixture is being heated continuously. The sharp "breaks" in the titanium - nickel compounds are observed in the synthesized product for the same time moments of mechanical activation.

The dynamic structures were plotted in three ways: attractor type [1], through the "clouds" of experimental data [2], and self-similarity of Bernoulli diagram [3].

Fig. 1 illustrates the frequency diagram for the fraction sizes after grinding in a planetary mill. Fig. 2 shows the wavelet diagram consisting of three zones separated from each other by sharp "peaks" in the «temperature - time of mechanical activation» coordinates. Every zone has 5 trajectories directed to one attractor. The number of trajectories was determined by three heating rates and two sizes of initial nickel powder.
Fig. 3 illustrates the reflexion of third subsystem state in the «TiNi content - time of MA» coordinates. In this case the data cloud curves are used.

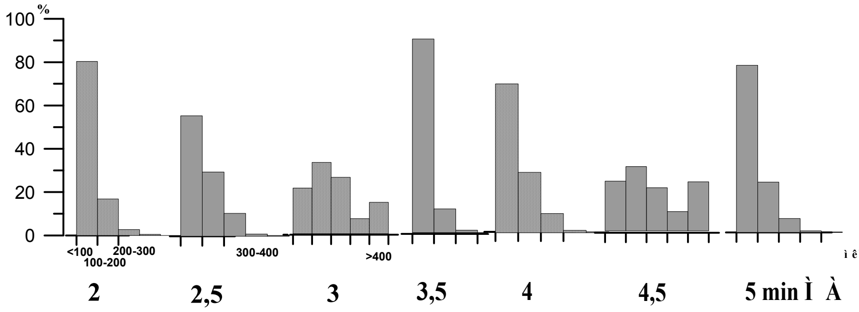

Fig.1. Histogram of the size fraction distribution versus the time of mechanical activation.

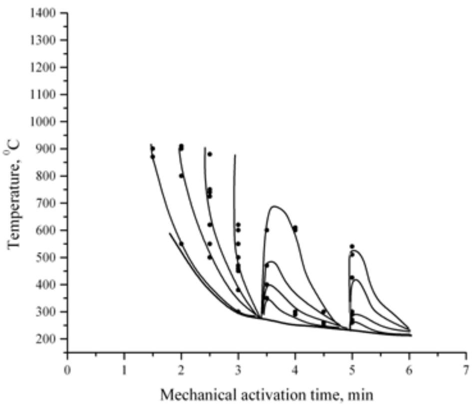

Fig.2. Wavelet is the state diagram in the «temperature - time of mechanical activation» coordinates.

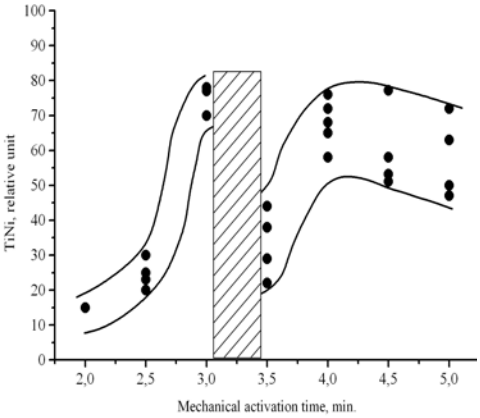

Fig.3. The TiNi content in a product as a function of mechanical activation time.

Conclusions: The behaviour of the nonlinear system «Mechanoactivation - explosion - synthesis» evidently complies with synergetic rules.

The optimal mechanical activation times were revealed to produce needed phase compositions.

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3B-3

ACTIVATED COMBUSTION FEATURES IN THE Ni-Al SYSTEM

Sloyan L.H.[1], Baghdasaryan A.M.[1,2], Khachatryan H.L.[1], Hobosyan M.A.[2], Grigoryan Y.G.*[2], Niazyan O.M.[2], Kharatyan S.L.[1,2]

[1] Yerevan State University, Yerevan, 1, A. Manukyan str., AM- 0025, Armenia
[2] A.B. Nalbandyan Institute of Chemical Physics NAS RA, Yerevan, 5/2, P. Sevak str., AM-0014, Armenia
*yeva@ichph.sci.am

Nowadays several methods are developed for promoting the combustion processes. Among these methods mechanical activation (MA) and chemical activation (CA) approaches are used most widely. These methods enable to control the combustion conditions; hence govern products microstructure and phase composition.

In this work CA method is used and the combustion, phase and microstructure formation laws in Ni-Al system are explored. Polytetrafluorethylene (PTFE) was used as a chemical promoter. The efficiency of CA was evaluated by varying the amount of promoter. Two type of Al were used as initial reactants: Al powder with particle size less than 40 μm (further marked as Al_{cr}), and fine-powdered Al (particle size less than 5 μm, further marked as Al_f). According to experiments the combustion did not take place when Al_{cr} was used. When Al_f was used, rather than Al_{cr}, the interaction took place in the self-sustaining mode; however in this case the reaction did not proceed completely and the end-products contain some amount of non reacted initial reactants. Moreover, in this case the end-products are mainly agglomerated. For the purpose of governing the microstructure of the end-product the CA was applied. Thus, using negligible amount of PTFE (less than 0.4 wt %) results in formation of pure NiAl. In order to obtain better understanding of combustion characteristics in the system under study, it is essential to have a clear picture of reaction mechanism. For these purpose thermogravimetric and differential thermal analyses for the (i) Al + Ni, (ii) Al + Ni+PTFE systems are performed (Fig. 1). When heating of Al+Ni mixture an exothermal interaction is observed just at Al melting point 660°C (Fig.1,(i) curve). According to XRD the end product of this interaction mainly consists of Ni_2Al_3 and NiAl phases.

In the Al+Ni+PTFE system, according to DTA trace, three exothermic and one endothermic effects are recorded ((ii) DTA curve).

As can be seen the first exothermic effect fits with decomposition temperature of PTFE. This leads to the conclusion that just after decomposition of the PTFE (520-610°C), Al reacts with the yielded compounds (please refer to Fig.1 stage 1, DTA curve), otherwise the endothermic effect would be recorded (decomposition of PTFE is endothermic). According to XRD analyses of quenched samples, the end-products mainly consist of non reacted Ni and Al; small amount of some aluminides were detected too. At higher temperature (Fig.1, stage 2, DTA curve, 620-650°C) a second stage of the reaction was recorded. According to XRD analyses, the product of second stage mainly is the Ni_2Al_3 phase. It must be noted that at this temperature the reactants are solid, and thus, the reaction takes place in the solid phase. The participation of gas phase also is not excluded. At 660°C Al melts (stage 3, endothermic effect), then follows exothermal reaction where the curve is much broadened (reached up to 880°C, stage 4). The end-product of the 4th stage was mainly NiAl. One can assume that in this stage the reaction between Ni_2Al_3 and Ni took place.

Summarizing, one can conclude that by application of a chemical activation approach it is possible to synthesize pure NiAl intermetallic compound.

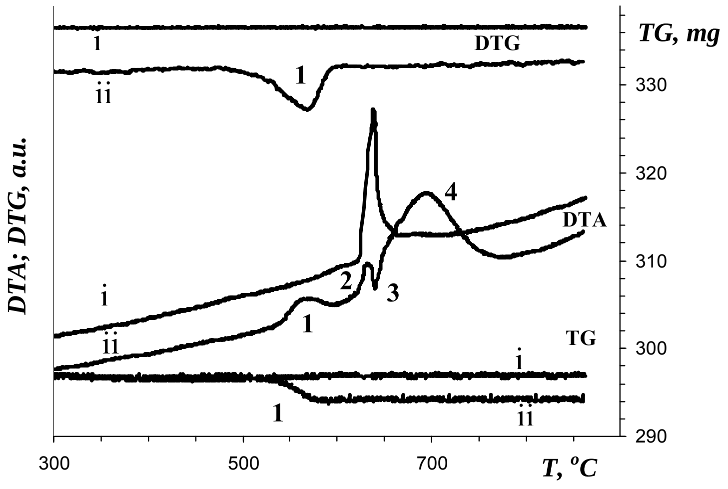

Fig.1. DTA study of Al-Ni (i) and Al-Ni-PTFE (ii) mixtures in He atmosphere; V=20°C/min.

3B-4

SOME THERMODYNAMIC ASPECTS FOR SHS OF CAST ALLOYS AND EXPERIMENTS UNDER NORMAL AND HIGH GRAVITY

Derin B.*[1], Altinordu O.[1], Alkan M.[1], Sonmez S.[1], Yücel O.[1],
Sanin V.N.[2], Andreev D.E.[2], Yukhvid V.I.[2]

[1]Istanbul Technical University Metallurgical and Materials Eng. Dept.,34469,Maslak, Istanbul, Turkey
[2]Institute of Structural Macrokinetics and Materials Sciences, ISMAN, Chernogolovka, Moscow Region, Russia
*bderin@itu.edu.tr

The thermodynamic aspects of cast alloys and some experiments via self-propagating high temperature synthesis methods were studied by investigating the effects of normal and high gravity conditions. In this study, the modeling of the SHS processes were carried out by using FactSage 6.1 thermochemical software in order to calculate adiabatic temperatures and molar composition changes of the cast alloys such as Ni-Cr-Al, Ni-Co-Al and Co-V-Al. The advanced thermochemical simulations of the reactions were investigated in detail including different ratios of initial mixtures, appropriate flux, heat sinker or increaser additions as well as different initial temperatures in order to reduce the number of experiments. A small example from the simulation studies is shown in Figure 1.

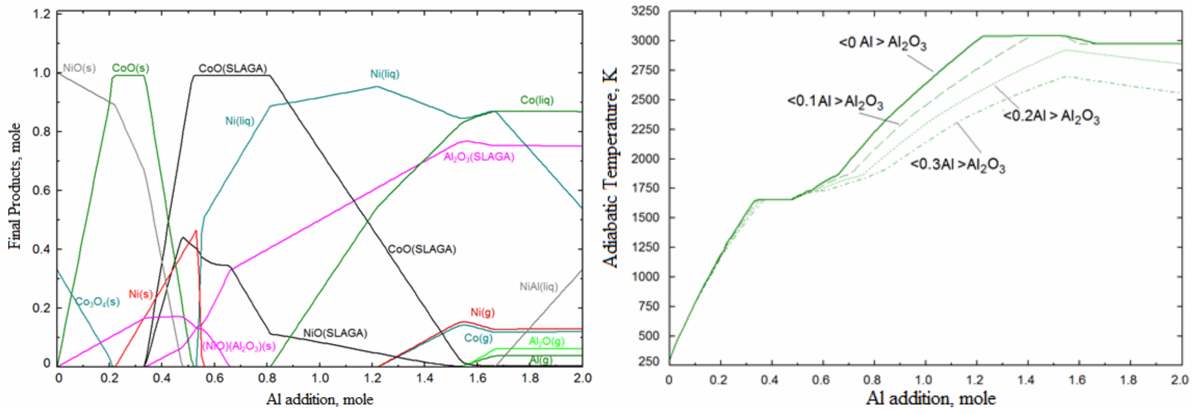

Figure 1. Possible product composition change and estimated adiabatic temperature values of SHS reaction of initial NiO:Co_3O_4:Al mixture with molar ratios of 1:0.33:<0-2>.

After suggested conditions were simulated with the advanced thermochemistry program, the optimum parameters (adiabatic temperature, initial temperature, ratio of initial metal oxides, flux, heat changers etc.) of the above mentioned cast alloys were determined experimentally.

SHS-processes were carried out in the open/closed crucibles (a = 1-g) and also in radial centrifugal machines (a = 1 - 400-g). At the end of SHS experiments, a good separation between multi-phase alloys and slag phases were occurred.

In the experiments with under normal earth-gravity conditions (1-g), the influences of the initial compounds ratio, functional additives (flux, heat sinker or increaser materials), initial temperature, and grain size on combustion regularities, chemical conversion, and the structure and microstructures of above mentioned SHS-produced Ni, Co, Cr based alloys were examined.

The re-melting and purifying studies of the SHS-alloys were also carried out in order to obtain end-products.

The control of characteristics of SHS-processes (combustion velocity, combustion temperature, degree of separation of liquid metal and oxide phases) and products (chemical and phase composition, structure and microstructure etc.) were carried out by variation of initial mixture composition, functional additives, particle size of reagents, under higher gravities provided with centrifugal force up to 400-g.

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3B-5

MACROKINETICS OF SHS-PROCESS UNDER THE EFFECT OF CENTRIFUGAL FORCE

Ksandopulo G.I., Baideldinova A.

Combustion Problems Institute - 172, Bogenbai batyr St., Almaty, 050012, Kazakhstan
abaid@inbox.ru

Widening the range of SHS usage base on combustion with the aim to obtain impurity-free metallic alloys, special ceramic materials with enhanced strength and thermal characteristics on account of effect of centrifugal acceleration is a practical task of this investigation. The employment of centrifugal force in SHS-method in layer oxide systems opens the prospect of using high temperature interactions for creation of a wide range of target products differing in composition and properties.

On the basis of the principle scheme used in the carried out investigation we have created a rotation reactor taking into account the conditions under which the processes proceed in it: a high temperature of SHS-reactions – up to 3000 K; a high rotational speed – up to 15 000 r/min. In the course of the carried out investigations centrifugal acceleration varied within 35 – 2000g/ alundum glasses jr quartz tubes with the diametr of 35 mm and length of 130 mm were used as crucibles for the reactor. Mechanical strength is provided by placing the crucible in a metallic shell closed by covers on both sides. After the system acquires the designed frequency of rotations, an electric impulse is applied to the upper layer of the reagents mixture to initiate the process of combustion.

Theoretical description of physico-chemical processes which place in a closed reactor rotating with a high angular speed is based on the notions on decomposition of the reduced metal drops in a viscous medium of melted slag according to the equation of Adamar-Rybchinski and their intrusion into the granular mixture of initial components compacted by centrifugal forces. The increase in centrifugal acceleration contributes to the increase in the speed of travel of dense particles of the melt and decomposition of smaller drops. Intrusion of hot melt the space between particles of the non-reacted substances contributes to formation of numerous sites for ignition and to the increase of heat evolution per time unit.

This results in the decrease of the lower concentration limit of combustion and the increase in the yield of the reduced metal with formation of a compact ingot. As a result, there appears the possibility to extract rare elrments from diluted mixtures and poor raw materials withot using flues and other additional components polluting the final products of ssynthesis. So, the combustion limit of diluted mixture on the basis of molybdenum oxide changes from 33.6% of Mo in the initial charge under the conditions of natural gravitation to 24.4% at 1000 r/min and to 16.8% at 3000 r/min. In combustion of nicel oxide under similar conditions concentration limit have the values: 46.9% of Ni; 35.2%; 26.0%, respectively.

As far as centrifugal acceleration influences the rate of the melt travel, temperature of the process and viscosity of the liquid phase, it effects the formation of the composition and structure of intermediate and final products of synthesis. The effect of rotation speed on the composition of oxide phases was studied on oxide systems, the combustion of continuous solid solution, e.g. Cr_2O_3 in Al_2O_3 or chemical compounds, such as spinels. Parameters a and c of a hexagonal crystalline lattice of corundum, α- Al_2O_3 make up 4.751 and 12,97 □, respectively, for Cr_2O_3 – 4.95 and 13.57 □. The change in their values can indirectly indicate the changes in chromium concentration in the crystalline lattice of aluminium oxide taking place due to superposition of centrifugal forces.

X-ray phase analysis shows that distortion of the crystalline lattice has its maximum at rotation frequency of 3000 r/min. The same is indicated by observed changes in the macrostructure of synthesis products of the system under study. In addition, the investigations carried out have shown that parameters of the crystalline of solid solutions also change by the length of the sample. The main factors effecting such changes area; the value of centrifugal acceleration depending on the radius of the trajectory of rotating point in combustion front and the increase in temperature along the reactor axis.

Production of pure spinel as an additional precious product of a metallothermic process is a positive practical result of investigation on the process of combustion and self-propagation high temperature synthesis under the conditions of actions of centrifugal acceleration. Thas, the use of centrifugal acceleration in the course of furnace out high temperature synthesis of materials provides a high degree of the contact of reagents, completences of chemical reactions procedure and separation of synthesis products according to their density. Owing to this, it is possible to extract precious metals from low concentrated ores obtaining multicomponent oxide materials possessing high refractory and abrasive properties in the composition of slags.

4C-K – KEYNOTE TALK

STRUCTURAL POLYMORPHISM AND SELF-ORGANIZATION OF COMBUSTION PRODUCTS AT NITRIDE SYNTHESIS BY SHS

Borovinskaya I.P.

Institute of Structural Macrokinetics and Materials Science RAS,
8 Institutskaya ul., Chernogolovka, Moscow region, 142432 Russia
inna@ism.ac.ru

Self-propagating High-temperature Synthesis (SHS) based on combustion processes is close to extreme processes by its character (combustion temperature – 1500-4000ºC, combustion wave propagation velocity ≥0.5-20 cm/s, a substance warming-up rate – 10^3-10^6 K/s, cooling rate – fast quenching, exposure at high temperature) and provides obtaining of substances at various states: amorphous, metastable, solid solutions, melts, etc.

Structures of the synthesized products can undergo different transformations resulting from synthesis and cooling terms.

The paper demonstrates the experimental results of the mechanism of combustion product crystal formation at the synthesis of silicon, aluminum nitrides and SiAlONs. The dependence of structure and phase formation of the combustion products on the terms of the process (high pressure of gaseous nitrogen, up to 100 MPa, combustion at condensed SHS, crystallization from melts) is considered for the systems of silicon-nitrogen, aluminum-nitrogen, and in complicated green mixtures for synthesizing SiAlONs.

A possible formation mechanism of “skeleton” and “antiskeleton” crystallites, dendrite units, metastable phases of various modifications (α- and β-silicon nitride), nanoparticles is discussed. Possible structure formation mechanisms of silicon and aluminum nitrides and SiAlONs are considered for the cases when some additives providing gaseous intermediate product formation are introduced. Combustion product characteristics obtained by various methods of chemical and X-ray analysis as well as morphological studies and power-dispersion analysis by SEM are demonstrated.

4C-1

PREPARATION OF ZINC ANTIMONIDE COMPOUNDS USING SHS

Rouessac F.[*], Ayral R.M.

Institut Charles Gerhardt, UMR 5354 CNRS, Université Montpellier 2, CC 1504 Place Eugène Bataillon, 34095
Montpellier Cedex 5, France.
* Florence.Rouessac@univ-montp2.fr

INTRODUCTION

Development of reliable, low temperature operating thermoelectric generators is becoming necessary today for converting the waste heat arising out of huge numbers of personal computers, automobiles and even from the domestic cooking ovens and hot plates [1]. In a typical TEG device, the conversion efficiency (η_{TE}) is proportional to a quantity called 'figure of merit' (ZT). For all the thermoelectric materials, ZT is theoretically defined as $ZT= (\alpha^2\sigma/k)T$, where σ and k are respective electrical and thermal conductivities and α is the Seebeck coefficient. Thermoelectric materials must have low thermal and high electrical conductivities for achieving high heat conversion efficiency. For this, they have to be as pure as possible. Zinc antimonides are thermoelectric materials with the figure of merit value ZT~ 1.3 in the intermediate temperatures (<400 °C). They are synthesized, usually by melting the high purity metallic Zn and Sb powders taken in the mole ratio of 53:47 with 2–5 at% excess Zn, in an evacuated quartz ampoule followed by granulation and hot pressing [2,3]. However, due to the high temperatures reached during the combustion, SHS is an interesting way to be explored in thermoelectricity science in order to obtain free-impurities materials. But, due to very low exothermicity, the reaction between Zn and Sb is rather difficult to initiate and to propagate. The present work will study the combustion synthesis of Zn_4Sb_3 and ZnSb material and will show the different characterizations including phase stability as a function of temperature using Raman spectroscopy.

EXPERIMENTAL PROCEDURE

The experiments were carried out in a conventional system SHS reactor under argon (between 0.2 MPa and 1.5 MPa). Ignition is provided by a tungsten wire. Zinc and antimony powders were used as reactants, mixed mechanically in a jar closed under argon and compacted in a floating die at a pressure ranging from 75 MPa to 600 MPa. During the reaction, the temperature control was performed thanks to an acquisition card «Hi-speed USB Carrier» coupled with Labview software. In each case, the products were characterized by X-ray diffraction at $2\theta = 20$ to 70° (XPert pro, CuKα radiation). The morphology and composition of the compound were examined by scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy (EDS). Raman spectroscopy (LabRAM - Isa – Dilor) was used to study the stability of the obtained materials as a function of temperature up to 300°C.

RESULTS

The study was made on two different mixtures: Zn+Sb on 1:1 and 4:3 ratios corresponding to the formation of ZnSb and Zn_4Sb_3 phases respectively. Thermal profiles obtained by thermocouples indicated a maximum temperature of 1200°C for both mixtures. The combustion rate was estimated to be around 5mm/s for each synthesis. In order to improve these conditions, compaction pressure and argon pressure were varied: no significant effect was observed on the materials. The macroscopic observation of these compounds reveals melting of a part of the sample. This is in total agreement with the binary phase diagram of the system Zn-Sb which shows melting point of these materials not higher than 800°C.

The XRD patterns of these phases show that for the 1:1 mixture there is only one phase which is obtained: ZnSb. It seems to be more difficult for 4:3 phase. Indeed, X-ray diffractogram reveals a mixture of the two compounds Zn_4Sb_3 and ZnSb. The Raman spectra show the stability of the Zn_4Sb_3 and the ZnSb pellets up to 350°C even after the back to room temperature.

CONCLUSION

These preliminary results encourage continuing this study on the application of the SHS process for the preparation of zinc antimonides. Efforts have now to be devoted to optimization of the final purity of the material in order to control the thermoelectric properties.

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4C-2

IN SITU TRANSMISSION ELECTRON MICROSCOPY INVESTIGATIONS OF SOLID-STATE SYNTHESIS IN THIN FILMS

Zharkov S.M.*[1], Altunin R.R.[2], Semenova Yu.G.[1,2], Moiseenko E.T.[1], Varnakov S.N.[1,3]

[1] L.V.Kirensky Institute of Physics of Russian Academy of Sciences, Krasnoyarsk, 660036, Russia
[2] Siberian Federal University, Krasnoyarsk, 660041, Russia
[3] Siberian State Aerospace University, Krasnoyarsk, 660014, Russia
* zharkov@iph.krasn.ru

Transmission electron microscopy (TEM) allows one to conduct *in situ* heating experiments and to study phase transformations such as solid-solid transitions or chemical solid-state reactions [1]. A specimen can be heated up to 1200ºC in vacuum of 10^{-5} Pa or in gaseous environments up to the pressures of 10^3 Pa. Dynamic events at the atomic level can thus be recorded in real time. It is possible to study the change of the sample morphology by obtaining TEM images, or the change of the phase composition by obtaining electron diffraction patterns during heating. A cross-section of a multilayer sample can be prepared making it possible to investigate interfacial reactions.

In situ heating experiments were conducted with a JEOL JEM-2100 (LaB_6) transmission electron microscope at an accelerating voltage of 200 keV. For the heating experiments a Gatan 652 double tilt heating holder was used. The holder allows heating of a specimen from room temperature up to 1000ºC with a controllable heating rate up to 20ºC/s. The TEM is equipped by a Gatan ES500W Erlangshen CCD Camera which allows acquiring up to 15 frames/s, so that the time resolution of the video recording is ~0.06 s.

The processes of solid-state synthesis in thin bilayer (Al/Au, Al/Ni, Cu/Au, Fe/Si, et al.) and multilayer (Fe/Si) films were studied by *in situ* transmission electron microscopy. The total thickness of a film was from 40 to 100 nm. The goals of the investigation were to study: the structural phase transformations; dynamics of solid-state reactions; change of the morphology during the interfacial reactions; in thin bilayer (or multilayer) films with different composition. The obtained information could help to establish the mechanisms of structural phase transformations, and, to explain the anomalously high rates of the mass-transfer of the reaction products during the solid-state synthesis in thin films.

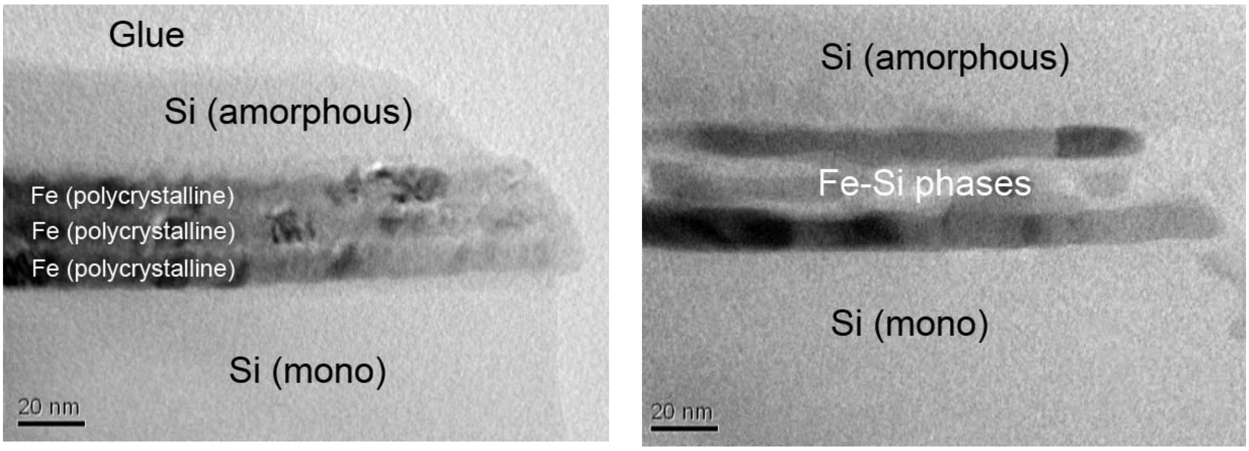

Fig.1 Cross-sectional TEM images of the Fe/Si multilayer film at the initial state, before heating (left image), and, at a temperature equal to 620ºC (right image).

As an example, the result of *in situ* TEM investigation of solid-state synthesis in a Fe/Si multilayer film is demonstrated in Fig.1. The film was obtained in ultra-high vacuum (10^{-7} Pa) and had the following structure: 3×(Fe(9nm)/Si(2 nm)) / Si (substrate). The thickness of an individual Fe layer was 9 nm, and that of a Si layer was 2 nm. As a substrate monocrystalline Si was used. The film was covered by a protective amorphous Si layer with the thickness of 30 nm. A cross-section specimen of the Fe/Si film for the TEM investigations was obtained by the cross-sectional sample preparation method, including cutting, gluing, mechanical thinning, and dimpling procedure, followed by Ar+ ion-beam milling until perforation [2]. The ion milling was performed using a Gatan 691 Precision Ion Polishing System (PIPS). The milling parameters were 5 keV, 25 μA ion current at a milling angle of 6° with respect to the specimen surface. A TEM bright-field image of the cross-section of the Fe/Si sample before heating is shown in Fig.1 (left image). The sample was heated from room temperature up to 750ºC at the heating rate of 10ºC/min. Fig.1 (right image) shows the Fe/Si cross-section TEM image at T=620ºC.

This work was supported by the Russian Foundation for Basic Research (grant # 10-03-00993).

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4C-3

COMBUSTION SYNTHESIS OF WC/C & Mo_2C/C CATALYTIC SYSTEMS

Zurnachyan A.R.[1*], Mnatsakanyan R.A.[1], Manukyan Kh.V.[2], Kharatyan S.L.[2]

[1] A.B. Nalbandyan Institute of Chemical Physics NAS of Armenia, 5/2, P. Sevak str., Yerevan, 0014, Armenia
[2] Yerevan State University, 1, A. Manukyan str., Yerevan, 0025, Armenia
A_Zurnachyan@yahoo.com

It is well known that transition metal carbides (WC and Mo_2C) possess catalytic activity in many reactions [1]. In recent years in addition to the traditional methods new methods were suggested [2] for synthesis of carbides with high specific surface area. In this research new catalytic systems, based on carbon coated tungsten carbide (WC/C) and molybdenum carbide (Mo_2C/C) were prepared under the *impregnation combustion synthesis* (ICS) method [3] and the effect of combustion temperature and precursor's nature on the phase composition and microstructure of tungsten and molybdenum carbides were studied. For this purpose carbon black (Vulcan XC-72R with specific surface $250m^2/g$) was impregnated with the tungsten and molybdenum water-soluble peroxo-complexes as described in [4,5] with the followed drying and calcination. For synthesis of desired end products a magnesiumathermic reduction of obtanined intermediates was performed in combustion mode. The combustion experiments were performed in the laboratory constant pressure reactor in Ar atmosphere (P=2 MPa).

Prior to the experiments preliminary thermodynamic analysis for WO_3-3Mg-C and MoO_3-3Mg-C systems were performed by "ISMAN-THERMO" software. The results of analysis shown that within the 1550-2500°C interval W_2C carbide is the main equilibrium product of reaction. At temperature below 1550°C WC phase is stable in this system. Whereas in the MoO_3+3Mg+C system, Mo_2C is a stable phase in the whole temperatures range and Mo_3C_2 – at temperatures above 2000°C.

Experimental investigations have shown that combustions of WO_3-3Mg-C and MoO_3-3Mg-C mixtures proceed quite violently. Sodium chloride was used as a diluent agent to moderate combustion temperature for both systems. Controlling the process temperature by this way it is possible to regulate phase composition and microstructure of the resulting products. It is worthy to note that the phase composition of products can be regulate both by changing temperature regime of interaction and, which is more important, by carbon amount. From this point of view the phase composition of products depending on combustion temperature and carbon amount was studied. The obtained carbides were investigated by SEM and XRD analyses. BET method was used for controlling products' specific surface area. The results of XRD analyses have shown that depending on the combustion parameters carbides with different phase composition can be obtained: WC with $11m^2/g$, W_2C with $60m^2/g$ and Mo_2C with $4m^2/g$ specific surface areas. The synthesized carbides were tested in catalytic reactions of (i) isopropyl alcohol dehydration (very high activity), (ii) cyclohexane dehydration and (iii) dry reforming of methane.

(MoO_3+3Mg+C)+*n%NaCl*					
n, %	T_c, °C	2θ	*peak's half width*	2θ	*peak's half width*
0	>2500	34.52	0.25	39.46	0.22
40	2120	34.56	0.1	39.57	0.125
70	1950	34.35	0.09	39.38	0.105
90	1900	34.38	0.08	39.41	0.095

It is known that the geometric factor has great influence on the catalytic activity. Influence of combustion temperature for MoO_3+3Mg+C mixture on the interplanar spacing and microstructure of crystals are shown in the table. It is seen that the combustion temperature affects not only on the interplanar spacing, but also on the perfection and size of crystals, as seen from the change of diffraction lines halfwidth.

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4C-4

COMBUSTION SYNTHESIS AND CHARACTERISTICS OF ALUMINUM OXYNITRIDE CERAMIC FOAM

Zheng Y.T.*, Zhou T., Zhang X.K., He X.D.

Center for Composite Materials and Structures, Harbin Institute of technology No.92 West Da-Zhi Street,
Harbin, P.R.China
* zhengyt@hit.edu.cn

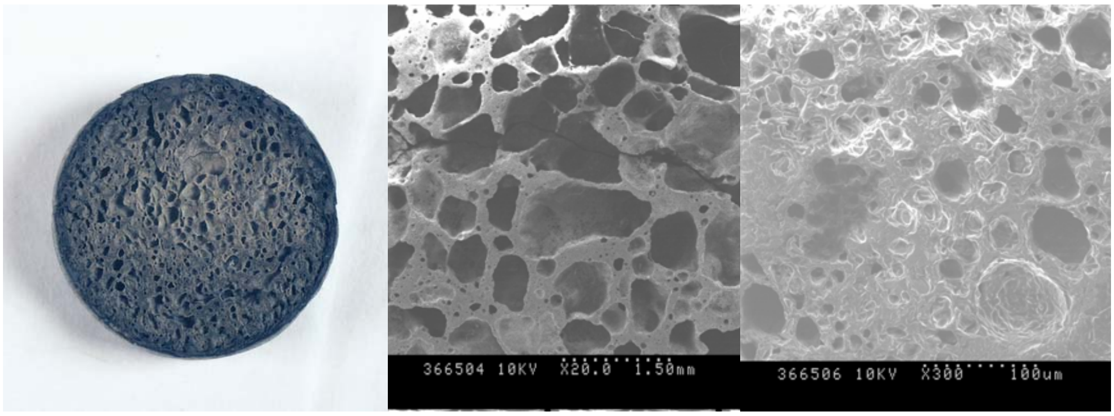
Foam ceramic is a novel material with excellent performance for application in molten metal filter, catalyst carriers, bioceramics and high-temperature thermal-insulation field because of its high-temperature stability, corrosion resistance, high porosity (70%-90%) and low density (0.3-0.6g/cm^3) [1]. As a solid solution of AlN and Al_2O_3, AlON ceramic is an ideal candidate for high temperature structural materials because of its good high temperature properties, thermal shock and oxidative resistance [2]. At present, most foam ceramics were prepared by the methods of addition of pore-forming agent, foaming process, polymeric sponge impregnation and sol-gel process [3]. These preparation methods used to fabricate foam AlON are highly involved and complicated, resulting in low productivity, high costs, and manufacturing problems during scale-up.

Combustion synthesis (CS) (self-propagating high temperature synthesis, SHS) provides a cheap and efficient method for the manufacture of inorganic refractory materials due to the advantages of high-temperatures, fast heating rates, short reaction times and no external power supply. AlON powder has been prepared by combustion synthesis under low air pressure using Al and Al_2O_3 powder as starting materials [4], however, only a few papers have reported the preparation of foam AlON ceramics by combustion synthesis [5].

In this paper, foam aluminum oxynitride (AlON) ceramics were prepared by combustion synthesis using Al and Al_2O_3 as starting materials under high nitrogen pressure. By introducing $Al(NO_3)_3$ into reactants as active pore-forming agent, foam AlON ceramics with well-distributed pores were fabricated efficiently and cost-effectively. The combustion synthesis reaction in this study can be expressed as follows:

$$\mathrm{Al + Al_2O_3 + Al(NO_3)_3 + N_2 \rightarrow AlON(foam) + Q} \qquad (1)$$

AlON foam ceramic was synthesized under 50MPa N_2 pressure in the super-high pressure SHS reactor. The combustion temperature, ranging from 2165 ºC to 2650 ºC, was higher than the melting point of Al_2O_3 (2065 ºC). At the same time, the massive gas decomposed from $Al(NO_3)_3$ can produce high pressure and the pressure increased as the temperature rised. The high pressure separated the gas from the liquid AlON and formed open pores. We also can observe fractal character of the pore structure of the final product. The influences of $Al(NO_3)_3$ content on the combustion process and pore structure were studied. Experiment results show that increased $Al(NO_3)_3$ content can lead higher pressure and temperature, this is favorable for forming better pore structure.



a b c

Fig.1 The apperance and the micro structure of the product. a: the general appearance, b: ×20, c: ×300

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4C-5

STRUCTURAL STATE OF Ti–Al AND Ni–Al POWDER MIXTURES UNDER MECHANICAL ACTIVATION

Kovalev D.Yu.*, Ponomarev V.I., Kochetov N.A.

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Russia
* kovalev@ism.ac.ru

The influence of mechanical activation (MA) on the structural state of a Ti–Al and Ni–Al powder mixtures investigated**.** Kinetic features of accumulation of deformation defects in reagents under MA are consider. Deformation degree and structure of mechanically activated Ti–Al and Ni–Al powder mixtures was characterized by X-ray diffraction analysis. The size of coherent scattering areas (CSA) and microstresses [1] were calculated based on XRD data (Fig. 1).

Mechanical activation (planetary mill, 90 *g*) caused material stress, decreased the size of CSAs, and partial amorphization of material crystal structure. After 8-min MA, microstress in the Ni–Al mixture was 500 MPa for Ni and 200 MPa for Al; in case of the Ti–Al mixture (after 20 min MA), 200 and 180 MPa, respectively.

A decrease in Al CSA was 100 nm after 8-min MA for Ni–Al and 40 nm after 20 min MA for Ti–Al. With increasing MA duration, a marked drop in the intensity of Al diffraction peaks and stronger background was observed. In case of Ti–Al mixture, the Al diffraction lines disappeared in 25 min of MA. This effect associates with an Al transition to an x-ray amorphous state.
Preferred orientation of crystal Ni и Ti under MA was observed. In case Ni–Al mixture a rolling texture along the (111) plane of maximum packing are formed. For Ti-Al similar texture along the (100) Ti plane are realized. Metallographic analysis showed the formation of flaky composite particles as a result of joint deformation.

Within a composite particle, lengthy phase interfaces were made up between mixture components. Polycrystalline layers have preferred orientation: (111) for Ni and (100) for Ti. The crystallographic conformity between the structural parameters of Ni, Al and Ti, Al is considered based on the appearance of crystallite texture during MA. It was assumed that the damage of long-range ordering in Al structure and local temperature rise during MA leads to correspondence between the parameters of crystal structure of mixture components. This is one of the factors causing a change in reactivity of powder mixtures in particular to decrease of ignition temperature [2].

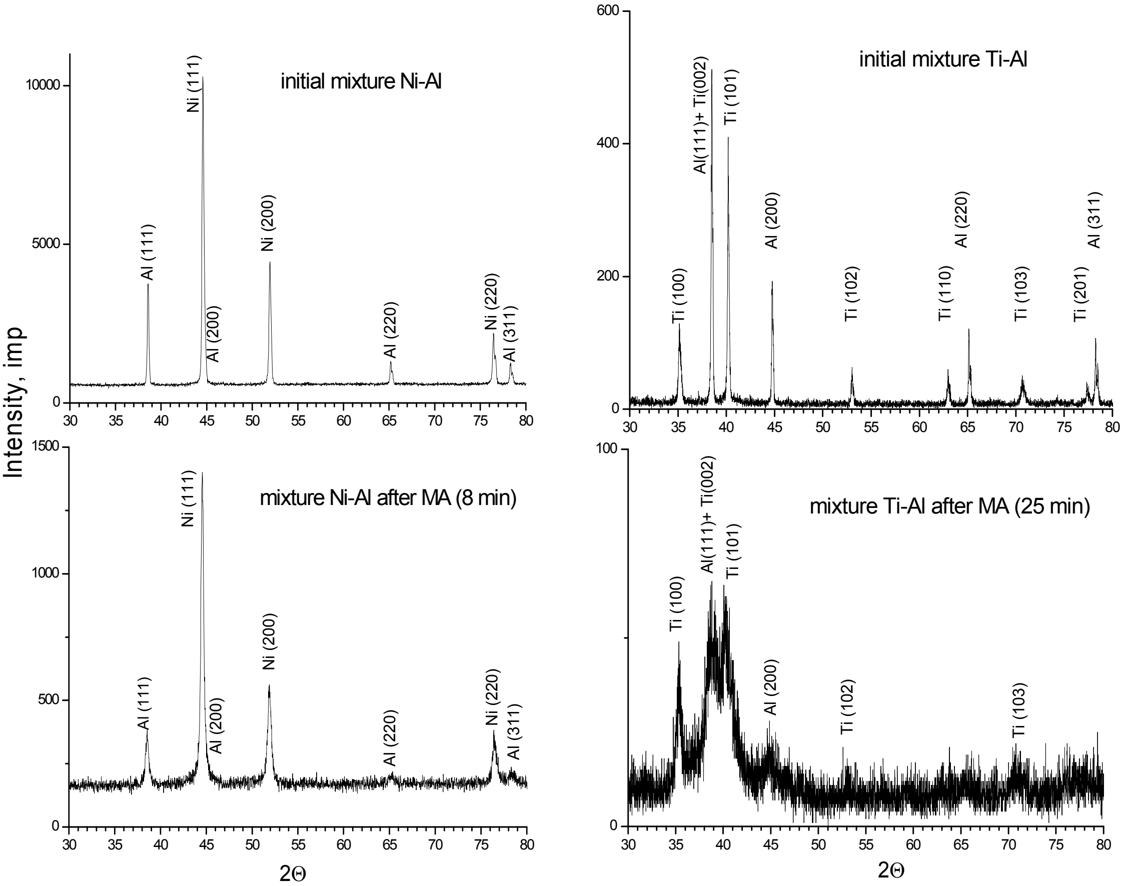

Fig.1. Diffraction patterns of Ni–Al and Ti–Al before and after MA.

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ORAL PRESENTATIONS

C: Chemistry and Technology of SHS processes

7A-K – KEYNOTE TALK

COMBUSTION SYNTHESIS OF ALN POWDER TOWARDS HIGH THERMAL CONDUCTIVITY CERAMICS THROUGH MICROWAVE SINTERING AND REHEATING

Chung S.L.*[1], Hsieh C.Y. and Chang C.W.

[1] Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101, Taiwan, ROC.
*slchung@mail.ncku.edu.tw

Aluminum nitride (AlN) has been acknowledged as an important industrial material because of its unique combination of the properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, moderately low dielectric constant, good thermal shock resistance and good corrosion resistance.[1,2] It has been considered for many applications such as a filler for EMC (epoxy molding compound) for microelectronic encapsulation, substrates for semiconductor chips, and an insulating material for RF and microwave packages.[3,4] Recently, it is also considered[3] for application as a loading substrate for high power LED chips because of its high thermal conductivity.

A combustion synthesized AlN powder was investigated for use as starting material for obtaining a high thermal conductivity AlN by microwave sintering followed by microwave reheating under a reducing atmosphere. The AlN green compact was microwave sintered in a TE_{103} single mode cavity with an adjustable microwave power in the range of 0-3 KW at 2.45 GHz. The specimen was embedded at the center of a volume (7.8 cm^3) of AlN packing powder contained in an AlN crucible (31 mm in diameter and 25 mm in height). The temperature of the specimen was measured by both a two-color pyrometer and a thermocouple with an extrapolation technique. The detailed specimen arrangement, insulation package, temperature measurement and experimental procedure were described in our previous study[9] and were not repeated here. All the specimens were sintered at 1900^{o}C with various soaking times (5 □ 180 min) under a constant flow of N_2 gas (450 ml/min).

To study the effect of heat treatment on sintered specimens under a reducing atmosphere, some of the specimens after sintering for a period of time (5 □ 180 min) were placed back into the cavity and were microwave reheated. The specimen arrangement and insulation package for reheating were both the same as that for sintering with the only difference that the AlN packing powder was uniformly mixed with a small amount of carbon powder (under 150 mesh and 0.2 □ 1 wt% based on the weight of the AlN packing powder). The reheating was carried out at 1800^{o} with a holding time ranging from 30 to 180 min.

To get an understanding of the effect of the reducing atmosphere on the sintering of the AlN specimen, some of the sintering experiments were carried out under the reducing atmosphere, i.e., with addition of small amounts of carbon powder to the AlN packing powder.

Microwave sintering was found to proceed very quickly that a density of 99.5 % of theoretical with a thermal conductivity of 165 W/mK was achieved after sintering at 1900^{o}C for 5 min. The thermal conductivity could be improved by prolonging the soaking time, which is attributed to decreases in both oxygen content and secondary phases by evaporation and sublimation of the secondary phases. The reducing atmosphere was created by adding carbon particles to the AlN packing powder surrounding the specimen, thus enabling adjustment of the degree of reducing of the atmosphere. Reheating of the sintered specimen under the reducing atmosphere was found to be an effective method to substantially increase the thermal conductivity (up to 235 W/mK). This is attributed to enhanced removal of the secondary phases by the reducing atmosphere. The reheating time was found to be more effective in enhancing the thermal conductivity than the soaking time.

Acknowledgment

Support of this research by the National Science Council of the Republic of China under Grant No. NSC 93-2214-E-006-013 is gratefully acknowleged.

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7A-1

COMBUSTION SYNTHESIS AND STRUCTURAL CHANGES OF STRONTIUM ALUMINATES

Tanaka H.*, Gubarevich A.V., Wada H., Odawara O.

Tokyo Institute of Technology, J2-48, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
* station@echem.titech.ac.jp

A strontium aluminate ($SrAl_2O_4$), which is a well-known host material for utilizing in luminescent applications[1], has been synthesized by a solution combustion synthesis technology[2] with the reactants of strontium nitrate, aluminum nitrate and urea. In general, luminescent intensity and afterglow lifetime are controlled by arranging the Sr-positions of $SrAl_2O_4$ structure (SA) in the relation of doping ions (Eu^{2+}, Dy^{3+}, etc.). The phase transition temperature of SA is 923 K, where monoclinic SA(α-SA) changes to hexagonal one (β-SA).
In order to make clear the effects of reactant concentrations and pre-heating temperatures of solution combustion synthesis, structure changes of combustion synthesized strontium aluminates have been investigated under various pre-heating conditions (370 K to 1270 K) and urea ratios (1.0 to 2.0 times excess from the stoichiometric ratio). Solution combustion synthesis proceeds as (1) to mix the optimum amounts of urea, $Sr(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$ and water, (2) to heat the mixtures in an electric furnace up to optimum temperature, and (3) to induce combustion synthesis.

As a result of X-ray diffraction (XRD), only $Sr(NO_3)_2$ is identified in products when the furnace temperatures are lower than 770 K with no existance of Al_2O_3 phase. Since $Al(NO_3)_3 \cdot 9H_2O$ decomposes to amorphous Al_2O_3 phase, the present XRD data would not be enough to show the evidence. It is only suggested that the main synthesis reaction cannot not attained less than 770 K. At higher temperatures above 870K, the combustion synthesis reactions could be confirmed, where the peaks of monoclinic-$SrAl_2O_4$(a-SA), hexagonal-$SrAl_2O_4$ (b-SA), $Sr_3Al_2O_6$ (S_3A), and $Sr_2Al_4O_7$ (SA_2) were identified.

The results of TG/DTA measurements show that an exothermic peak is clearly observed at 430 K. With the increase of temperatures from 430 K, the gradual decrease of exothermic process was observed up to 530 K. At 870 K, an endothermic peak was observed. The former gradual decrease would be caused from the decomposition of $Al(NO_3)_3 \cdot 9H_2O$ and $CO(NH_2)_2$, and the DTA peak of 870 K corresponds to the thermal decomposition of $Sr(NO_3)_2$ to SrO. Solution combustion synthesis would be a suitable technology to synthesize compounds which are composed of elements with large differences in reaction temperatures such as the present system. Within the range of pre-heating temperatures tested between 870 K and 1270 K, α-SA, β-SA, $Sr_3Al_2O_6$(S_3A), and $SrAl_4O_7$(SA_2) could be identified. The β-SA existed in whole temperature ranges, and the maximum ratio of α-SA could be found at 1270 K. At higher temperatures, the ratio of S_3A increased and that of SA_2 decreased. In the case of the urea amount of 1.5 times excess from stoichiometric ratio, the ratio of α-SA was the maximum (more than 70 % of the product) in the present work (Figure 1). These results suggested that phase composition of strontium aluminates can be controlled by changing solution combustion synthesis condition, such as furnace temperatures and urea amount.

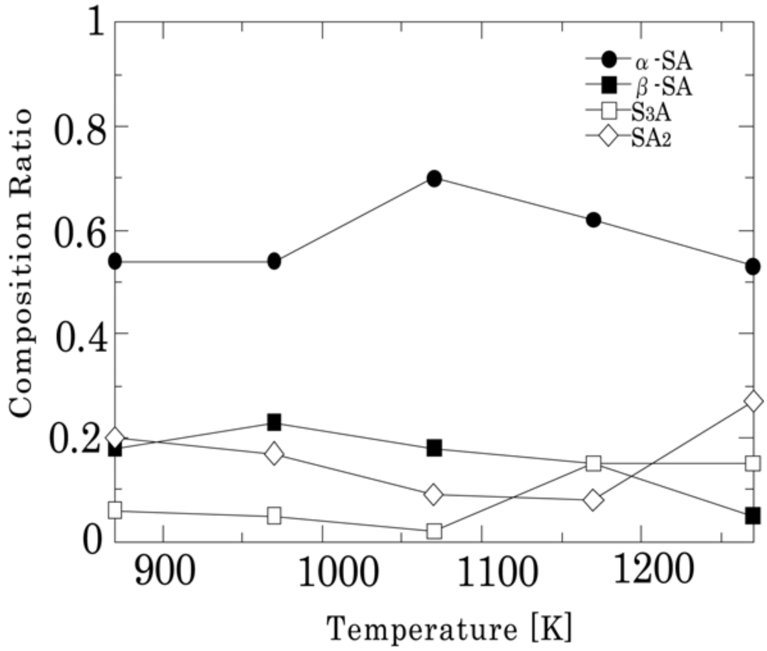

Figure 1 Composition ratio to total amount of products
(urea ratio of stoichiometric amount: 1.5)

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7A-2

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF α-Si_3N_4 USING SUBMICRON SILICON POWDER AND GASIFYING ADDITIVES

Zakorzhevsky V.V., Borovinskaya I.P.

Institute of Structural Macrokinetics and Materials Science RAS Chernogolovka,
Moscow region, 142432 Russia
zakvl@ism.ac.ru

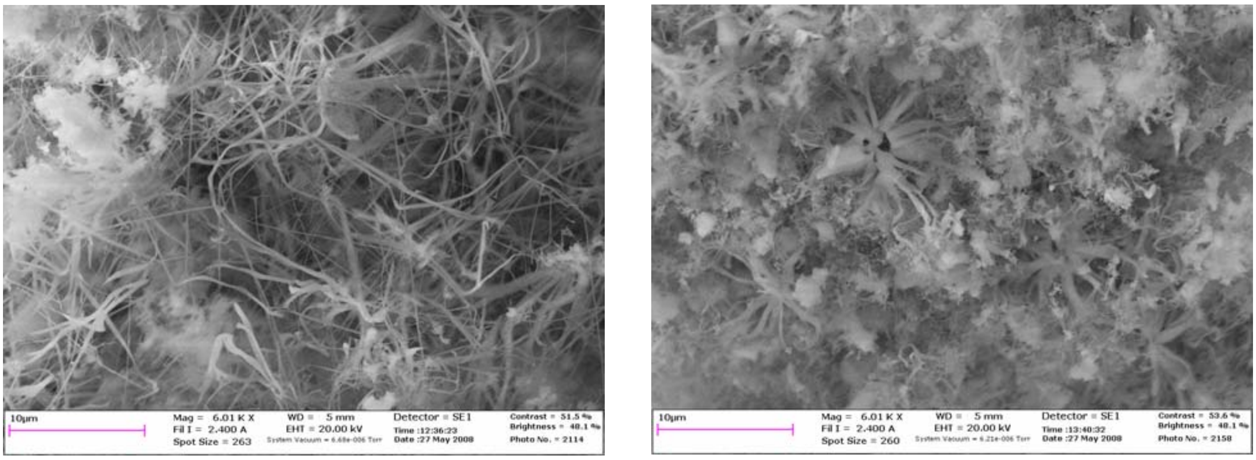
Use of submicron-nano powders allows improving ceramic material characteristics by 15 – 30 %. Therefore, one of the tasks of materials science is to obtain submicron-nano powders of refractory compounds, including silicon nitride. One of the methods of silicon nitride nano-powder production is gas-phase synthesis. It has already been established that during SHS of silicon nitride using polydispersed silicon powder and ammonium halides, the gas-phase mechanism of the synthesis is also realized with participation of silicon submicron particles [1]. The paper demonstrates the investigation results of α-Si_3N_4 synthesis using submicron silicon powder, an inert diluent (α-Si_3N_4) and gasifying additions (GA) (NH_4Cl, NH_4F). The aim of the work is to realize the gas-phase mechanism at SHS of α-Si_3N_4 and to obtain submicron-nano powder of silicon nitride. The influence of GA on synthesis parameters (combustion temperature and velocity) and product characteristics is considered.

In order to prepare the reaction green mixture we used a classified submicron silicon powder with the average particle diameter 200 nm (S_{sp}=12.0 m^2/g) which contained up to 25 mass.% of nano-sized particles (d<100nm) and dispersed silicon nitride powder (α-Si_3N_4) as an inert diluent with the specific surface area of 6.5 m^2/g. Ammonium chloride and fluoride additives were introduced into the green mixture for realizing the gas-phase mechanism.

The green mixture components were mixed in the ball mill during 1 h. The initial nitrogen pressure in the reactor was 5,0 MPa. The green mixture was placed onto a graphite boat. The boat and the mixture were covered with the heat-insulating layer (α-Si_3N_4 powder) in order to decrease heat losses, since the synthesis should be carried out at minimum temperatures for realizing the gas-phase mechanism.

We established that in the case of the determined initial conditions of the experiment the combustion threshold by the gasifying additive content in the mixture was 6 mass.%. When the content of the additives was increased from 0 up to 6 mass.%, the combustion temperature was lower - 1465ºC instead of 1600ºC, α-phase content grew from 89 to 97%, and the specific surface area – from 5 up to 12.6 m^2/g.

Due to our investigation silicon nitride was synthesized; its specific surface area was 12.6 m^2/g and α-phase content – 97 %. The synthesis product mainly consisted of fine-fiber particles of 0.1-0.3 µm in diameter and 10 µm in length (Fig.1a). Also there were a lot of elongated particles of 1-2 µm in width and up to 5 mm in length (Fig.1b). The size of these particles was higher than that of the particles of the initial components. It proves the fact that the dry mixing did not provide a homogeneous mixture of Si-Si_3N_4. That is why many submicron silicon particles formed large Si_3N_4 ones and that resulted in a significant decrease of the specific surface area of the final product.



a b

Fig.1. Morphology of silicon nitride particles obtained by gas-phase SHS.

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7A-3

THE EFFECT OF MECHANICAL ACTIVATION OF A REACTION MIXTURE ON THE VELOCITY OF THE WAVE PROPAGATION OF SHS REACTIONS AND MICROSTRUCTURE OF TiC–Ni HARD ALLOY

Kochetov N.A.*[1], Rogachev A.S.[1], and Pogozhev Yu.S.[2]

[1] Institute of Structural Macrokinetics and Material Sciences, Russian Academy of Sciences,
ul. Institutskaya 8, Chernogolovka, Moscow region, 142432 Russia
[2] Moscow Institute of Steel and Alloys (State Technological University), Leninskii pr. 4, Moscow, 119049 Russia.
*kolyan_kochetov@mail.ru

An experimental investigation into the effect that the MA of the 80% (Ti + C) + 20% Ni mixture has on the mechanism of the SHS process and the structure of synthesized products in the TiC–Ni system was carried out. It is shown that the MA of the starting mixture affects the sequence of physicochemical transformations in the SHS wave. The combustion rate decreases if the Ti–Ni or Ni–C pairs are subjected to activation. This is explained by the fact that the conglomeration of components leads to the inhibition of the Ti + C main exothermic reaction. For other MA schemes, this rate does not vary in comparison with non activated compositions.

It is shown that the MA can be used as an effective method to obtain a fine-grained structure of TiC–Ni hard alloys. The average grain size can be decreased more than by a factor of two.

This work is supported by the Russian Foundation for Basic Research, grant 10-03-00217-a.

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7A-4

FORMATION OF CAST Ni–Cr(Co)–Al AND Fe–Co–V–Al ALLOYS DURING SHS IN THE FIELD OF CENTRIFUGAL FORCES

Andreev D.E.[1]*, Sanin V.N.[1], Ikornikov D.M.[1], Yukhvid V.I.[1], Derin B.[2], Sonmez S.[2], and Yücel O.[2]

[1]Institute of Structural Macrokinetics and Materials Science (ISMAN),
Russian Academy of Science, 142432 Chernogolovka, Russia
[2]Istanbul Technical University, Applied Research Center of Materials Science and Production Technologies, 34469, Maslak, Istanbul, Turkey
* ade@ism.ac.ru

Metal alloys based on intermetallides of nickel, cobalt, chromium, and iron are widely used in metallurgy as master alloys and modifying agents of steels to produce protecting heat- and wear-resistant coatings by mans of plasma spraying and electric arc surfacing or complex multicomponent alloys intended for powerful energy setups of a turbine type.

All industrial methods used so far in the production of such alloys are highly energy consuming. The most commonly employed methods of such alloy production are electric vacuum and powder metallurgy. In the latter case, starting raw materials to have high-quality alloys are expensive pure metal powders, while high-cost equipment is needed for the case of electric vacuum metallurgy. Complexity and multistage character of the technologies and expensiveness of the initial components of alloys determine high cost of the resulting alloys thus narrowing the range of their practical applications.

One of the most energy-saving methods of producing composite, metallic and ceramic materials is self-propagating high-temperature synthesis (SHS). Its advantages are most definitely observed in SHS metallurgy of cast hard alloys and wear-resistant coatings [1, 2].

In the present investigation of cast Ni-, Co-, and Fe-based alloys were synthesized. Since the experiments were focused on the regularities of combustion, metal and oxide phase separation in the melt as well as the influence of the gravity increase (up to 1000 g) on the product chemical composition, the combustion process was carried out in centrifugal setups. The overall scheme to obtain the alloys can be presented as follows:

$$(M_1 + M_2 + \dots M_i) + R + F_{add} \rightarrow [\text{Alloy}] + Al_2O_3 + Q,$$

where M_i denotes oxides of Ni, Co, Cr, V, Mn etc., R is a reducing metal (Al), F_{add} is a functional additive, and Q is the reaction heat.

Quantification of the adiabatic temperature and the final product composition performed according to the THERMO program showed that the temperature realized in all systems except that of NiO–Cr_2O_3–Al constituted 3000 ± 150 K. At the increase in the Cr_2O_3 additive content in the mixture, the combustion temperature lowered from 3000 down to 2300 K, the gas phase in the system in turn became lower and the combustion products were converted to the condensed state.

In the experiments on the Ni–Cr–Al, Ni–Co–Al and Co–V–Al systems the Ni/Cr, Ni/Co and Co/V ratios were varied. Analysis of the obtained data revealed that variation of the component ratio resulted in the synthesis of alloys of different composition.

Preliminary series of the experiments under ambient conditions (a = 1g и P = 1 atm.) showed that the combustion process was accompanied by the reaction product dissipation, the yield of the desired phase into the ingot passed the maximum dependent on the ratio of the components in the green mixture. A certain composition was chosen for each system to be synthesized in the field of centrifugal forces. It was found that an overload produced a favorable effect on the processes of phase separation between the metal and oxide components in the ingot, significant reduction of the content of the nonmetal inclusions in the alloy, and on the structure formation of synthesized alloys.

The present investigation was financially supported by RFBR (Grant 10-03-91219-ST).

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7A-5

PHASE FORMATION MECHANISM IN THE MOLYBDENUM OXIDE REDUCTION BY Mg + C MIXTURE

Aydinyan S.V.[1*], Aghajanyan A.A.[1], Manukyan Kh.V.[1,2], Grigoryan E.G.[2], Niazyan O.M.[2], Kharatyan S.L.[1,2]

[1] Department of Inorganic chemistry, Yerevan State University, 1, A. Manoogian str., Yerevan, 0025, Armenia
[2] Laboratory of Kinetics of SHS Processes, A.B. Nalbandyan Institute of Chemical Physics NAS RA, 5/2, P. Sevak str., Yerevan, 0014, Armenia
*a-sofya-1984@rambler.ru

In recent years novel methods to control thermite-type reactions were proposed to produce advanced materials including ceramics, metal powders and composites [1-3]. An example of such controlled thermite reaction is the magnesium reduction of MoO_3. To regulate process conditions magnesium was partly substituted either by zinc [2] or carbon [3]. This approach enabled to moderate reaction conditions and produce molybdenum powder. Such promising approach to control violent reaction condition in thermite-type reaction is opening new prospective to produce nanostructured metals and alloys. Application of reducer mixtures in thermite reactions enables to tune reaction temperature (by changing the reducers' ratio) and in such way to control microstructure of materials obtained. However, little is known about phase transformation mechanism in such complex reacting systems. In the present study we investigate reduction mechanism in the MoO_3 + Mg + C system. As it was shown in [3] combustion of MoO_3 + 1.5Mg + 1.25C mixture yields molybdenum powder with low level of carbon and oxygen contaminations (0.3 wt.%). The measured reduction temperature for this mixture is about 2100°C. To study phase formation mechanism magnesia (MgO) was added as diluent material MoO_3 + 1.5Mg + 1.25C. Thermodynamic calculations show that temperatures higher than 1300°C Mo, MgO, CO and CO_2 are the equilibrium products of reaction, while below this temperature product contain Mo, MoO_2, Mo_2C, CO and CO_2. XRD analyses of products for magnesia added mixtures confirm this feature. Magnesia additions allow to decrease both the reaction temperature and heating rate of materials within the reaction zone. At low heating rates temperature-time profiles (Fig. 1) contain several braking points and plateaus. Comprehensive investigation of combustion parameters, products microstructure, DTA investigations of selected mixtures and phase composition of products helped us to propose possible reduction mechanism. According to which in the very initial stage of the process the following low exothermic reaction takes place at combustion of the MoO_3 + Mg + C mixtures:

$$2MoO_3 + C = 2MoO_2 + CO_2 \quad (500\text{-}600^{o}C) \qquad (1)$$

MoO_3 (MoO_2) reduction by magnesium starts with magnesium melting at 650°C. Consequently during the combustion of MoO_3+Mg+C mixtures the reactions (2) and (3) proceed at temperatures higher than 650°C. Obviously these two reactions are responsible for main heat generation.

$$MoO_3 + 3Mg = Mo + 3MgO \qquad (2)$$

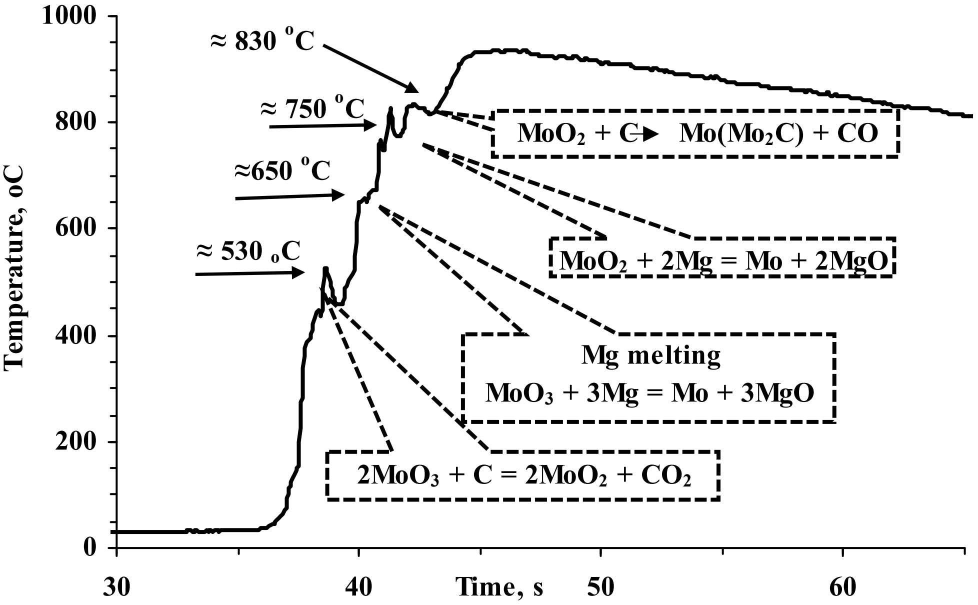

Fig. 1 Temperature-time history at combustion of $MoO_3 + 1.5Mg + 1.25C + 5MgO$ mixture

$$MoO_2 + 2Mg = Mo + 2MgO \qquad (3)$$

Heat allocated from (2) and (3) reactions provides reduction of remained MoO_2 by carbon according to the following endothermic conversion:

$$MoO_2 + 2C \rightarrow Mo(Mo_2C) + 2CO \qquad (4)$$

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7A-6

PROSPECTS FOR SYNTHESIS OF POROUS OXYNITRIDE CERAMICS BY SHS

Maznoy A.S.*[1], Kirdyashkin A.I.[2], Maksimov Yu.M.[2], Kazazaev N.Yu.[1]

[1] Tomsk State University, 36 Lenin Avenue, Tomsk, 634050, Russian Federation
[2] Department of Structural Macrokinetics of Tomsk Scientific Center SB RAS, 10/3 Akademicheskii Avenue, Tomsk, 634021, Russian Federation.
* maznoy_a@mail.ru

INTRODUCTION

Ceramics are extensively used for production of porous penetrable materials because of their high strength, wear resistance, and resistance to aggressive media. However, it is known that introduction of nitrogen into ceramic structures considerably improve their operational characteristics. One of the advanced methods for production of porous penetrable materials from oxynitrides is the method of Self-propagating High-temperature Synthesis (SHS) [1]. In the centre of attention of our studies there are ways of synthesis of porous oxynitride SHS-ceramic. Casting technique may be used for production of highly porous preforms from reagents for consequent combustion synthesis of oxynitride ceramics. Porous space of preforms is formed by gassing in the volume of slurry. In our case, there is an interaction between aluminium and water. The preforms are combustion synthesized, which involves mass transfer between a porous body of preforms and nitrogen, which a priori requires a connected-pore system penetrating the entire volume of the material.

INVESTIGATION TECHNIQUES

We found that SHS of preforms with the composition $Si_4Al_2O_2$ (basis of β-SiAlON with Z=2) did not lead to a high nitrogen saturation degree – we got only 0.46. (Nitrogen saturation degree is defined as a ratio between nitrogen trapped in the volume of preforms resulting from CS and nitrogen required for the total conversion of nitride-generating reagents. Assume that only silicon and aluminium powders react with nitrogen, low-probability reaction of silicon oxynitride formation was not taken into account.) It is explained by the presence of melt regions in the preform structure. Nitrogen cannot penetrate into those regions. A XRD analysis shows *β-SiAlON* phases, but the residual components of the charge are also present. Additives are usually used to decrease the maximal reaction temperature and/or to separate silicon grains in order to improve their reactivity in the liquid state. Therefore, we studied how the dilution rate depends on CS parameters. From the point of view of cost-effective production, using sialon powders or silicon nitride powders as dilatants is not desirable [2]. We used an alumina as a dilution agent.

The starting materials used were: 1). Aluminium ASD-4 (D_{Av}=10 μm); 2). Silicon dust CR-1 (D_{Av}=10 μm); 3). Kaolinite clay produced by the company «TGOK «Il'menit» (D_{Av}< 63 μm); 4). Alumina, (D_{Av}=10 μm). The experimental procedures were as follows: 1). Alumina was put in addition to the mass of reaction charge (the charge was kept constant at the level 70 g), which were thoroughly mixed according to the formula $Si_4Al_2O_2$. That is, the mass of the diluted preforms increases with increasing dilution rate by the value of the rate; 2). Water/solid ratio for temper of charge was 0.625; 3). Slurry was cast in a cylindrical mold with V=105.62 cm^3 (D=41 mm, H=80 mm); 4). Porous preforms were produced using endothermic sponging of the slurry in a muffle furnace with a programmed heating controller in the air (Know-how). The preforms were further roasted in the muffle at 600 ^{0}C for 45 minutes each; 5). Combustion synthesis of preforms was performed in an autoclave in the nitrogen atmosphere at 8 MPa pressure; 6). The maximal temperature of combustion wave was estimated using a W-Re thermocouple. The combustion rate was calculated as height-to-time ratio.

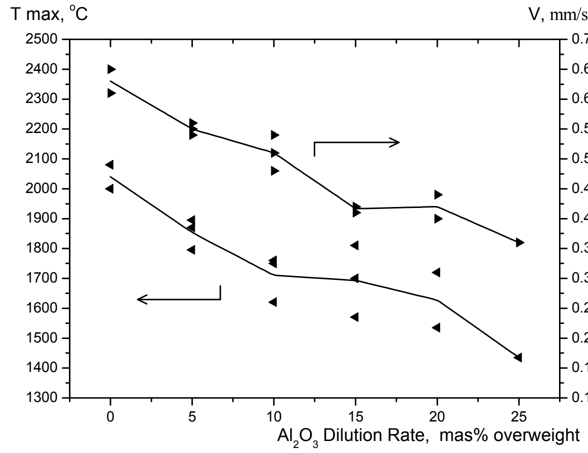

Fig.1. Maximal SHS temperatures & Combustion rates versus Al_2O_3 dilution rate.

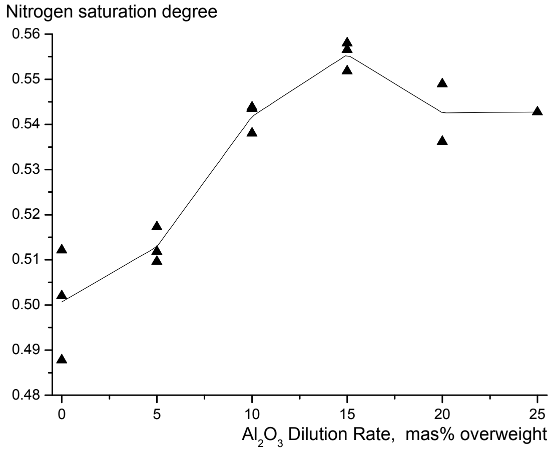

Fig.2. Nitrogen saturation degree versus Al_2O_3 dilution rate.

Figures 1,2 are respectively shown the rate of synthesis, maximal temperature of the combustion wave, and nitrogen saturation degree depending on the Al_2O_3 dilution rate of the charge. The CS rate and the maximal temperature decrease with increasing the dilution rate. The maximum nitrogen saturation degree 0.55 was reached for the 15% dilution rate. When the dilution rate was higher than 15%, the nitrogen saturation degree started decreasing. This occurred because of the change in the combustion wave type. We observed a spin regime and a self-oscillation regime rather than the conventional layer-by-layer regime. Some of the samples were even not synthesized in the self-propagation mode. A considerable variation of the maximal temperature for the same synthesis conditions can be explained by the position of the thermocouple tip in the pore structure of the preform. The temperature measured in a pore is lower than that measured at the contact of the skeleton material.

CONCLUSION

We have shown that: 1). The rate of weight loss during preform roasting increases with the Al_2O_3 dilution rate despite the overall increase in the density of the preforms; 2). The maximal temperature and the rate of combustion synthesis are significantly reduced with increasing of dilution rate. A change of the synthesis regime from layer-by-layer to self-oscillating or spin was observed; 3). By reducing the influence of coagulation of a low-melting component, an increase in nitrogen saturation degree up to 0.56 was revealed. To increase the nitrogen saturation degree we are intend undertake further studies as to how nitrogen pressure affects on the CS, and assess the prospects of using special fluoride additives [3] facilitating the process of nitrogen infiltration into the reaction zone.

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8B-1

IN SITU SYNTHESIS AND MECHANICAL PROPERTIES OF $M_{N+1}AX_N$ PHASES BY SHS/PHIP

He X.*[1], Ying G.[1], Du S.[1], Zheng Y.[1], Zhu C.[2]

[1]Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China
[2] College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150001, China
*Corresponding author. Tel.: +86-451-86412513; Fax: +86-451-86402333.
hexd@hit.edu.cn

The layered ternary $M_{n+1}AX_n$ phases (where n=1,2,3, M is an early transition metal, A is a □A or □A element and X is C or N), have been attracted increasing interest due to the unique combination of the properties of both metals and ceramics [1-3]. However, the weaknesses such as low hardness and unsatisfied strength limit their widespread applications. Considerable efforts to strengthening of $M_{n+1}AX_n$ phases, second phase formed from quaternary system needs to be incorporated for forming a composite [4-6]. Self-propagating high-temperature synthesis (SHS) has been identified to a low-cost and significant technique for the synthesis of $M_{n+1}AX_n$ phases [4, 7-15]. And the $M_{n+1}AX_n$ phase matrix composites prepared by SHS with the pseudo–hot isostatic pressing (SHS/PHIP) was identified to be a strategy for improving the mechanical properties of monolithic $M_{n+1}AX_n$ phase [4, 10, 16].

In this paper, we first introduce the synthesis of Ti_3SiC_2, Ti_3AlC_2, Ti_2AlC and Cr_2AlC by SHS/PHIP. Then, the $M_{n+1}AX_n$ phase matrix composites with the high strength and toughness are presented. [4, 9-16]

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8B-2

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF NONSTOICHIOMETRIC MANGANESE OXIDE

Hiramoto M.*[1], Okinaka N.[1], Akiyama T.[1]

[1] Center for Advanced Research of Energy Materials, Faculty of Engineering, Hokkaido University,
Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-0813, Japan
* m-hiramoto@eng.hokudai.ac.jp

INTRODUCTION

The nonstoichiometric transition metal oxides of $Mn_{1-\delta}O$ ($0 \leq \delta \leq 0.150$) crystallize in the simple rock salt structure with varying degrees of intrinsic defects [1]. As a result of the aggregation of intrinsic point defects, the sample behaves as a semiconductor even without the addition of rare metal dopants. However, nonstoichiometric transition metal oxides have been conventionally produced based on equilibrium. The conventional method suffers from limitations of being time- and energy-consuming, because the raw materials must be kept at a high temperature for an extended period in order to reach the equilibrium compositions of the products. To overcome the problems, we applied self-propagating high-temperature synthesis (SHS) utilizing thermal energy generated by an exothermic chemical reaction between metal powders and an oxidant of raw materials. The purpose of this study was to synthesize nonstoichiometric $Mn_{1-\delta}O$ using the SHS method, in which the mixing ratio is systematically varied to control the value of δ.

EXPERIMENTAL

The raw materials used for preparing samples are commercial reagents: Mn (99.9% purity, Kojundo Chemical, ca.10 μm), $NaClO_4$ (98%, Aldrich), and MnO (99.9%, Kojundo Chemical, 5–10 μm). The synthesis reaction is expressed by the following equation, $(0.4-\delta)$ Mn + 0.1 $NaClO_4$ +0.6 MnO (diluent) → $Mn_{1-\delta}O$ + 0.1 NaCl(g) (δ = 0 to 0.150). The three reagents were mixed for 3 hours under air atmosphere using a ball mill with 60 rpm in the mass ratio.

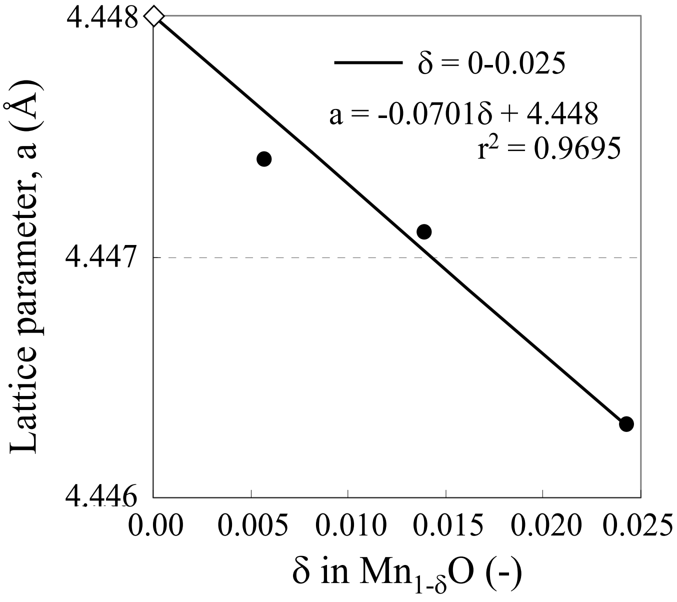

Fig.1 Lattice parameter of the SHSed $Mn_{1-\delta}O$ (δ = 0 to 0.025), together with the liner least square fit and correlation coefficient.

The milled-powder of 10 g was poured into a graphite crucible (30 mm × 12 mm × 100 mm) and then it was ignited by an electrically heated carbon foil for 5 seconds under Ar atmosphere. The product obtained was then ground to less than 25 μm in size using a zirconia mortar and pestle after the NaCl in product was removed by using ultrasonic cleaning. Each product was characterized by X-ray diffraction (XRD) employing CuKα radiation (λ = 1.5418 Å). A thermogravimetric analyzer (TGA) was used to evaluate the nonstoichiometry, δ, of nonstoichiometric $Mn_{1-\delta}O$.

RESULTS AND DISCUSSION

In all the experiments, the mixtures of raw materials were successfully ignited and propagated. Successful completion of the SHS yielded a blackish green and spongy agglomerate. According to XRD analysis, single phase $Mn_{1-\delta}O$ products containing nonstoichiometric defects were obtained for $0 < \delta \leq 0.025$. Figure 1 shows the lattice parameters of SHSed $Mn_{1-\delta}O$ (δ = 0 to 0.250), along with the linear least square fit and correlation coefficient. The lattice parameter of 4.448 Å at $\delta = 0$ was taken from the literature [2]. As the value of δ increased, the lattice parameter decreased by the introduction of Mn defects. The lattice parameter, *a*, of the products was well explained by the linear equation: $a = -0.0701\delta + 4.448$. The results reveal the possibility of a new production route for $Mn_{1-\delta}O$ with the benefits of a simplified production procedure and minimized production time.

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8B-3

FABRICATION OF TiN PARTICLE-DISPERSED Al_2O_3 COMPOSITES UTILIZING HIGH N_2-PRESSURE SHS

Hirota K.*, Yagura H., Takaoka K., Kato M.

[1] Doshisha University, Kyo-tanabe, Kyoto, 610-0321, Japan
*khirota@mail.doshisha.ac.jp

As metal nitrides reveal characteristic properties such as high melting temperatures (T_m), high hardness, excellent wear resistance and high chemical stability[1,2]), they have been widely used as thin films in home appliances and industrial fields. However, it is very difficult to fabricate the dense bulk materials because of their poor sinterability due to the high T_m and low diffusibility of constitution elements in the compounds. On the other hand, as the formation energies of refractory metal nitrides are generally very high, SHS between metal and nitrogen can be induced; however, the control of densification and grain growth during sintering on the SHS process based on solid/gas reaction is much difficult. Therefore, monolithic bulk metal nitrides with high density have not been obtained. In the present study, a fabrication of bulk Al_2O_3/TiN composite materials have been tried directly from the mixed powder compact using high-N_2 pressure hot isostatic pressing (HIP) because Ti requires high-N_2 pressure to form pure TiN in SHS[3]).

Synthesis of dense composite materials with the compositions of Al_2O_3/TiN=100/0~90/10 vol% has been conducted directly from Al_2O_3/(Ti,$TiN_{0.30}$) mixed powder compacts using capsule-free N_2 hot isostatic pressing (HIP). Fine Ti powders (Φ~0.3 μm) with a small amount of $TiN_{0.3}$ phase were prepared by thermal decomposition of pre-ball-milled fine TiH_2 powder at 400°C for 1 h in a vacuum, followed by thermal treatment in N_2. Then, the mixed powder compacts with homogeneously dispersed Ti particles (relative densities of 57.2-57.8%) were prepared and then heated up to 1350°C under 6 MPa N_2 and kept for 1 h, followed by the heating at the same temperature for 2 h under 196 MPa-N_2. During the first stage of heating [1350°C/6MPa/1h], solid/gas reaction of SHS between Ti and N_2, was induced to form TiN (Fig. 1). Then, after the successive second stage of HIPing [1350°C/196MPa/2h], the most of sintered composites consisting of Al_2O_3 and TiN phases reached to a higher relative density than 98.5 % with closed pores (Fig. 2). Dispersion of TiN particles (Φ 0.30~0.35 μm) just SHS-derived suppressed the grain growth of Al_2O_3 during sintering. Mechanical properties, such as bending strength (σ_b), Vickers hardness (H_V), fracture toughness (K_{IC}), and other properties have been evaluated as a function of TiN content. The maximum values of σ_b=640 MPa, H_V=19.5 GPa, and K_{IC}=4.5 $MPam^{1/2}$ were obtained in the Al_2O_3/TiN=97/3~95/5 vol% composites (Fig. 3).

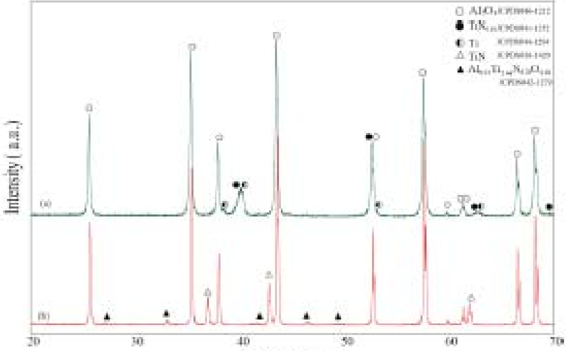

Fig. 1 XRD patterns for (a) the powder compact and (b) pre-sintered body after the 1st HIPing (1350°C/6MPa/1h), in which SHS was induced.

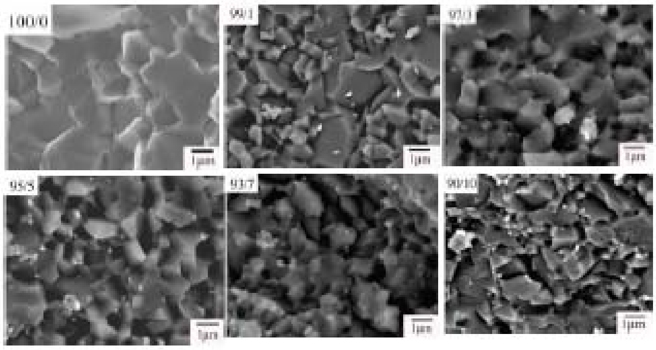

Fig. 2 SEM photographs for the fracture surfaces of Al_2O_3/TiN composites with the various compositions after the 2nd HIPing (1350°C/196MPa/2h), in which the densification was enhanced.

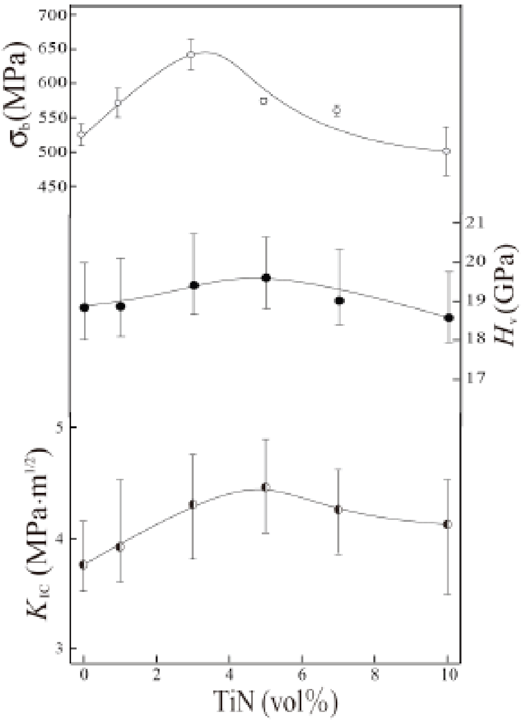

Fig. 3 Mechanical properties of Al_2O_3/TiN composites (a) bending strength σ_b, (b) Vickers hardness H_v , (c) fracture toughness K_{IC} as a function of TiN content.

Thus, pure titanium nitride TiN was prepared by SHS under high-N_2 pressure using capsule-free HIPing from the fine Ti particles dispersed in the Al_2O_3 matirix. Fine TiN particles in the composites brought the improvement of mechanical properties of Al_2O_3 ceramics.

From the present study, it is cleared that metal nitrides with much difficulty in formation by conventional process, adoption of both N_2 high-pressure using an HIP and homogeneous dispertion of metal particles to other ceramic matrix can make it possible to introduce the controlled SHS for metal-nitrization.

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8B-4

SYNTHESIS OF REINFORCED MATERIALS BY THERMAL EXPLOSION

Kamynina O.K.*, Sytschev A.E., Boyarchenko O.D., Vadchenko S.G., Umarov L.M., Gutmanas E.[1] and Gotman I.[1]

Institute of Structural Macrokinetics and Materials Science RAS, 142432, Chernogolovka, Russia
[1]Faculty of Materials Engineering, Technion, Haifa, 32000 Israel
*kuz@ism.ac.ru

At present, metal matrix composites have great potential as materials of high service parameters (strength, wear and high corrosion resistance at elevated temperatures [1, 2]) determined by volume of the reinforced phase, its content, microstructure and characteristics of phases interface. Such materials are traditionally manufactured by methods of powders metallurgy, infiltration, casting, etc. In this work we studied formation of dispersion-strengthened Ti–Al-based alloys reinforced with B_4C particles. It is known that in the high-temperature synthesis B_4C particles serve both as a power and structure forming reagent. We investigated behavior of Ti + 3Al + (10-60) wt.% B_4C system by thermal explosion (TE). In experiments the influence of initial structure of B_4C powder on the structure of produced materials was studied and B_4C powder with particles coated TiB/TiC (diffusion barrier) were used. Analysis of the thermograms and video frames allowed us to elucidate the features of the TE processes. Synthesized materials were characterized by SEM, EDS and XRD. The strength properties were determined by Instron-1195.

As a result, the optimal content of B_4C was selected in experiments and dispersion-strengthened Ti–Al-based alloys of required structure and properties were manufactured. It was also shown that increase of B_4C content does not effect on macrokinetics parameters of a reaction and causes improvement of viscoplastic materials characteristics. Applying powders with the diffusion coating allows one to obtain materials of more homogeneous structure and better strength properties.

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8B-5

SHS JOINING OF INTERMETALLICS WITH METAL SUBSTRATES

Sytschev A.E.*, Vadchenko S.G., Vrel D.[1], Sachkova N.V., and Kovalev D.Yu.

Institute of Structural Macrokinetics and Materials Science, Chernogolovka, 142432 Russia
[1]LIMHP, Universitй Paris 13, CNRS, 99 Av. Jean-Baptiste Clйment, 93430 Villetaneuse, FRANCE
* sytschev@ism.ac.ru

The joining of intermetallic parts to the metals (Ti, Al, Cu, Ni) or different intermetallics (e.g. NiAl, TiAl) is important for high-temperature applications. Traditional fusion welding is difficult to apply due to the large thermal expansion mismatch between the intermetallics to be joined and the filler material. Brazing and diffusion bonding are also inefficient, energy-consuming, and must be carried out in vacuum or protective atmosphere. Meanwhile, Self-propagating High-temperature Synthesis (SHS) that is widely used for production of powders, compact materials and parts holds considerable promise as a method of joining various component parts.

In this communication, we report on a new SHS-based approach to joining TiAl and NiAl intermetallics with metal substrates Ti and Ni. The adiabatic combustion temperatures for the systems under study and stoichiometric ratios of green mixtures were determined by thermodynamic calculations. Experiments were performed in the modes of pressure-assisted thermal explosion and combustion wave propagation, with the samples placed between the punches of experimental set up.

Investigated were the processes taking place in thermally treated Ti or Ni plates mechanically impregnated (by Mechanically Activation or Vibration Milling) with a mixture of metallic particles. Vibratory treatment of an Al and Ti surfaces in a powder mixture of metals was found to result in destruction of the surface oxide film and formation of extensive physical contacts between the Ni or Ti matrix and the metallic particles mechanically impregnated into the near surface layer of Ni or Ti.

Subsequent thermal treatment was then used to launch chemical reaction yielding intermetallides within the impregnated layer. Performing SHS reactions yielding melted intermetallides in the coatings (or pellets) deposited (or placed) onto the surface of thus treated Ti or Ni plates, one can obtain strong weld joining between solidified SHS products and substrates. This approach can also be used for deposition of coatings with a desired composition onto substrates. The proposed technique seems attractive for repair operations and for deposition of coatings in special-purpose applications.

This study was supported by the Program of OKhNM RAS and Service des Relations Européennes et Internationales, Université Paris 13. .

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8B-6

PREPARATION OF MO-ADDED ZIRCONIUM CARBOSULFIDES BY SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS

Tomoshige R.*[1], Itaya S.[1], Oikawa K.[2], Ishida K.[2]

[1] Sojo University, 22-1 Ikeda 4-chome, Kumamoto-shi, Kumamoto 860-0082, Japan.
[2] Tohoku University, 6-6 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan.
* tomosige@nano.sojo-u.ac.jp

Molybdenum and tungsten disulfides have been utilized as good solid lubricants [1, 2]. The solid lubricants are used, for example, under hyper-low temperature or vacuum. It is believed to be attributed their excellent solid lubricity to their layered structures. Japanese industries depend on importation from foreign countries on supply of such sulfide minerals. Under the circumstances, industrial cost and stable supply of the mineral are very important factors. On the other hand, self-propagating high temperature synthesis (SHS) is known as low cost and industrial promising processes. Our research group has prepared titanium carbosulfide and chromium sulfide [3] that are expected to have such properties as MoS_2. In this study, molybdenum-added zirconium carbosulfides which are from the same transition metal as titanium were prepared by SHS. Zirconium, graphite, sulfur and molybdenum powders as raw material were wet-mixed in ethanol for 1 hour in molar ratio of Mo: Zr: Mo: C: S = (2-x): x: 1:1 (x = 0 to 1.0), followed by sufficient drying the mixtures. It should be expected the addition of molybdenum with higher melting point than zirconium to suppress intensive reactions of the carbosulfides. The powder mixtures were hydraulic pressed for shaping a pellet. SHS was carried out with nichrome heating-coil contacting at the top of the pellet. Reactions were terminated in a few seconds. The synthesized materials were investigated on microstructures, phase identification, hardness and thermoproperties. As a result, it was difficult to collect the sample with the original shape due to its intensive reaction in the composition without molybdenum. However, XRD patterns indicated that $Zr_4C_2S_2$ phase was detected in the product with byproducts of some hard carbides. Similar results were found in the other compositions. Slight peak shift was also observed in those diffraction patterns. On the other hands, hardness test values tended to increase with the amount of molybdenum. This tendency suggested solid solution hardening in the $Zr_4C_2S_2$ phase or hardening of the synthesized materials accompanied with a formation of carbide phase. In thermogravity measurements, the sample with the composition of Zr: C: S = 2:1:1 indicated good resistant-to-oxidation up to 500 °C with slight weight increment due to the oxidation. Figure 1 shows TEM image of the sample in molar ratio of Zr: Mo: C: S = 1.6: 0.4: 1: 1. This sample had a layered structure, which is preferable for the appearance of good solid lubricity. Furthermore, the microstructures of the sample were similar to those of MoS_2. Thus, the sample is expected to be useful solid lubricants.

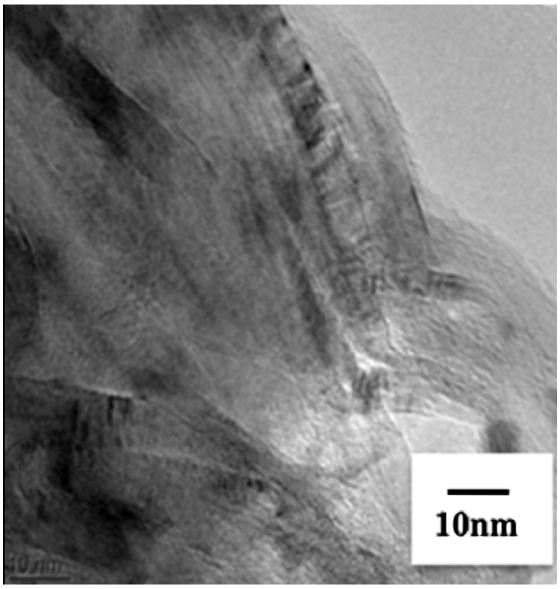

Fig. 1 TEM image of the synthesized carbosulfide with the composition of Zr: Mo: C: S = 1.6: 0.4: 1: 1.

Acknowledgements: This study was supported in part by a Grant-in-Aid for Scientific Research (C)(20560695) from JSPS and Strategic Research Foundation Grant-aided Project for Private Universities (S0801085) from MEXT.

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ORAL PRESENTATIONS

D: SHS of advanced materials: nanomaterials, metals, ceramics, intermetallics, composites, etc.

4A-K – KEYNOTE TALK

REACTION PROPERTIES, PHASE TRANSFORMATIONS, AND NOVEL APPLICATIONS FOR REACTIVE LAMINATE FOILS AND PARTICLES

Weihs T.P.

Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD, 21218, USA
* weihs@jhu.edu

Vapor-deposited laminate foils provide an ideal geometry for studying the properties of self-propagating exothermic formation reactions as shown in Figure 1(a) [1]. The average reactant spacing is well defined and consistent throughout the foils and such uniformity aides characterization of the physical parameters that control ignition and propagation. Using a combination of experiments and continuum modeling we have identified the impact of microstructure and chemistry on ignition thresholds, reaction velocities and reaction temperatures. An example of the strong dependence of reaction velocity on bilayer thickness is shown in Figure 1(b) for Ni/Al multilayer foils. Both the measured and predicted velocities increase as the bilayer thickness decreases. However, when the bilayer thickness becomes quite small the as-deposited intermixing at each Ni/Al interface becomes a significant volume fraction and the stored energy decreases. This reduces the driving force for the reaction and therefore velocities drop steeply as bilayer thickness decreases further [2].

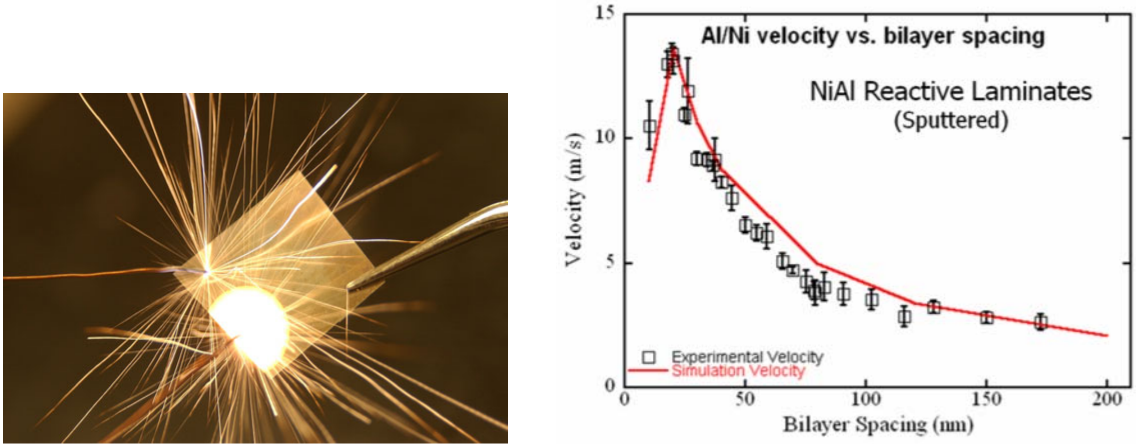

Figure 1: (a) Photo of an exothermic reaction propagating in a Ni/Al laminate foil and (b) velocities plotted versus bilayer spacing or average reactant spacing.

Beyond reaction properties we have also used *in situ* X-ray diffraction to identify the metastable phases and morphologies that appear in these foils under very rapid (~10^6 K/sec) heating conditions. Note in Figure 2 that Ni and Al peaks disappear rapidly and that peaks for the B2 NiAl intermetallic and a liquid Al-Ni solution appear within 100's of microseconds [3]. Similar initial phase formations are observed in Dynamic TEM experiments and in MD simulations. The final stable phases only appear at much longer times. An different squence of phases is obtained using slow heating experiments (DSC).

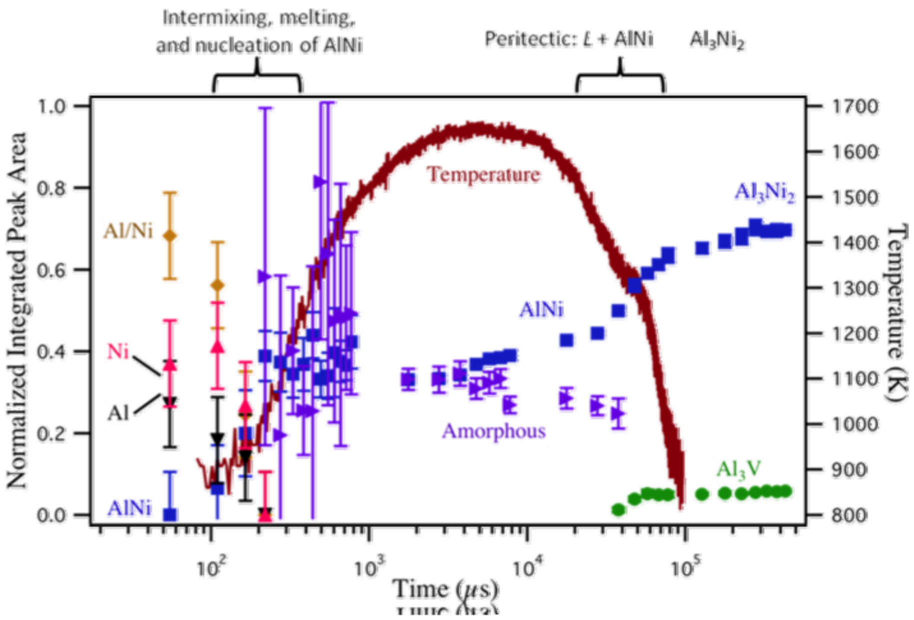

Figure 2: Normalized integrated peak area versus time for an *in situ* XRD study of a self-propagating reaction in a Ni/Al foil leading to the formation of Ni_2Al_3.

In addition to these scientific studies, we have developed commercial applications for reactive laminate foils, including their use as local heat sources for soldering and brazing. This talk will touch on applications prior to focusing on scientific studies of reaction properties and rapid phase transformation in laminate foils and particles.

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4A-1

PREPARATION OF ZnO POROUS MONOLITHS VIA SHS OF ZnS PREFORM

Perraud I.[1*], Rouessac F.[1], Ayral R.M.[1], Ayral A.[2]

[1]ICGM - C2M UMR 5253 CC1504, Université Montpellier 2, Place E. Bataillon,
34095 Montpellier cedex 5, France
[2]IEMM UMR 5635 CC047, Université Montpellier 2, Place E. Bataillon,34095 Montpellier cedex 5, France
[*] igor.perraud@univ-montp2.fr

Today, we have to take care of every technology's environmental effects. The removal of H_2S and other sulfur compounds in hot gas enters this ecological aspect in several industrial processes. To do so, cylindrical ZnO extrudates are usually used in fixed beds in industrial plants. Zinc oxide is used here because it shows the ability to reversible chemisorption of hydrogen sulfide, H_2S, and other sulfur compounds, with current industrial applications as a regenerable sorbent for gas desulfurization [1]. Now, macroporous ZnO monoliths are studied as an alternative. Sol-gel routes have already been used to prepare ZnO-based microporous or mesoporous supported membranes [2, 3]. However, to be consistent with this sustainable development policy, other ways of synthesis can be implemented like Self-propagating High temperature Synthesis [4]. In fact, SHS offers a lot of advantages, like rapidity, low energetic cost and high purity of products. Moreover, the generated porosity can be controlled and so appeared as a great benefit for the industrial application referred The goal of this work is the preparation by SHS, of macroporous ZnO monolithic filters with high capacity and easily regenerable, and their optimization with the control of porosity.

Because of its highly explosive character [5, 6], the SHS of ZnO-based materials cannot be easily controlled. That's why a two-step synthesis was developed. First, preparation of ZnS monoliths by SHS, then, conversion into ZnO of those monoliths by heat treatment in air. Morphology and porosity of the final product can be controlled during the first step by varying the experimental parameters like green pellets compaction pressure, argon pressure in the reactor and addition of porogens in the initial Zn-S powder mixture. Then, during second step, additional porosity can appear due to variation of volume cell.

Syntheses are performed in a high pressure reactor (1-15 bar). The reaction is ignited by an electrically heated tungsten wire. The reaction's combustion front is monitored in real time using a thermal camera (FLIR A320). Thanks to that experimental plant, we have access to a vast source of information, like real temperatures reached during the reaction, propagation and cooling's velocity, combustion type. To control the samples final morphology, it is necessary to study the influence of preform compaction pressure, argon pressure in the reactor and the addition of diluents in the initial mixture. Thus, the reaction between zinc and sulfur in argon leads to a thermal explosion, and reaction temperatures are closed to 1600 °C. The ZnS-based monolith obtained has a significant macroporosity and mainly inhomogeneous. The addition of ZnS as diluents, or NaCl as porogen, varying the weight percentage in the initial mixture, allows a better control of the reaction by lowering the temperatures reached during combustion. Then, NaCl is easily removed by lixiviation. We finally obtain materials with controlled and uniform porosity. The resulting materials were characterized by X-ray diffraction and scanning electron microscopy.

From there, the second step of the preparation consists in the oxidation of ZnS under air. We first performed a thermogravimetric analysis on our samples. The results have shown that the conversion occurs between 700 and 800 °C. The experimental parameters such as heating rate, processing temperature and holding time at this temperature remain to be studied to optimize the thermal post-treatment.

The feasibility of preparing ZnO porous monoliths via SHS of ZnS perform had already been demonstrated in a previous study. In this work, we have tried to optimize the way of preparation, searching best experimental parameters. We also tried to optimize the initial mixture composition by searching the best diluent and its percentage. This optimization was facilitated by using the thermal camera and the considerable information given by this technology.

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4A-2

THE INFLUENCE OF TECHNOLOGICAL PARAMETERS ON THE Fe-Al PHASE FORMATION CLOSE TO SHS REACTION UNDER ISOTHERMAL CONDITIONS

Pocheć E.*, Jóźwiak S., Bojar Z.

Department of Advanced Materials and Technology, Military University of Technology Kaliskiego 2 St.,
00-908 Warsaw, Poland
*epochec@wat.edu.pl

The phenomena preceding and accompanying the SHS reaction between Fe and Al elemental powders during sintering were investigated. Many theories have been developed to explain the mechanisms occurring during Fe-Al phase formation. One of the main was described by Deevi and Gadevanishvili [1]. They observed that during the heating of Fe and Al powders mixture two exothermic reactions have occurred, which are responsible for the formation of Fe_2Al_5 phase and FeAl secondary solid solution. Our experiments showed that besides generally known above mensioned phases also high-aluminum phases $FeAl_2$ and $FeAl_3$ are formed [Fig.1].
SEM technique and XRD analysis were used to observe mechanisms of Fe-Al intermetallic phases creation. Due to the large reaction rate, classical methods do not allow to investigate the kinetics of phase transformations. Therefore, DSC technique using JMA (Johnson-Mehl-Avrami) model were used. This approach allowed to calculate Avrami coefficients which characterize the speed and the manner of particular phase transformation. The activation energy of formation of Fe-Al phases was calculated using Kissinger method.
The effect of sintering process temperature and pressure on the phase transformations were examined. It have shown a strong influence of these parameters on the process.
The changes of lattice parameter, content of aluminum and microhardness were also observed.
All the investigations allowed to choose the optimum conditions for obtaining Fe-Al sinters.

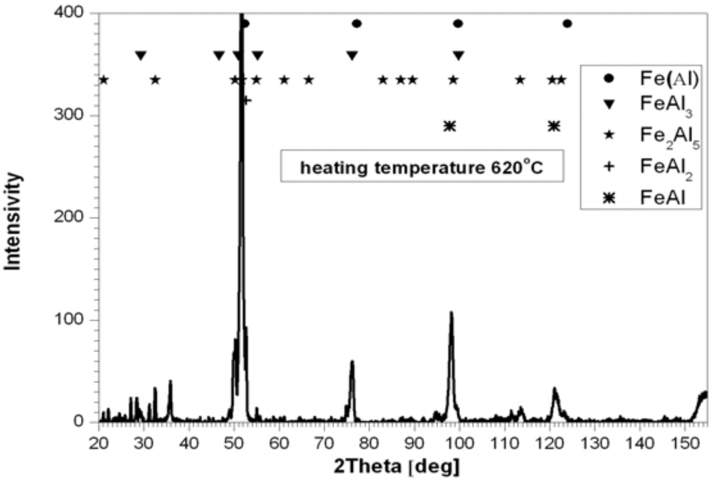

Fig.1 XRD pattern for sample after sintering at temperature of 620°C

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4A-3

SOLUTION COMBUSTION SYNTHESIS OF NANOMATERIALS AND THEIR PROPERTIES

Nagabhushana B.M.*[1], Nagabhushana H.[2]

[1]Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore-560 054, India
[2]Department of PG studies in Physics & Research, Tumkur University, Tumkur - 572 103, *India.*
* bmnshan@yahoo.com

This presentation would review the published literature on solution combustion synthesis, characterization and various studies like magetoresistance (MR), pahotocatalytic, adsorption and luminescence properties of combustion derived products. The solution combustion method was developed by K.C. Patil [1] and it has the advantage of choice of a wide variety of fuels, rapid cooling leading to nucleation of crystallites without any growth and also has the potential to scale up. Because of the gas evolution, large particles or agglomerates can be disintegrated during the process and the products formed are of high purity and nano dimension. The combustion method has been preferred over various traditional and sophisticated synthetic methods such as sol-gel, hydrothermal, micro-emulsion, co-precipitation etc. This method has been used by authors to synthesize metal oxides (CaO, CeO_2, Gd_2O_3, Nd_2O_3, ZnO, MgO), silicates (Ca_2SiO_4, Mg_2SiO_4, $CaSiO_3$, Zn_2SiO_4), and doped manganites (alkaline earth doped $LaMnO_3$). These materials were prepared by respective metal nitrates as oxidizers and organic fuels and products are characterized by PXRD, SEM/TEM, FTIR and surface area measurements. Then, the well characterized samples were used for studying various properties like adsorption, catalytic, photoluminescence, thermoluminescence, COD and color removal, antibacterial, etc [2-23].

The mechanism of the combustion reaction is quite complex and has been studied during the last decade by number of research groups processing parameters such as type of fuel, the amount of gaseous. The products released during combustion, water content, flame temperature (T_f), or the ignition temperature (T_0), addition of extra oxidizer, fuel-to-oxidizer ratio (F/O), furnace temperature etc., play an important role in deciding material properties and phase formation. During presentation, the processing parameters influencing the morphology and their effects on various properties will be presented.

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4A-4

SHS CATALYSTS BASED ON Ni AND Co INTERMETALLIDES FOR DEEP OXIDATION AND FISHER-TROPSH PROCESSES

Sanin V.N.[a)], Borshch V.N.[a)], Andreev D.E.[a)], Yukhvid V.I.[a)],
Lapidus A.L.[b)], Eliseev O.L.[b)], Kazantsev R.V.[b)]

a) Institute of Structural Macrokinetics and Materials Science Russian Academy of Science
Institutskaya street 8, Chernogolovka, Moscow region, 142432, Russia
b) N.D.Zelinski Institute of Organic Chemistry Russian Academy of Sciences,
Leninski prospect, 47, Moscow, 119991, Russia
svn@ism.ac.ru

Deep oxidation of CO and hydrocarbons as well as NO_x reduction is the key problem in purification of exhaust gases from internal combustion engines and effluent gas flows from different industrial enterprises. To date, the catalytic systems for purification of exhaust gases normally contain precious noble metals such as Pt, Rh, and Pd. Meanwhile, an alternative to the above systems can be Ni based polymetallic alloys [1,2] obtained from SHS intermetallides of 3*d* metals. Co based polymetallic alloys can be highly active catalysts in Fisher-Tropsh syntesis of hydrocarbons from $CO+H_2$ as well.

The general scheme of our investigations consists of the following stages:
1. Study of the effect of synthesis conditions on formation of the phase composition and intermetallide structure.
2. Preparation of catalysts by grinding the synthesized cast intermetallic alloy and subsequent leaching of aluminum to obtain highly porous metallic materials with a branched surface.
3. Study of catalytic activity of the obtained catalysts.

In a general form, the chemical scheme for producing cast multi-phase alloys using the SHS metallurgy technique can be represented as follows:

$$(Ox_1 + Ox_2 + Ox_3 + \dots Ox_n) + R \rightarrow \text{[intermetallic alloy]} + R_kO_l + \mathrm{Q},$$

where Ox_i – oxides of Ni, Co, Fe, Mo, V, Mn and so on, R – metal reducer (Al), [intermetallic alloy]- alloys based on aluminides of Ni, Co, Fe *etc.,* Q – thermal effect of the process.

Since the combustion temperatures are extremely high (2000–3000 K), the combustion products (alloys and oxides) appear in the their liquid state. In this communication the combustion was carried out in the centrifugal machine under high gravity in the range 1–1000*g*, where *g* is free fall acceleration.

Figure 1 shows the microstructure of leached samples surface Co–Ni–Al catalysts. The surface is highly eroded. On some sample sections, we can easily see a thick layer of nanosized plates 1–2 μm in diameter and 80–90 nm thick.

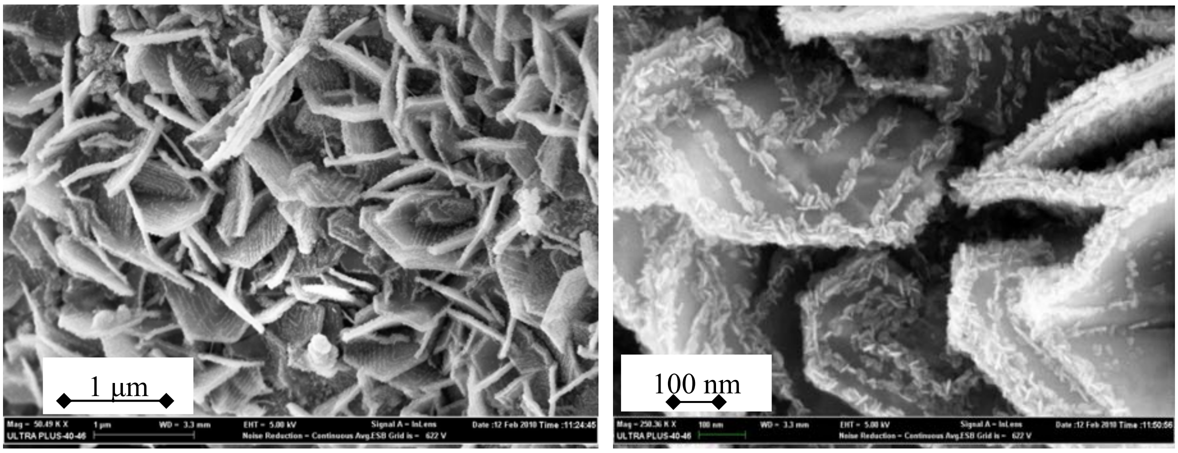

Fig. 1. Microstructure of the surface of Co-Ni-Al catalysts.

The studies of the obtained Ni based catalysts showed that the samples under analysis are characterized by high catalytic activity. The temperature of a 100% conversion of CO is 175°C for the most active catalyst sample. For propane, a 90% conversion is achieved at 250°C. The catalysts of such type are shown to be highly active and their development is a novel challenging direction in the catalysis of deep oxidation processes.

The studies of the obtained Co based catalysts in Fisher-Tropsh processes revealed that obtained hydrocarbons consist predominantly of linear paraffines (ratio of linear to iso-paraffines is equal 6.7) and were characterized by value of a parameter of chain growth $\alpha = 0.92$, that indicates the high contents of a diesel fraction and firm paraffines. These data testify to a capability of an effective utilization of the obtained catalysts for producing higher hydrocarbons.

The work was supported by RFBR, grant № 10-03-91219 and the Program of basic research of chemical department of RAS (program № 7) nanotechnology and nanomaterials.

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4A-5

OBTAINING OF CARBIDE OR TITANUM SILICIDES-CARBIDE WITH SHS METHOD WITH THE USE OF TITANUM ALLOYS

Shulpekov A.M., Lepakova O.K.

10/3 Akademicheskii ave., Tomsk, Russia PO box 634021
Department for Structural macrokinetics of Tomsk Scientific Centre of SB of the RAS
shulp@yandex.ru

Heat resistant and high temperature materials on the base of refractory compounds of transition elements find wider and wider use as constructional materials: injectors, dies, blades of engines of jet aeroplanes etc.[1]. Special steel qualities, intermetallic alloys and compounds of titanium, aluminum are more widely used. Titanium carbide, especially in metallic bundle, is one of the prospective materials for refractory cutting tools, injectors, dies etc.[2] It has decomposition temperature of 3054 ºC, temperature of onset oxidation in air of 850–1200 ºC in dependence of stoichiometry. Family of so-called MAX – compounds, comprising carbides, nitrides, corresponding to formula $M_{n+1}AX_n$, where M is transition material, A is element of IIIA or IVA group, and X is carbon or nitrogen refer to a number of the most novel materials. Titanium silicide-carbide Ti_3SiC_2 is the most studied and prospective one among compounds of this class. Owing to peculiarities of structure of crystalline lattice Ti_3SiC_2 is characterized by unique combination of physical-chemical –mechanical properties: high temperature of decomposition (2300 °C), low density (4,5 gr/sm^3), high values of moduli of elasticity (326 hPa) and shear (135 hPa), and not very high (for carbides) hardness simultaneously (4 –7 hPa). Material is treated like graphite and is weakly sensitive to thermal shocks [3, 4]. The use of expensive powders of titanium and silicon as starting reagents is one of the retarding factors for wide use of Ti_3SiC_2 in material science.

The aim of this work is development of the method of synthesis of materials on the base of carbide and titanium silicide carbide with SHS from cheap raw material – ferroalloys (ferrotitanium and ferrosilicium) as well as titanium-nickel alloy.

Powders of FeSi (FS-75), ferrotitanium (75 mass % of Ti), soot (PM-15) were used for synthesis of samples. Determination of structure of activated powders and synthesized samples was carried with X-Ray analysis. Video recordings were carried out on X-Ray device «XRD - 6000» Shimadzu (Cu K_α). Powders of reagents were mixed in required proportions and thoroughly grinded in porcelain mortar up to homogeneous mixture .The mixture was subjected to cool one-sided compaction in steel press form at pressure P=40-80 kg(f)/sm^2 in order to obtain samples in the form of the cylinder with Ø = 15 or 20 mm. Synthesis was conducted in air and reactor of constant pressure in argon.

Investigation of phase composition and microstructure of products , where Ti-N- alloy (12 mass % of Ni), was used as reagent showed , that in Ti-Ni-C system nickel doesn’t form solid solution and is separated as independent phase, and TiC of various stoichiometry is formed as the main phase. The content of binded carbon correlates with its content in starting mixture. In synthesis products of NiTi-Si-C system the main phase is titanium carbide TiC, peaks, belonging to $TiSi_2$, Ti_3SiC_2 are also present. Two phases – TiC and Fe were detected in the system ferrotitanium and carbon with X-Ray phase analysis. Size of particles of ferrotitanium powder, carbon content in charge and other synthesis parameters effects, substantially, on combustion velocity and parameter of TiC lattice. In this case the decrease in size of ferrotitanium particles increases combustion rate and parameter of TiC lattice.

Since due to insufficient heat extraction during synthesis, the reaction proceeds incompletely, titanium carbide is unstoichiometric one. To increase the thermicity of the process and the degree of stoichiometry, the part of ferrotitanium was substituted for titanium PHT. Substitution of ferrotitanium for titanium leads to regularly increase of parameter of TiC lattice, besides the combustion velocity is also rising. The material, obtained with the substitution of ferrotitanium for 40 mass % if titanium doesn't differ from titanium carbide powder, obtained from titanium carbide mixture, according to its characteristics. In products of synthesis of FeTi-Si-C system, the main phase is titanium carbide TiC, reflections, belonging to $TiSi_2$ and Ti_3SiC_2 as traces are also observed.

Thus, method of obtaining of refractory electric conductive materials on the base of carbide from titanium-containing alloys with SHS, were suggested as a result of the work conducted. The technology allows to obtain materials, which don't give way to titanium carbide, obtained from pure powders, according to characteristics and to lower their cost.

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5B-1

A NEW STRATEGY FOR THE SYNTHESIS OF HIGH LUMINESCENCE RED-EMITTING $M_2Si_5N_8$:Eu^{+2} PHOSPHOR

Nersisyan H.H.*, Won C.W., Won H.I.

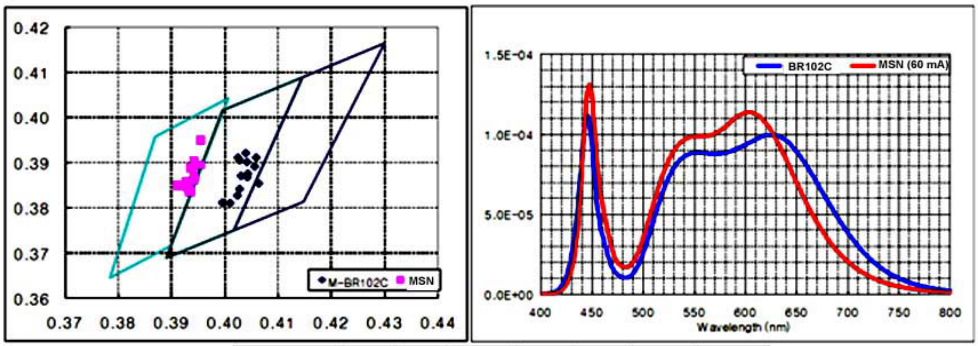
[1] Rapidly Solidified Materials Research Center (RASOM), Chungnam National University,
220 Kung-Dong, Yuseong-gu, Daejeon, 305-764, Republic of Korea
* nersisyan_hayk@cnu.ac.kr

Using a one-pot solid-state combustion synthesis procedure, we have successfully prepared silicon-nitride-based red-emitting $M_2Si_5N_8$:Eu^{2+} (shortly CS-MSN) phosphor fine powder under the nitrogen atmosphere. The phosphors synthesized by the developed method show good emission characteristics and high performance in LED package. Our technology holds considerable promise for the large-scale and low-cost production of $M_2Si_5N_8$:Eu^{2+}phosphors.

Eu^{2+}-activated $M_2Si_5N_8$ (M is Ca, Sr, Ba) are promising down-conversion red phosphors candidates for the white LEDs application. Nitridosilicates $M_2Si_5N_8$: Eu^{2+} show red emission and has high quantum efficiency and very low thermal quenching, which makes them an encouraging red phosphors for use in white light-emitting diodes to improve the color rendering index. Four synthetic strategies for $M_2Si_5N_8$:Eu^{2+} have been proposed in the literature: solid-state reaction (SSR) gas reduction and nitridation (GRN), carbothermal reduction and nitridation (CRN), and high pressure ammothermal methods [1-3]. In addition to existing techniques we have developed a combustion route for synthesising of $M_2Si_5N_8$:Eu^{+2} phosphor powders under the nitrogen pressure. This is a high temperature process with an abrupt temperature increase from 25 °C to 1740 °C occurring in the first part of the reaction zone; a long tail and an after-burning zone with a maximum temperature of about 1830 °C then followed. According to XRD analysis single-phase phosphors of $M_2Si_5N_8$ compoition can be obtained by the developed combustion process. Generaly, CS-synthesized $M_2Si_5N_8$:Eu^{2+} phosphor show good dispersion and mean particle size from 0.5 to 7 μm.

The PL characteristics of red-emitting CS-MSN ***phosphor powders*** itself is studied and their luminescent properties are compared to those of reference sample, commercial silicon-nitride-based red (BR102C, Mitsubishi, Japan) phosphor. Red-emitting nitride phosphors obtained by CS shows emission spectrum exhibiting a peak from 620 to 650 nm under the excitation of 450 nm. This broad band emission of CS-MSN phosphor at excitation of 450 nm is assigned to the allowed $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion. The emission spectrum of CS-MSN powder with 620 nm emission peak (0.05 mole Eu^{2+}) indicates that relative intensity of red phosphor prepared by the combustion method is more than 90 % compared to the reference sample. Increasing of Eu^{2+} concentration from 0.05 to 0.5 mole shift the emission peak from 620 nm to 650 nm and the emission intensity drops from 90 to 80 %.

Tests performed in LED packages have shown high-performance of combustion synthesized phosphor powders. At least similar or stronger luminescence effect of the LED product (100-105%) was achieved by using only 50-70 % quantity of our phosphor powder (in comparison to commercial phosphor) (Fig.1).



Model	Vf (V)	If (mA)	CD	x	y	CCT (K)	CRI
M-BR102C	3.16	60	5.84	0.40	0.38	3504	83.8
CS-MSN	3.16	60	6.64	0.39	0.38	3739	83.2

Fig. 1. LED package testing results for warm light application.

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5B-2

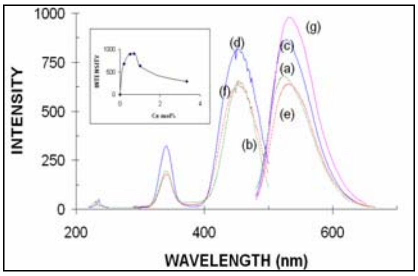
SYNTHESIS OF MULTICOMPONENT CERAMIC PHOSPHORS FOR SOLID STATE LIGHTING USING SHS PROCESS

Yadav P.J.[1], Joshi C.P.*[1], Moharil S.V.[2]

[1] Applied Physic Department, R. K.N Engineering College, Katol Road, Nagpur 440 013, India
[2] Physics Department, RTM Nagpur University, Nagpur 440 010, India
*joshicp@rknec.edu, charusheela_4253@yahoo.co.in

About 50% of the world's need of lighting is provided by artificial lighting [1]. In last decade world has witnessed rapid shift from conventional Hg based lighting to LED based solid state lighting (SSL). SSL technology extensively uses YAG:Ce phosphor for production of white light LEDs[2]. Part of the blue light from the (In,Ga)N LED chip is absorbed by a thin layer of Ce^{3+}-doped YAG and is converted into yellow light. The combination of blue and yellow gives a bright white light source with an overall energy efficiency exceeding that of the compact fluorescent lamp.

Several soft chemical routes have been explored for synthesis of YAG, but are discarded due to their complex nature, high cost for the industrialization, phase impure materials etc. In this paper we describe rapid one step modified SHS synthesis [3] of YAG:Ce^{3+} and related phosphors carried out at 500 C using mixed fuel. Photoluminescence spectra of YAG:Ce and LED prepared with thereof are comparable with commercial phosphors.



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5B-3

ACTIVATION OF SHS BY RAPID DECOMPOSTION OF SILICON NITRIDE

Kata D., Lis J.

[1] AGH- University of Science and Technology Al. Mickiewicza 30, 30-059 Kraków, Poland
* kata@agh.edu.pl

The last decade has shown that SHS can be activated by several techniques. Mechanical alloying and field activation play a significant role in self sustaining solid state reactions and can bring perspective results for nanopowders preparation and their densification. The combination of rapid prototyping techniques and SHS can bring promising results for joining different kind of metals and ceramic also. Present study shows that rapid silicon nitride decomposition can activate formation of solid solution because specific mechanisms of SHSynthesis.

Experimental study has been placed on solid solution formation in the O'sialon and X-sialons systems. The both sialons are not determine yet because preparation difficulties by conventional methods. It has been amply demonstrated that rapid silicon nitride decomposition in SHS conditions play a crucial role in formation of solid solution in the Si and N based systems. Experimental work shown that combustion in all S-Al-O-N systems propagated with formation of transient Si_3N_4 phase resulted in either: O'sialon and X-sialons nanosized products. To elucidate role of silicon nitride decomposition on products formation, thermodynamic data, temperature profiles, morphology (SEM, TEM), dispersion (BET) and phase composition (XRD) of products were evaluated. It was found, that silicon nitride forms transiently at early stages of combustion because thermodynamic and kinetic considerations. Two steps of reaction were detected: (i) nitridation of the silicon surface during initial stages, (ii) simultaneous decompostion of silicon nitride and reaction with silica resulted in pure sialon nano-powder.

Finally, it was demonstrated that SHS in the formation of sialon powders by decomposition of Si_3N_4 is very efficient and provide nano-sized products. Obtained powders are well sinterable and after further processing can be used in wide range of application as refractory materials, ceramic armour, elements of chemical equipment.

5B-4

POROUS FEAL INTERMETALLICS MATERIALS FABRICATED BY SHS REACTION

Karczewski K.*, Jóźwiak S., Chojnacki M., Stępniowski W., Bojar Z.

Military University of Technology, Warsaw, Gen. S. Kaliskiego 2 str., 00-908, Poland
*kkarczewski@wat.edu.pl

The influence of organic compounds additions on the SHS reaction in the Fe-Al system has been investigated in this paper. Porous FeAl intermetallics were fabricated by the Self-propagating High-temperature Synthesis (SHS) from the iron and aluminum elemental powders and organic compounds additives mixtures compacted into cylindrical pellets. In order to maintain shape of the final products experiments were conducted in the volume-controlled environmental reactor designed by the authors and described in paper [1]. Porous structures of FeAl intermetallics fabricated in the reactor were investigated using SEM and XRD analysis. The results explicitly indicate that it is possible to obtain porous intermetallic materials with use of environmental reactor. It was found that the type of additives have a significant effect on the final structure of porous FeAl sinters.

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5B-5

COMBUSTION SYNTHESIS OF FERROTITANIUM ALLOY REINFORCED BY CERAMIC PHASE

Asatryan A., Avetisyan A., Davidova A., Khachatryan H.L.*

Yerevan State University, Yerevan, A. Manukyan str., 1, AM-0025, Armenia
*haykh@ysu.am

In this work is presented the results of synthesis of ferrotitanium alloy under the combustion mode. *In situ* reinforcing of formed alloy by titanium nitride, control of its amount and distribution into metallic matrix, as well as the ration of metals in the alloy was investigated. The effect of initial mixture composition, reactants' particle size, and other operating conditions, such as gas pressure and initial mixture's density on the combustion front propagation velocity and maximum combustion temperature as well as product microstructure and its phase composition was investigated. The combustion was performed in the nitrogen atmosphere. Utilizing heat released from titanium-nitrogen reaction ferrotitanium alloy was formed. In order to govern filtration process and formation of titanium nitride some amount of titanium was replaced by titanium hydride. Thus, the titanium hydride restricts impregnation of nitrogen into reacting zone due to released hydrogen; hence varying hydride's amount it is possible to control amount of infused nitrogen and such manner to govern amount of formed titanium nitride. Experiments have shown that in the Ti- Fe system increasing concentration of Ti in the initial mixture causes the decrease of combustion parameters and when amount of iron was 40 wt.% the combustion limit was appeared.

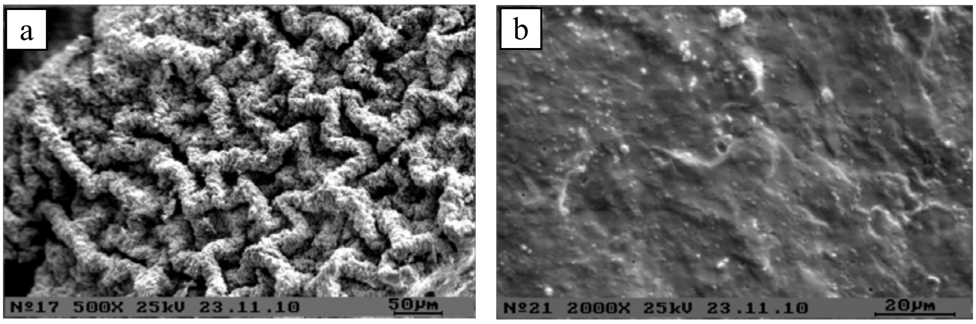

Fig. 1. Micrograph of combustion product obtained from the Ti-20%Fe reacting system; a – upper site, inner site. P_{N2}= 5atm

Products morphology and compositions were examined using XRD, and SEM analyses. Microstructure analyses have shown that surface of alloys has jagged structure (figure 1a) which mainly was titanium nitride while inside has even appearance (figure 1b).

The oxidation resistance was examined using DTA technique. According to results obtained the ferrotitanium alloys withstands to oxidation up to 900^{o}C while pure titanium and iron powders start oxidized at ~650^{o}C and 550^{o}C, respectively.

7B-1

SHS OF INORGANIC MATERIALS WITH DESIRED STRUCTURE AND POROSITY

Boyarchenko O.D.*, Barinov V.Yu., Vadchenko S.G., Sytschev A.E.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
*olgaboyarchenko@gmail.com

Metallic and ceramic materials with open porosity are being used as filters, catalyst supports, implants, sound-proofing items, etc. Besides sintering, such materials can also be fabricated by SHS method. Since the regulation of porosity characteristics (open to close porosity ratio, size distribution of pores) in SHS-produced items is a rather complicated problem [1, 2], it seemed interesting to perform SHS reactions in preliminary structured green compositions.

Investigated was an SHS-based process for fabrication of inorganic materials with desired structure and porosity. Starting 5Ti + 3Si, Ni + Al, and 0.45Ti + 0.3Al + 0.25Nb + 0.35C powder mixtures were rolled to obtain the corrugated tapes which were then cut into pieces, stacked into sandwiches, and ignited under some clamping pressure.

In this work, the latter ones were prepared by either powder rolling to obtain planar tapes [3] followed by its corrugation or tape rolling to obtain profiled tapes [4, 5]. Then the corrugated or profiled tapes were cut into pieces, stacked into sandwich-type structures, and ignited to initiate SHS reaction under some clamping pressure.

Powders of desired composition were first rolled into a planar tape and then corrugated with gear rolls to obtain corrugated tapes with pitch a and goffer amplitude b. This technique is applicable only to powder mixtures of ductile metals; in case of metal–nonmetal mixtures, it requires the use of plasticizing agents.

Corrugated tapes were cut unto 20 × 20 mm pieces and stacked into sandwiches.
Tapes with a single-sided profile were fabricated by rolling either a preliminary fabricated planar tape or directly, by rolling starting powders mixtures in profiled rolls. Both types of profiled tapes were used in experiments.

A combustion wave in the systems under consideration is known [6, 7] to propagate from layer to layer by the so-called relay race mechanism.

Porous combustion products were obtained from sandwiches of rolled 5Ti + 3Si and 0.45Ti + 0.3Al + 0.35C + 0.25Nb mixtures. The formation of conjugation bridges between the tapes ensures the mechanical strength of porous material.

The EDS data for combustion products derived from 5Ti + 3Si mixtures—72–75 wt % Ti and 28–25 wt % Si—are consistent with Ti_5Si_3 as a product: 73.96 wt % Ti and 26.04 wt % Si. The composition of combustion products derived from 0.45Ti + 0.3Al + 0.35C + 0.25Nb mixtures was found to be localization-dependent.

Suggested is the process for fabricating materials with a regular porous structure from starting 5Ti + 3Si, Ni + Al, and 0.45Ti + 0.3Al + 0.25Nb + 0.35C powder mixtures. The technique may turn out promising for SHS production of bone implants, filters, and catalyst supports.

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7B-2

INFLUENCE OF MECHANICAL ACTIVATION ON SHS AND STRUCTURE FORMATION IN NANOSTRUCTURED TI ─ BN AND TI ─ SIC ─ C SYSTEMS

Shkodich N.F.[1]*, Vadchenko S.G.[1], Rogachev A.S.[1], Sachkova N.V.[1], Neder R.B.[2], and Magerl A.[2]

1 Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
2 Institute of Crystallography and Structural Physics, University of Erlangen-Nürnberg, Staudtstraße 3, Erlangen, D-91058 Deutschland
* n.f.shkodich@mail.ru

During past years, ever-growing interest was displayed in the methods of mechanical activation (MA) and self-propagating high-temperature synthesis (SHS) to develop a new approach to production of nanostructured materials. Mechanical activation provides the possibility of both modificating the conditions of the chemical reaction run and changing the thermal parameters of the synthesis (temperature, combustion velocity, heating rate, and others) thus leading to the different structures and properties of the final product.

Our investigation aimed at establishing the influence of MA on SHS. The Ti ─ BN and Ti ─ SiC ─ C systems were studied. Green mixtures were prepared by dry mixing of the initial components in china crucibles at the stoichiometric ratios corresponding to the following reactions : $3Ti + 2BN = 2TiN + TiB_2$ and $3Ti + SiC + C = Ti_3SiC_2$.

Preliminary MA was preformed in a water cooled planetary ball mill (AGO-2) type at room temperature under argon. The milling procedure was carried out at the ball/mill ratio of 20 : 1. The milling time varied within 0.20, 40 s, 1, 3, 6, 9, 12, 15, 20, 25, 30 min.

The resultant mechanically activated particles were composed of layers of the initial components alternating with each other at the nano level.

The products from the mechanically activated Ti + BN and Ti ─ SiC ─ C mixtures were obtained by SHS method. Experimental investigation of the combustion temperature and velocity were performed under argon in a constant-pressure chamber (1 atm). Prolongation of the MA time led to a 1.5 − 2-fold increase in the combustion velocity. Besides, MA resulted in reduction of the combustion temperature by about 400ºC and 360ºC in the Ti + BN and Ti ─ SiC ─ C systems, respectively.

The dependences of the ignition temperature on the MA duration, the heating rate, and the way of the sample preparation were studied. It was found that after the MA time within 0 − 30 min the ignition temperature lowered by approximately 600°C.

For the determination of the internal microstructure, the particle size and microstrains of mechanically activated powders and of the combustion products were analyzed by X-ray powder diffraction on a Huber Guinier diffractometer at the Institute of Crystallography and Structural Physics, in Erlangen, Germany.

Analysis showed that an increase in the MA duration of the Ti + BN and Ti ─ SiC ─ C mixtures led to a decrease in the peak intensities and broadening of the Ti peaks. With increasing activation time, the BN reflexes in the Ti + BN reaction mixtures were instantly broadened and in three minutes their intensity became comparable to that of the background. Similar behavior was also observed in case of graphite in the activated Ti ─ SiC ─ C mixtures. This evidences the destruction of the crystal structure (amorphization) of boron nitride and graphite in the MA process.

The effect of milling time on the crystalline size and strain in the powder mixtures and SHS products we determined from line broadening analysis of the XRD peaks. The Rietveld full profile refinements were carried out with the Fullprof Suite. Best refinement results were obtained with the Thompson-Cox-Hastings Pseudo-Voigt profile-function. As a result of up to 30 min MA, the average size of the Ti crystallites was found to reduced down to 25 and 50 nm in the Ti + BN and Ti ─ SiC ─ C systems, respectively. Mechanical activation was found to affect the size of product crystallites. The value of the micro stains increased with the MA duration.

Formation of nanocomposites at the stage of mechanical activation provides proper conditions for synthesizing nanostructured SHS materials with a complete inherence of the precursors' structural morphology.

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Acknowledgement

The present work was supported by the Russian Foundation for Basic Research (Project no. 10-03-00217-a) and the Council of the RF President Grants for Support of Leading Scientific Schools (Grant no. NSh-6497.2010.3).

7B-3

SINTERING AND HOT-PRESSING OF SHS DERIVED POWDERS IN Ti-Al-C AND Ti-Al-N SYSTEMS

Chlubny L.*, Lis J.

[1] AGH-University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Ceramic Technology and Refractories , al .Mickiewicza 30, 30-059, Krakow, Poland
*leszek@agh.edu.pl

In the Ti-Al-C and Ti-Al-N systems exists group of interesting materials called MAX-phases. This materials are characterised by heterodesmic layer structure. Their specific structure consisting of covalent and metallic chemical bonds strongly influence their semi-ductile features locating them on the boundary between metals and ceramics [1]. This fact may lead to many potential applications, for example as a part of a ceramic armour.

Self-propagating High-temperature Synthesis (SHS) with local ignition system was applied to obtain sinterable powders of nanolaminate materials in Ti-Al-C and Ti-Al-N systems. Synthesized compounds were Ti_2AlC, Ti_3AlC_2 and Ti_2AlN. As a precursors for synthesis of ternary materials intermetallic compounds, namely TiAl and Ti_3Al were used. These intermetallic compounds were also synthesized by SHS method. Others substrates that were used were metallic powders of titanium, aluminium and graphite as a source of carbon and also high purity nitrogen gas. Phase compositions of obtained powder were examined by XRD method.
After phase analysis, selected powders, containing highest amount of ternary phase were used for sintering in various temperature both in a presureless sintering and hot-pressing process, in argon atmosphere in case of Ti_2AlC, Ti_3AlC_2 and in nitrogen atmosphere in case of Ti_2AlN. Changes in phase composition were observed both during pressureless sintering and hot pressing method. These phase composition evolution was examined by XRD method. In case of Ti_2AlC pressureless sintering was conducted in temperatures between 1000ºC up to 2070ºC. The hot-pressing process was realized up to 1350ºC. For Ti_3AlC_2 pressureless sintering was conducted in temperatures between 1000ºC up to 1930ºC. The hot-pressing process was realized up to 1350ºC. While in case of Ti_2AlN pressureless sintering was conducted in temperatures between 1000ºC up to 2200ºC. The hot-pressing process was realized up to 1600ºC [2, 3, 4].

In case of all of SHS obtained powders it can be easily observed characteristic transformation from hexagonal structure into regular structure of TiC and TiN respectively. Also chemical reaction undergoing during the sintering process is observed. This reaction promotes forming of additional amounts of ternary nanolaminate compounds in a sintered dense body. For hot-pressed Ti_3AlC_2 it was possible to obtained 96% of MAX phase in a final product. The same situation was observed in hot-pressed ternary nitride, where was possible to achieve 76% of MAX phase in the final product.
Mechanical properties of obtained dense polycrystalline materials will be examined.

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7B-4

MODIFICATION OF THE SHS ASSISTED SINTERING OF Fe-Al INTERMETALLIC MATERIALS BY SMALL ADDITIONS OF LOW MELTING ELEMENTS

Chojnacki M.*, Jóźwiak S., Karczewski K., Bojar Z.

Military University of Technology, Warsaw, Gen. S. Kaliskiego 2 str., 00-908, Poland
* mchojnacki@wat.edu.pl

The manufacture of FeAl intermetallic materials with use of the elemental powders sintering techniques is associated with the Self-propagating High-temperature Synthesis. The highly exothermic nature of this reaction often leads to harmful swelling and high porosity of sinters. The main objective of this study was to investigate the possibility of control of the SHS reaction and decrease of its intensity. An attempt to modify sintering process of iron and aluminum elemental powders with use of small additions of low melting elements was presented in this paper. The kinetics of such modified sintering were investigated using DSC technique, XRD analysis and SEM observations. This work is the direct continuation of the studies presented in paper [1].

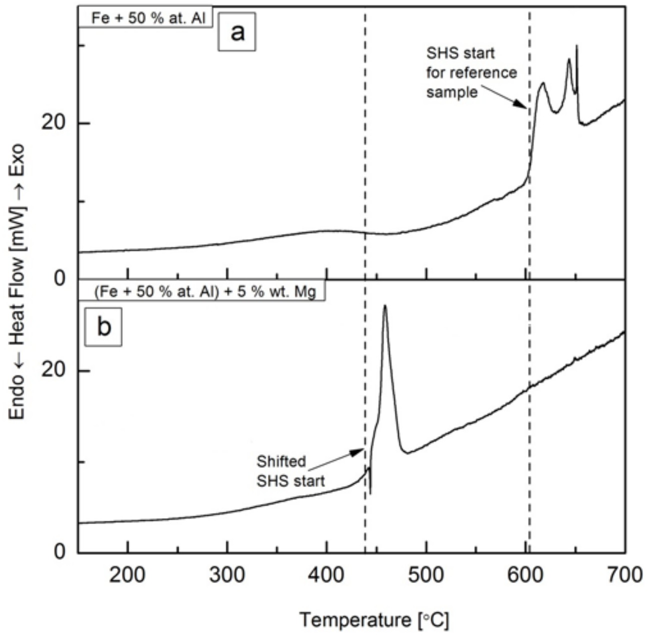

Fig. 1. Comparison of the DSC curves obtained for reference (a) and Mg alloyed compositions (b) sintered under argon flow with a heating rate of 1 deg/min

Some of the investigated elements induced significant changes in the mechanism of exothermal formation reaction of Fe-Al intermetallic phases. Elements that forms low melting eutectic and intermetallic phases with aluminum (for example magnesium) are changing the reagents' state of aggregation, from solid – solid to liquid – solid before the synthesis reaction. Aluminum-based liquid favours diffusion processes allowing high-aluminum phases to be formed at relatively low temperature resulting in an almost instantaneous SHS initiation. Initiation temperature of SHS reaction was pronouncedly shifted to lower value as compared with undoped composition (Fig. 1). resulting in noticeable decrease of the reactions enthalpy. On the other hand, some of the elements, despite forming low melting eutectic phases with aluminum, also forms high melting intermetallic phases (with aluminum and/or iron) which immediately consume the entire addition- or aluminum-based liquid solution. In this case the influence of such occurrence on the SHS reaction's kinetics is minimal if any at all.

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7B-5

FABRICATION OF SHAPE MEMORY ALLOY IN Mn-Ni-Sn THERNARY SYSTEM

Baghdasaryan R., Kirakosyan H.V., Kharatyan A.S., Khachatryan H.L.*

Yerevan State University, Yerevan, A. Manukyan str., 1, AM-0025, Armenia
*haykh@ysu.am

Shape memory alloy (SMA, smart metal, memory alloy, smart alloy) is an alloy that "remembers" its original, cold, forged shape, and which returns to that shape after being deformed by applying heat. This material is a lightweight, solid-state alternative to conventional actuators such as hydraulic, pneumatic, and motor-based systems.

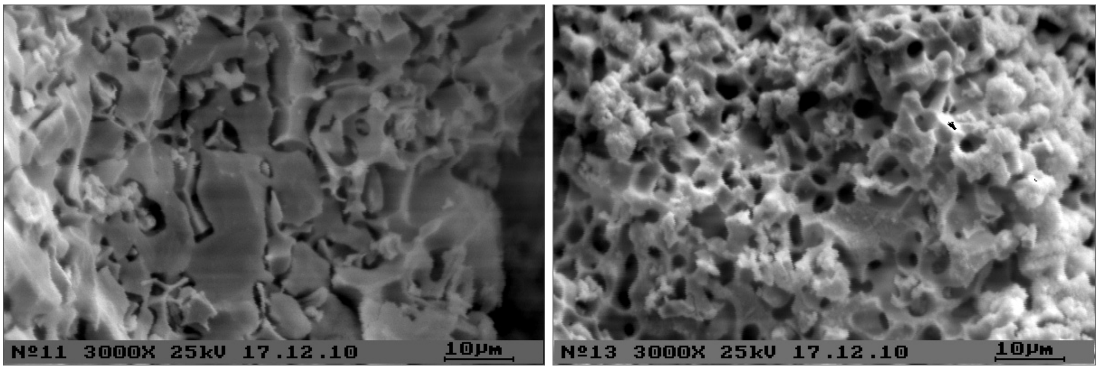
In the presented work Ni:Mn based SMA was synthesized using oxide source. As initial mixture the Mn_2O_3- Ni(NiO)-Mg systems were chosen and the combustion laws were investigated. It must be emphasized that adding third element (e.g. Ge, Sn, In, etc.) into Ni:Mn matrix makes its shape memory alloy.

As shown experiments in the Mn_2O_3-Mg-nNi system the increased concentration of nickel in the initial mixture causes the decrease of combustion parameters and when amount of Ni was exceed 70 wt.% the combustion limit appears. According to XRD analyses the combustion products consisting of Ni:Mn alloys and magnesia. In order to remove the MgO acetic acid was applied which enables to remove magnesia without harming metal alloy.

In order to add third element into Ni:Mn alloy and to synthesize SMA a $SnCl_2$-Mg mixture was added into green mixture. According to the thermodynamic calculation $SnCl_2$-Mg reaction is very exothermic, $\Delta H = -311.78$ kJ/mol and corresponding adiabat temperature is mounts up to $T_{ad} = 2277^{o}C$. The experiments have shown that using [Mn_2O_3-Mg-Ni] – [$SnCl_2$-Mg] system allows to synthesize $MnNi_2Sn$ thernary intermetallic compound.

The effect of initial mixture composition, type of used reactants, gas pressure on the combustion front propagation velocity and maximum combustion temperature as well as product phase composition and microstructure was investigated. Products morphology and compositions were examined using XRD, and SEM analyses. The XRD analyses testified that $MnNi_2Sn$ thernary intermetallic compound forms at certain composition of initial mixture. Varying this composition yields to formation other by-products such as $Mn_{3.7}Sn$, Ni_3Sn, etc.

Microstructure analyses have shown that the formed intermetallic compound uniformly distributed into MgO matrix (figure 1).



a) b)

Fig. 1. Micrographs of the combustion product obtained from a) [Mn_2O_3-Mg-50%Ni] – 50%[$SnCl_2$-Mg] and b) [Mn_2O_3-Mg-30%Ni] – 50%[$SnCl_2$-Mg] reacting systems

The shape memory effect was examined using DTA technique. According to results obtained reversible phase transformation take place at 720 -780°C range (Figure 2).

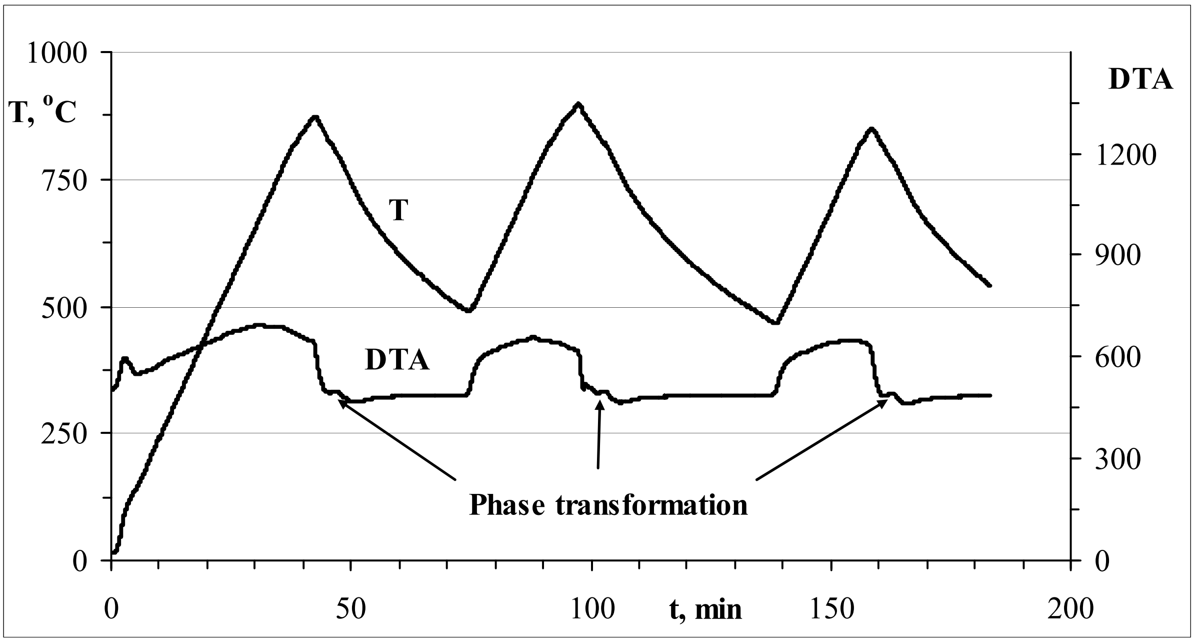


Figure 2. Reversible phase transformation in $NiMn_2Sn$ intermetalic SMA.

7B-6

FABRICATION OF MICROCHANNEL-TYPE TRANSPIRATION COOLING DEVICES BY REACTION SINTERING AND SHS

Ohmi T.*, Omura M., Kumagai T., Iguchi M.

Hokkaido University, Sapporo, Hokkaido, 060-8628, Japan
* ohmi@eng.hokudai.ac.jp

The transpiration-cooling technology using liquid water as a coolant is one of the most effective thermal protection method. Recently, this technology has attracted attentions in various fields. It is expected to be used for a disaster preventing robot working in a fire [1], a thermal protection suit [2], a drain for molten steel from a blast furnace [2], and a hypersonic space plane [3], etc.

In this study, we propose a novel transpiration-cooling system which can be designed for small parts with complicated geometry. In this system, the parts consist of open porous metal and contain microchannel networks. The microchannel networks act as flow passages for cooling water like leaf veins of plants or blood vessels of animals. The cooling water delivered via the microchannel networks seeps out to the surface of the porous metal to be vaporized absorbing the latent heat of evaporation.

We examined a powder-metallurgical microchanneling process to produce such a device consisting of a thermally-resistant Ni-Al alloy. We used powder mixture of nickel and aluminum as a body metal, and aluminum wire as a sacrificial core. The body metal reacted to produce an open porous Ni-Al alloy. The sacrificial core was to melt and migrate to the body-metal region to give the shape of the microchannel. Ni-33mol%Al elemental powder mixture containing an aluminum wire 0.5 mm in diameter was heated from room temperature to a given temperature above the melting point of aluminum.

When the heating rate was 0.4 Ks^{-1} and the initial porosity of the green compact was less than 59.8 %, a SHS reaction occurred and the resultant specimens cracked significantly. In contrast, microchannels were produced in reaction-sintered specimens in the cases of higher initial porosities.

We also examined a thermite-type SHS reaction expressed by the following equation.

$$3a_T\mathrm{NiO}+3(1-a_T)\mathrm{Ni}+(1+2a_T)\mathrm{Al}=\mathrm{Ni_3Al}+a_T\mathrm{Al_2O_3}$$

where a_T is the ratio of the thermite reaction to the thermite-type SHS reaction. When a_T was 0.02, microchannels were produced even when the SHS reaction was occurred.

A water-flow examination was carried out for a reaction-sintered specimen with a zigzag microchannel. As shown in Fig. 1, seeping water delivered via the microchannel was observed on the entire surface of the specimen.

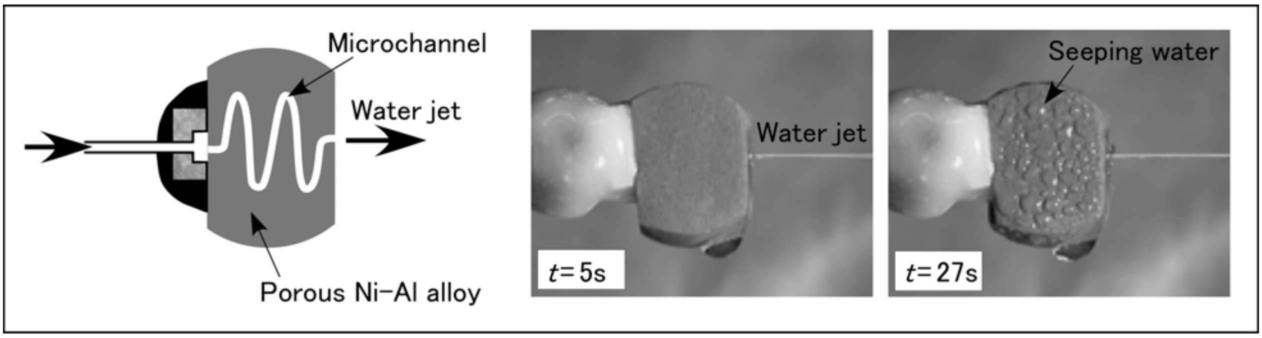


Fig. 1 Flow examination for a Ni-Al reaction-sintered specimen.
Water flow rate was 2.5×10^{-6} m^3s^{-1}.

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7C-K – KEYNOTE TALK

SHS OF CAST OXIDE AND OXYNITRIDE CERAMICS

Yukhvid V.I.

Institute of Structural Macrokinetics and Materials Science RAS,
8 Institutskaya ul., Chernogolovka, Moscow region, 142432 Russia
yukh@ism.ac.ru

The paper reviews the main results obtained by the author and his colleagues since 1980 in synthesizing cast oxide and oxynitride materials. Two approaches are used to synthesize cast oxide ceramics: 1 – combustion of thermite mixtures with complete reduction of initial oxides and formation of high-temperature two-phase melt of combustion products, the process being followed by gravity separation and crystallization of oxide and metal phases; 2 – combustion of mixtures based on peroxides with their incomplete reduction when a single product is formed – cast oxide material [1, 2]. Lately, we have found out that cast oxynitride ceramics can be formed at combustion under nitrogen pressure in the case of introduction of nitride additives to thermite mixtures, [3].

Much attention has been paid to experimental and theoretical study of phenomenology and regulations of combustion of thermite mixtures, control of phase separation under gravity, and formation of combustion product composition. The experimental investigation has proved that it is possible to change combustion, phase separation and melting characteristics as well as to obtain cast oxide and oxynitride ceramics of various structures, chemical and phase compositions by varying the parameters of the process (gas pressure, reaction volume size, centrifugal effects, etc.) and the reactive mixture (reagent ratio and dispersion, introduction of functional additives, etc.), Fig. 1.

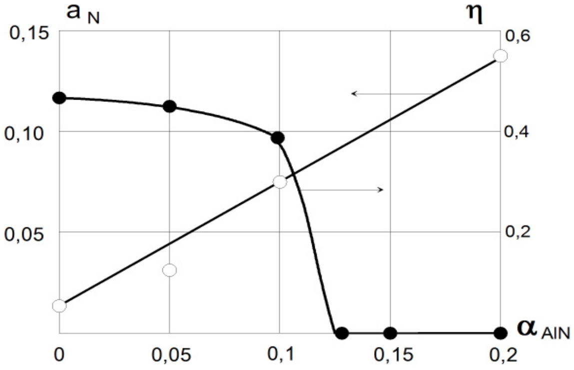

Fig.1. Dependence of nitrogen content in oxynitride layer (a_N) and metal and oxynitride phase separation degree on AlN content(η) in the initial mixture, Fe2O3+4Al+αAlN.

Based on the results we have developed the ideas on the synthesis mechanism, combustion and gravity separation processes.

The knowledge on controlling autowave synthesis of cast ceramics allowed us to develop materials for industrial application:

1. Cast oxide solid solutions Al_2O_3 x Cr_2O_3 with random Al_2O_3/Cr_2O_3 ratio, Fig.1. A mixture of chromium oxide with aluminum and corundum and quartz additives was used. The oxide ceramics containing 5 – 10 % of chromium oxide was called “L-Rubin” due to its color. L-Rubin is characterized by unique properties – high resistance to metal melts, strength, hardness, wear resistance, etc. which allow applying it for making molds and abrasive tools;
2. Cast oxide solid solutions SiO_2 x Cr_2O_3 containing 10 – 20 mass % of Cr_2O_3. They are characterized by amorphous structure, high resistance to nickel and cobalt-based melts, zero coefficient of thermal expansion, excellent solubility in alkalis. It allows using them for manufacturing removable forming rods;
3. Cast lanthanum chromite $LaCrO_3$ stabilized with calcium and aluminum oxides. It is characterized by high conductivity and can be used for manufacturing high-temperature heaters;
4. Cast oxynitrides Al-O-N, Al-Si-O-N, Al-Cr-O-N, etc. can be used for producing high-strength transparent glasses.

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7C-1

WELDING OF ALUMINUM ALLOYS USING Al-CuO COMBUSTION SYNTHESIS REACTION

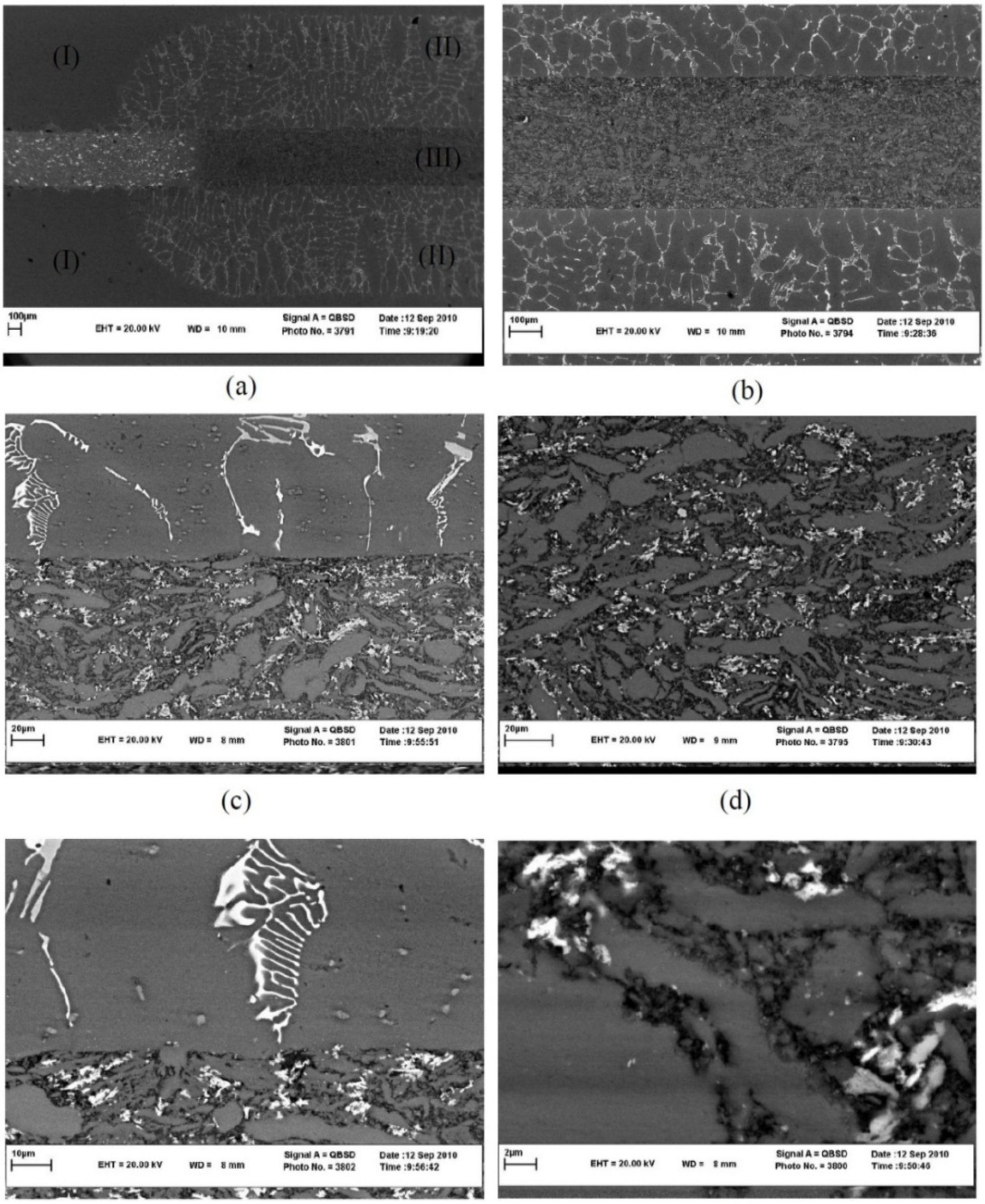
Bahrami Motlagh E.*, Vahdati Khaki J., Haddad Sabzevar M.

Department of Materials Science and Engineering, Engineering Faculty, Ferdowsi University of Mashhad,
Mashhad, Iran
*ebahramimotlagh@gmail.com

Thermite reactions have been utilized in rail welding for nearly 100 years [1]. Recently, some methods are devised to decrease the ignition temperature of thesekinds of reactions such as highenergy ball milling (HEBM) [2] and arrested reactive milling (ARM) [3, 4]. Among different combustion synthesis reactions Al–CuO thermite is of particular interest because the reaction is highly exothermic and it’s a diabatic temeperature can be adjusted [2, 5].

In this work, the released heat from the "14Al+Ni+3CuO" combustion synthesis reaction was used for welding of aluminum alloys (Al1100). The drawback for this process has been the high ignition temperature of the reaction which is higher than the melting point of aluminum. Using arrested reactive milling (ARM) and adding a small amount of elemental nickel to the thermite mixture its ignition temperature was decreased, so that this thermite mixture became applicable for welding of non-refractory materials. Welding procedure was as follow. First of all, aluminum 1100 plates were selected as the joining parts and cut into samples measuring 20 mm×20 mm×5 mm. Their largest surfaces were ground manually up to grit 1200 finish, using SiC grinding paper. Afterwards, the milled powder mixture was cold-pressed into a cylindrical compact in a steel mould by applying 276 MPa uniaxial pressure.In the next step, this compact was pressed between the two surface prepared aluminum 1100 plates under 157 MPa pressure. Finally, this three ply stack was secured in a steel fixture and undergone a 40 minutes thermal cycle up to 650^{o}C. When the reactive media reaches to its ignition temperature the combustion synthesis reactions in powder mixture commences and the released heat causes surface melting of the aluminum 1100 plates in both sides and weld them to each other. In situ fabrication of Al_3Ni_2 and Al_7Cu_4Ni intermetallic compounds as well as Al_2O_3 particles in the interface was confirmed by XRD experiment.

Figures 1(a) to (f) show the SEM micrographs of the cross section of the aluminum 1100 plates which have been welded using combustion synthesis reactions. Three regions are distinguishable in figure 1(a); they are illustrated by I, II and III which are parent alloys, weld zones and reacted powder compact, respectively. The thickness of the weld zone layer in each side is about 750 µm. The mean shear strength of the obtained joints wa sabout 27 MPa.



(a) (b)

(c) (d)

(e) (f)

Figure 1. SEM micrographs from the cross section of two Al1100 plates which have been welded via combustion synthesis reactions at different magnifications.

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7C-2

ULTRA-FAST GROWTH OF SILICON CARBIDE NANOWIRES: PARAMETRIC STUDIES

Huczko A.*, Soszyński M.

Laboratory of Nanomaterials Physics and Chemistry, Department of Chemistry,
Warsaw University, 1 Pasteur str., 02-093 Warsaw, Poland
*ahuczko@chem.uw.edu.pl

Silicon carbide (SiC) is considered as a high-performance, high-temperature, semiconducting (wide band-gap compound) ceramic material because of a set of attractive properties, such as high strength and stiffness, good wear and corrosion resistance, and chemical inertness. One-dimensional (1-D) SiC nanomaterials are expected to exhibit even more interesting properties due to their low dimensionality, quantum confinement, and shape effects. For example, Zhou et al. showed an improved photocatalyst property of 3C-SiC nanowires (SiCNWs) [1]. The excellent field emission from SiCNWs was also noted [2]. Recently, we developed a simple, autogeneous and efficient production method of 1-D SiC via combustion synthesis (SHS) route using Si/PTFE powdered reactants [3]. We observed tunable photoluminescence of SiCNWs [4]. SiC nanowires were also found to promote polymerization processes [5] and positively modified the properties of composites [6]. Recently, Busiakiewicz et al. [7] studied the defects of produced SiCNWs by STM and STS.

Any further and wider applications of SiCNWs will call for the mass production. Thus, the process optimization is of the highest concern. We present here the continuation of our parametric studies.

Instead of micrometric Si we used silicon nanopowder (0,1 μm). Surprisingly, regardless the combustion atmosphere, the reaction yield was lower comparing to 40 μm Si particle size. One of possible explanations could be related to the presence of silica layer covering Si core and hampering direct fluorination of silicon.

We also carried out the comparative runs using polyvinylidene fluoride $(C_2H_2F_2)_n$ instead of PTFE $(C_2F_4)_n$. The results were unexpected and rather spectacular. Not only SiC nanowires were efficiently formed (fig. 1), but also their morphology was different comparing to previous PTFE (Teflon powder) combustion processing. The nanowires are capped with spherical tips (liquid globules?) which points to the VLS (Vapor-Liquid-Solid) crystal growth mode characteristic for gas phase condensation of one-dimensional crystallites [8]. The TEM/EDX studies are under way to determine the morphology and composition of those nanowire heads.

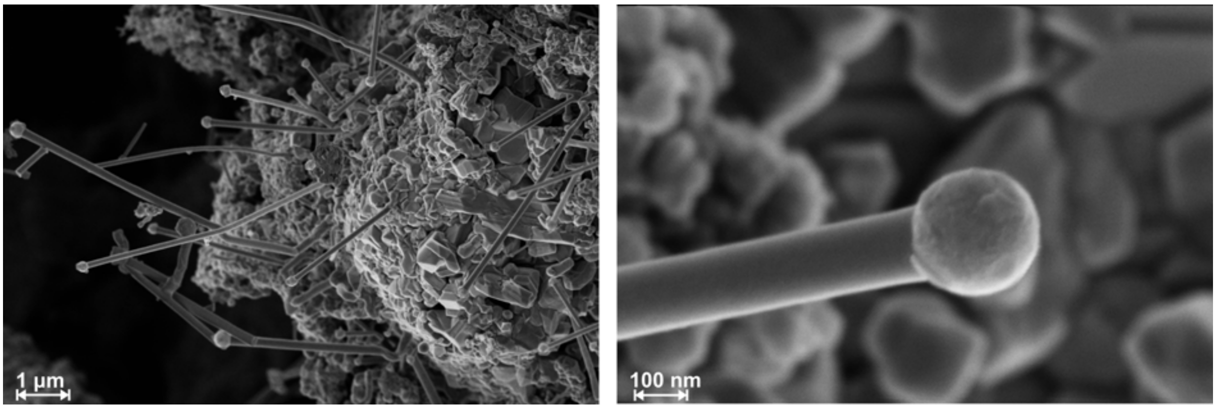

Fig. 1. SEM images of products resulting from the combustion synthesis in Si/$(C_2H_2F_2)_n$ system

Acknowledgements: This project is funded by the European Regional Development Fund within the Innovative Economy Operational Program 2007-2013 ("Development of technology for a new generation of the hydrogen and hydrogen compounds sensor for applications in above normative conditions") under No UDA-POIG.01.03.01-14-071/08-04.

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7C-3

CERAMIC JOINING BY COMBUSTION SYNTHESIS OF NiO-Al SYSTEM

Wu W.W.*, Gubarevich A.V., Wada H., and Odawara O.

Tokyo Institute of Technology, J2-48, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8502 Japan

*wu.w.ab@m.titech.ac.jp

Combustion synthesis technologies have been widely applied to join ceramics [1]. Volume combustion synthesis of NiO-Al system is considered can be applied to join Al_2O_3 ceramics. Process control by changing components and reactant powder characteristics should be much interested in order to establish highly efficient joining technology, and the effects on interface layer reactions relating with combustion initiation and heat transfer have not been discussed so much yet.

In the present work, Al_2O_3 ceramic joining by combustion of NiO-Al compacts or powders has been performed in the Volume Combustion Synthesis mode, that is, when the entire sample is heated uniformly in a controlled manner to keep its thermal gradient low during pre-heating. The ignition behavior of NiO-Al combustion has been investigated upon variation in starting composition, particle size of Al, and packing density of reaction powders. The process was then applied to join oxide ceramics, and microstructures of joint interfaces were analyzed and characterized in order to shed light on the mechanism of joining.

The combustion synthesis behavior of NiO-Al mixtures was investigated on the basis of following composition:

$$3NiO + 2Al = Al_2O_3 + 3Ni \qquad \cdots\cdots\cdots\cdots (1)$$

The adiabatic temperature calculated for above formula (1) is 3514 K, which is much higher than the melting point of Al_2O_3 (2327 K) and Ni (1728 K). Flake-like Al powders of ~ 40 μm and sphere-like NiO powder of ~ 3 μm were dry-mixed by following formula (1) and two other compositions with excess of Al were also prepared with the composition of 3NiO + 2.6Al and 3NiO + 3Al. Alumina ceramics of 99 % Al_2O_3 were used as sample plates for joint experiments. The joining surfaces of them were scratched before experiments by B_4C particles thoroughly. The joint experiments were carried out by setting the powder mixtures with optimum thickness between the sample plates. For attaining smooth reactions, a compact with fixed composition of 3NiO + 2Al (diameter of 15 mm, thickness of 1 mm), was placed at the edge of the powder layer to have a little contact with the powder mixtures. In order to obtain uniform contact between the reactant and sample surfaces and to keep the position of plates, the test sample system was loaded by applying some force on the top. The test sample system with the load was then placed into a furnace and heated up at rate of 10 K/min from room temperature to 1273 K to initiating the reaction, and then cooled down in air. The temperature at which the combustion reaction took place during heating was defined as ignition temperature (T_{ig}).

The typical results obtained with the joint experiments results are shown in Table 1. The ignition temperature is seen to be influenced by powder mixture composition, and powder layer thickness.

While powders with a composition of 3NiO + 2Al are difficult to ignite, the ignition of composition with excess of Al is much easier. The reactions of powders with composition of 3NiO + 2.6Al are very smooth, but composition of 3NiO + 3Al with too much Al will cause the reaction becoming violent. The increase of thickness of powder layer and compact can decrease T_{ig}. However, if the thickness was too high, the heat generated will become too much and cause the joining layer porous resulting in heavy cracks on the matrix Al_2O_3 plates.

Table 1 Results obtained with the present joint experiments

No.	Powder layer		Al_2O_3 plates surface	T_{ig} (K)	Combustion process	Products state	Joining
	Composition	Thickness (mm)					
1	3NiO + 2Al	4	scratched	×	×	powder	×
2	3NiO + 3Al	4	scratched	903	violent	droplets	×
3	**3NiO + 2.6Al**	**4**	**scratched**	**1133**	**smooth**	**layer**	**O** **(with coating)**
4	**3NiO + 2.6Al**	**3**	**scratched**	**1148**	**smooth**	**layer**	**O** **(with coating)**
5	3NiO + 2.6Al	2	scratched	×	×	powder	×
6	3NiO + 2.6Al	3	no scratched	×	×	powder	×

The optimum joining of Al_2O_3 plates with NiO-Al powder could be attained in the present work with the composition of 3NiO + 2.6Al and thickness of 3 mm at 1148 K of T_{ig}. By coating on the Al_2O_3 sample plates with an Al_2O_3 paste, optimum joining of matrix Al_2O_3 plates could be performed without any crack on surfaces of each other.

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7C-4

IN SITU SYNTHESIS AND MECHANICAL PROPERTIES OF TI_2ALC-TI_3ALC_2 COMPOSITE BY SHS/PHIP

Ying G.*[1], He X.[1], Du S. [1], Li M.[2], Zheng Y.[1], Zhu C.[2]

[1]Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China
[2]National Key Lab for Precision Hot Processing of Metal, Harbin Institute of Technology, Harbin 150001, China
[3]College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150001, China
*Corresponding author. Tel.: +86-451-86412513; Fax: +86-451-86402333.
yinggb001@yahoo.com.cn

As the members of $M_{n+1}AX_n$ phases (where n=1,2,3, M is an early transition metal, A is a ⅢA or ⅣA element and X is C or N), Ti_2AlC and Ti_3AlC_2 have been attracted increasing interest due to the unique combination of the properties of both metals and ceramics [1-3]. However, they have the same weaknesses of low hardness and unsatisfied strength, which would limit their widespread applications [1-5]. Considerable efforts to strengthening of Ti_2AlC and Ti_3AlC_2 phases, second phase needs to be incorporated for forming a composite. Ti_2AlC and Ti_3AlC_2 can be fabricated from Ti-Al-C system, and the binary TiC could be derived in the same system by self-propagating high-temperature synthesis (SHS) [6]. The $M_{n+1}AX_n$ matrix composite by SHS with the pseudo–hot isostatic pressing (SHS/PHIP) is identified to be a strategy for improving the mechanical properties of monolithic $M_{n+1}AX_n$ phase [7]. Therefore, the composite combined of Ti_2AlC-Ti_3AlC_2 phases with second phase TiC by SHS/PHIP would exhibit a high hardness, strength and toughness.

In this paper, Ti_2AlC-Ti_3AlC_2 composite is successfully fabricated by SHS/PHIP. Then, the mechanical properties of Ti_2AlC-Ti_3AlC_2 matrix composites are determined.

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7C-5

MACROKINETIC FORMATION FEATURES OF Ti_3Al IN THE THERMAL EXPLOSION MODE IN MECHANICALLY ACTIVATED POWDER MIXTURES

Filimonov V.Yu.*[1], Dudina D.V.[2], Ditenberg I.A.[3], Tyumentsev A.N.[3], Korchagin M.A.[2], Lyakhov N.Z.[2]

[1]Altay Technical State University, Barnaul, Lenina str.46, 656038, Russia
[2]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Kutateladze str.18, 6300128, Russia
[3] Institute of Strength Physics and Materials Science SB RAS, Tomsk, pr. Akademicheskii, 2/4, 634021, Russia.
*vyfilimonov@rambler.ru

Due to the combination of attractive properties, the Ti_3Al intermetallic is of great interest for application in aircraft industry and shipbuilding. However, it is difficult to produce a single phase Ti_3Al compound using traditional high-temperature methods. The goal of this work was to find the optimal mechanical activation (MA) parameters of Ti-Al powder mixtures and those of the subsequent high-temperature synthesis in the thermal explosion (TE) mode in order to obtain the single phase Ti_3Al.

Powder mixtures were prepared using Ti (99%, PTOM-2) and Al (98%, PA-4) elemental powders. The mechanical activation of the mixtures was carried out using a planetary ball mill of the AGO-2 type with water-cooled vials. The volume of each vial was 160 cm^3, the ball diameter was 8 mm, the mass of the balls in each vial was 200 g, the mass of the powder sample was 10 g. The centrifugal acceleration of the milling balls was $400 m/s^2$ (40 g). In order to prevent oxidation, the mechanical activation was performed in an atmosphere of argon. The mechanically activated mixtures were discharged from the vials in a glove box in argon.

X-ray diffraction and Electron Microscopy studies have shown that in the mechanically activated mixtures highly defect structures are formed. These structures show high crystal-lattice curvatures (up to 40 degrees/μm) and high density of boundaries with varying misorientation vectors. Such states act as sources of increased local internal stresses with maximum values reaching the theoretical strength of the crystal while the disclination character of the defect structure causes high local stress gradients ($\sim E/20\ \mu m^{-1}$).

TE and its macrokinetic parameters were studied using experimental techniques previously described by Korchagin et al [1]. With the time of mechanical activation, the ignition temperature, the maximum synthesis temperature and the average self-heating rate decrease, as is seen from Fig.1. It was found that as the average heating rate decreases, the effective activation energy of the reaction decreases as well, as was determined based on the analysis of the thermograms in the form of Arrhenius plots. The activation energy of the reaction in non-activated 3Ti-Al powder mixtures is 313kJ/mol [2]. In the mechanically activated mixtures, it decreases monotonically with the time of activation reaching anomalously low values ($10 \div 15$kJ/mol in the mixture mechanically activated for 7 min).

The macrokinetic parameters of the TE in the 3Ni-Al system studied in [1] followed similar trends for powder mixtures mechanically activated for different durations.

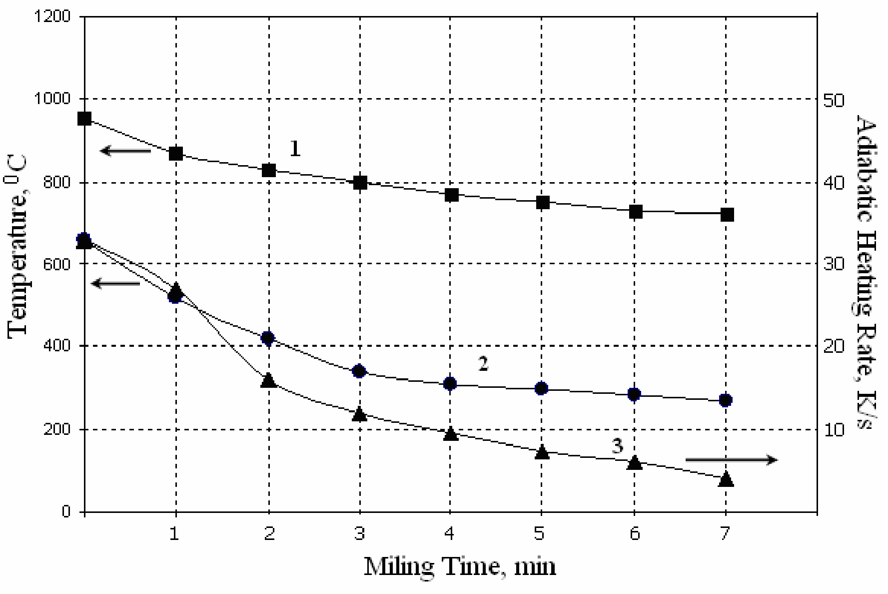

Fig.1. Variation of the maximum temperature during the synthesis (1), ignition temperature (2) and average adiabatic heating rate of the mixtures (3) with the time of mechanical activation (TE occurred at the heating rate 50 ºK/min).

The phase composition and microstructure of the synthesis products also depend on the time of mechanical activation. The optimal parameters of the preliminary mechanical activation and TE have been found ensuring the formation of the single phase Ti_3Al.

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7C-6

COMBUSTION SYNTHESIS OF Eu-DOPED α -SiAlON PHOSPHORS FOR WHITE LEDs

Han L.[1,2], Li J.T.[1], Borovinskaya I.P.[3], and Smirnov K.L.*[3]

[1] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
[2] Graduated School of the Chinese Academy of Sciences, Beijing, China
[3] Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia
* kosm@ism.ac.ru

α-SiAlON ceramics are well known excellent structural materials due to their high strength and high thermal and chemical resistances [1]. Recently, rare earth-doped α-SiAlONs have received significant attention because of their encouraging luminescent properties (excitability by blue light, high conversion efficiency, low thermal quenching, high chemical stability), and high potential for use in white LEDs [2]. For preparing α-SiAlON phosphors such methods as solid-state reaction at high temperature and high pressure [3], carbothermal reduction and nitridation [4], and gas reduction and nitridation [5] are used. These methods, however, suffer various drawbacks such as critical synthesis condition, impurity contamination, and poor crystallization. Consequently, developing new efficient methods for synthesis α-SiAlON phosphors is a hot subject of research.

In this work, solid solutions based on silicon nitride or α-SiAlONs represented by the general formula $(Eu,Me)_{m/\gamma}Si_{12-m-n}Al_{m+n}O_nN_{16-n}$ (where Me is one of the metals Mg, Ca, Y, Nd, and γ is the valence of this element) were selected for investigation. Combustion synthesis (CS) was realized through the exothermic chemical reaction of powdered mixtures that contain Si, Al, $MeO_{\gamma/2}$ and Eu_2O_3 with high pressure N_2 gas. Phase composition and lattice parameters of the product were studied by the method of X-ray analysis (Cu-K_α, X' Pert PRO MPD). The morphology of the synthesized α-SiAlONs was observed with scanning electron microscope «HITACHI S-4300». Emission spectra were measured at room temperature using a fluorescent spectrophotometer (Hitachi F-4500).

The following characteristics of considered reaction systems and their relationships were defined experimentally: - influence of the product high-temperature dissociation and sintering in the combustion wave on the nitriding process and terms providing the highest conversion of the reagents; threshold values of the combustible component content in the green mixture; dependence of the product microstructure, phase composition, crystal structure of the synthesized solid solutions and the range of their homogeneity on such factors as the maximum temperature in the combustion wave, dispersion of the initial components, presence of halogen-containing compounds in the green mixture, and additional warming-up.

Spectral characteristics of the synthesized α-SiAlONs doped with Eu (2+) cation were investigated. Their absorption spectrum covers the area from 250 to 520 nm and has two peaks; their position actually does not depend on the elemental composition of the α-SiAlONs. Their emission spectrum is able to cover the area from 500 to 750 nm and has only one peak. Its position depends on both the type of the metal used for α-SiAlONs formation and Eu (2+) cation content (fig. 1). The minimum values of the emission spectrum were noticed in the case of α-SiAlONs with Mg application, and the maximum ones – in the case of α-SiAlONs with Y.

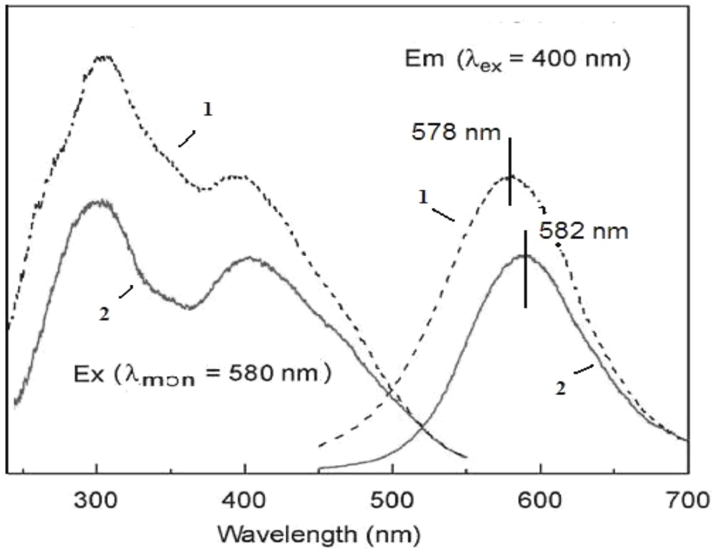

Fig.1. Excitation and emission spectrum of Eu-doped Ca-α-SiAlON: $Ca_{0,9}Eu_{0,1}Si_9Al_3O_{1.05}N_{14,95}$ (1) и $Ca_{0,6}Eu_{0,4}Si_9Al_3O_{1.2}N_{14,8}$ (2).

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ORAL PRESENTATIONS

E: Non–conventional SHS processes: New methods and applications

4B-K – KEYNOTE TALK

COUPLING REACTIONS IN SHS.
NEW POSSIBILITIES FOR MATERIALS SYNTHESIS

Kharatyan S.L.[1,2], Merzhanov A.G.[3]

[1] Yerevan State University, Yerevan, 1, A. Manukyan str., AM-0025, Armenia
[2] A.B. Nalbandyan Institute of Chemical Physics NAS RA, Yerevan, 5/2, P. Sevak str., AM-0014, Armenia
[3] Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432, Russia
suren@ichph.sci.am

The phenomenon of thermal coupling of chemical reactions in a single combustion process has long been known and were applied, particularly for smelting of pig iron (blast furnace process). Creation of a new autothermal system by coupling an endothermic (or low exothermic) to an exothermic reaction demands the matching of the thermal requirements of the two reactions. In this matter of particular interest is also the design of reactors in which these reactions are thermally coupled.

In [1] thermally coupled and chemically independent reactions in SHS were analysed in the simplest formulation, namely at proceeding of strongly and weakly exothermic reactions in spatially separated mixtures with the purpose to design a new temperature controlled self-sustaining process of the material synthesis and its optimization.

In this work different aspects and coupling schemes of reactions occurring simultaneously in SHS wave in an integrated and quazi homogenized mixture to synthesize new materials are considered.

Preliminary thermodynamic calculations confirmed the existence of new routes for materials synthesis by coupling the various type of reactions into single combustion process. The following schemes are possible, which enhance the opportunities for designing new energy-efficient processes:

- poorely thermal coupling of reactions;
- thermo-chemical coupling of reactions;
- coupling reactions to ensure the end products separation;
- kinetic coupling for increasing selectivity of desired end product;
- combined schemes of reactions coupling.

Thermodynamic and kinetic aspects of reaction coupling with particular examples for each type of coupling are discussed.

Thermo-chemical coupling of reactions often allow: (i) to perform interaction with high selectivity, (ii) increase the yield of desired end product, (iii) simplify the process, etc. In the work the approach was applied to the production of WC, Mo_2C, Mo, Cu, Ni and Co powders, Fe-Mo, Cu-Ni, Ni-Zr alloys under the combustion mode. It is worthy to note, that in some cases the desired end product is the only condensed product of the process.

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4B-1

SYNTHESIS AND DENSIFICATION OF TIAL ALLOYS BY ALTERNATIVE SINTERING TECHNIQUES

Lagos M.A.*[1], Agote I., Azurmendi N., Minster-Blondeau T.

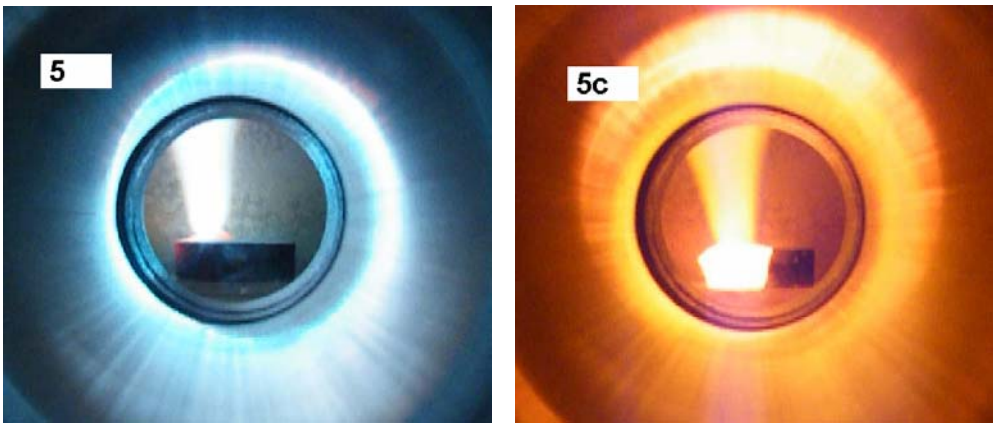
Tecnalia, Paseo Mikeletegi 2, Parque Tecnológico E-20009 San Sebastian, Spain
* miguel.lagos@tecnalia.com

TiAl alloys are increasing in interest due to low density and good high temperature properties. These alloys have great potential in replacing nickel based super alloys in automotive, energy production and aerospace applications for a temperature range between 500-800 ºC. Until now the material has been produced using a variety of processing means including forging, extrusion, casting, HIP, reactive sintering, SHS, etc. Some of these production methods often demand careful processing control and are slow, energy consuming, and expensive. Alternative processing means are needed for faster, cheaper and more energy efficient production.

This paper presents two alternative methods to the synthesis and densification of TiAl alloys: Spark Plasma Sintering (SPS) and microwave sintering. In both methods, the raw materials were elemental powders, and the synthesis of the intermetallic and the densification were carried out in a single step. The selected composition for the alloy was Ti-48Al-2Cr-2Nb.

Regarding SPS, this method is found to compact powders satisfactorily through the simultaneous application of direct current pulses of high intensity and pressure. The electric current induces a temperature elevation within the sample by Joule's effect. The process is very fast and it is possible to obtain fine microstructures. In the recent years, some works have studied the densification of TiAl by SPS [1-2], but the majority of them uses pre-alloyed powder as raw materials. Few works [3] have studied the densification of elemental powders and it seems that the sintering can be easier than for pre-alloyed powders. With elemental powders, when the material reaches the melting point of the aluminium, the exothermic reaction between the titanium and aluminium takes place and the whole material is in plastic stage. This is the reason why the compaction is easier. This work presents the effect of the parameters of the process (current pulses, temperature, heating rate) on the density and microstructure of the final products. It is important to take into account that in this process a commercial composition was selected (Ti-48Al-2Cr-2Nb) and it is important to study the diffusion of the elements (chromium and niobium) into the sample.

The other technology used in this work is the SHS induced by microwaves. A new generation 2.45GHz single-mode microwave featuring a rotating platform which incorporates a hydraulic press was used. At the start of the experimental run the sample was heated by microwave energy; the electromagnetic energy enters the metal powder at its respective skin depth and forms eddy currents in the particles. At a certain point in the process a pulsed plasma is produced. At this stage, it is considered further heating is related to the plasma, and not to microwave heating. The formation of the plasma drastically depends on the atmosphere of the chamber. When the reaction was completed, the pressure was applied with a hydraulic press. The main parameters of the process were studied and the properties of the final products are presented.



SHS reaction induced by microwaves

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4B-2

NANO SCALE AL/PD MULTILAYER SYSTEMS FOR REACTIVE BONDING IN MICROSYSTEMS TECHNOLOGY

Braeuer J.*[1], Besser J.[1], Wiemer M.[1] and Gessner T.[1,2]

[1]Fraunhofer Institute for Electronic Nano Systems, Chemnitz, Technologie-Campus 3, 09126, Germany
[2]Chemnitz University of Technology, Chemnitz, Reichenhainer Str. 70, 09126, Germany.
joerg.braeuer@enas.fraunhofer.de

The system integration and packaging of microelectronics and micromechanical systems (MEMS) is increasingly affected by three dimensional chip stacking [1]. Major roles therein play the fabrication of Through Silicon Vias (TSV) and the wafer bonding [2]. When it comes to combining different functionalities such as electronics, mechanics or optics the bonding process has to fulfill several conditions. The most important requirements on the joint interface are the mechanical strength, electrical conductivity and in most cases also hermetical tightness. Typical bonding processes nowadays are silicon direct bonding, anodic bonding or adhesive bonding [3]. For most applications, however, the bonding process has to be limited regarding to temperature (<400 °C). Therefore new low temperature processes have been under investigation recently [4]. This paper introduces a new method of local heating for wafer bonding processes which is based on reactive nano scale multilayer systems. Such systems typically consist of several (up to hundreds) alternating layers of two different thin metallic films each with thicknesses in the range of tens of nanometers. With the application of an initial energy pulse, the system starts to rapidly form intermetallic phases by interdiffusion of adjacent material layers. By choosing material combinations with negative enthalpy of formation this reaction can be running exothermic [5].

Reactive bonding is conventionally applied for joining of macroscopic components with the help of freestanding Nickel/Aluminum foils in combination with solder pre-forms [6]. However, for bonding techniques in microelectronics and MEMS with bond frame dimensions of a few ten microns, this method is not similarly applicable. This is due to the fact of handling issues and the limited ability of patterning such foils with smaller dimensions. Our approach focuses on the direct deposition of thin film reactive multilayer systems onto 6 inch silicon wafers. Therefore, we applied physical vapor deposition (PVD) to generate multilayer films of aluminum (Al) and palladium (Pd) with individual layer thicknesses in the nano scale. The individual layer thicknesses are chosen to obtain the desired 1:1 stoichiometry. Patterning of the multilayer films was done by lithographic techniques and wet etching procedures. After patterning electrochemical deposition of Sn was used to generate our so called integrated reactive systems.

The reaction of multilayer systems was initiated by an electrical spark. The route of the reaction front was observed by using high-speed camera imaging. We observed a constant combustion velocity (higher than 50 m/s). The microstructure of the deposited films and the reaction product as well as the patterned systems were characterized by using Scanning Electron Microscopy (SEM) in combination with special preparation techniques like the Focused Ion Beam (FIB) liftout method. In further experiments we used the integrated reactive systems to create thin bonding interfaces. Figure 1 shows SEM images of the bond interface prior and after the reaction front has passed. The produced interfaces were characterized by Energy-dispersive X-ray spectroscopy (EDX) line scan and mapping.

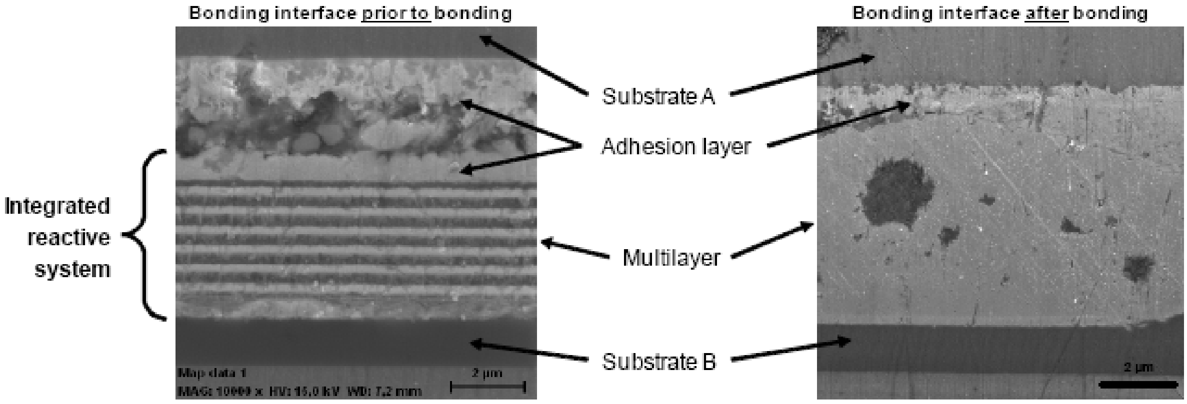

Figure 1: Bonding interfaces (SEM images) prior to bonding (left) and after bonding (right)

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4B-3

HEAT IMPULSE THERMOSYNTHESIS METHOD OF (Pd- Ag)/GLASS FIBER CATALYSTS OF ACETYLENE SELECTIVE HYDROGENATION

Kotolevich Y.S.[1], Mikenin P.E.[2], Goncharov V.B.[2*], Nizovskii A.I.[2], Tsyrul'nikov P.G.[1]

[1]Institute of hydrocarbons processing Siberian Brunch RAS, Omsk, Neftezavodskaya st. 54, 644040, Russia
[2]Boreskov Institute of Catalysis Siberian Division RAS, Novosibirsk, Lavrentieva prospect 5, 630090, Russia
*gvb@catalysis.ru

Thermosynthesis of various materials is widely used: self-propagating high-temperature synthesis (SHS) [1], solution combustion synthesis (SCS) [2], surface selfpropagating thermosynthesis (SST) [3], etc. We developed the heat impulse thermosynthesis (HIT). This method based on short time heat action on the support with supported precursors during sample moving through narrow high temperature region ("chink"). The residence time is varied from 0.1 up to 30 minutes. The temperature on the samples surface can reach 800ºC. This method of catalyst preparation was used for obtaining (Pd-Ag)/glass fiber catalyst for the gas-phase selective hydrogenation of acetylene. The HIT realization scheme presents on Fig. 1.

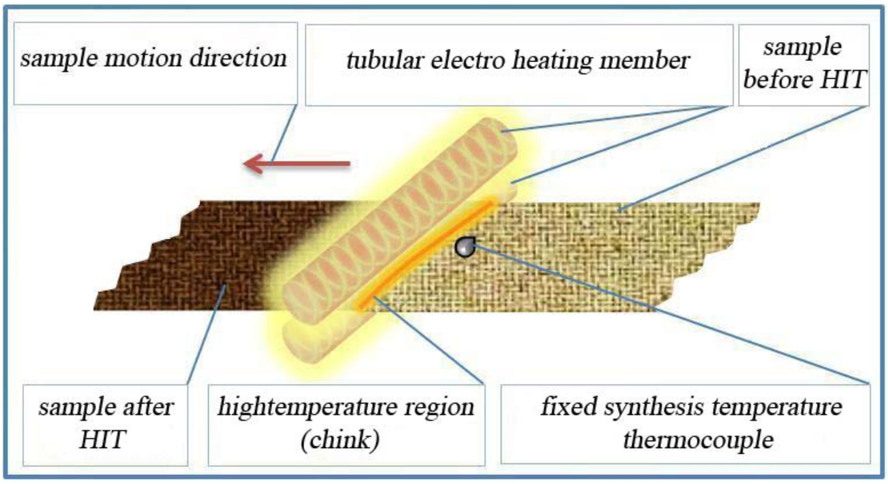

Fig.1. HIT realization scheme

HIT as compared with traditionally catalysts synthesis method allows expressively obtaining more defective and dispersing supported systems.

We used an open worked modified by rare earth oxides silica fiber glass as a support. The active component precursors were CH_3COOAg and $Pd(NO_3)_2$; as the fuel additive (for HIT) was taken the D-glucose. Ag content was 0.5% mass. Molar ratio Ag:Pd was 4:1, 7:1 and 10:1. Dried samples were underwent of HIT, the preparation temperature being 470ºC and the contact time τ=10 min. The process of acetylene selective hydrogenation conditions: the gas phase composition, % vol.: 51.9% C_2H_4 + 0.8% H_2+ 0.8% CH_4+0.5% C_2H_2 with a traces of CO and C_2H_6, Ar – balance; stainless steel reactor, V = 8 cm^3, pressure 20 bar, temperature was varied from 55 up to 145ºC with the step 15º. The catalyst loading was 3.4 g and the gas velocity was 3000 l/h. The inlet and outlet gas composition was analyzed chromatographically. All principal data are presented in the Table 1.

Table 1. Conversion and selectivity (Pd-Ag)/GFS catalysts with different ratio Pd:Ag in the acetylene hydrogenation at 115ºC

Sample	Content of Pd, % by mass	X (C_2H_2), %	S(C_2H_4), %
Pd-Ag(1:4)/GFS	0.13	76	80
Pd-Ag(1:7)/GFS	0.07	25	81
Pd-Ag(1:10)/GFS	0.05	21	81

As shown, with Pd content increasing the acetylene conversion increases ~ 3.5 times, being the selectivity practically constant: 80 – 81 %. Note that the activity (X) and selectivity (S) of industrial Pd-Ag catalysts are higher, but at the temperature interval 30-200ºC [4], where as the working temperature for (Pd-Ag)/GFS catalyst (115ºC).

This work was supported by the Russian Fund for Basic Research under Grant 10-03-00451a.

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4B-4

NON CONVENTIONNAL SOLID COMBUSTION OF NEW REDOX BINARY MIXTURE FOR HYDROGEN GENERATION

Goudon J.P.*[12], Yvart P.[2], Bernard F.[1]

[1] University of Burgundy, Laboratoire Interdisciplinaire Carnot de Bourgogne, Dijon, 21078, France
[2] SNPE Matériaux Energétiques, Laboratoire Balistique, Comportement et Fonctionnement,
Vert-Le-Petit, 91710, France.
* jp.goudon@snpe.com

Many innovative self-propagating high-temperature synthesis (SHS) techniques such as thermite process, field activated combustion, solid-state metathesis or flame synthesis crystallise currently scientific interest for the synthesis of “advanced materials” [1]. On the same way, in the field of “fuel cells systems”, an innovating gas producing self-propagating process using redox mixtures initiated at low temperature has been used for the generation of hydrogen [2]. Indeed, for a wide range of civil and military on-board applications such as for emergency power supplies or future vehicle, the problematic of solid hydrogen storage is not an easy way : pressurized vessels (~200 up to ~750bar) present safety sizeable risks which reduce their utilization whereas cryogenic tanks (20K) present as for them risks of boil off. So, optimizing both gravimetric and volumetric hydrogen densities require therefore using solid storage at room temperature [3].

In such context, SNPE Matériaux Energétiques has developed a novel solid hydrogen generating composition, without binders and catalysts, in the field of gas generators [2]. Based on a high exothermic self-propagating solid-solid reaction (Tad~1300K) between a hydrogen-rich compound, the ammonia borane complex BH_3NH_3 (19.6%wtH) [4], and an oxidizer salt, the strontium nitrate $Sr(NO_3)_2$, this technology generates gaseous hydrogen on demand and a small quantity of nitrogen depending on the stoichiometric ratio. In a technological point of view, this technique presents several intrinsic advantages: being safe compared to others solid hydrogen storage solutions, having a fair energetic density (>10%wt), and a long life time with no maintenance costs.

In such a way, this paper will be first focused on physico-chemical characterizations (Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray Spectrometer (EDXS), X-ray Photoelectrons Spectroscopy (XPS), Dynamic Vapour Sorption (DVS)…) realized on each material in the field of morphological, microstructural, thermoanalytical and hygroscopical aspects. In a second time, a combustion chamber specifically realized, in the one hand, to the “in-situ” study of this combustion reaction and the visualization of the propagation front and, on the other hand, to evaluate the influence of two mechanical mixing processes, a turbula shaker mixer and a rotary grind machine, will be presented. The “ex-situ” characterization of combustion products (solid residues, condensates and gas phase composition) in both qualitative and quantitative aspects will be also presented. The whole obtained results allow us to determine a macroscopic mechanism.

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4B-5

STUDY OF DYNAMIC CONDITIONS OF THE SHOCK INITIATION OF POWDER AND LAYERED ENERGY MATERIALS

Dmitrieva M.A., Leitsin V.N.

I.Kant Baltic Federal University, Kaliningrad, 236041, Russia
*dmitrieva_m@inbox.ru

In connection with the some problems in obtaining experimental data on the characteristics of diverse physical and chemical processes that occur over short microsecond time of shock compression, there are significant difficulties in conducting experimental studies and theoretical modeling. At present, almost there are no theory that adequately describe the basic mechanisms of shock synthesis, heterogeneous heating of real powder materials, phase transitions and the conditions of the reactions, characterized by nonstationarity of the state and structure parameters at all stages of physical and chemical transformations.

Theoretical and experimental studies of the behavior of multicomponent powder reacting systems allowed to conclude that the concentrations inhomogeneity factor of the components of chemically reacting system has decisive influence on the degree of activation of the reacting components, the conditions of shock initiation of chemical transformations, the kinetics of chemical processes, product structure of shock synthesis and other parameters of reactive systems.

There is a stage of melt of low-melting component of the reacting mixture, moreover, in many systems the intensive interaction of the components takes place after the melting of one of them. For the implementation of certain conditions of synthesis, and also the possibility of obtaining a wide range of new materials, the mechanical activation of the reacting components , i.e. increase their reactivity (lowering the threshold of the reaction initiation and reducing the duration of interaction between the components) due to non-thermal effects is a governing factor.

Shock compression of chemically reacting materials, allows to combine the technological processes of mechanical activation, melting and the initiation of chemical transformations. Processes in chemically reacting systems is significantly multiparametric, and the macroscopic structure of concentration inhomogeneity of powder systems is the reason for the significant scatter of the observed conditions of synthesis and structure of the final product [1]. Layered (foil) chemically reacting systems are concentration-deterministic, that makes them an attractive object of study for construction a theory of multicomponent chemically reacting systems, and for experimental studies of the chemical processes kinetics [2]. Nature of the mechanical modifications of reactive medium is defined by the processes of energy dissipation in the local micro-volumes, characterized by different times of damage, phase transformations of components, initial conditions of non-stationary processes of dynamic compression, and, in turn, determines the degree of mechanical activation of the reacting components. The resonant modes of energy exchange in shock-compressed heterogeneous medium to assess the conditions of shock compression and chemical reactions initiation is studied. A dynamic theory of mechanical modification of layered materials, allowing to predict the structure of the emerging activated areas of reagents is constructed. The possibility of changes in proper frequencies of microvolumes due to compression and change of the concentration-phase composition is taken into account. The feasibility of non-stationary processes of mechanical modifications, under the conditions of the resonant modes of shock compression is investigated. Evaluation of dynamic characteristics of the shock compressed reactive compacts allows to formulate a criterion for the onset of unsteady regimes of shock compaction and run chemical reactions with taking into account the proper frequencies of structural elements (including the frequency of Rayleigh waves for multilayered compositions).

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5A-K – KEYNOTE TALK

HIGH DENSITY NANOENERGETIC GAS GENERATORS: FUNDAMENTALS AND PERSPECTIVES

Martirosyan K.S.

Department of Physics and Astronomy, University of Texas at Brownsville, Brownsville, TX, 78520
karen.martirosyan@utb.edu

Major progress has been made during the past two decades in developing energetic materials such as Metastable Intermolecular Composites (MIC) or so-called Nanoenergetic Materials (NM). These materials can rapidly release temperature and pressure waves and have extensive potential applications as propellants, explosives and primers and currently are the subject of extensive research [1]. They can have higher energy densities than conventional explosives and can generate shock wave with velocities of up to 2500 m/s [2]. The composites are mainly mixtures of two nanoparticles components, one of which is defined as a fuel and the second as oxidizer. The use of nanoscale particles instead of micro particles increases the intimate contact between the fuel and oxidizer. This decreases mass transport limitations which increases the reaction rate and reactivity of the mixtures. Thermodynamic calculations of the adiabatic temperature, equilibrium composition, and reaction enthalpy help select a MIC mixture from a large number of candidate thermite mixtures. The shock wave velocity and rate of energy release increased by up to 3 orders of magnitude when the particles size of either aluminum and/or the oxidizer were reduced to a nanosize range.

This lecture covers recent progress on the development of Nanoenergetic Gas-Generators (NGG) reactant mixtures having high PV (pressure x volume) values that may have several civil and military emerging applications. Our long term research focuses on the finding and characterization of new NGG formulations that rapidly releases a large amount of gaseous products and generates a fast moving thermal wave during the explosion. This involved a systematic study of various nanoenergetic reactants, their synthesis, fabrication and determination of the peak gas pressure evolution and rate of gas release. We have recently shown that among common thermite reactions, the Al/Bi_2O_3 and Al/I_2O_5 mixture generated the highest pressure pulse [3-6]. A possible explanation for the high pressure rise during the combustion of Al/Bi_2O_3 and Al/I_2O_5 nano systems is that the reaction product (bismuth or iodine) boils at a temperature of 1560 and 184 °C, respectively, that is lower than the maximum reaction temperature ~2000 °C. This causes bismuth or iodine evaporation and increases the released gas pressure. The energy densities per volume of monomolecular composites such as TNT-2,4,6-Trinitrotoluene, RDX-1,3,5-Trinitroperhydro-1,3,5-triazine, PETN-Pentaerythritol tetranitrate were ~7 kJ/cm^3; ~10 kJ/cm^3 and 10 kJ/cm^3, correspondingly. The thermodynamic analysis and comparison of energy densities between MIC and monomolecular composites demonstrate that the volumetric energy of thermites based materials can easily exceed the best existing molecular explosives by about a factor of two and can be reached to 25.7 kJ/cm^3 for iodine based thermite. The HR TEM images in Figure 1, (left) show that most Al particles which were used for NGG systems are spherical with a diameter from 50 to 150 nm and coated by about 4 nm aluminum oxide layer. The values of the peak pressure generated during the combustion of different reactant mixtures are shown in Figure 1 (right). It can be seen that the Bi_2O_3 nanoparticles synthesized by combustion synthesis is generated more than three times large pressure than commercial Bi_2O_3 nanoparticles. The Bi_2O_3-Al and I_2O_5-Al mixtures generated the highest pressure peak of ~ 11 MPa.

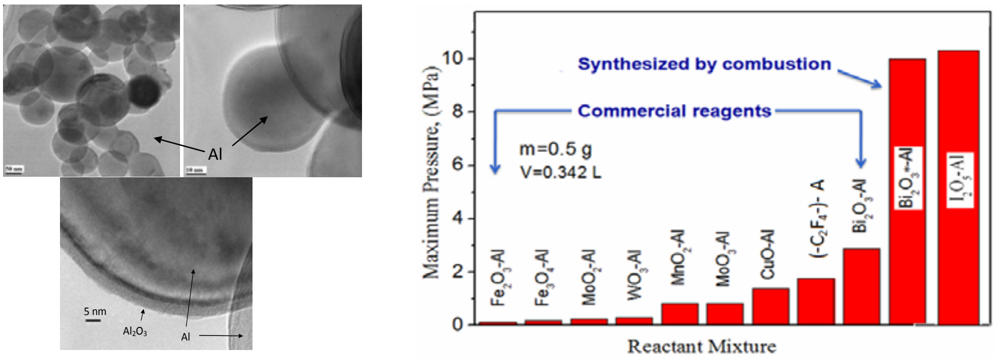

Figure 1: (left)- TEM images and morphology of Al particles used in NGG systems; (right)- The values of the peak pressure obtained during the explosion of different nanoenergetic thermite formulations.

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5A-1

INNOVATIVE COMBINATIONS BETWEEN COMBUSTION SYNTHESIS AND ELECTROPHORETIC DEPOSITION TECHNIQUES

Rosa R.*[1], Veronesi P.[1], Colombini E.[1], Michelazzi M.[1], Leonelli C.[1], Boccaccini A.R.[2]

[1] Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università degli Studi di Modena e Reggio Emilia,
via Vignolese 905, 41125 Modena, Italy
[2] Institute for Biomaterials, Department of Materials Science and Engineering,
University of Erlangen-Nuremberg, Germany
* roberto.rosa@unimore.it

Electrophoretic deposition (EPD) is a simple and cost effective technique, which allows the production of dielectric coatings over conductive substrates, with little or no substrate shape restrictions [1]. The principle on which EPD relies is that dielectric particles, suitably dispersed in a liquid medium acquire a determined surface charge, which can be varied by addition of a proper charging agent. Applying an electric field to the suspension, by means of submerged electrodes, the particles are forced to migrate toward the oppositely charged electrode, forming a deposit; particles accumulated at the electrode are held together only by weak forces, thus a further consolidation step (melting, sintering) is required in order to develop satisfactory mechanical properties [2]. This high temperature step represents, from an economical and energetical point of view, a major inconvenience to an otherwise inexpensive technique.
The combination of CS and EPD, two simple and potentially complementary techniques is here investigated for the first time: sub-micrometric ZrO_2 particles were electropheretically deposited on Ni + Al and Ti + Al reactive powders compacts, used as electrodes, and subsequent ignition of the exothermic reactions involving metallic precursors was performed by means of microwave irradiation in order to obtain in a single step the synthesis of the desired intermetallic phase and the sintering of the previously deposited ceramic coating. Schematic representation of the here proposed innovative approach is reported in Figure 1.
Preliminary results concerning a different combination approach among these two techniques, i.e. the EPD of reactive metal particles and subsequent CS, will be presented as well.

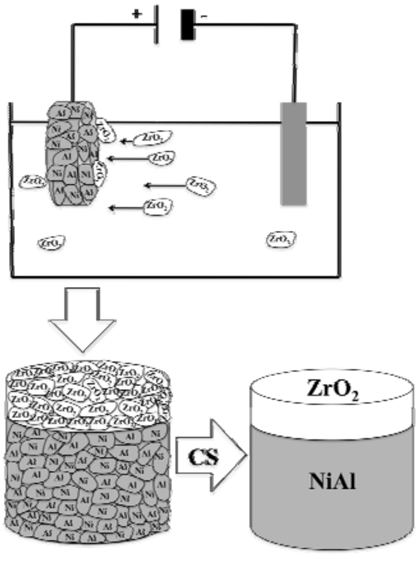

Figure 1. Schematic representation of EPD process combined with the CS one.

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5A-2

NEW COMPOSITE MATERIALS BY SHOCK WAVE AND SHS PROCESSING

Pervukhina O.L.*, Saikov I.V.

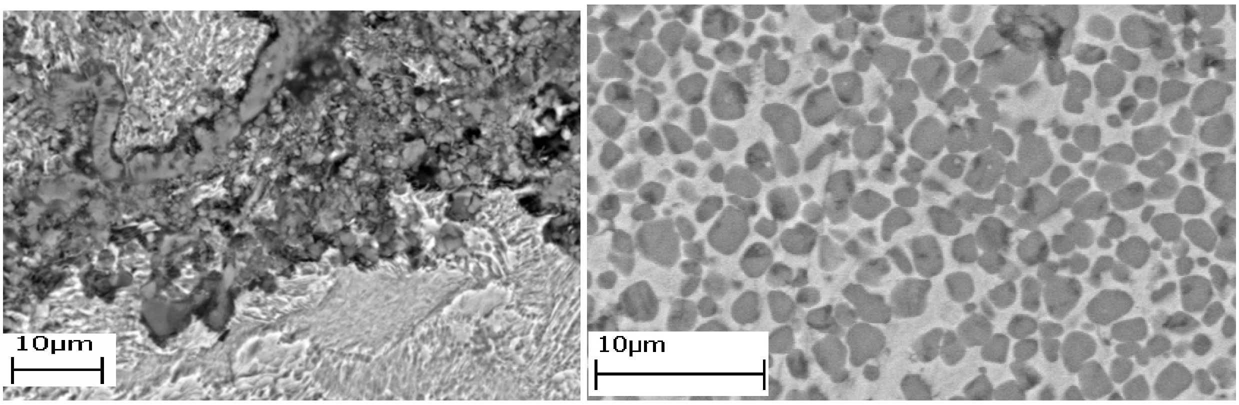
Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,
Chernogolovka, Moscow, 142432 Russia
*opervukhine@mail.ru

New promising materials including laminate metal and metal ceramic ones can be produced by shock-wave processing combined with SHS [1]. As it known, metals and ceramics are very difficult to combine in a bulk cermet material because of marked differences in physical parameters, and clad metals can be produced by explosive welding. We explored the feasibility of fabricating layered cermet materials by combined use of explosive welding (compaction) and SHS in Ti + C + Ni system.

Investigation was done in two lines of research: (1) initiation of SHS by shock wave impact during explosive welding when a steel cladder was thrown by blasting charge onto steel backer with grooves filled with green SHS mixture. Explosive detonation rate was about 2500 m/s; (2) initiation of SHS by shock wave impact after explosive welding followed by synthesis under heating. Then the fabricated intermediates were heated in a furnace at 800–1200°C or with a thermochemical tape providing 1600°C.

The temperature was measured with a pyrometer, the synthesized materials were characterized by phase and structural analyses while welded areas were tested in ultrasound. It was discovered that initiation of SHS did not take place under conditions of explosive welding.
Under impact of thermochemical tape on the pressed green SHS mixture placed onto steel substrate, titanium carbide was obtained as a result of SHS.

FeNi alloy with gradient distribution of Ni was obtained as a bonding agent. In the grain boundary area, Fe prevailed and its distribution diminished while moving off the grain. Good adhesion between metal and ceramic layers was reached (Fig. 1a) and penetration of some TiC grains into steel was stated at the depth up to 120 μm.



(a) (b)

Microstructure of final product

The structure with TiC grains uniformly distributed over a matrix (Fig. 1b) was produced by sintering a preliminary sealed green mixture in the furnace. It was defined that SHS after shock-wave impaction starts after a furnace was heated to 1100°C. Hardness of the cermet TiC–Ni layer shows a good correlation with that of materials produced by other techniques.

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5A-3

CONTAINERLESS COMBUSTION SYNTHESIS PROCESSING IN MICROGRAVITY LEADING TO PRODUCT FABRICATION AND RESOURCE UTILIZATION ON ISS

Guigné J.Y.

University of Bath, Bath, England, BA2 7AY, UK
jguigne@nl.rogers.com

In an effort to conduct containerless materials processing experiments involving Combustion Synthesis or Self-Propagating High Temperature Synthesis (SHS) on the International Space Station (ISS), a unique facility called Space-DRUMS was developed and installed on ISS. Containerless processing eliminates unwanted interactions between a container and the material being processed. Such interactions include contamination of the melt and of the catalysis of unwanted reactions or nucleation-induced reactions of the melt [1]. In certain conditions, detrimental heterogeneous crystallization or nucleation can occur at the interface between the material and the container. In addition, in order for a material to be produced by the SHS technique, the chemical reactions involved in the process must be highly exothermic and the heat loss must be kept to a minimum such that a self-sustaining combustion reaction wave is generated [2]. Hence a container has also a direct effect in lowering the reaction temperatures as the container acts as a heat sink. It also induces unwanted micro-flows in the resultant material's internal structure during reactions.

The opportunity to fabricate components in a space environment such as the International Space Station has opened the way to consider and fully exploit the advantages of using SHS. The technology of SHS allows for the synthesis of a wide range of materials that could be used for producing form-fitted or graded fabrications in the long duration microgravity environment as offered by the ISS. The resulting reactions can be engineered to deliver custom products fully embracing the low gravity ambient environment, be it oxygen free or oxygenated. Generally on ISS the SHS reactions would not be affected by gravity and within the dynamic environment created by the multi-acoustic beams within the Space-DRUMS facility, the SHS samples would be held during their internal phase front propagation within a true containerless condition.

In conventional acoustic levitators, using resonance or interference principles, a standing wave is set up between the projector and a reflector. Samples to be processed can be levitated in the energy wells present in this space. The depth of the energy wells depends on the amplitude of the projected acoustic waves, whereas the distance between the two adjacent wells is equal to half a wavelength. Typically, these levitators have a number of deficiencies, restricting their practical usage for containerless material processing in space. Control over sample position and stability would be non-existent during an SHS reaction, as the sample would undergo a high temperature exothermic reaction, which would alter the shape of their supporting well. The position of the sample, even though the sample would be very small in form, is maintained by adjustments to the magnitude of the acoustic radiation force. This directly alters the shape of the well thus causing instabilities, which cannot be corrected.

In contrast, the Space-DRUMS's containerless facility on ISS was specifically designed to handle SHS processes by relying on 20 programmable-pulsed acoustic pencil beams operating at 64kHz. The acoustics are positioned at the vertices of a dodecahedron to create a gentle restoring force on a sample from any direction. This polyhedron, possessing 12 faces, provides for equal distance and equal angle on the energy propagation to the sample. Only if the sample is partaking in motion away from its central position does an acoustic force be conveyed onto the sample in the counter direction of its movement, thus providing for a precise restoring condition. Active control of the sound pressure levels is achieved by controlling the amplifiers that drive each projector. Since gentle propagating acoustic pulses or waves produce the forces on the SHS sample, there is no perturbation imposed on the SHS process as the time duration on the sample is in milliseconds. There is not a limitation on the size of the sample that can be manipulated as a result of the acoustic field generated as the criteria is for the processing of large sample sizes .In fact, Space-DRUMS works very well with samples having diameters of 5 cms.

Space-DRUMS is a unique SHS facility on ISS that mitigates or eliminates gravity and container effects on the combustion synthesis characteristics of the SHS process, as well as on the microstructure and properties of the products formed including both porous and dense ceramics, intermetallics, metal-ceramic composites and glass matrix composites.

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5A-4

ADVANCED SHS-ELECTRODES BASED ON TiC-TiNi FOR PULSED ELECTROSPARK DEPOSITION

Pogozhev Yu.S.*[1], Kudryashov A.E.[1], Novikov A.V.[1], Levashov E.A.[1], Kochetov N.A.[2], Rogachev A.S.[2]

[1] National university of science and technology «MISIS», Moscow, Leninsky prospect 4, 119049, Russia.
[2] Institute of structural macrokinetics and material sciences of Russian Academy of Sciences, Moscow region, Chernogolovka, ul. Institutskaya 8, 142432, Russia.
* pogozhev@rambler.ru

Electrodes that usually are used in PED (Pulse Electrospark Deposition) technology for deposition of functional coatings are normally made of metals, their alloys, graphite, and hard alloys (mainly WC-based). However, coatings deposited with using of the above electrode materials not always exhibit desired service properties (such as hardness, heat-, wear-, corrosion resistance, friction coefficient and etc.). In this context, rather promising seems to be use of electrode materials based on titanium carbide with modified structure [1]. At present study advanced electrode materials in TiC-TiNi system were produced by SHS (self-propagating high-temperature synthesis) technique using focused alloying of initial reactionary mixtures by nanoparticles of refractory compounds such as tungsten carbide, zirconium dioxide and alumina. The regularities of influence of the initial temperature of SHS process, the composition of initial reactionary mixtures and additives of refractory nanoparticles on macrokinetics of combustion process were studied during the synthesis of composite ceramic materials. For investigation the mechanisms of combustion process of green mixtures and structure formation of the synthesis products some experiments on quenching of the combustion front in a copper wedge were conducted with the following electron microscope and microprobe analysis of specific areas of the combustion front. That allowed us to provide the dynamics of chemical transformations in the combustion wave of investigated ternary system. The effect of additives of refractory nanoparticles on the mechanisms of combustion process and structure formation of the synthesis products is shown. Based on the obtained results, we suggest that the doping of the initial compositions by nanoparticles of refractory compounds leads to inhibition of the reaction of TiC formation due to partial blocking of the reactionary surface of carbon black, as the most highly dispersed component in the system, and the leading reaction becomes the reaction of TiNi formation. In this case, the chemical reactions in the combustion zone does not occur in parallel (as in the mixtures without nanoparticles), and occurs sequentially. In addition, the introduction of nanocomponents contributes to the formation of finer grains of TiC and TiNi in the combustion zone. This effect is consistent with the assumption about the change in staging of chemical reactions in the combustion wave, when the formation of titanium carbide grains begins at a later stage with the presence of nanoparticles of the inert component in the green mixture. At the same time inert nanoparticles, getting into the high-temperature nickel-titanium melt, sharply increase the number of crystallization centers, and it leads to the formation of submicron grains of TiC on the first stage of structure formation [2]. In addition, the change in concentration of nickel titanium from 60 to 90 % in the synthesis products composition also leads to significant refinement of grains of the main wear-resistant phase. According to the results of comprehensive studies of the properties of obtained materials it was found that the concentration of titanium carbide in the synthesis products without nanoparticles exerts the biggest influence on the mechanical characteristics of the compact materials. In this case, the values of hardness, flexural strength and elasticity modulus of composite materials do not depend on the average grain size of TiC, despite the significant effect of structure modification with increasing the concentration of TiNi. At the same time, it was determined that the alloying of the green mixtures by refractory nanoparticles gives a positive effect on physical and mechanical properties and heat-resistance of the compact synthesis products. The application of the obtained materials, dispersion-strengthened with nanoparticles, as electrodes for the deposition of multifunctional coatings by PED technology [3] allows to produce coatings with enhanced service properties, due to their high erosive capability because of finer structure.

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6B-1

COMBUSTION SYNTHESIS OF POROUS ZIRCONIUM ALLOYS WITH CONTROLLED PROPERTIES

Kirakosyan Kh.G.[1,2*], Amirkhanyan N.H.[1], Yeghishyan A.V.[2], Manukyan Kh.V.[1,2],
Kharatyan S.L.[1,2] and Bossert J.[3]

[1] Yerevan State University, 1, Manukyan str., Yerevan, 0025, Armenia
[2] A.B. Nalbandyan Institute of Chemical Physics NAS of Armenia, 5/2, Sevak str., Yerevan, 0014, Armenia
[3] Institute of Materials Science and Technology, Friedrich Schiller University Jena, Löbdergraben 32
Jena, D-07743, Germany
* mkhachatur@gmail.com

Porous metallic materials have been considered as important components for cancellous bone repair and replacement. It is known that the accepted range of pore size in porous orthopedic materials providing bone cell ingrowth is 100-500 μm. There have been numerous efforts to develop porous alloys with the proper characteristics [1]. Many existing metallic biomaterials (e.g., plasma-sprayed titanium, porous sintered powder metallurgy materials), however, do not easily lend themselves to fabrication into porous structures [2].

In the present research chemical interaction in the Ni+Zr and Co+Zr mixtures with small amounts (1-2wt.%) of polytetraflourethylene additions was investigated to produce porous Zr-based materials. These mixtures were selected in a way that chemical reaction may be performed under the self-propagation combustion mode. To govern pore sizes and their distribution in the products, granules of so *called space holding agents (SHA, e.g. ammonium carbonate or urea)* were well mixed with the initial reagents. It was shown that preliminary thermo-vacuum treatment of initial samples allows to create desired pores by evaporation of granulated SHA. After the combustion reaction in these samples molten, porous (porosity 60-75%) zirconium-based alloys with 100-600 μm pore sizes were obtaned (Fig. 1a). The average pore size in these products was determined to be in the range of 200-315 μm.

Besides, the porosity, surface chemical composition of metallic implants should mimic the composition of natural bone to stimulate bone ingrowth and fixation. An approach to make metallic materials bioactive is coating of the surface with hydroxylapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) which is the main constituents of bone. To test apatite forming ability of produced materials their interaction with stimulated body fluid (SBF) was studied at 36.5°C and pH=7.25 conditions. It was shown that 20 days-long interaction allows to produce needle type hydroxylapatite crystals with 200 nm in diameter and 1-2 μm in length on the surface of porous alloys (Fig. 1b). Biocompatibility of HA/NiZr material was tested *in vitro*. Results of these investigations show that cells originated from the human bone tissue can be attached to the surface of HA-coated porous alloys.

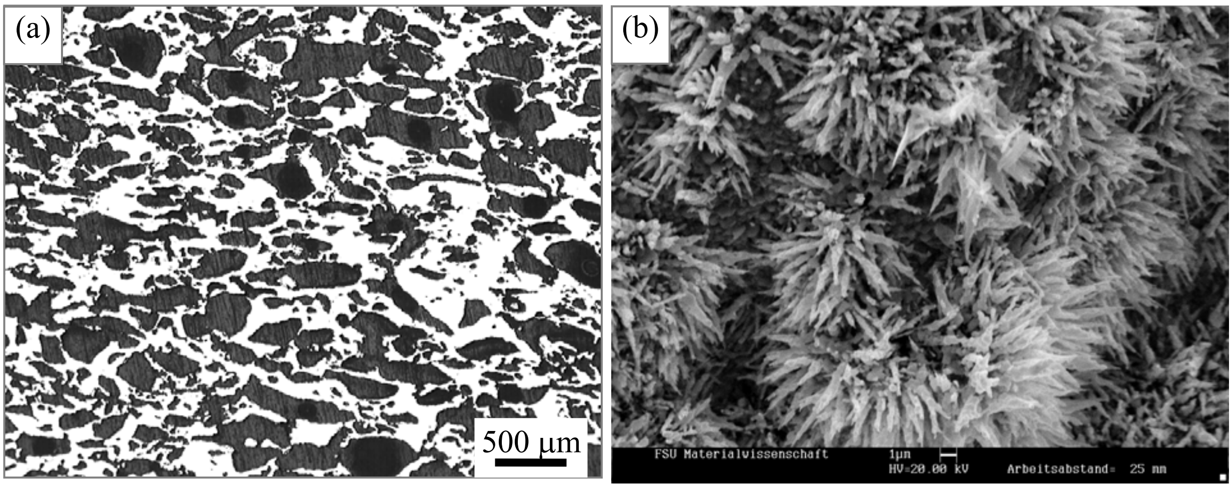

Fig. 1 Microstructures of porous ZrNi-based alloy (a) and hydroxylapatite crystals obtained on its surface (b)

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The authors would like to thank for the financial support provided by Joint Project NoECSP-09-13/B40 of National Foundation for Science and Advanced Technologies (NFSAT), State Committee of Science (SCS) of Armenia and USA Civilian Research and Development Foundation (CRDF) and International Bureau of German Federal Ministry of Education and Research (Project No ARM10/002).

6B-2

COMPOSITE COATINGS IN THE SYSTEM AL-NI-NIO BY *IN-FLIGHT* COMBUSTION SYNTHESIS DURING THERMAL SPRAYING

Marinou A. [1,2], Xanthopoulou G.[1], Vekinis G.[1], Lekatou[2] A., Vardavoulias M.[3]

[1]Institute of Materials Science, NCSR "Demokritos", 15310, Athens, Greece
[2]University of Ioannina, Department of Materials Science and Engineering, Ioannina 45110, Greece
[3] Pyrogenesis SA, Lavrion Technological Park, 19500 Lavrion, Greece

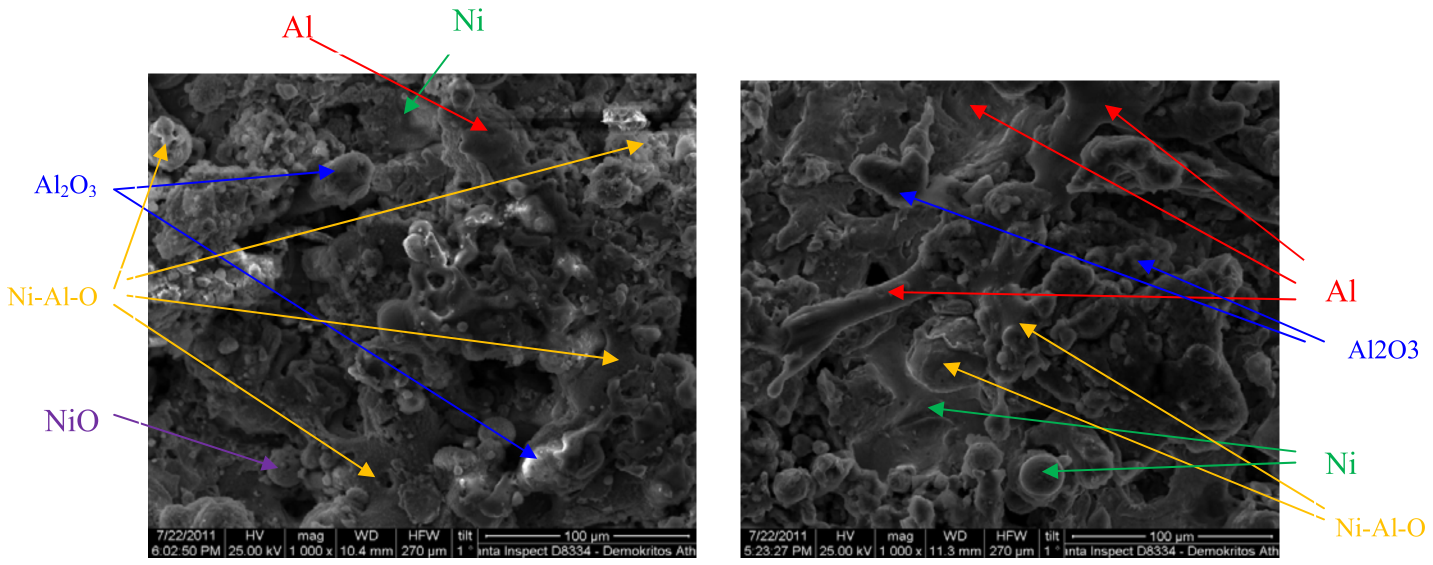
Lately nickel aluminides have attracted considerable attention because of their great potential for high temperature applications, due to their high melting points, excellent resistance to environmental degradation and good mechanical and chemical stability at high temperatures. Much effort is still needed to reduce processing cost and improve their ductility and creep properties before these intermetallic compounds can be more widely utilized in bulk form. Nevertheless, to take advantage of the unique properties of these intermetallics, many researchers have been developing them as protective coating materials.

This paper presents the results of our work to produce self-reacted intermetallic coatings by *in-flight* combustion synthesis during thermal spraying of Ni - Al and NiO - Al powder mixtures. The initial compositions tested were: 58%NiO + 42%Al and 59-86%Ni + 41-14%Al. The process developed is now undergoing patent assessment. It should be noted that no previous reports of in-flight SHS in a thermal spray were found in the literature and only very few in a Plasma spray.

Stainless steel (304) samples of size 50 × 40 × 5 mm were used as substrate. Prior to spraying the composite coatings all the samples were sand-blasted to obtain a rough surface. Thermal spraying was carried out using a Sulzer's Metco 5P-II Thermospray Gun with a high-oxygen acetylene-oxygen mixture providing a flame of temperature about 3000°C. SHS ignition was obtained in nearly all cases of the Ni-Al and NiO-Al composite powders, as confirmed by later characterization of the coatings.

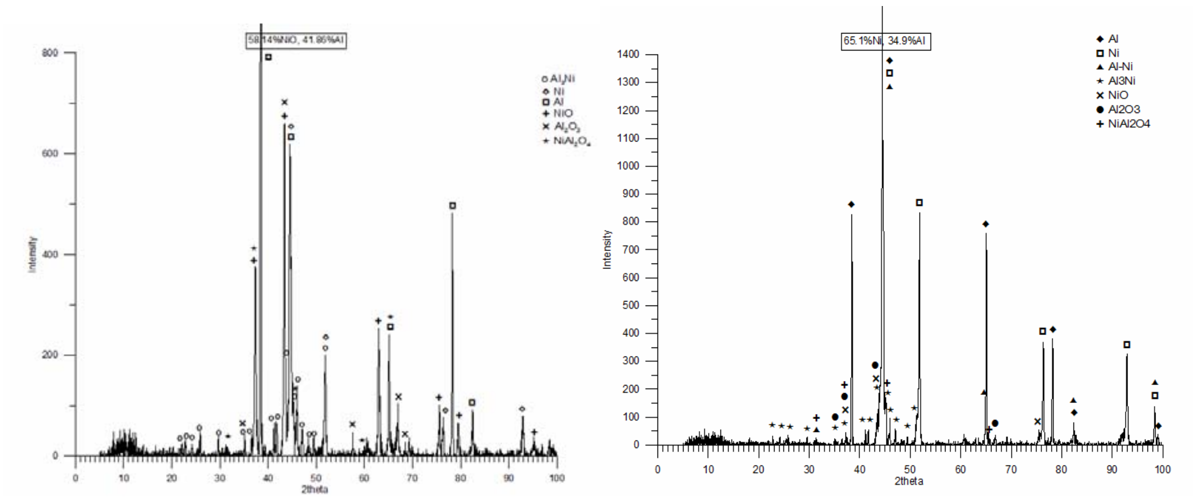
During SHS, the possible reactions that take place for the systems NiO-Al during flight are the following: 1)$Al + 3NiO \rightarrow 3Ni + Al_2O_3$, 2)$3Al + Ni \rightarrow NiAl_3$, 3)$Al_2O_3 + NiO \rightarrow NiAl_2O_4$. For the Ni-Al system they are: 1) $Al + Ni \rightarrow NiAl$, 2) $3Al + Ni \rightarrow NiAl_3$, 3) $3Al + 2Ni \rightarrow Ni_2Al_3$, 4) $2Ni + O_2 \rightarrow 2NiO$ 5) $4Al + 3O_2 \rightarrow 2Al_2O_3$ 6) $Al_2O_3 + NiO \rightarrow NiAl_2O_4$.

The morphology, microstructure and atomic structure of the composite powders and coatings were determined by means of scanning electron spectroscopy (SEM), optical microscope (OP) and X-Ray Diffraction (XRD). Properties of the coatings, such as porosity, surface roughness, hardness and adhesion were measured. Figure 1 shows typical SEM microstructures of the coatings and Figure 2 gives the X-ray diffraction spectra of the phases in Figure 1. It was found that SHS in the NiO-Al produces coatings made of mixtures of Al_3Ni, Al_2O_3, Ni, Al and NiO, which indicates that NiO and Al reacted only to a limited extent, probably because of the inadequate flight time of reaction (2-3 seconds). A small amount of $NiAl_2O_4$ spinel phase was also found which was due to the reaction $Al_2O_3 + NiO \rightarrow NiAl_2O_4$. Nevertheless, the presence in the coating of intermetallic Al_3Ni shows that melted Al and Ni must have reacted. In the Ni-Al system, the SHS was more complete during flight and the coating contained Al, Ni, Al-Ni, Al3Ni and small amounts of NiO, Al_2O_3 and spinel $NiAl_2O_4$.



(a) (b)

Fig 1.SEM photos of a)NiO-Al and b)Ni-Al composite coatings



(a) (b)

Fig 2.Typical XRD spectra of the systems a) NiO-Al and b) Ni-Al

The SEM/EDAX results, in combination with the XRD results for both mixtures tested, show that the coatings are composite with various phases in the system Ni-Al-O. Cross sectional analyses showed that the surface of the coatings had different phases than the bulk inside. The presence of oxide in almost every part of the coating is expected due to particles' oxidation by the flame. The grey phase above is sometimes a Ni-rich, Al-rich or intermetallic phases (Al_3Ni, NiAl). The light grey zones are the oxides Al_2O_3 and NiO. The $NiAl_2O_4$ phase was not found on the surface. In short, the microstructure of the composite coating is dominated by three phases with different morphologies: Metallic/Intermetallic phase, Oxide phase and a Spinel phase. The results show that this method offers an easier and cheaper, potentially mobile alternative to the normal spraying of intermetallic powders and has obvious potential in industry. It is the first time that in-flight SHS was demonstrated during thermal spraying with good quality hard coatings.

6B-3

COMBINATION OF THE SOL-GEL AND SHS-TECHNOLOGIES FOR OBTAINING THE CARBONAUCES REFRACTORIES

Mansurov Z.A.*, Dilmukhambetov E.E., Fomenko S.M.

Combustion Problems Institute, 172, Bogenbay Batyr Street, Almaty, 050012, Republic of Kazakhstan
* Zmansurov@kaznu.kz

The goals of the present study are to develop a high-carbon lining paste-like substance (mass) with minimum refractory quality 1850 °C based on the SHS and sol-gel technology for application instead of the graphite crucibles in the induction furnaces for melting nonferrous metal such as aluminum and its alloys, copper, brass, bronze etc.

Conventional technologies of obtaining carbonaceous refractories, as a rule, include high temperature roasting and smelting in reducing or inert atmosphere. They are quite power consuming and require complex equipment. In this connection, the technology of self propagating high temperature synthesis (SHS) of refractory material and products from them is very perspective. [1,2]. In this work, the properties of carbon containing SHS-refractories, which are perspective when melting bronze copper and others in induction furnaces, have been studied.

The general approach to synthesis of carbon containing refractory materials is carrying out of aluminothermal solid phase combustion of metal oxides under the conditions of SHS in the presence of carbon. At high temperatures of synthesis -1500 °C the reduced metal may interact with excess carbon forming carbides The use of silica sol as a binder has a new effect – heterocoagulation of sol [3]. We studied silica sol obtained by different methods: the ion – exchange method from sodium silicate solution, by hydrolysis of tetraetoxysilane and silicic acid ether – ethylsilicat.

The optimal conditions for production of sol silica by hydrolysis ethyl silicate present in figure 1.

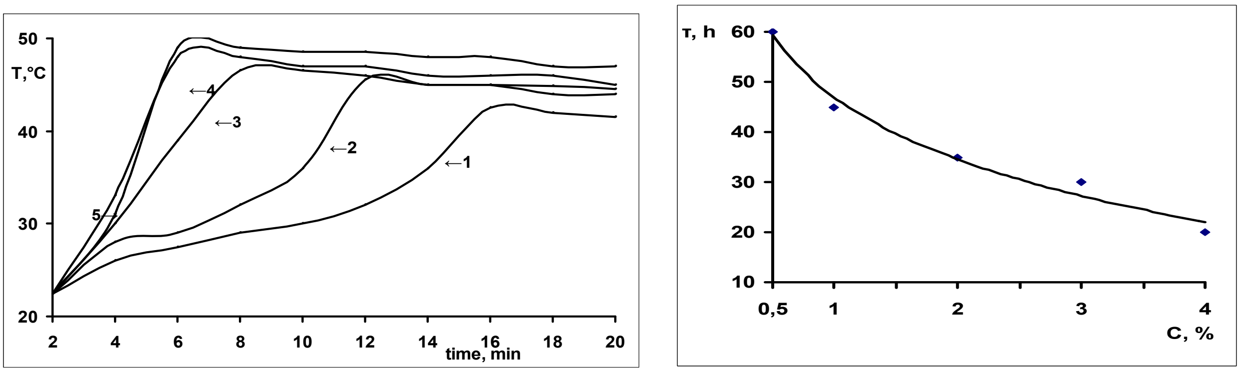


Fig.1. The optimal conditions for production of sol silica by hydrolysis ethyl silicate: a) -the temperatures of hydrolysis with present of H_2SO_4: 1 – 0,5 %; 2 – 1,0 %; 3 – 2,0 %; 4 – 3,0 %; 5 – 4,0 %; b) -the time stability of sol silica

An optimum composition of hydrolusate having a sufficient resistance to sol coagulation was determined: ethylsilicate ES -40 – 55 %, 0,5 % sulphuric acid solution – 45 %.

The presence of nanodisperse silica contributes to initiation of SHS at relatively low temperatures of system heating up to 850-900 ° C. For cubic specimen with the sizes 2 × 2 × 2 cm, and cylindric specimen with the diameter of 2 cm and height of 4 cm pressed from exothermic mixtures moisturized by silica sol, after carrying out SHS, burning off of the products in air was determined. For this, the specimens were subjected to cyclic thermal treatment at 950 ° C with 30-minute exposure in each cycle.

Physico-mechanical properties of synthesized refractories are present. Table 1

Table 1. Compressive strength of carbonaceous SHS refractories before and after cyclic thermal treatment

Specimen, No,	1	2	3	4	5	6	Graphite	Graphite-fireclay refractory
C, %	30	40	50	30	40	50		
σ_1, MPa	4,0	6,4	12,0	7,2	3,2	6,4	11,2	3 – 5
$\sigma_{2.}$, MPa	4,4	6,8	12,4	6,4	6,4	7,2	6,0	-

σ_1, σ_2– compression strength directly after SHS and after 5 cyclic thermal treatment.

Highly carbonaceous materials worked out in this work on the basis of SHS – and sol-gel technologies surpass conventional carbonaceous and carbongraphite refractory materials by their main characteristics.

These materials can be used not only as a lining material when repairing induction furnaces for melting non-ferrous metals but also for production of small highly refractory products: moulds, crucibles, glasses, metal wire, by the method of pressing followed by SHS.

Acknowledgement
This study has been accomplished with support from the US Civil Research and Development Fund (CRDF, AW KAE1-4024-AL-07).

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6B-4

MECHANICAL ACTIVATION ASSISTED SHS OF MAX-PHASES $Cr_xTi_{(2-x)}AlC$

Kurbatkina V.V.*[1], Levashov E.A., Patsera E.I., Rupasov S.I.

[1] National University of Science and Technology "MISIS".
* vvkurb@mail.ru

Class of refractory oxygen free compounds with a layered structure and a unique combination of metal and ceramic properties, which are generally described by the formula $M_{n+1}AX_n$ and well known as MAX-phases [1] are presented. MAX- phases based materials are advanced for application in different branch of industry due to a number of excellent properties: low density; high thermal conductivity, electrical conductivity, relatively high strength, reduced (when compared with ceramic materials) elasticity modulus, excellent corrosion resistance in aggressive external media, resistance to high temperature oxidation, and resistance to thermal shocks. Moreover, these materials are easily subjected to mechanical treatment [1-2].

The problem in obtaining the MAX- phases is that the final products contain impurity phases (for example, TiC, $TiAl_3$, Cr_2Al, Cr_7C_3, etc), which exert a substantial effect on their exploitation characteristics. The main cause of the phase nonuniformity in the synthesis of similar compounds is multistage solid state interaction, when thermodynamically stable compounds such as titanium carbide are formed during intermediate stages. In addition, local violations in the stoichiometric composition take place. They are associated, for example, with the partial evaporation of aluminum at high temperatures.

Taking into account the positive experience of applying mechanical activation (MA) to the problems of increasing the transformation depth and structural and phase uniformity of the SHS-product, in order to increase the content of the MAX phases, the initial exothermic mixtures were subjected to MA in a planetary mill.

By search of optimum modes MA we have tested some ways. The first is traditional way, including only variation of the time MA at constant speeds of rotation and a ratio mix/ball. Optimal mode corresponds to maximum of heat evolution.

Another way consists of consecutive addition of components mixture in drums, i.e. chrome and carbon are activated at first, then the titanium and aluminum are involved. Such approach allows to prevent appearance of interaction products in drum mill.

When analyzing the known mechanisms of formation of the MAX phases [1-3], as well as allowing for the combustion experiments, we can assume that these phases are formed due to the solid phase diffusion. In this case, the structural factors are of importance, namely, the phase size and the component distribution throughout the mix volume. It was confirmed with our researches.

First of all we have tried to increase internal energy of systems and probably burning temperature by assistance of MA. However this approach was not effective. The subsequent annealing though raise the quantity of MAX-phases, but it is not essential.

Then we have decided to increase time MA, despite formation of products in mill drums. As the MA time increases to 60 min, the fraction of the agglomerated particles reaches 90–95%, while the average agglomerate size decreases to 10 μm. The separate layers are not thicker than several micrometers.

More significant result was reached in mixture with X=1.5 $Ti_{2-x}Cr_xAlC$. The final product of MASHS consists of three MAX phases: $(Cr,Ti)_3AlC_2$, Cr_2AlC, and $(Cr,Ti)_2AlC$. The rest of samples amount of MAX-phase bigger, than the same from nonactivated mixtures. Also we could increase content MAX-phases from 8% till 45% in the samples with X=1.

When investigating the materials obtained from the activated charge, it was established that heat resistance of synthesized products in general somewhat higher than that of the materials not subjected to MA, and the alloys with a high chromium content are better in this respect.

For all considered mixtures in system $Ti_{2-x}Cr_xAlC$ the main contribution MA consists in possibility to intensify the phase formation due to decomposition and homogenization of components. For all investigated samples increase of a share of MAX-phases was observed.

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6B-5

MAGNETIC PROPERTIES AND MICROSTRUCTURE PARAMETERS OF COBALT-BEARING HEXAFERRITES SYNTHESIZED BY SHS

Minin R.V.*[1], Itin V.I.[1], Naiden E.P.[1,2], Zhuravlev V.A.[2], Maksimov Yu.M.[1]

[1]Department for Structural Macrokinetics of the Tomsk Scientific Center of Siberian Branch of the Russian Academy of Science, Tomsk, 10/3 Akademichesky ave., 634021, Russia
[2]National Research Tomsk State University, Tomsk, 36 Lenin Prospekt, 634050, Russia

Hexagonal oxide ferrimagnetics (hexaferrites) represent the main group of compounds used to produce materials for biological protection against electromagnetic radiation, decreasing the radar detection of various objects, and electromagnetic compatibility of radioelectronic facilities. To produce hexaferrites, it is commonly used the multioperational and energy-consuming ceramic technology including ferritization at high temperature.

To produce hexaferrite powders with a narrow particle size and shape distribution, the new methods were proposed. They involve mechanical activation of the reagent mixture in a high-energy device, self-propagating high-temperature synthesis, and subsequent ferritization [RF Patents No. 2303503, 2391183]. These methods, unlike the traditional ceramic process, use the chemical energy of the initial reagents and differ with a high product yield and low power and material costs for production.

This work represents the research results in a phase composition, structural parameters, and basic magnetic properties of $BaCo_{2-x}Zn_xFe_{16}O_{27}$ hexaferrites with the concentrations x=1.0 ÷ 1.4 synthesized by SHS in the vicinity of the EMP ↔ EMC ↔ EMD spin reorientation transition.

To produce oxide hexagonal ferrimagnetics, one part of oxygen oxidizer is added to the green mixture in a solid state (in the BaO_2 composition) and another part is provided by filtration of an active gas from the environment during chemical reactions. The initial components of the mixture were weighed and mixed for mechanical activation in a planetary ball mill, and then self-propagating high-temperature synthesis (SHS) and final sintering (ferritization) were conducted.

The crystal structure parameters, phase composition, and dispersity of synthesized hexaferrites powders were investigated with an X-ray diffractometer (Shimadzu XRD 6000, CuKα - radiation) and scanning electron microscope (Phillips SEM 515).

The magnetic measurements included the investigation of magnetisation curves in the fields up to 7 кOe. The saturation magnetization (M_S) and anisotropy fields (H_a) were calculated by using the method of singular point detection. The temperatures of the plane-cone easy magnetization spin-reorientation phase transitions ($T_{pl\text{-}cone}$) and Curie's temperature (T_C) of the synthesized powder materials were determined from the thermogram of initial magnetic permeability. The anisotropy fields and gyromagnetic ratios were calculated from the ferromagnetic resonance spectra in the frequency range of 27 - 37 GHz.

The work represents the basic static and dynamic magnetic characteristics of $BaCo_{2-x}Zn_xFe_{16}O_{27}$ hexaferrites with the concentrations x=1.0 ÷ 1.4 synthesized by SHS. The saturation magnetization, magnetic crystallographic anisotropy field, and spin-reorientation phase transition

temperatures were determined; the spectra of ferromagnetic resonance, magnetic and dielectric permeability were analyzed.
Mechanical activation, used to produce nancrystalline states in hexaferrites, is found out to be a method for controlling an effective anisotropy field and spectra of high-frequency magnetic permeability accordingly. It allows radio absorption to be optimized in the wider frequency range in comparison with the use of traditional materials with a similar composition [RF Patent No. 2382804].

The received results have demonstrated that hexaferrites synthesized by the SHS method show magnetic and dielectric properties highly competitive with those of the materials synthesized by a conventional ceramic technology. The use of the SHS method to synthesize barium hexaferrites allows power and material costs to be reduced due to the decrease in numbers and duration of technological operations, and final sintering temperature as well.

ORAL PRESENTATIONS

F: Industrialization of SHS

6A-K – KEYNOTE TALK

CONTRIBUTION OF SHS TO DECISION OF PROBLEMS OF SURFACE ENGINEERING

Levashov E.A.

National University of Science and Technology, Moscow, Leninsky prospect, 4, 119049, Russia
levashov@shs.misis.ru

Overview of recent progress results on synthesis of composite cathodes-targets for PVD (magnetron sputtering, cathodic arc evaporation) and PLD (pulsed laser deposition) are presented. The Ti-Al-N, Ti-Cr-N, Cr-N coatings are widely used in practice for cutting and forming tools because of their high mechanical and tribological properties, good thermal stability and excellent oxidation resistance. Recent research has been extended to multicomponent systems. The Si incorporation into the Ti-Al-N coatings resulted in the formation of nanocomposite structure with the (Ti,Al)N crystallites embedded to amorphous SiN_x matrix. Nanocomposite structure of the Ti-Al-Si-N coatings promoted to the increasing of the hardness and maximal usage temperature. C- and B- doped Ti-Al-N and Ti-Cr-N coatings are characterized by improved tribological properties due to the solid lubricant effect of the amorphous carbon or h-BN. Addition of the optimal amount of Y drastically improved the oxidation behavior of the Ti-Al-N-based coatings and promoted grain refinement resulting in lower residual stresses in coatings. So, problem of multicomponent (Ti,Cr)-(Al,Si,Cr,Y)-(C,B,N) coatings deposition stimulated studies on SHS of composite targets with different metals/nonmetals ratios Ti-Al-Si-C-N, Ti-Cr-Si-C-N, Cr-Ti-Al-C, Ti-Cr-B, Ti-Ta-C, Cr-B-Al-Si. Some peculiarities of combustion and structure formation in these systems are considered. Multicomponent nc-coatings (Ti,Cr)-(Al,Si,Cr)-(C,B,N) deposited by ion implantation assisted magnetron sputtering technology were found to be much better on the combination of physical mechanical, tribological properties and heat resistance as to compare well known analogs. Investigation results on the deposition of nc-coatings in a system (Ti,Cr)-Al-(C,N) by magnetron sputtering of SHS- composite targets based on MAX- phases $Cr_xTi_{2-x}AlC$ (x=0, 0,5, 1,5, 2) are discussed as example. It was found the film compositions which have a dense and defect free structure consist of cubic (Cr,Ti)(C,N), h-AlN, cubic (Ti,Al)(C,N) nanocrystals and amorphous phase. Coatings are characterized by unique combination of properties: high hardness 30-45 GPa; high wear resistance; relatively low friction coefficient less than 0.17; high thermal stability up to 1200^0 C in vacuum and high oxidation resistance in air. Low oxidation layer thickness 200-500 nm at 1000^0C was accompanied by a loss of nitrogen and diffusion of Al to the surface of coating resulting in the formation of a layered barrier structure consisting of Cr_2O_3, Al_2O_3, Cr_7C_3 and AlN_xO_y sublayers from the top to deep of the coatings. Nc-coatings demonstrated high positive value of corrosion potential in a 1 N H_2SO_4. Moreover corrosion resistance becomes high when nitrogen concentration in coating is raised.

Second part of talk is devoted to nanostructured electrodes which are successfully used in pulse electrospark deposition (PED) and chemical reaction assisted PED (CRAPED). The follow requirements to electrodes are proposed: high volume fracture of grain boundaries; average grain size of refractory compound phases could be less than 100 nm; precipitated or/and involved nanosized particles are distributed homogenously on the grain boundaries around refractory phases; refractory compound phases of electrode material could be wetted by the melt of substrate metal. Two groups of SHS- electrodes are presented: 1- dispersive-hardening ceramics (DHC) with effect of simultaneous strengthening of carbide grains and binder result in precipitations; 2- disperse-strengthened ceramic with modified structure produced using focused alloying by nanosized refractory compound which are modificators affected to the process of melt containing structure formation and lock the recrystallization.

Mechanisms of concentration separation of supersaturated solid solutions are discussed. Combination of the force SHS-pressing followed by annealing makes it possible to synthesize composite materials with desirable structure and properties. DHC based on Ti-xC, Ti-Me–xC (Me= Nb, Zr, Ta) systems were produced by SHS. Composition and structure of synthesis products before and after annealing were studied. Carbide grains and intergranular phase just after combustion process is not equilibrium: supersaturated solid solutions are formed because of high gradient of temperature in combustion zone and further high speed cooling. Precipitates 20-200 nm appear result in concentration separation of supersaturated solid solution via two schemes:

$(Ti, Me)_{x+y}C = (Ti, Me)_xC + y(Me\text{-}Ti)$, where Me- Nb, Ta, Zr (less 6%)

or $(Ti, Zr)_{x+y}C = (Ti, Zr)_xC + y(Me\text{-}Ti) + z(Zr, Ti)_zC$.

Coatings thickness (more than 50 μm) at density till 100%, lower roughness (less than 0.1 μm) were achieved due to high energy expended to erosion of nanostructured anode at high frequency and relatively lower pulse discharge energy.

6A-1

PRODUCTION AND APLICATION OF POROUS SHS CERAMICS

Maksimov Yu.M., Kirdyashkin A.I.

Department for Structural Macrokinetics, Tomsk Scientific Centre of SB RAS,
10/3 Academichesky ave., Tomsk, 634021, Russia
maks@dsm.tsc.ru

The work represents the research results of porous ceramics synthesis in a combustion mode. The results show that it is possible to obtain the various structures of a final product depending on the thermal SHS modes: periodic gradient structure, slotted structure, and drop structure [1]. The last structure type is optimal for materials with a high open porosity and gas permeability.

It was developed the technology for production of intermetallic and metallic oxide compositions with various forms by the SHS method.

The units based on SHS porous materials were constructed for water, water vapor, and wastewater purification, and technical oil purification from mechanical impurities as well. The general characteristics of porous products (pipes) are following: the length is up to 1500 mm, diameter is 350 mm, porosity is 65 %, pore size is 20-300 mm, thermostability is 1000-1500 K, and compression strength is 25-40 MPa.

The next application of porous SHS ceramics is the construction of gas burner units for heat generation. Porous SHS burners have a higher radiant heat transfer in comparison with flame burners, which allows natural gas costs to be reduced by 15 %, and harmful impurity emission to be decreased. The series of burners with a capacity up to 3000 kW were constructed on the basis of pipes from SHS ceramics and successfully tested at Siberia plants.

The use of SHS opens new possibilities to produce block porous catalysts. Catalytic converters for oil gas processing [2] can be produced by adding different catalysts to a green mixture.

At Tomsk Scientific Center of SB RAS, on the basis of the nickel-containing block SHS catalyst, it was constructed an autothermal synthesis gas reactor that carried out catalytic methane conversion during partial oxidation by air oxygen. The generator with a capacity of 50 m/hour provided with the conversion degree of natural hydrocarbons up to 90-95 %.

The generator operation showed high stability of its characteristics. Macro and microstructures of the catalytic block did not change during operation. Stability of the catalytic block properties is explained by the fact that during operation an oxide matrix continuously releases catalytic active centers (submicron particles of nickel) replacing losses due to a gas stream and corrosion deactivation.

Carbonization is eliminated by adding the air to a fuel mixture, which allows a catalytic activity of the block to be completely restored. The produced synthesis-gas is suitable for its subsequent conversion into liquid hydrocarbons by the Fischer-Tropsch process. Preliminary laboratory investigations have shown that this method can be used to produce C_8-C_{15} hydrocarbons useful as a motor fuel.

Porous SHS shape memory materials from nickel-titanium are successfully used in medicine. The new class of porous functional materials was developed for implantation in an organism at the Medical-Engineering Center of the Siberian Physico-Technical Institute at Tomsk State University. Body tissues grow well through the porous structure of intermetallic compound, which allows them to apply in traumatology, otolaryngology, and backbone surgery.

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6A-2

ALUMINA NANOFIBERS MASS PRODUCTION VIA AIR-EXPOSED COMBUSTION SYNTHESIS

Amel-Farzad H.*, YousefiMashouf H.

Bu-Ali Sina University, Hamadan, Iran
hh_amel@yahoo.com

Alumina fibers of nanometer diameter are of special interest as insulators and etc. It was known from previous work that, under special conditions, metal/gas (such as O_2 and N_2) combustion reactions can lead to the fibrous morphology of ceramics (oxides and nitrides) [1]. The temperature must be high enough for evaporation of the metallic component, but, not so high that all the products evaporate. Since T_{ad} is so high for most metallic oxides and nitrides, another ceramic component has to be added to reduce it. The following simply air-exposed combustion reaction was designed to provide all discussed necessities,

$$Al+xMgO+O_2 \Rightarrow Al_2O_3+xMgO$$

where x is varied from 2 to 3.

The micrometer-sized particles of Al and MgO were ball milled in a high energy planetary machine using Alumina jar and balls. Both the components were severely refined to the range of about 100 nanometes in diameter. No special phase was detected through the further XRD tests. The mixed powders were then pressed to form cylinders of 1mm diameter and 1mm height with relative density of 50%. The reactions were simply ignited using electric arc. No special atmosphere was used.

At last, MgO were easily leached in light HCl and pure Al_2O_3 fibers were simply gathered, the same as nanopowders produced by Won et.al [2]. The Al_2O_3 fibers were usually of about 100 nanometers diameters and about 100 micrometers length, leading to aspect ratio of about 1000.

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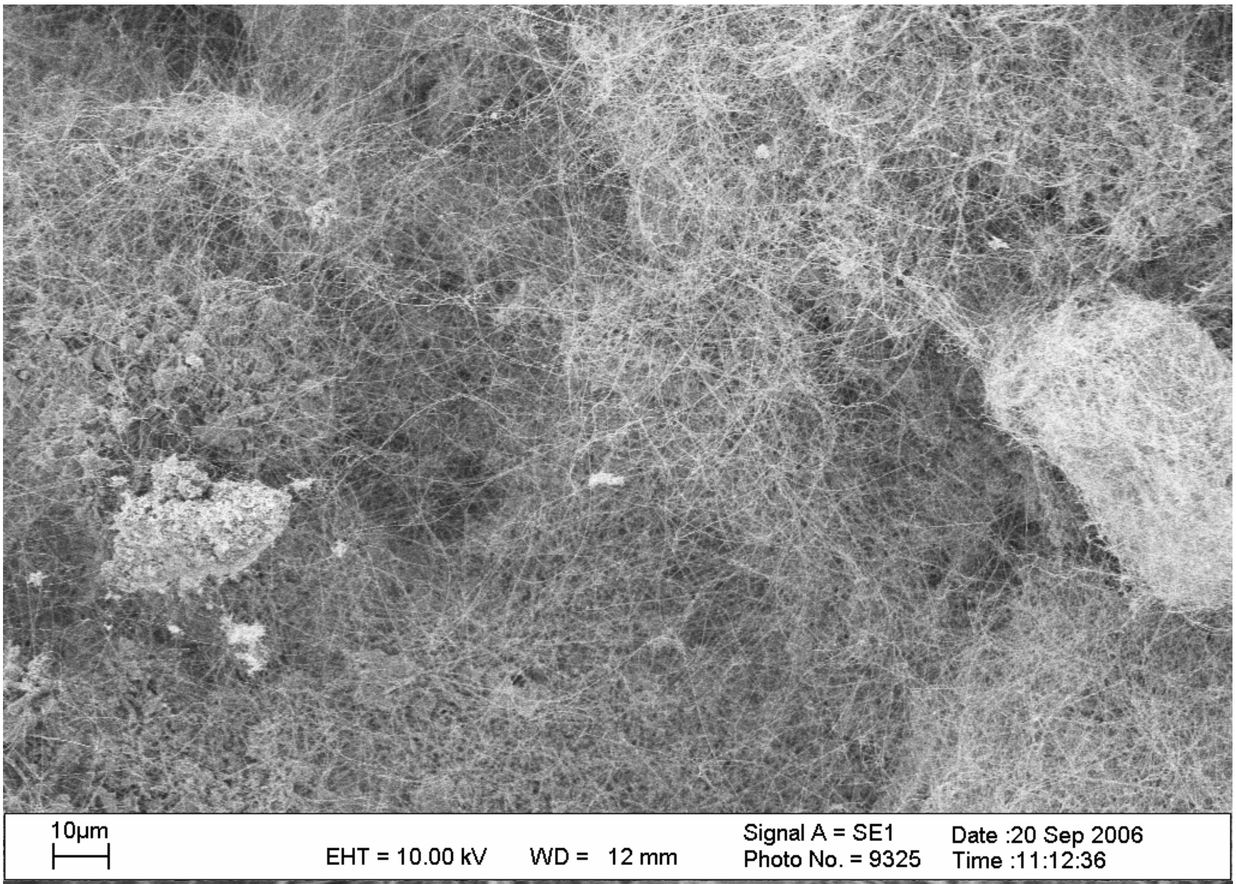
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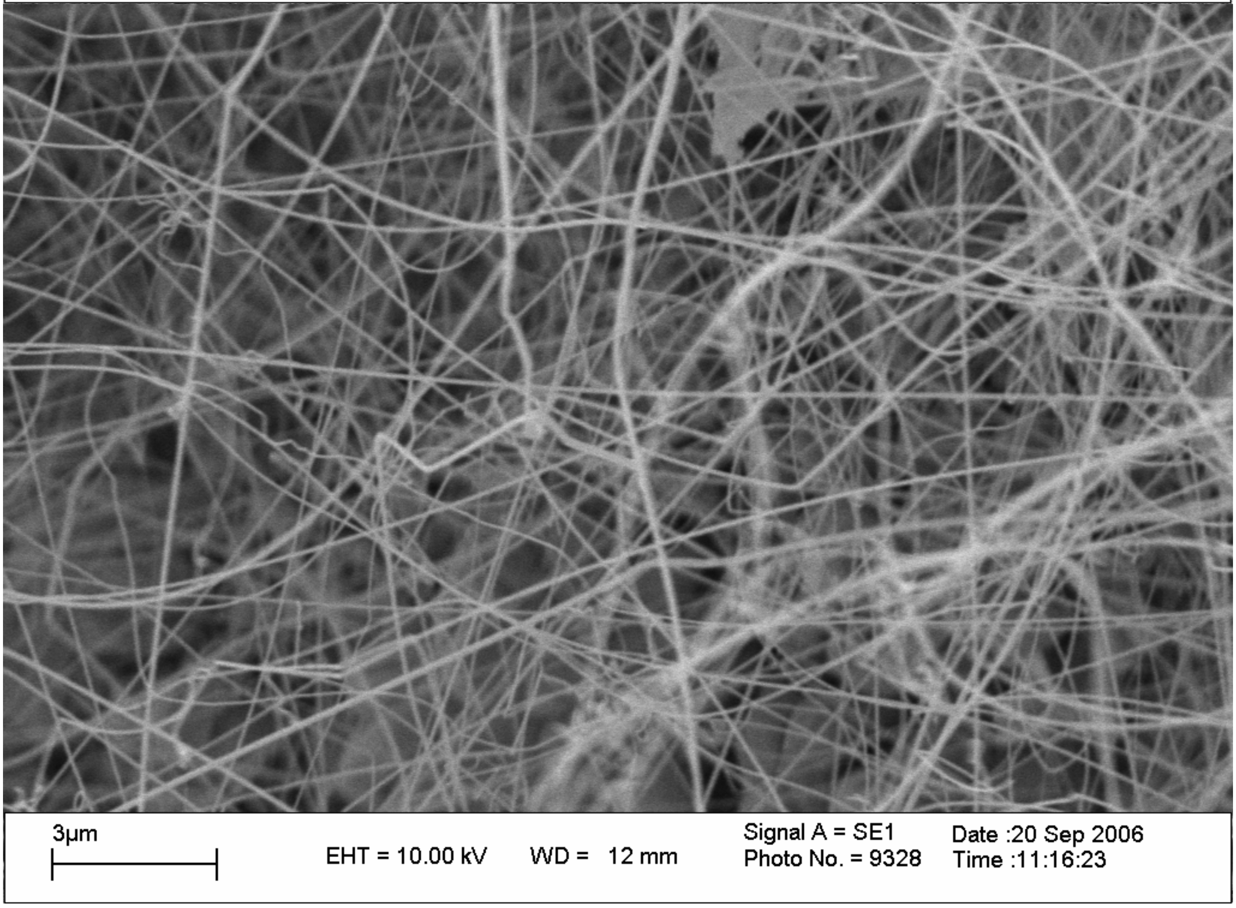
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6A-3

ALUMOSILICATE REFRACTORY COMPOSITE MATERIALS FOR HEATING AGGREGATES INSULATION FROM HIGH TEMPERATURES

Kapustin R.D.*, and Pervukhin L.B.

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,
* kapustin-roman@mail.ru

In many industrial branches, refractory linings used in heating aggregates are often subjected not only to high temperature effects but also to simultaneous influence of abrasive wear or hostile media. As a result of such conjugated action of crushible factors the lining refractory materials used are destroyed thus creating the necessity of a considerable outlay to the basic repair.

However it is not always reasonable to substitute refractory or heat-insulating material that does not meet contemporary requirements for a more stable and more expensive analog.
At present, protecting refractory coatings have been developed with the use of advanced technology of self-propagating high-temperature synthesis (SHS). Such coverings deposited onto the surface of refractories can expand the region of their thermal application, lead to significant reduction of physicochemical and mechanical erosion on their surfaces, and result in a pronounced (up to 200°C) increase in the material heat-resistance under the condition of static and dynamic forces of hostile media and high-temperature gas and dust currents.

However practical employment of such coatings is limited because of insufficient knowledge of the changes in them taking place during SHS and impossibility of reliable forecast of their final physicomechanical and performance properties. Besides, available technologies do not allow their employment in thermal aggregates that cannot generate temperatures required for initiation of the synthesis process (tubes, reactors, and the like).
The objective of investigations was the attempt to improve the technologies of production of aluminosilicate refractory composite materials and articles from them intended for preventing overheating of thermal aggregates based on the data obtained in thee experimental and theoretical studies of synthesis of mullite structures and corundum in the surface layer based on aluminosilicate SHS materials (AS-materials).

Investigations involved

- calculation of the adiabatic temperature according to the known methods including specified computer software ISAMAN-THERMO;
- the experiments on various approaches to SHS in thin coatings of AS-materials and further investigation of the final products by an X-ray analysis and scanning electron microscopy.

The experimental procedure presupposed quenching of the samples composed of SHA+OCP M-1 in accord with various step-wise heating regimes of an electrical furnace chamber.

It was found that because of a significant heat escape it was necessary to arrange heating of the thin surface layer based on AS-aluminosilicate to the temperatures above 1300°C for initiation of synthesis of mullite structures. However heating up of the entire aggregate up to such temperatures requires high energy consumption and is not always technically possible and economically reasonable.

The experiments were performed with the use of the shamotte compositions SHA+ OCP M-1. The surface was heated by igniting a flexible pyrotechnic tape (LTH-100) based on ferroaluminum thermit (TI-5M) attached to the sample surface, which allowed the combustion temperature up 2000°C. We also elaborated a heat-insulating dressing based on a heat-resistant cellular concrete (VBF-400).

As a result of experiment, the technology of synthesis of composite material shamotte SHA+ OCP M-1 by means of surface heating with a pyrotechnic tape (LTH-100) helping to the synthesis of a mullite structure and corundum in the surface layer has been developed. Such arrangement of the process in turn results in elevation of the operation characteristics of the composition and makes the range of the material application much wider.

6A-4

EXOTHERMIC REACTION CHARACTERISTICS OF CONTINUOUSLY BALL-MILLED Al/Ni POWDER COMPACTS

A. Hadjiafxenti[1,2], I.E. Gunduz[1,2], T. Kyratsi[1], C.C. Doumanidis[1], C. Rebholz*[1,2]

[1] University of Cyprus, Department of Mechanical and Manufacturing Engineering, 1678 Nicosia, Cyprus
[2] Northeastern University, Department of Mechanical and Industrial Engineering, Boston, MA 02115, USA
* claus@ucy.ac.cy

Nanoscale materials that exhibit self-propagating exothermic reactions are promising energy sources for thermal manufacturing, owing to their ability to provide intense localized heat. These materials are often manufactured in the form of bimetallic multilayer foils (MFs) using magnetron sputtering. One possible economic processing route is the use of ball milling (BM), which can produce similar nanoscale lamellae within the powders of Al and Ni through mechanical deformations. Such powders have been shown to be highly reactive when milling is interrupted before any intermetallic phases form [1-3].

In this study, self-propagating high temperature reactions in consolidated pellets of continuously ball milled aluminum (Al) and nickel (Ni) powders at a composition corresponding to $AlNi_3$ have been investigated. The reaction characteristics of the samples (observed using high speed optical and infrared imaging) revealed that the thermal wave velocity, maximum reaction temperature and ignition initiation duration decreased with increasing milling times after 1 hour. The formation of a bi-modal structure with nanoscale lamella of Al and Ni and a reduction in overall powder size at longer milling hours was observed. BM produces near optimum microstructures after 4 hours of continuous milling with nanoscale lamella and some relatively thick nickel layers, suggesting that the thermal characteristics of the powders can be improved by using smaller Ni particles in the starting mixture. The heat output of the powder mixtures was close to the formation enthalpy of $AlNi_3$, which is somewhat reduced by the remaining Ni solid solution. BM beyond the optimum point increases the solid state diffusion that negatively impacts the heat output and the thermal wave velocity. Ignition experiments indicated near adiabatic reactions occurring within the pellets, which could easily be ignited with a locally applied heat source. X-Ray Diffraction (XRD) analysis after ignition tests showed that the $AlNi_3$ amount increased with increasing milling time. Thermal analysis using interrupted Differential Scanning Calorimetry (DSC) in combination with XRD revealed that the ball milled pellets have similar characteristics to nanoscale magnetron sputtered multilayer foils in terms of phase formation sequence and exothermic peak shifts. Powder mixtures consolidated into a more optimum form (for example, very thin layers or compacts further thinned with rolling) can potentially be ignited using a spark source similar to MFs and be used for thermal manufacturing applications.

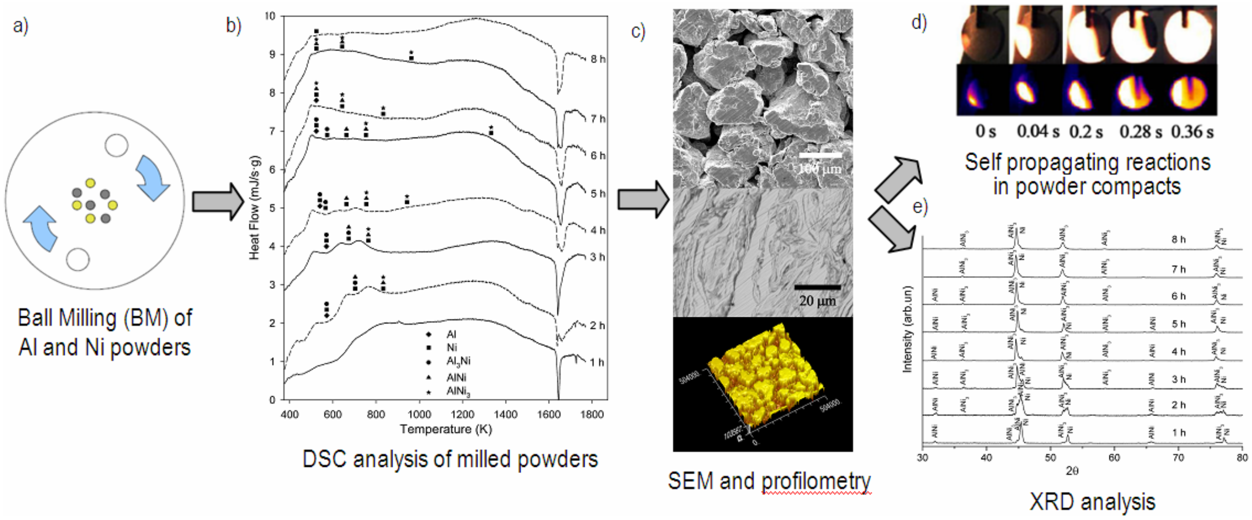

Fig. 1. Graphical abstract, showing schematically BM of Al and Ni powders (a), results on DSC scans for samples milled between 1 and 8 hours (b), SEM and profilometry images for samples milled for 4 hours (c), IR and high-speed camera images of reactions in powder compacts milled for 4 hours (d), and XRD patterns for between 1 and 8 hours milled powders after ignition tests (e).

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6A-5

MECHANOCHENICAL ACTIVATION AND REACTIVITY OF SHS-SYSTEMS ON THE BASIS OF QUARTZ

Mofa N.N.*, Mansurov Z.A.

Combustion Problems Institute, Bogenbay Batyr str., 172, Almaty, Kazakhstan
*Nina.Mofa@kaznu.kz

Intensive dispersion in the mill results in not only grinding of particles but also saturation of them with defects determining the different level of the energy state of the material and, hence, its chemical activity. The work deals with the effect of different parameters of mechanochemical activation on the change in the structure and power characteristics of silicon dioxide (quartz). The presence of defects in quartz after mechanochemical treatment was evaluated by widening X-ray lines at semiheight of the peak and by the size crystals. After treatments of quartz in the mill in the presence of different modifiers: butyl alcohol, silicic and acrylic acids, polystyrene, one can observe the formation of chemical compounds on the surface of a quartz particle, in particular, with participation of carbon. The presence of carbon on the surface of modified quartz is verified by the results of electron microdiffraction and absorption-weight method.

On the basis of a complex investigation on the structure and properties of quartz particles modified by different organic compounds it was earlier shown [1] that the use of structurally complex modifiers provided the formation of nanostructurized carbon containing films of different density of morphology on the surface of particles. So, modification of quartz particles by acrylic acid in the process of mechanochemical treatment results in formation of a dense, quite homogeneous organic film and the presence of highly disperse crystallites in the surface polymer layer. At the combined treatment of quartz with polystyrene there takes place a simultaneous destruction of a quartz particle and destruction of polystyrene into polyenic and aromatic components. Depending on the amount of the modifier being used, the time of mechanical action as well as the variation of action conditions there form structurized films of different morphology cross-linked with the particle surface or rolled in the form of tubes of different configurations the size of which reaches 50÷70 nm.

Beside silicon, oxygen and carbon, in formation of the surface layer structure, an active part is taken by iron which is ground in the form of nanoparticles and included into the surface of quartz. Thus, particles of quartz modified in the process of mechanochemical treatment are a complex formation. On the surface of particles there are reducers: carbon and iron introduced into a polymerized surface layer which provides not only encapsulation of the power state of the activated particle but also prevents nanosized inclusions of iron from untimely oxidation.

The relation of the structural state of the charge material particles and thermokinetic characteristics of SHS process was stated. When studying the peculiarities of combustion of the systems with activated and modified quartz, we constructed thermograms of combustion and determined the induction period, the self-ignition temperature, the process rate and maximum temperature of combustion. The use of modifying additives results in not only the increase of maximum temperature of combustion but also the increase of the combustion process period as well as the change in the phase composition of synthesis products [2]. Quartz modified by acrylic acid most completely reduces to Si and aluminium is oxidized to Al_2O_3. Besides, $3Al_2O_32SiO_2$ (mullite), SiC are formed and admixtures of Fe uptaken into quartz from steel balls in the course of milling form $FeSi_2$. When using polystyrene as a modifying additive under similar conditions of treatment and synthesis, the process of combustion of SiO_2 with Al develops like that for quartz modified by acrylic acid differing only in noticeable increase in the amount of formed SiC on account of carbon of the modified surface of particles. Finally, mechanochemical treatment of quartz determines stationary of the process development and completeness of Si reduction.

The effective method of influencing the combustion process of the substance being synthesized is a scale (size) factor. When changing the sizes of the sample (product) being synthesized, it is possible to change the conditions of heat removal, kinetics of the reaction development and temperature in the combustion wave. Finally, this effects the phase composition, structure and properties of the material being created.

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8A-K – KEYNOTE TALK

SOLUTION COMBUSTION SYNTHESIS OF CATALYSTS: METHODOLOGY AND APPLICATIONS

Wolf E.E. and Mukasyan A.S.

Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN, 46556 USA
ewolf@nd.edu

In this talk we describe methodology for solution combustion synthesis (SCS) of various multi-component catalysts, including complex oxides, metal and alloys and demonstrate their applications in catalysis on the example of hydrogen production from methanol and bio-ethanol. In one of the method used, referred as Impregnated Layer Combustion Synthesis (ILCS) a reactive solution containing the catalysts' precursor and a fuel, such as glycine, is impregnated into a thin cellulose paper or into a porous support. After drying, the impregnated cellulose is ignited at one end resulting in a combustion front that moves in a self-sustained mode, leaving behind the desired oxides with high surface area. A high speed IR and conventional video recording cameras are used to follow the temperature–time evolution and reaction front structure during ILCS. Fig. 1 shows a schematic diagram of the propagating reaction front with the temperature profile superimposed onto the video image. Also inserted are statements describing the type of reaction occurring in each zone before and after the reaction front [1] determined from x-ray diffractions and SEM micrographs. A theoretical model of the ILCS process for catalysts preparation was developed on the basis of these front propagation experiments [2]. The model include the two reaction zones in which heat conduction and convection and heat generation by the reaction occurs and it captures qualitatively the features experimentally observed.

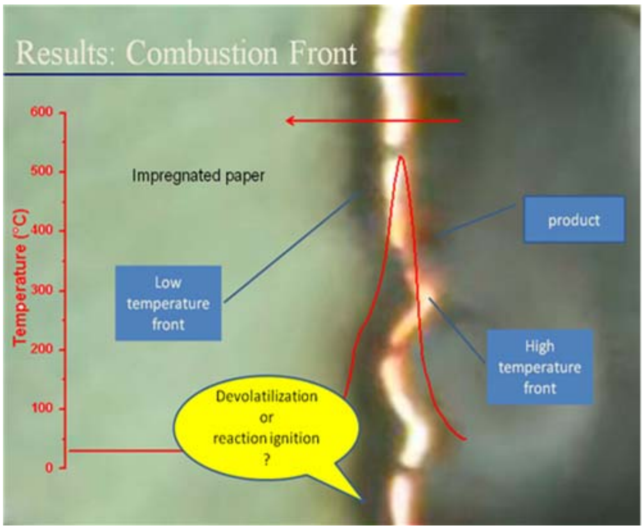

Fig 1. Video image of the moving front on the impregnated cellulose paper. The temperature profile was obtained from the IR emission camera.

Complex catalysts containing copper, zinc and zirconium were prepared by ILCS. Palladium was added into the mixture during ILCS or by a subsequent impregnation of a previously synthesized Cu/Zn/Zr catalyst (second wave impregnation). The activity and selectivity of these catalysts for hydrogen production from the oxidative reforming of methanol was measured under various conditions. The catalysts were characterized by various techniques to determine surface area and bulk composition. Structure and oxidation state during reaction were obtained by in-situ Extended X-ray Absorption Fine Structure (EXAFS) and x-ray absorption near edge spectroscopy (XANES).

Characterization results correlating the catalytic role of the various components during methanol oxidative reforming are also discussed.

We also report the application of solution combustion synthesis (SCS) to prepare metal-based catalysts for hydrogen production from bio-ethanol [3,4]. Catalysts containing Ni, Cu and Fe and their alloys were synthesized from an aqueous solution of their nitrate precursors and variable amounts of glycine as a fuel and reducing agent. This solution was heated over a hotplate until the mixture ignited locally and then the reaction front propagates to the bulk of the mixture to yield crystalline materials with the desired composition. The amount of glycine was optimized to get pure metals as well as metal oxides. The presence of metallic phases is an important factor in the activity and selectivity, and if so, increasing the oxides surface area and its reducibility increases the number of active sites. Due to the vigorous nature of the combustion synthesis reaction and the evolution of large amount of gas phase products a unique surface morphology was produced. The gases evolved during the combustion synthesis reaction, form channels in the resulting solid product and hence the product is porous in nature as shown in SEM images (Figure 2). High magnification images show the presence of particles smaller than 500 nm agglomerated together forming a micro-porous structure. The multicomponent catalysts prepared by SCS were very effective for ethanol decomposition as well as ethanol partial oxidation. Kinetics and FTIR studies are combined with EXAFS results to correlate the oxidation state of the active metal with the catalyst preparation.

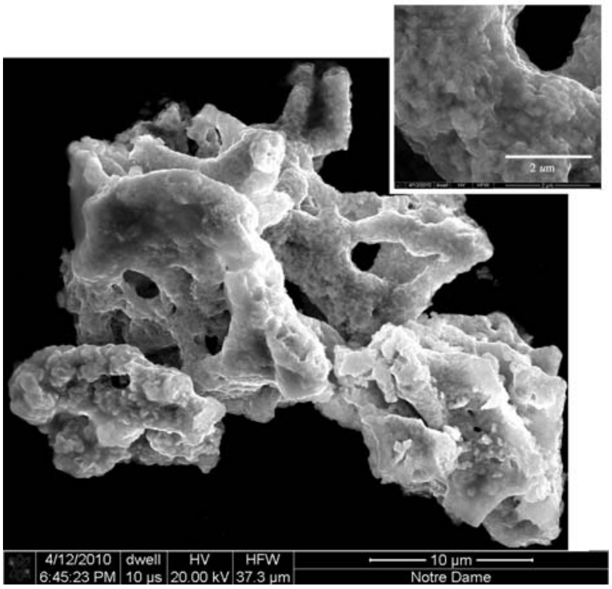

Figure 2: SEM image of $Ni_1Fe_1(Cu_7Zn_3)_{0.5}$ nanoparticles

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8A-1

FRONTAL COMBUSTION OF ENERGETIC COMPOSITIONS INTO THE ENVELOPE: USING FOR HEAT SOURCES "RUNNING HEATWAVE" TYPE

Kobyakov V.P.

Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Institutskaya str. 8,
Moscow Region, 142432, Russia.
koba@ism.ac.ru

Various kinds of solid-phase energetic compositions (SEC), burning without oxygen was investigated. Interdisciplinary studies of the combustion in the envelope and heat-evolve SEC, as well as heat transfer through the shell to the environment was conducted. The results obtained are discussed in the report by the example of a composite mixture $Fe_2O_3/TiO_2/Al$ system with various additives and with different ratios of the components. Technological research aimed at developing various structures of heat sources was carried. This report focuses on the practical application of the research and development. In particular, we consider the development intended for the oil and gas industry. Specifically, it concerns the creation of heat generators for the treatment of the bottom-hole formation zone containing hydrocarbons, with a view to increasing the productivity of oil and gas wells, and heat monitors for drilling-through perforated wall of the well casing. The results of these studies led, in particular, develop a method of thermo pulse treatment of the bottom-hole formation zone; devices to implement this method (heat generator TTG type and the generator initiating electro-pulse GID type); not detonate heat-generating mixtures, burning of solid-liquid-phase mechanism, which are characterized by combustion heat of 4-5 MJ/kg; advanced technologies for producing these mixtures and devices. Heat generator TTG type is a new effective and relatively inexpensive device designed to enhance well production, rehabilitation of uneconomic wells and resuscitation of dormant wells, and to extract residual oil reserves and development of oil fields with heightened viscosity. It is these issues today are most relevant to oil and gas industry, and not just Russian.

Principle of action of TTG and technology of thermo pulse treatment of bottom-hole zone are as follows. TTG, equipped with an adapter with a hermetic electrical leads, attached to a standard cable lugs and with a standard hoist lift and standard cable-rope lowered in the range of treatment. Remote feed over a cable-rope current pulse from the generator electro-pulse GID type initiates local inflammation of the fuel filling. A powerful heat pulse causes rapid overheating of the wellbore fluid with the formation of vapor-liquid mixture and the formation of high-pressure pulse. The both thermal and hydraulic shock penetrates through the perforations of the casing and influences on the bottom-hole formation zone, causing an increase in its filtration properties, both due to melting and removal of bridging pollutions, and due to expansion of the old and the formation of new channels in the surrounding borehole collector.

Field tests of this innovative development were carried out in the oilfields of Republic Belarus. The 1st test in June and July 2007 was processed uneconomic (about 1 ton per day) well number 126 Vishansky deposits (Fig. 1). The 2nd test in August 2008 was processed well number 2 West Davydovsky deposits which before was in the prime.

Effectiveness of thermo pulse treatment of the Vishansky well can be characterized by the following data:

-

- Since the beginning of testing and the end of 2009 the total increase in oil production was approximately 5400-5500 tons.
- Income from additional oil production (the period from late 2007 to late 2009), taking into account the average cost of petroleum of mark Urals USD$70 per barrel or $490 per ton amounted to ≈ $2,6-2,7 million. The comparison of this profit with the cost of TTG (not more than $10000) speaks for itself.
- Duration increased productivity of the well has already exceeded 3 years.

At the West Davydovsky well to processing oil production rate was very low (0.4 tons per day), and water cut crude oil exceeded 70%. Work in this well was stopped, and from December 2007 to August 2008 the well was in the prime. That well after treatment was gushed with almost waterless oil (previously used a rod pump) and output between 20-40 tons per day.

The innovative development is protected by patents, has a Certificate of Conformity and ROSTECHNADZOR's Permission for use it in oil and gas industry, and so was awarded the Gold and Silver medals in innovative exhibitions.

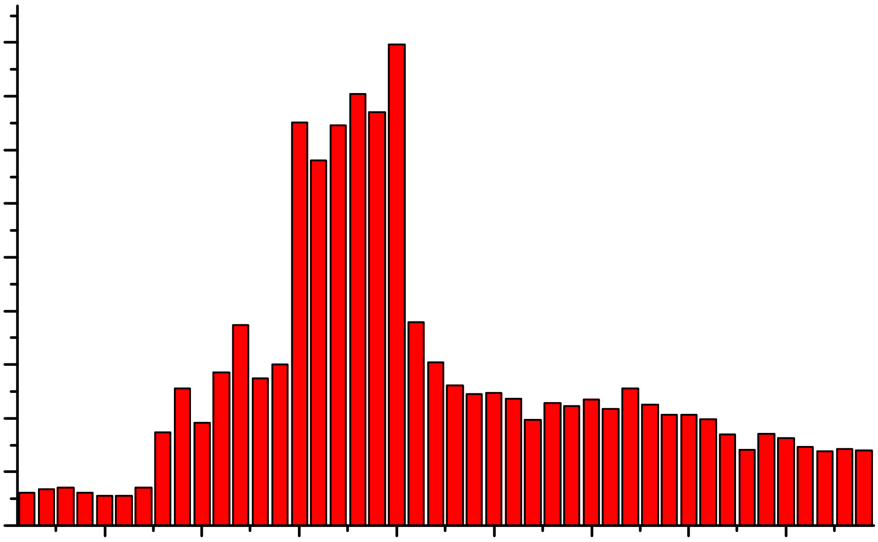


Fig.1. Results of 1st field test. Oil out-put of Vishansky well number 126.

8A-2

PRODUCTION OF Ti/TiB MASTER ALLOY BY SHS PROCESS FOR THE OBTAINING Ti COMPOSITES FOR THE AERONAUTIC INDUSTRY

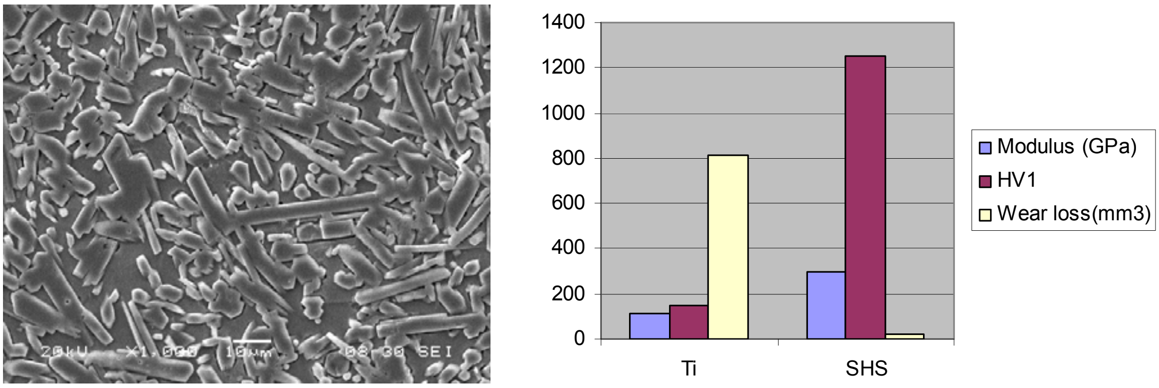
Agote I.*, de Cortazar G., Lagos M.A., and Gutiérrez M.

Tecnalia, Paseo Mikeletegi 2, Parque Tecnológico E-20009 San Sebastian, Spain
* inigo.agote@tecnalia.com

Titanium and titanium composite materials have been widely investigated during the last decades for aeronautical applications. Today many components are made with titanium alloys in the aeroplanes but also in race cars, leisure sports, biomaterials, jewellery…the titanium is now becoming a very popular metal [1]. Concerning titanium matrix composites reinforced by continuous monofilaments, several investigations were done in the 80 and 90’s and only few applications are effective nowadays. There is a technological and an economical reason of this. The technical reason is the difficulty to make the material and mainly to associate without any mechanical or chemical damage the filament and the matrix. The matrix is usually the well known Ti-6Al-4V alloy and the reinforcement is most of the time the SCS-6 or SM-2156 silicon carbide monofilament. On the economical side, the prohibitive cost of the reinforcement associated to the complexity of the process to achieved a good material have been the main reasons why only restricted applications have been developed. However titanium matrix composites have several advantages on their mechanical and physical properties, i.e. strength, stiffness, hardness at room and at medium temperatures (less than 600°C). The direction of the reinforcements dictates the properties, providing the option to tailor specific properties in specific directions [2.3].

This work studies the production and properties of Ti based composites obtained by SHS technology and followed by casting process. Firstly a heavy loaded master alloy was obtained by SHS technology. Secondly this alloy was added to the molten Ti alloy to obtained the final reinforced component.

It was observed that the SHS technology is a very useful process to obtain a suitable boron source to be added in the investment casting process and thus, to produce discontinuously TiB-reinforced titanium matrix composites via casting. By means of the SHS technology, highly reinforced Ti/TiB (TiB>60wt.%) master compounds (as can be seen in the figure). The obtained mechanical properties (young modulus, hardness and wear resistance) are much better that for pure titanium, especially the hardness and wear resistance (see the graph).



Micrograph of the obtained master alloy (left) and the properties obtained in the final reinforced material (right).

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8A-3

SHS COMPACTING MULTI-COMPONENT CATHODES ON THE BASE OF HIGH-MELTING TITANIUM COMPOUNDS FOR ARC-PHYSICAL VAPOUR DEPOSITION OF NANOCOMPOSITE COATINGS

Amosov A.P.*, Fedotov A.F., Ermoshkin A.A., Altukhov S.I., Smetanin K.S., Latukhin E.I., Lavro V.N.

Samara State Technical University, 244, Molodogvardeyskaya St., Samara, 433100, Russia
*mvm@samgtu.ru

This work is devoted to development of construction and technology for producing by one-stage method of SHS-pressing multilayer multi-component cathodes of intricate shapes for arc-physical vapour deposition of nanocomposite coatings in industrial installations of the Union type. The cathode has the shape of truncated cone with a cylindrical water-cooled bottom with a coupling flange (Figure 1, a). An article of such intricate shape can not be produced by the method of SHS-pressing in free-flowing sandy shell. In this connection the construction of multilayer cathode was developed (Figure 1, b, c) which consist of metallic bottom 1, the evaporating working layer 3 from high-melting SHS product, the layer of SHS brazing solder 2 for joining the working layer 3 to the bottom 1, and the intermediate layer 4 (if necessary).

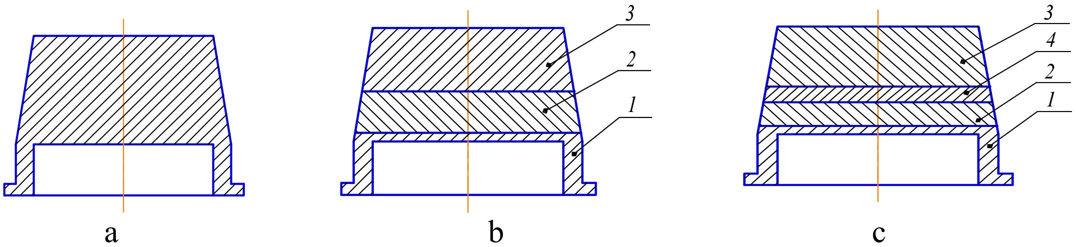

Fig. 1. Constructions of (a) monolithic, (b) tree-layer, and (c) four-layer cathodes

A means was specially designed to join the multilayer cermet part of the cylindrical shape to the metallic bottom an once during the process of the SHS pressing. The multilayer green part in diameter 54 mm was pressed previously in a cylindrical die up to relative density 0.5 – 0.55. Then the synthesis and forced compaction of the hot synthesis product was performed in a cylindrical press-mold-reactor in diameter 125 mm with sandy shell by Hydraulic Press D-1932. First the multilayer green part in the sandy shell was pressed with pressure 18 MPa and ignited by an electrical coil. After 3 – 5 sec upon completion burning the pressure 125 MPa was applied to combustion product and held for 20 – 25 sec. The synthesized part was placed in a furnace with the temperature 700 – 750 °C and cooled together with the furnace down to the room temperature to eliminate the possibility of the part cracking in the course of cooling. The synthesized part was ground to make the shape of truncated cone with flat top.

On development of the technology of SHS compacting the multilayer cathodes, the following problems were solved:

1) end compositions multi-component working layer of the cathode were selected which could be compacted to a nonporous condition and were not cracked both during SHS compacting and during cooling to the room temperature;

2) compositions and thicknesses of the layer of the SHS brazing solder and the intermediate layer were selected which could provide continuous joints (welding or brazing) all layers together and with the metallic bottom and hold the continuous joints during cooling without separation into layers;

3) formation of cracks in the working layer was eliminated during grinding the synthesized part. Compositions of SHS brazing solders are TiB-10%Ti and TiB-25%Ti for the titanium bottom and TiB_2-45%Cu for the bottom made from stainless steel 12X18H9T. In the latter case, there is an intermediate layer of composition TiB_2-75% (Cu-30%Ni) as well.

Possibilities for producing the cathodes with working layers from multi-component materials on the base of high-exothermic SHS systems Ti-C and Ti-B doped with such components as Al, Si, Ni, Cu have been investigated. The best producibility on SHS pressing and machining was shown with materials on the base of nonstoichiometric titanium carbide $TiC_{0,5}$ synthesized in the Ti-C system: $TiC_{0,5}$-25%Al; $TiC_{0,5}$-30%Al; $TiC_{0,5}$-50%$Ti_{0,4}Al_{0,6}$; $TiC_{0,5}$-20%Si; $TiC_{0,5}$-25%(Al-3%Si); $TiC_{0,5}$-20%(Al-10%Si); $TiC_{0,5}$-25%(Al-10%Si); $TiC_{0,5}$-50%($Ti_{0,4}Al_{0,6}$-10%Si); $TiC_{0,5}$-10%(Cu-30%Ni); $TiC_{0,5}$-15%(Cu-30%Ni). Materials of the working layer on the base of the Ti-B system was found to be significantly the less producible. For producing nondefective synthesized parts and cathodes, these materials were bound to contain a sufficient amount of free titanium as a ductile binder: no less than 35% for the Ti-B-Al system, no less than 10% for the Ti-B-Si system. As this takes place, the content of Al and Si in these systems was bound not to exceed 23 and 15% respectively: (TiB-35%Ti) + 15%Al; (TiB-35%Ti) + 20%Al; (TiB-35%Ti) + 20%$Ti_{0,4}Al_{0,6}$; (TiB-35%Ti) + 50%$Ti_{0,4}Al_{0,6}$; (TiB-10%Ti) + 60%Ti_5Si_3; (TiB-20%Ti) + 40%Ti_5Si_3; (TiB-20%Ti) + 50%Ti_5Si_3; (TiB-20%Ti) + 60%Ti_5Si_3. Materials of the Ti-B-Al-Si system were found not to be producible both on SHS pressing and in machining.

Certain of the produced cathodes allowed us to obtain arc-PVD nanocomposite coatings with mechanical properties which were much higher than that of the TiN coating.

8A-4

COMBUSTION SYNTHESIS OF SILICON BASED OXY-NITRIDE PHOSPHOR FOR LED APPLICATION

Won H.I.*, Nersisyan H.H., Won C.W.

Rapidly Solidified Materials Research Center (RASOM), Chungnam National University, Yuseong,
Daejeon 305-764, Korea.
* rotc4379@hanmail.net

Recently, white LED has been developed under great attention in lighting industry for new light source because of many merits such as a high efficiency, long life-time and low power consumption [1-3]. Silicon based oxy-nitrides (SiON) have been actively investigated in recent years because these phosphors are fitted to excitation condition of white LED application and have many attractive luminescence properties such as high luminescence intensity, good chemical stability and broad excitation band [4-5]. SiON phosphors are usually used as powder form and they are usually prepared by solid state reaction. The mixture of starting materials is calcined at high temperature (1500-2000°C) under the pressure of nitrogen. To make single phase, the reaction needs at least 5hours at high temperature so that high energy consumption is always pointed out as a drawback of solid state reaction.

In this study, we applied combustion synthesis for preparing $SrSi_2O_2N_2$ phosphors, and flake type $SrSi_2O_2N_2$ green phosphors having good luminescent characteristics were successfully prepared. Strontium salt (SrX, X is halogen element), silicon dioxide (SiO_2), combustion agent (CA) and silicon is starting materials for combustion system. Figure 1 is a cross section photo of combusted pellet. As seen, the pellet is consisted of two parts: black colored surface and yellow-green colored center. XRD verified yellow-green colored center to single phase $SrSi_2O_2N_2$. Figure 2 shows excitation and emission spectra of $SrSi_2O_2N_2$ phosphor prepared from combustion synthesis. With the excitation wavelength at 450 nm, the powders exhibited a green emission spectrum in the range of 500 to 600 nm, with the main emission peak at 535 nm.

Figure 1. A cross section photo of combusted pellet.

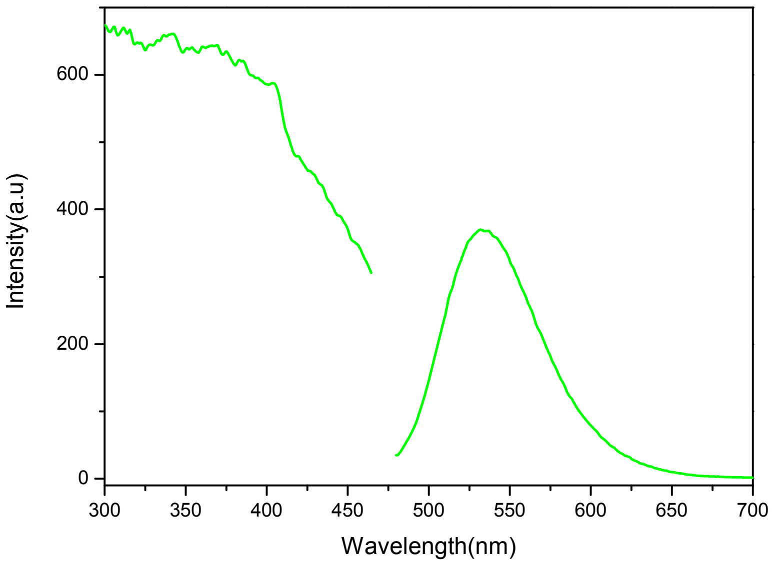

Figure 2. Excitation and emission spectra of $SrSi_2O_2N_2$ phosphor.

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8A-5

THERMAL DECOMPOSITION OF SHS-PRODUCED TiH_2 POWDER

Kovalev D.Yu.*, Prokudina V.K., Ratnikov V.I., Ponomarev V.I.

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Russia
kovalev@ism.ac.ru

The process of thermal decomposition in vacuum of SHS-produced TiH_2 powder was studied during heating up to 570°C. The sequence of phase transitions to result from thermal decomposition is determined by time-resolved X-ray diffraction (TRXRD) techniques, which allowed for in-situ investigation of the dynamics of rapid phase transformations at thermal treatment [1].

On base of pressure changes during heating it was showed, that hydrogen removal from TiH_2 gets started around 360°C. The absence of visible changes in the diffraction pattern until 450°C (fig.1) can be associated with the existence of a homogeneity range in TiH_2. Hydrogen removal from TiH_2 takes place without changes in its structure, which is evidenced the shift of TiH2 lines toward higher angles at temperatures above 360°C, despite the fact that thermal expansion normally produces a shift toward lower angles.

It was revealed, that process of phase transformations had a two-stage character. The process gets started with transformation of starting TiH_2 into solid solution of hydrogen in β-Ti (β-Ti[H]) and then followed by the polymorphic transition cubic phase β-Ti[H] to hexagonal phase α-Ti[H] and subsequent hydrogen elimination from α-Ti[H]. At continuous heat up to 570°C with heating rate 12 deg/min, the time of full dehydrogenation of near-surface layer is equal 25 min. Marked changes in the phase composition of starting TiH2 were found to get started around 450°C. Dehydrogenation of TiH2 at temperatures below 600°C can be expected to produce Ti powders with mean particle sizes not exceeding those of starting titanium hydride.

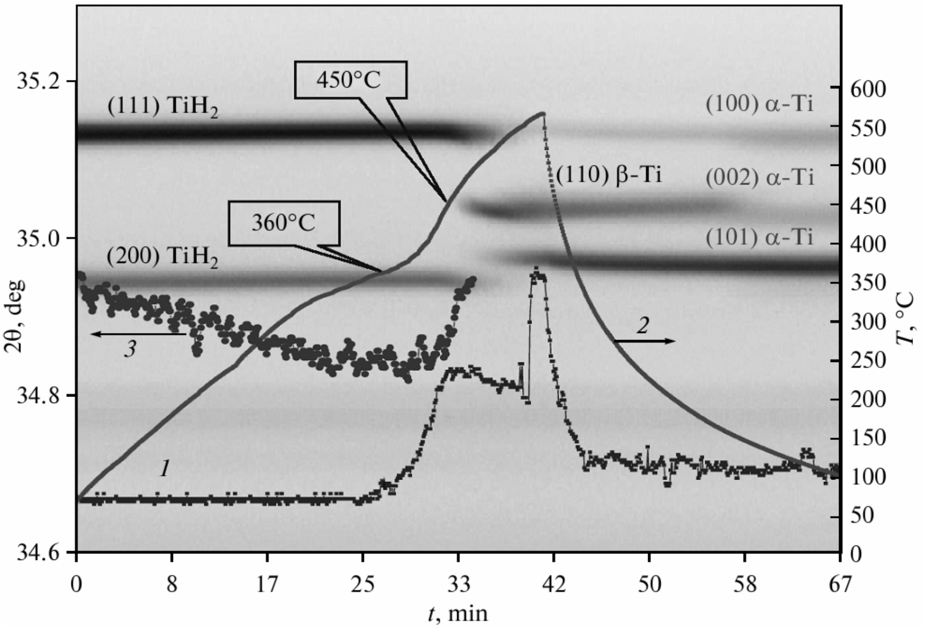

Fig.1 Diffraction pattern along with superimposed pressure profile (1), temperature profile (2), and variation in the 2θ value for the (111) TiH_2 peak (3)

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POSTER PRESENTATIONS

A: Combustion theory and modelling

P-A1

MODELLING OF AN ELECTROTHERMAL EXPLOSION IN THE TI+C SAMPLE ENCIRCLED WITH A FINAL PRODUCT LAYER

Bostandzhiyan S.A., Gordopolova I.S.*, and Shcherbakov V.A.

RAS Institute of Structural Macrokinetics and Materials Science, 142 432 Chernogolovka, Russia
* gis@ism.ac.ru

An electrothermal explosion (ETE) is used in investigations of macrokinetic regularities of fast-running high-temperature interaction in heterogeneous condensed systems [1]. The experiments involving mixtures of titanium, tantalum, silicon with carbon and boron showed ETE occurring required preliminary thermo-vacuum treatment to reduce electrical resistance of the green compositions and remove impurity gases that could hinder the experimental run [2, 3]. However the thermo-vacuum procedure resulted in accumulation of a considerable amount (≈30%) of the final product in the sample thus affecting much the macrokinetic parameters of interaction.

This drawback appeared to bring about serious limitation to the method potential, since it gave no possibility of registering kinetic data at the initial stage of the electrothermal process in condensed systems.

In the present study it was found that the sample surrounded with a conducting porous layer of the final product (a coating) was protected from crushing under the action of the impurity gases released in thee course of ETE. Under the given conditions the sample and the porous layer it is in was heated with the electric current. Such an arrangement offered two regimes of electrothermal interaction in the heterogeneous system.

In one case, where Joule heat release in the sample was higher or of the same order with that in the coating, the ETE regime is expected to occur. In the other, the regime of ignition is observed, since Joule heat is predominantly released in the coating.

The problem with a cylindrical sample involves consideration of equations of thermal conductivity of the sample, the coating, and the reactor shell with chemical and electrical sources of heat evolution and the kinetic equation of the first-order reaction under the boundary conditions of the forth kind.
Both modes of exothermic reaction were found to occur under the proposed conditions.
The increase in the induction delay time was observed at the decrease in the electric power applied.
The effect of the heating rate produced on the ETE parameters, namely the induction period, the ignition temperature, and the maximum temperature of the final product was found and studied.

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P-A2

RESEARCH OF FORMATION OF THE TRANSITIVE LAYER AND ITS INFLUENCE ON PROCESS OF CONDENSED REACTIVE SUBSTANCES INITIATION AT INFLUENCE OF POWERFUL RADIATION PULSE

Burkina R.S.*, Burkin V.V., Domukhovskii A.M.

Tomsk State University, Tomsk, 36б Lenin aven. , 634050, Russia
* roza@ftf.tsu.ru

The powerful stream of radiation (~ 10^9 W/m^2) falling on substance can cause complex structural changes of its near-surface layer. Destruction and fracturing of a near-surface layer, origin of an erosive stream from a surface of substance, melting of a fusible components in porous multicomponent structure, change of porosity and gas permeability, origin and development of a high-temperature centers within substance are possible [1, 2] . The distinguished structural changes of a substance lead to qualitatively new laws of its initiation and burning, in comparison with thermal influences of moderate intensity (~ 106 W/m2).

The laws of destruction of a near-surface layer of condensed reactive substances (CRS), formation of a transitive layer, its influence on ignition CRS at action on the surface of substance by powerful radiation pulse from area of the electrodischarge plasma arising in CRS at the electrical discharge or electroexplosion of a conductor are studied in the contributed paper. Studying of these processes is important for the decision of initiation questions of SHS-systems especially in a case of hard ignition compositions.

It is considered a condensed reactive substance in which the flat foil is located as the conducting bridge initiating discharge. Electroexplosion of a foil and the following electrical discharge in a electroexplosion products generate electrodischarge plasma in CRS. The area occupied with electrodischarge plasma is model as the flat layer (cavity). The process flow diagram is shown in fig. 1.

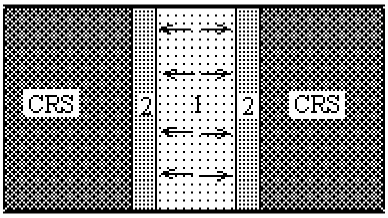

Fig.1. Process flow diagram: 1 - electrodischarge cavity, 2 - transitive layer, CRS - condensed reactive substance

Thermal radiation from an electrodischarge cavity influences on the CRS surface, which being contiguous with it. As a result of powerful thermal influence the CRS surface is destroyed, and destruction products form the transitive layer between CRS and electrodischarge cavity. The formed transitive layer absorbs radiation of electrodischarge cavity partially and thereby protects CRS from it. So there is a warming up of a transitive layer and CRS, and CRS ignition is realized in case of sufficient energy of the discharge. In paper [3] it has been shown, that only the mathematical model which is taking into account presence of a transitive layer, allows to reproduce laws of CRS ignition process by electroexplosion, which are observable in the experiments.

In the mathematical model of process it is supposed, that the substance is opaque and originally a radiation stream from an electrodischarge cavity is absorbed by CRS surface. Heat is transferred into substance by the thermal conduction mechanism. There is destruction (evaporation) of near-surface substance when CRS surface temperature reaches up to the value T_{Ph}. Products of destruction form a transitive layer. Warming up of a formed transitive layer occurs due to heat conductivity and as result absorption of a radiation stream from electrodischarge cavity under Buger law. It takes place the ideal thermal contact between a transitive layer and the condensed substance. The chemical process passes with a simple kinetic and Arrhenius dependence of speed on temperature in CRS. Products of chemical process are solid. The laws of change of the parameters of the radiation pulse are determined at the calculation of energy balance of the discharge cavity formed at electroexplosion of a conductor in condensed substance [4]. The results of research are obtained from numerical methods. The basic laws of formation of a transitive layer and feature of CRS ignition are determined at various parameters and energy of radiation pulse.

The paper is supported by the Russian Foundation for Basic Research (project number is 11-03-00136-á)

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P-A3

INTERACTION MODES IN MOLYBDENUM/SILICON DIFFUSION COUPLE AT NON ISOTHERMAL CONDITIONS

Chatilyan H.A.[1], Aghayan M.A.[1], Kharatyan S.L.[1,2]

[1] A.B. Nalbandyan Institute of Chemical Physics NAS RA, Yerevan, 5/2, P.Sevak str., AM-0014, Armenia
[2] Yerevan State University, Yerevan, 1, A. Manukyan str., AM-0025, Armenia
hakob@ichph.sci.am

In [1] the phase formation laws and kinetics of heat release during the interaction of molybdenum wire with silicon layer (δ_{Si}=0.01-3μm) under conditions of rapid linear heating (V_h=75000 °/s) up to 1600°C were studied. It was shown that the interaction starts before reaching the melting point of silicon (I stage) and more intensively continues after the melting of silicon (II stage). The dependence of maximum heat release rate in the primary - second stage vs. the thickness of silicon layer has a maximum (Fig. 1, curve 1).

The aim of present work is to study the influence of heating rate on the patterns of chemical heat release, as well as on the phase and structure formation laws in the nanosize range of silicon layer thickness and temperature-time region comparable to the conditions of molybdenum disilicide synthesis in combustion wave.

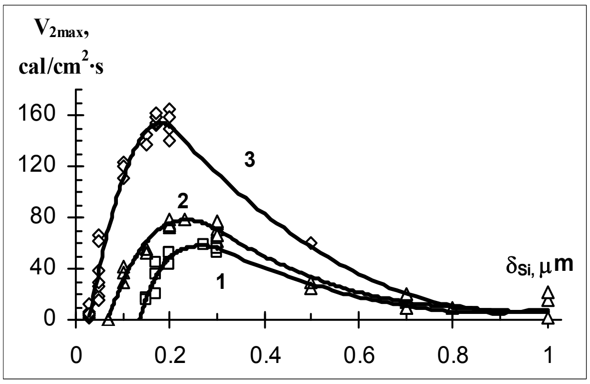

Fig.1 The dependence of maximum heat Release rate vs. silicon layer thickness.
1 - V_h = 4000, 2 - 13000, 3 – 75000 °/s

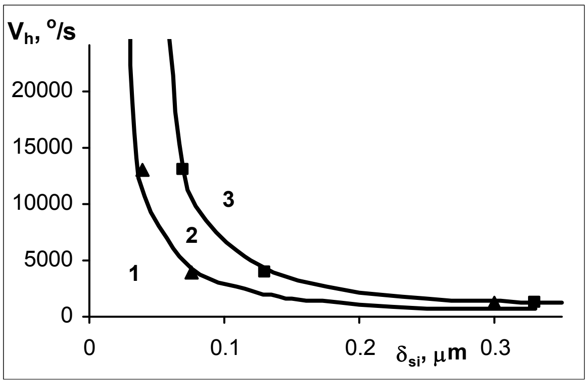

Fig. 2 V_h - δ_{Si} diagram of molybdenum siliconizing modes

The experiments were conducted on high-speed scanning electrothermography (HS SET) set up [2] by direct, resistively heating of the samples, representing Mo wire (99.97%, ESPI Metals) 100 μm in diameter covered with a silicon layer of varying thickness. Heating rate of the samples ranged from 1.10^3 to 75.10^3 °/s.

It was established that when changing the heating rate the overall type of dependency of maximum heat release rate vs. silicon layer thickness is preserved (Fig. 1, curves 2,3). However, with decreasing heating rate the location of the peak shifts to the thicker silicon layers and its absolute value decreases. On the other hand, as it follows from Figure 1, with decreasing the heating rate a significant expansion of the region by silicon layer thickness is observed, in which the interaction of molybdenum with silicon ends at the first stage, i.e. second stage is absent.

Based on the data obtained a V_h - δ_{Si} diagram of molybdenum siliconizing modes was constructed (Fig.2), where four characteristic parametric regions can be distinguished:

- In the region 1 all silicon reacts with molybdenum before the reaching to the melting point of silicon, by the mechanism Mo(s) + Si(s) with formation of $MoSi_2$;
- In the region 2 the interaction starts by the mechanism Mo(s) + Si(s) and ends during the melting of remained silicon (at $T_{melt.}$) with formation of $MoSi_{2;}$
- In the region 3 the interaction has two-stage character: I stage: Mo(s) + Si(s) and second one: Mo(s) + Si(l);
- At silicon layer thickness δ_{Si}>0.3 μm (region 4, not shown in diagram) the interaction also proceeds almost single stage, but already at the maximum temperature and by the mechanism of Mo(s)+Si(l) to form $MoSi_2$.

Taking into account that the thickness of silicon layer simulates the molybdenum particle size, which corresponds to one or another silicide phase stoichiometry of the formed Mo-Si product, in particular, Mo:Si =1:2, it can be concluded that for sufficiently small Mo particles non isothermal siliconizing of Mo in a wide range of heating rates can proceed by a purely solid-phase mechanism.

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P-A4

INTERACTION BETWEEN THERMAL DIFFUSION AND GAS FILTRATION AS A KEY PARAMETER MANAGING SPIN COMBUSTION IN REACTIVE GAS-SOLID SYSTEMS

Filimonov I.A.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
fil_limonov@hotmail.com, fax: (7495) 9628025

It has now been widely recognized in combustion community [1-2] that spin combustion is a consequence of 2D instability (usually the thermal one) of a plane combustion front. Therefore observation of the corresponding unstable modes in experiment or calculation of them in theory is not an easy experimental (numerical) problem. The paper presented aims at an attenuation of these shortages. The reason is that we have successfully used the theory of strongly developed spin combustion [3-5] to investigation of thermally activated spinning combustion modes under external electric fields [6-10]. Urgency of these investigations is explained by the fact that the reacting sample diameter was previously considered as a main governing parameter. Nevertheless, we have later understood that the sample diameter is not the best experimental parameter which can be easily changed under the other equal conditions [6-10]. Investigation of the external electromagnetic field effects provides the theory and experiments with the other governing parameters which are often more simple, effective and more useful for theoretical and/or practical applications. The initial green mixture temperatures, as well as the rate of heat removal to the sample center or forced filtrational flows belong to them. We have already experimentally confirmed [11] the theoretical conclusions [6-10] that changing the green mixture temperatures only one may distinctly observe a thin way of transition from the layer-by-layer steady combustion mode to a spin mode and next to extinction in a single row of measurements. We have also developed the theoretic approach of Novozhilov [3-5] to gas-solid reactive systems [12]. It turns out that there is a possibility for valuable contribution of gas filtration into thermal diffusion equation (24) (see [12]) determining the parametric range of spin existence (see the terms containing the filtrational Peclet numbers) and into the gas-solid temperature gap. Nevertheless, till now nobody has studied in details this possibility and certainly the question about an effective interaction between thermal diffusion fluxes and filtration flows in terms of the gas-solid spin mode region of existence. Our calculations in the wide parametrical range with respect to the filtrational and thermal Peclet numbers have revealed that the most effective case of thermal flux and filtration flow interaction can be realized when the flux and flow vectors are collinear(the co-flow scheme of forced filtration [13]). Under these conditions only the increase in filtrational gas flow leads to the parametrical region of spin existence expanding sharply for the low-temperature brunch (LT) of spin solution while the high-temperature brunch of the solution (HT) almost doesn't change

The other schemes of forced gas filtration (counter-flow, inclined or perpendicular-flow schemes) are considered in terms of the effective influence on the parametric region of spin existence

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P-A5

THERMODYNAMIC MODELING OF ILMENITE REDUCTION IN THE SHS REGIME FOR PRODUCING COMPOSITE POWDERS FOR THERMAL SPRAYING

Formanek B.*[1], Khina B.B. [2], Letsko A.I. [3], Ilyushchenko A.F.[3]

[1] Silesian University of Technology, 8 Krasinskiego str., Katowice 40019, Poland
[2] Physicotechnical Institute, 10 Kuprevich str., Minsk 220141, Belarus
[3] Institute of Powder Metallurgy, 41 Platonov str., Minsk 220071, Belarus
* boleslaw.formanek@polsl.pl

SHS is efficiently used for producing composite powder materials with a unique combination of physical and mechanical properties, which can be tailored to particular applications. For example, coatings obtained from SHS-powders by thermal spraying, which are supposed to possess a combination of wear and corrosion resistance, should contain uniformly distributed hard inclusions (carbides, borides, etc.) in a ductile matrix featuring anticorrosive properties. To apply SHS for producing such powders, it is necessary to determine the initial composition and the mass ratio of inert additives to the reactive components so that the heat release of exothermal reactions should be sufficient to melt the charge and produce the target material.

The ultimate goal of this research is producing powder compositions using cost and energy efficient SHS method for subsequent thermal spray deposition of protective coatings on working surfaces of thermal equipment, particularly boilers of electric power stations, which are exposed to the furnace gas flow. The coatings should possess high corrosion resistance in a hostile gas atmosphere and withstand erosion by the fly ash particles at elevated temperatures. The most suitable powder composition for such coatings is a nichrome (80% Ni + 20% Cr) or ferrochromium (70% Fe + 30% Cr) matrix, which features high resistance to gas corrosion and good plasticity, containing uniformly distributed intermetallic particles FeAl and/or TiAl (compounds with excellent gas-corrosion resistance at elevated temperatures) and fine hard oxide (Al_2O_3) and carbide (TiC) inclusions that possess a high hardness and can ensure the material structure stability in the conditions of erosive wear (hereinafter the concentration is expressed in wt.%). During the thermal spray process, both the matrix and intermetallic inclusions can completely or partly melt in a plasma or oxygen-fuel torch (for nicrome of the above composition T_m=1692 K, for ferrochromium T_m=1800 K, T_m(FeAl)=1583 K, T_m(TiAl)=1752 K) and then crystallize to produce a coating with good adhesion to a substrate material, while both Al_2O_3 (T_m=2327 K) and titanium carbide (T_m=3213 K) remain solid. For producing the target powder composition, a local raw material, viz. ilmenite ($FeTiO_3$) was used. Hence it appears necessary to estimate the adiabatic SHS temperature, T_{ad}, of the chosen systems and their equilibrium phase composition at both T_{ad} and at lower temperatures (corresponding to thermal spraying and subsequent cooling) to predict the coating composition and stability.

In this work, thermodynamic modeling (TM), which is known as a versatile tool for studying SHS processes with a reduction-oxidation stage [1,2], has been employed to solve the above formulated problem. A versatile software program ASTRA-4 [3], which performs the Gibbs energy minimization of a multicomponent system using a vast thermodynamic database (TDB) on inorganic compounds, was used for TM in both adiabatic (SHS) and isobaric-isothermal (cooling after SHS or thermal spray process) conditions. A new methodology of TM has been developed, which employs iterative calculations using the ASTRA-4 program, comparing the results with all the available binary and ternary equilibrium phase diagrams for the examined systems, and adding new compounds to the TDB. For multicomponent melts that can form at high temperatures, the model of ideal solution of the interaction products [4] was used, while for binary Fe-Cr and Ni-Cr solid (α (bcc) and γ (fcc) phase, respectively) and liquid solutions the quasi-subregular solution model [5] was applied.

Two groups of charge compositions were considered: (i) ferrochromium (about 25%) as an inert matrix, reduction of ilmenite is performed by aluminum according to reaction $FeTiO_3 + 4Al \rightarrow FeAl + TiAl + Al_2O_3$ or by both Al and carbon so that reaction $FeTiO_3 + 3Al + C \rightarrow FeAl + TiC + Al_2O_3$ could occur, and (ii) about 25% nichrome as a matrix, reduction of $FeTiO_3$ is performed as in the previous case.

As a final result of TM, the values of T_{ad} and the equilibrium compositions of the SHS products were evaluated and the evolution of phase composition during subsequent cooling was tracked. Stability of the SHS-produced phases at subsequent heating and cooling during thermal spraying was revealed, and the optimal charge compositions were determined.

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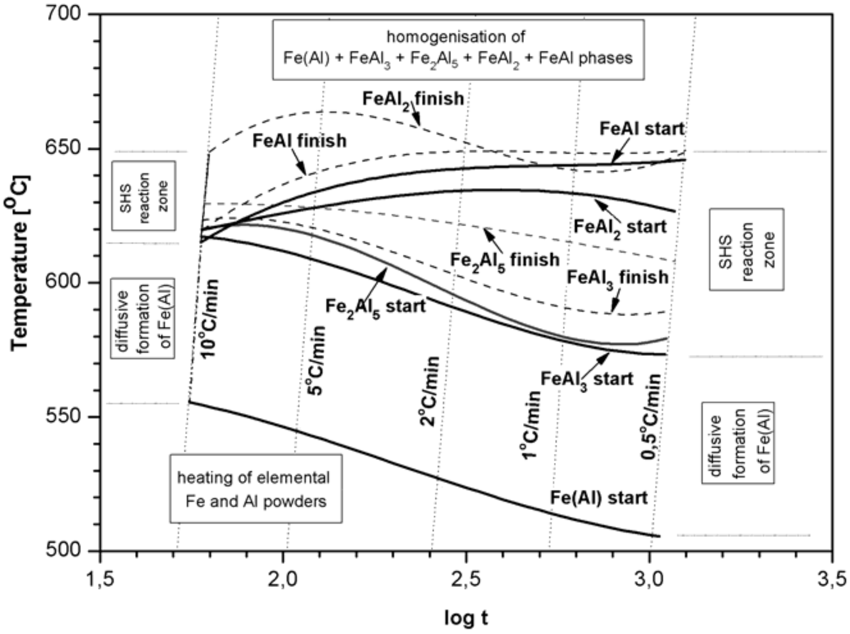
P-A6

THE DTA INVESTIGATION OF SHS REACTION CHANGES DURING NON-ISOTHERMAL SINTERING PROCESS OF Fe AND Al POWDERS

Jóźwiak S., Karczewski K., Bojar Z.

Military University of Technology, Warsaw, Gen. S. Kaliskiego 2 str., 00-908, Poland
*kkarczewski@wat.edu.pl

Powder metallurgy (PM) eliminates many of the limitations during the fabrication process, but in case of the Fe-Al phases, the use of this method is limited by the necessity of controlling of the SHS (self-propagating high-temperature synthesis) reaction. SHS performed during sintering of Fe and Al elemental powders mixture is very rapid and strongly exothermic, which unfortunately may cause unwanted porosity of the sinters. It was concluded that the mechanism of exothermic phase transformations is strongly correlated with many factors, such as chemical composition of the sample, elemental powder particles size, compact pressure and the heating rate. These parameters optimization were conducted on industrial-purity powders pre-mixed in the Uniball 5 ball Mill and compacted by uniaxial pressing with pressure of 300, 500, 700, 850 or 1000 MPa. Three different powder mixtures: 40, 45 or 50at.% Al were examined on DTA instrument with heating rates of 0.5, 1.0, 2.0, 5.0 or 10.0°C/min in an argon atmosphere up to 700°C. SEM (EDS) and XRD analysis showed that not only Fe_2Al_5 but also other high-aluminum phases - $FeAl_3$ and $FeAl_2$ could be found in the samples structure sintered at temperature lower than the SHS reaction temperature. This allowed to separate DTA curves into peaks attributed to particular phases and determine the maximum peak temperature and found the activation energy E_a of phase formation and finally determine the relationship between activation energy E_a and compacting pressure. The Kissinger equation analysis of each other heating rate allowed determine of this quantity value determining the correct sequence of phase transformations for optimum compacting pressure. The same heating rate value was determine from TTT diagram draw according of separate DTA curves data. Additionally, analysis enthalpy of phases formation determined as a integral area under heat flow curve allowed estimating of technological parameter optimum such as grain size of powders particles, compacting pressure and aluminum content in sintered mixture.



The TTT diagram for samples compacted at 700 MPa and heated with heating rate from the range of 0.5-10.0 deg/min

P-A7

THE TOPOLOGICAL REFORM OF COMBUSTION SCIENCE

Klyucharev V.V.

RAS, Institute of Problems of Chemical Physics, Chernogolovka, 142432, Russia
vvk@icp.ac..ru

The scale of donor may be larger, smaller, or equal in comparison with the scale of body reproduced in a unit time which is assigned to the passing of information from generation to generation [1]. In current combustion science it is taken that the second kind of the process limits extinction because this case is most advantageous in energy terms [2]. As a result the chemistry of combustion has run out of its own enclosed scene [3,4]. The reason of such case stands is the absence of geometric technique designed for chemical transformation understanding as the state of body [1]. The failure of researchers to distinguish between consuming, combustion and deflagration as radically different kinds of self-propagating chemical processes [5] and the inability of scientists to reconcile experimental data with combustion physics on first principle [6-9] arise just because.

Adequate method for solving the problem was found not long since classical geometry had made new step forward, namely, to the realm of bodies with fragments which disappeared and appeared alternatively [10,11]. Among other things it emerges that combustion, once defined as a body with the dimension of becoming $D_B = \log 3 / \log 2 \approx 1.5850$ in 2D-case or as a body with the dimension of becoming $D_B = \log 7 / \log 2 \approx 2.8074$ in 3D-case [1], has the capacity of random close packing at all scales. This geometrical discovery allows at last the limits of extinction for self-propagating chemical process to be calculated on first principle, taking into account the Lebesgue's non-arithmeticity of transformation [12, S. 177-178] as the factor of reactivity [13].

In the second half of the 20th century combustion science began moving from molecular chemistry to materials chemistry. However, chemists succeeded in the formation of the first bridge from the mole of molecular chemistry to the mole of materials chemistry only last year [13]. The challenge is now to turn the bridge into safety way for students and scholars. This seems quite possible in modern times, for example, in the framework of TEMPUS-IV [14].

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P-A8

LOW TEMPERATURE CONVERSION OF CARBON OXIDE TO CARBON DIOXIDE PROMOTED BY SINGLET DELTA OXYGEN

Sharipov A.S., Starik A.M.*

Central Institute of Aviation Motors, Aviamotornaya str. 2, Moscow, 111116, Russia
* star@ciam.ru

Carbon oxide (CO) is one of the key gaseous pollutants (along with unburned hydrocarbons and nitrogen oxides) produced during combustion of organic fuels, coals, biomass, waste, and etc. [1]. The formation of CO is usually attributed to incomplete oxidation of fuels. The presence of CO in the combustion exhaust is not only harmful of itself, but also suggests that not whole chemical energy stored in the reagents was converted into the heat during combustion process. In fact, the oxidation of CO to CO_2 occurs with the release of substantial energy: $CO+½O_2 \rightarrow CO_2+0.9$ eV.

As is known, carbon oxide transforms to carbon dioxide in the following sequence of elementary reactions:

$CO + O_2 = CO_2 + O$, and
$CO + O + M = CO_2 + M$.

However, such a "dry" oxidation is very slow process because of the high activation barrier of the reaction $CO + O_2 = CO_2 + O$. This reaction proceeds with a considerable rate only at relatively high temperatures. When gas temperature drops to 900-1100 K, the oxidation of CO terminates.

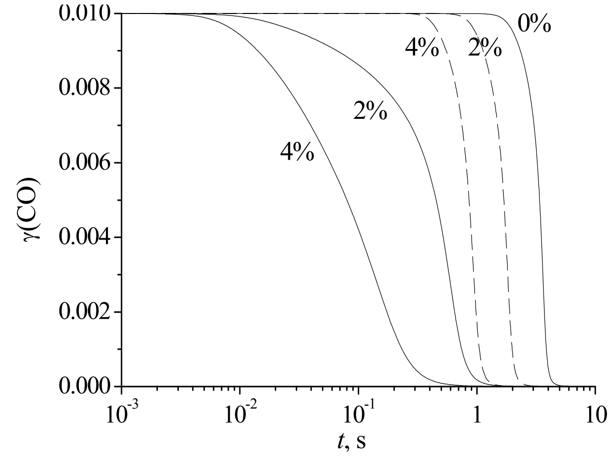

Fig. 1. Temporal profiles of CO mole fraction for $1\%CO-1\%H_2O-21\%O_2-77\%N_2$ mixture at T_0=900 K, P_0=1 bar with different $O_2(a^1\Delta_g)$ content: 0; 0.02; 0.04 (solid curves) and when $O_2(a^1\Delta_g)$ excess energy is spent on heating the gas (dashed curves).

As was shown previously, the excitation of O_2 molecules to the singlet electronic states $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ makes it possible to accelerate significantly the chain- branching paths in oxy-fuel systems [2, 3]. Therefore, practically interesting problem is to investigate how the abundance of $O_2(a^1\Delta_g)$ molecules in the mixture affects the oxidation of CO to CO_2 in the temperature range

900-1100 K. This work addresses the study of kinetic processes responsible for conversion of CO to CO_2 in CO-O_2, CO-H_2-air, and in CO-H_2O-air when $O_2(a^1\Delta_g)$ molecules are abundant in the gas. Note that singlet oxygen $O_2(a^1\Delta_g)$ can be produced in noticeable amounts by specially arranged electric discharge or by resonance laser radiation or due to photodissociation of O_3 molecule.

In order to analyse the kinetic processes in such mixtures the novel reaction mechanism involving the reactions with $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ and O_3 molecules was built. In order to estimate the rate constants of the reactions with excited oxygen molecules *ab initio* investigations of potential energy surfaces of the CO+$O_2(a^1\Delta_g)$, H_2+$O_2(a^1\Delta_g)$ and H_2O+ $O_2(a^1\Delta_g)$ were performed. These investigations exhibited that the reactivity of $O_2(a^1\Delta_g)$ molecules in the oxidation of CO is by a factor $10^3\div10^4$ higher than that of normal ground state $O_2(X\,^3\Sigma_g^-)$ molecules. It was shown that the presence of $O_2(a^1\Delta_g)$ in the CO-O_2, CO-H_2-air, and in CO-H_2O-O_2 mixtures even in small amounts (only 4% $a^1\Delta_g$ content in normal oxygen) results in the enhancement of oxidation process due to acceleration of chain-branching reactions. Adding singlet oxygen to the moist air with CO impurity allows one to convert CO to CO_2 with high efficiency even at low temperature. Fig. 1 depicts the temporal profiles of CO mole fraction γ_{CO} in the 1%CO-1%H_2O-21%O_2-77%N_2 mixture with T_0=900 K and P_0=1 bar for different singlet delta oxygen content in normal molecular oxygen. For comparison shown here are also the time evolution of γ_{CO} when $O_2(a^1\Delta_g)$ excess energy is spent on heating the gas. One can see that addition of $O_2(a^1\Delta_g)$ molecules allows one to shorten the time of CO oxidation significantly. So, if at zero $O_2(a^1\Delta_g)$ content the total CO conversion is achieved at the time instant t=4 s, whereas at $\gamma^0_{O_2(a^1\Delta_g)}=0.04\gamma^0_{O_2}$ these time is tenfold smaller. It is of great importance that the abundance of 4% singlet delta oxygen in the molecular oxygen allows us to convert 75% CO to CO_2 for the time of 0.2 s even at low temperature T_0=900 K.

This work was supported by the Russian Foundation for Basic Research (grants 10-08-90035 and 11-01-00920) and by the Federal Targeted Program “Academic and Teaching Stuff of Innovative Russia” (state contract No 2.740.11.0074).

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P-A9

HIGH-TEMPERATURE SYNTHESIS IN MECHANOACTIVATED SYSTEM WITH THREE REAGENTS

Smolyakov V.*[1], Lapshin O.[1], Prokofyev V.[2]

[1]Department for Structural Macrokinetics, Tomsk Scientific Center of SB RAS, 10/3 Academichesky ave., Tomsk, 634021, Russia
[2] Tomsk State University, 36, Lenina ave., Tomsk, 634050, Russia
*vsmol52@mail.ru

Mechanical treatment of heterogeneous system, capable to reaction, is effective method of control over chemical transformation, being used for stimulating of different solid phase reactions.

In practice, the idea of separation of stages of mechanical activation of powder mixture and chemical transformation is often used. Grinding and activation of the substance is conducted at the first stage during preset time, and chemical interaction under controlled conditions is conducted at the second [1]. Preliminary mechanical treatment is prospective method for realizing self propagating high temperature synthesis under weakly exothermal systems.

In the framework of macroscopic approach, the description of synthesis in mechanoactivated mixture includes equation of chemical reaction, which consider kinetic (mechanical activation of reagents), structural (milling of substances and of interface) thermal factors, as well as equations, describing the dynamics of excess energy in substances and temperature in powder sample [2].

Combustion of three-component sample, made from the mixture of condensed substances A, B and C, forming condensed products F and L in one-staged reactions, proceeding concurrently

$$A + C \rightarrow F \quad (1)$$
$$B + C \rightarrow L \quad (2)$$

is considered in the work.

Influence of characteristics of activated mixture on the synthesis dynamics, combustion velocity and structure of finite products was investigated by numerical methods. It was shown, that different scripts of development of high temperature synthesis in reaction system are realized, in dependence of what of the starting reagents were subjected to mechanical treatment.

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P-A10

PRE-FLAME PHENOMENA AND LOW TEMPERATURE IGNITION MECHANISMS IN KEROSENE-AIR MIXTURE

Starik A.M.*, Titova N.S., Torokhov S.A.

Central Institute of Aviation Motors, Aviamotornaya str. 2, Moscow, 111116, Russia
* star@ciam.ru

For past decades the great interest was paid to study the ignition and combustion of heavy normal alkanes as well as complex fuels such as aviation kerosene and diesel oil comprising mostly heavy alkanes and aromatic hydrocarbons. Despite significant achievements in understanding the kinetic mechanisms of high-order hydrocarbon combustion, until now there is no quantitative description of so–called "negative temperature coefficient" (NTC) in the behavior of temperature dependence of the induction time $\tau_{in}(T_0)$ and pre-flame phenomena in kerosene-air mixture. This paper addresses the study of kinetic mechanisms responsible for the appearance of cold flame and abnormal behavior in $\tau_{in}(T_0)$ dependence.

Kerosene was modeled by surrogate mixture consisting of 80% n-decane and 20% benzene (BD surrogate). As was shown previously [1], this surrogate reproduces the ignition and combustion characteristics of aviation fuel Jet-A quite adequately. The reaction mechanism built to describe the features of chain mechanism development in kerosene-air mixture combines the reaction mechanisms of n-$C_{10}H_{22}$ and C_6H_6 oxidation and includes both high and low temperature submechanisms [2]. The model reproduces the experimental data on ignition delay for kerosene-air mixture with higher accuracy than other reaction mechanisms and allows to predict the NTC in $\tau_{in}(T_0)$ behavior which is observed in the temperature range T_0=900 – 680 K. The NTC appears for all high-order alkanes, but the strongest NTC effect was recorded for lighter alkanes: n-C_6H_{14}, n-C_7H_{16}. Kerosene-air mixture demonstrates only slight NTC behavior. Note that at low initial temperature (T_0=700 – 900 K) before the ignition event there exists slight luminescence. This luminescence is associated with so-called cold and blue flames [3]. Our analysis shows that both NTC and pre-flame phenomena are in a close connection and caused by the low temperature path of chain mechanism development.

At the temperature below 900 K the chain process in the kerosene–air mixture occurs firstly through the following steps:

$C_{10}H_{22}+O_2 = C_{10}H_{21}+HO_2$ (1),
$C_{10}H_{21}+O_2 = C_{10}H_{21}O_2$ (2),
$C_{10}H_{21}O_2 = C_{10}H_{20}OOH$ (3),
$C_{10}H_{20}OOH+O_2 = O_2C_{10}H_{20}O_2H$ (4),
$O_2C_{10}H_{20}O_2H = C_{10}H_{20}O_3+OH$ (5).

At this stage, the appearance of the noticeable amount of OH radicals initiates rapid benzene oxidation in the course of reaction paths:

$C_6H_6+OH = C_6H_5+H_2O$ (6),
$C_6H_6+O = C_6H_5O+H$ (7),
$C_6H_5+O_2 = C_6H_5O+O$ (8),
$C_6H_5O+H_2O_2 = C_6H_5OH+HO_2$ (9) .

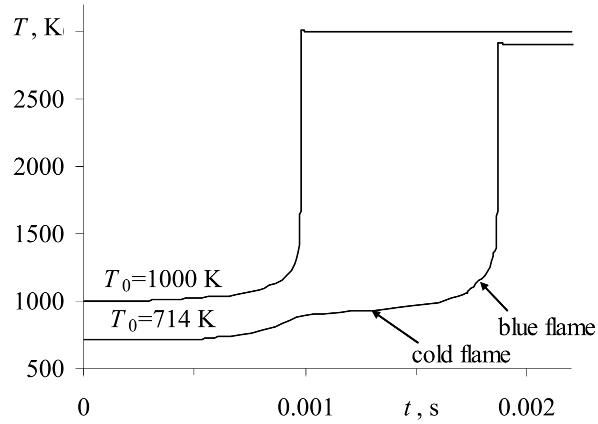

Fig. 1. Temporal temperature profiles during BD surrogate-air mixture ignition.

The principal features of low temperature chain mechanism in kerosene-air mixture is that, in contrast to high temperature way, where C_6H_6 reacts predominantly with O_2, at low T_0 the main reactions of chain initiation are the reactions of C_6H_6 with OH radical and O atoms that are produced due to n–$C_{10}H_{22}$ oxidation. Fig. 1 plots the temporal evolution of gas temperature in a stoichiometric BD surrogate-air mixture with P_0=20 atm at low and high values of T_0. At T_0=715 K non-monotonic behavior in the $T(t)$ dependence is observed at the time interval [0, τ_{in}]. First temperature growth (at t=1 ms) from 715 K to 900 K is caused by the occurrence of recombination reactions (2) and (4) and exchange exothermic reaction (6) and is associated with the cold flame. The formaldehyde CH_2O contributes mostly in the luminescence at this time interval. The second increase in the temperature from 950 to 1100 K, just before the ignition event, is associated with blue flame, caused by the luminescence of formyl CHO and hydroxyl OH radicals that arise in large amounts due to decomposition of H_2O_2 molecules. At T_0=1000 K such phenomena don't appear due to high temperature path of chain mechanism development at this temperature range.

This work was supported by the Russian Foundation for Basic Research (grants 11-01-00920, 11-08-00920) and Council of President of Russian Federation for support of Young Russian Scientists and Leading Scientific School (grant SS-3335.2010.8).

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POSTER PRESENTATIONS

B: Structural Macrokinetics of SHS processes

P-B1

TIME-RESOLVED X-RAY DIFFRACTION OF THE COMBUSTION SYNTHESIS OF TiC-Ni COMPOSITES

Boutefnouchet H.[1], Curfs C.[2], Triki A.[1], Boutefnouchet A.[3], Vrel D.[4]

[1] Laboratory of magnetism and spectroscopy of solids (LM2S) Badji Mokhtar University, B.P. 12, 23000 Annaba, Algeria
hafida.boutefnouchet@univ-annaba.org, triki.abdelhafid@univ-annaba.org
[2] European Synchrotron Radiation Facility (ESRF), B.P. 220- F- 38043 Grenoble, France
caroline.curfs@esrf.fr
[3] Laboratoire de transformations de phases (LTP) Université Mentouri-Constantine, Route Ain El-Bey, BP 233 25017 Constantine, Algeria
a.boutefnouchet@facmed-annaba.com
[4] Université Paris 13, CNRS, LSPM – UPR 3407, 99 avenue J.-B. Clément, 93430 Villetaneuse, France
dominique.vrel@lspm.cnrs.fr

Nickel is known to be a good sintering aid for titanium carbide. Since the first results published by Dunmead et al.[1], several investigations have been made on the Ti-Ni-C system to produce TiC-Ni cermets by SHS. Indeed, nickel addition provides to the TiC-Ni synthesised composite some very interesting structural and mechanical properties (high shear and compression strength, high service temperature capabilities), due to the combination of metallic (ductility and toughness) and ceramic (high strength and modulus) properties.

However, the reaction pathway followed by this kind of synthesis is unpredictable since many factors may influence its progress, and the final product may include some impurities, including Ti-Ni intermetallics; in addition, because the presence of nickel decreases significantly the final temperature, some quenching effect may arise, yielding an incomplete reaction and some remaining reactants.

To follow the TiC formation mechanisms, we carried out several experiments with different weight percentage of Ni (5w%, 10w% and 15w%), providing a composition range within which the reaction can take place. In the case of the 10w%Ni sample, we found in the resulting sample by-products together with the expected TiC and Ni, such as titanium-nickel intermetallics and metastable nickel carbide. To better understand the chemical pathway, a time-resolved X-ray diffraction experiment (TRXR) using synchrotron radiation was performed. This analysis clearly showed that the formation of these by-products clearly takes place during the cooling of the sample, when the crystallization of liquid nickel is taking place (Figure 1), and that the formation of TiC is undoubtedly the driving reaction of the synthesis. As a consequence, these by-products cannot be considered as "remaining intermediate compounds", and their origin should be attributed to the reaction of unburned remaining reactants, coming from an imperfect initial mixing and/or from a large initial grain size.

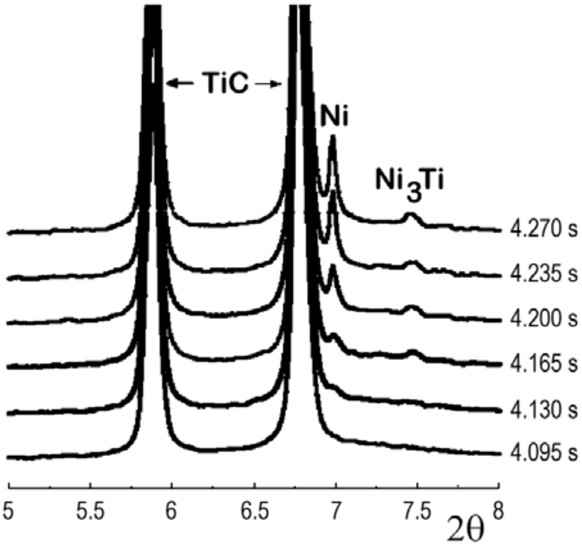

Figure 1 : Successive diffraction patterns during the cooling of the sample. Time is expressed in seconds, the origin being the observed onset of the TiC formation. X-ray wavelength was chosen to λ=0.2583Å.

All experiments were performed at ESRF (Grenoble, France) on the ID11 beamline. The authors would like to express their gratitude to G.B.M. Vaughan for the beamtime and to Irina Snigireva for her valuable help during the SEM investigations.

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P-B2

THE MODE EFFECT OF SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF TRANSITIVE METAL ALLUMINIDES ON CATALYTIC PROPERTIES DURING CARBON DIOXIDE METHANE CONVERSION

Naiborodenko Yu.S.[1], Kasatsky N.G.[1], Tsapalo L.I.[*2], Arkatova L.A.[2], Pakhnutov O.V.[2]

[1]Department for Structural Macrokinetics of Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Science, Tomsk, 10/3 Akademichesky ave., 634021, Russia
[2]National Research Tomsk State University, Tomsk, 36 Lenin ave., 634050, Russia
Tsapalo@sibmail.com

At present, carbon dioxide conversion of natural gas is of great interest caused by the production of synthesis gas, With the ratio of CO: H_2 =1:1. The work offers catalysts based on intermetallic compounds on the base of nickel and ferrum for this conversion. Alluminides were produced by SHS (self-propagating high-temperature synthesis) [1] using the various modes: layered combustion and thermal explosion [2, 3].

Investigations were generally conducted with alluminides having a stochiometric composition: 3Ni+Al, and 3Fe+Al. The powders of carbonyl and electrolytic nickel, spherical aluminum, and carbonyl ferrum were used for synthesis.

The samples of the 3Ni+Al (Ni+13.4% mas of Al) compound of 15mm in diameter and 40 mm in height were heated to 450-500°C for layered synthesis. The samples of the Ni+7.5% mas of Al and Fe+13.4%mas of Al were synthesized in a mode of thermal explosion. The Fe+13.4% mas of Al composition was preliminary mechanically activated. This approach allows high quality alluminides to be produced fast and effective. The mixture was mechanically activated in a M3 planetary mill with an acceleration of 45g; the ratio of the mixture to balls was 1:10. The synthesis products were investigated by the X-ray phase and metallographic analysis. To study the products catalytically, it was used a flow-catalytic set-up with chromatographic analysis on-line. The catalytic properties of the synthesized materials (Table 1) are close to the properties of industrial NIAP-22. The structural analysis has shown that products have a different phase composition and structure depending on a mode of synthesis and composition of fresh mixtures. All the samples are multiphase and contain free Ni and Fe in addition to the Ni_3Al and Fe_3Al main phases. Mechanical activation results in the formation of layered agglomerates that save the structure during the synthesis.

Table. 1: Catalytic properties of alluminides

System	T,°C	Rate of a mixture flow, cm^3/min	CO_2/H_2 (mol) in the initial mixture	Conversion, %		Yield, %	
				CO_2	CH_4	CO	H_2
Ni+7.5%mas of Al	800	100	1:1	0	13	2	5
	850			47	50	16	26
	900			93	87	28	19
	950			100	99	31	26
Ni+13.4%mas of Al	800	100	1:1	16	20	11	7
	850			39	41	19	21
	900			63	59	33	27
	950			94	87	47	42
Fe+13.4%mas of Al	600	100	1:1	1	1	1	0
	900			36	7	19	3
Fe+13.4%mas of Al MA	600	100	1:1	0	4	0	1
	900			94	98	44	51
NIAP-22	600	100	1:1	41	14	9	18
	900			91	92	46	44

The results of conducted catalytic experiments are given in Table 2. It was shown that the materials produced in a mode of layered combustion show higher catalytic properties during carbon dioxide conversion.

Table. 2: Catalytic properties of alluminides

Ni+13.4%mas of Al LC	600	100	1:1	6	18	5	7
	700			18	36	12	18
	800			46	53	18	22
	900			90	95	31	37
Ni+13.4%mas of Al TE	600	100	1:1	1	19	4	5
	700			10	30	8	8
	800			33	40	14	18
	900			71	82	28	34

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P-B3

FEATURES OF ALUMO-COBALT SPINEL SHS-SYNTHESIS

N.I. Radishevskaya[1], O.V. Lvov*[2], N.G. Kasatsky[1], A.Yu. Chapskaya[1], Yu.S. Naiborodenko[1]

[1]Department for Structural Macrokinetics of the Tomsk Scientific Center of Siberian Branch of the Russian Academy of Science, Tomsk, 10/3 Akademichesky ave., 634021, Russia
[2]National Research Tomsk State University, Tomsk, 36 Lenin Prospekt, 634050, Russia
* Lvovov@net-ka.ru

The ceramic spinel-type pigments were produced by self-propagating high-temperature synthesis (SHS) [1, 2]. The aim of this work is to investigate the features of high-melting pigment SHS-synthesis on the basis of spinels and alumo-thermal reactions, and produce products in a fine-dispersed state. The powders of metallic oxides and spherical aluminum were used to synthesize pigments. The preparation of a green mixture was following: the initial components (oxides of aluminum, cobalt, zinc, and magnesium, powdered aluminum, and magnesium nitrate) were weighed and carefully mixed by the dry method in a porcelain mortar. Self-propagating high-temperature pigment synthesis was conducted with an installation of constant pressure on the air. The mixture was placed in a container that was located in a resistance furnace to be heated up to 450-500 ºC. The samples were ignited by two methods: 1) from the Ni+Al (50 % of Al) ignition tablet; 2) the mixture was heated in the resistance furnace up to ignition. Tungsten-rhenium thermocouples, 100 μm in diameter, placed in the centre of the samples were used to control heating temperatures and record thermograms. The thermocouple data were recorded with a computer. Two thermocouples were used during combustion of the samples with big diameters; one of the thermocouples was placed in the centre of the sample and the second one was near to a lateral surface. The microstructure of the produced samples was investigated with an optical microscopy (Unimet, Axiovert 200M) and scanning electron microscopy (Camebax). The produced pigments were identified by the X-ray phase analysis using the DRON-UM1 diffractometer (filtered CO Kα-radiation) and infrared spectroscopy in the range of 4000-400cm^{-1} using the Nicolet 5700 IR Fourier spectrometer with a diffuse reflexion device.

Alumo-cobalt spinel is produced by the SHS method during short time. The maximum temperature of synthesis was 1600°C. The flat front of combustion was observed on the samples with a diameter of 0.010, 0.015, and 0.020 m and broken on the samples with the big diameters. Besides, the long fluorescence was registered on the big samples after front passage, which testified the development of postprocesses, in particular, oxidation of the cobalt released due to an alumo-thermal reaction and interaction with aluminum oxide during the spinel formation. It resulted in producing a qualitative product due to the increase in transformation depth. Despite all the features of combustion, alumo-cobalt spinel is formed in a fine-dispersed state in free filled systems having mainly the open porosity. The process is completed with the total interaction of a reactionary mixture, which is provided with the carefully selected structure and dispersity of the initial components. Producing the ceramic free filled spinel-type pigments by the SHS method in a fine-dispersed state is the complicated stage (combined) process proceeding with a reducing stage and simultaneous natural air filtration that provide with an external gas reagent due to the pressure drop in a reaction zone. In some cases, depending on the diameter, localized combustion is initiated on a surface; as a result, the appeared combustion sites can unite during the movement. In addition, a spin combustion site can be formed due to the temperature redistribution in a cylinder section. As a result, the rate slightly decreases on the samples with a big diameter.

Producing spinel-type ceramic pigments by the SHS method in a fine-dispersed state represents the complicated stage (combined) process proceeding with a reducing stage and simultaneous natural filtration of the air.

Cobalt, released during a thermit reaction, participates in the subsequent reactions. The heat release of these reactions increases the transformation depth, which improves the quality and color of pigments.

The flat combustion front, observed on the samples with small diameters, turns into multiple combustion sites on the samples with big diameters.

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P-B4

PLOTTING OF DYNAMIC STRUCTURE UNDER EXPERIMENTAL RESEARCH OF BEHAVIOR OF SHS SYSTEMS WITH COMPLEX ORGANIZATION

Raskolenko L.G., Shkoda O.A.

Tomsk Scientific Center of Siberian Branch, Department of Structural Macrokinetics, Russian Academy of Sciences,Academichesky Ave, 10\3, Tomsk, 623021, Russia
caryll@english.tsc.ru

The paper presents holistic approaches for experimental data processing during research into the behavior of a complex system of self-propagating high-temperature synthesis such as the Metal1 – Metal2 – Nitrogen system. The holistic approach takes into account that the combustion characteristics during self-propagating high-temperature synthesis are the characteristics for a high temperature chemical environment with heterocatalytical processes. Dissipative structures are plotted on the basis the following factors: analogies with well-known types of phase portraits, using known invariants, and observance of symmetry.

By the present time, the main principles of a new approach for investigation of complex systems have been thoroughly developed [1,2,3]. The main point is to understand that the properties of a particle, small part, and subsystem do not correspond to the properties of all system consisting of the parts under study.

SHS systems are the very convenient systems to obtain the regularities for plotting of dissipative structures. In particular, it is the «Ti - Mo - N» SHS system. The chemical reaction proceeds layer-by-layer along the porous sample. Each point on the plots corresponds to a separate experiment, i.e. new filling, mixture pressing, firing by a spiral and burning in a reactor under nitrogen up to the product formation in the whole sample. The relative density and initial structure were varied, and the combustion rate was measured.

At first the paper shows graphic figures constructed according to the "classical" principles and then plots which constructed in according to holistic approach. The deep analyze of the plot showed that the compositions chosen as invariants of a constant variable did not combine in the one curve representing the combustion rate versus a relative density. However, the points from different compositions formed the single curve for which it was necessary to search its invariant. The search of a new invariant was an important point to understand the physics of processes in a combustion wave. Each trajectory was found to correspond to the same formula of intermediate nitrides of molybdenum. As is seen from Fig. 1 the points were located on the straight lines converging in the origin of coordinates. Each straight line had its invariant Ki that was equaled to the atomic ratio of absorbed nitrogen to atoms of molybdenum.

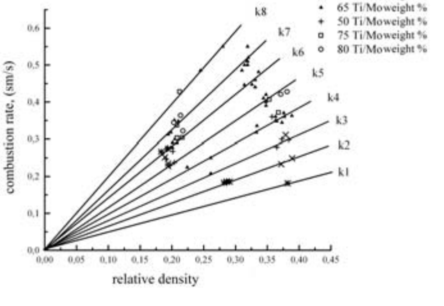

Fig.1. Dissipative structure of chemically active environment of combustion wave with point attractor (x,y)=0. Each straight line had its invariant K_1– K_8

In the same system of coordinates, the values of experimental combustion rate were combined by another way and another invariant was found, in particular, the values of conversion degree. Figure showed three closed cycles which are attractors, and the other trajectories try to combine with these attractors. In this case, each trajectory, that formed a closed cycle, had its value of conversion degree. Also, we found the coordinate space «the absorbed quantity of nitrogen is the atomic ratio of absorbed nitrogen to initial quantity of molybdenum» where combustion rates were combined into linear trajectories with chosen compositions.

CONCLUSIONS:

The plotting and analysis of dissipative structures representing a set of trajectories can provide an actual description corresponding to a reality.

Each set of trajectories represents a phase portrait that is defined by chosen and found invariants.

We have found the invariants that are the formulas of intermediate nitrides for one phase portrait and the conversion degree for another one in the same coordinate space for the Titanium - Molybdenum - Nitrogen system.

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P-B5

INVESTIGATION OF INFLUENCE OF MECHANICAL ACTIVATION TIME SUMMATION MODE ON SHS FOR POWDER SYSTEM Nb-Si

Shkoda O.A., Terekhova O.G.

Tomsk Scientific Center of Siberian Branch, Department of Structural Macrokinetics, Russian Academy of Sciences,
Academichesky Ave, 10\3, Tomsk, 623021, Russia
caryll@english.tsc.ru, terog@dsm.tsc.ru

Mechanical activation (MA) is widely used for stimulation of subsequent SHS process, since during MA, conditions intensifying combustion process are formed [1, 2, 3]. Different kind of devices use for MA, but efficient are planetary ball mill. Construction of many planetary ball mills not allows working uninterruptedly long time. For example: for 10 min of mechanical activation it is necessary to switch on and switch off some times.
The purpose of the paper is study of influence of summation mode of mechanical activation time on lay-by-lay SHS process behavior.

EXPERIMENTAL

MA of powder mixture Nb-Si was conducted in high power planetary mill (65 g). The time of mechanical activation varied from 15 s up to 10 minutes. The composition of powder was prepared as stoichiometric composition of $NbSi_2$.

Summation of MA time was conducted: 1 mode - 5 min MA + 15 min cooling (uninterrupted activation), 2 mode – 10 s MA + 15 min cooling (interrupted MA).

SHS in lay-by-lay regime of mechanical activated mixtures was conducted in constantly pressure bomb in argon. The maximum temperature T_{max}. was determined from thermograms. The structure and composition of powder mixtures and synthesis products under investigation were investigated with methods of electronic microscopy, optical metallography (Axiovert 200M) and X-ray phase analysis (DRON-UM).

RESULTS

MA of low - energy Nb-Si system allows realizing SHS without additional heating [3].
Experimental results indicate that different modes of MA time summation lead to differences in structure of MA mixture and combustion behavior.

The lay-by-lay regime of combustion possibly to realize: after duration of uninterrupted MA mode from 15 s up to 3 min. and after interruption mode from 1,5 min up to 5 min of total time.
There are differences in combustion velocity and combustion maximum temperature for powder mixtures prepared by different summary modes of MA time.
The combustion after 2 min MA summation time for different modes takes place in different phase interaction: in solid phase for uninterrupted mode and in liquid phase for interrupted MA mode of summation time.
Electron microscope study of powder mixture showed structural changes after different modes of MA summation time. This study showed that more strongly formation of agglomerates takes place during uninterrupted MA. Heating of drums and balls takes place during of uninterrupted MA and temperature factor effects on formation agglomerates. The effect of the temperature factor decreases during interrupted MA because of 15 min cooling.

RESUME

The mode of time summation for MA effects on combustion behavior and structure of synthesized product.

The agglomerate structure formed for MA has influence on formation of structure of synthesized product in combustion wave. Formation of agglomerates takes place more strongly during uninterrupted activation and dense structure influences on combustion behavior and structure of synthesized product.

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POSTER PRESENTATIONS

C: Chemistry and Technology of SHS Processes

P-C1

PREPARATION OF XELAT ADSORBENT CONTAINS ARSENATE GROUP AND STUDY OF ADSORBTION OF THIS ADSORBENT WITH Pd(II) ION

Aliyeva R., Abilova U.*, Chiragov F.

[1] Baku State University, Chemistry department, Baku, Z. Khalilov, 23 street, Az 1148, Azerbaijan
* u.abilova@mail.ru

One of the important ecological problem is control of heavy metals in natural and industrial objects on level their limit permissible concentration and below. Therefore arise a necessity in elaboration new methods of collection heavy metals with following determination different methods. For the extraction of precious metals and mercury are used complexing sorbents containing functional analytical groups of atoms of nitrogen and sulfur [1-3].

This invention censers to derivatives of copolymer of malein anhydride-styrene and can be used in analytical chemistry and hydrometallurgy for extraction of palladium (II) and its concentration. Essence of the invention is concluded in that Copolymer of malein anhydride-styrene modification with4-nitroanilin-2-arsenate acide. The Reaction is conducted on sand bath, under unceasing mixing. Whereas, reaction is conducted in water phase anhydride groups consist in copolymer hydrolyzes. In system from interaction phormaldehide and amine is formed unstable carbonylamin, which interacts with carbocsyl group consist in macromolecule with the result that amino fragment falls into macromolecule. The Announced sorbent possesses high sorption characteristic to palladium(II). As follows, sorption capacity to palladium ion in water solution 601mg /g and degree of sorbtion -94,2%.

The composition of obtained sorbent has been studied by the IR-spectroscopy method. By the potenthiometric method has been determined constant ionization of sorbent and constant stability complexes formed by the ions Pd(II). According to K^+ ion the static adsorption capacity (SST_K^+=8.1 mgr-ekv/gr) has been studied and the ionization constant of adsorbent has been found both calculation graphic methods due to volumetrik potensiometrik system ($pK_{graphic}$=7.52, $pK_{cal.}$=7.73).

It has been studied full static changed capacity for ion potassium.

In static condition has been researched influence pH an ionic strength liquid phase to sorption ion Pd(II) by the synthesized sorbent. This sorbent adsorb Pd (II) at pH 5.4 and the install time, sorption equilibrium does not exceed 24 hours. Palladium content in solutionwas determined by photometric method. Measured analytical signal of palladium at pH-3 λ = 490 nm. Number of adsorbed palladium was determined by the difference of the metal content before and after sorption. The effect of pH on the preconcentration of the ions Pd (II) in static conditions in the chelating sorbent in the pH range 1-8. At low pH of the liquid phase (pH 1.4), the low degree of extractionmay be associated with protonation of functional groups present in the sorbent phase and a low degree of swelling of the polymer. For these values of pH ions Pd (II) are $[Pd(H_2O)_{4-n}(OH)_n]^{2-n}$. With increasing pH of the liquid phase (pH 5-6) the degree of swelling of polymer sorbents increases. In aqueous solutions (pH>4) palladium ions can be present as $Pd(OH)_2$ [4].

For sorption recovery of palladium rational use of acidic and weakly acidic region, because at pH> 4 on a given sorbent can sorb metals and ions Pd (II) is hydrolyzed with the formation of soluble hydrolyzed forms.

It has been influence sorption processes from concentration of ion Pd(II) and time. It has been research influence equally capacity and concentration of acid $HClO_4$, H_2SO_4, HNO_3, HCl on desorption sorbed ion Pd(II) from polymer sorbent. The experiment shows that $HClO_4$ desorbs Pd(II) ion from the polymer adsorbent better than others. The study of increasing of the concentration of $HClO_4$ shows that the desorption process increases till 1.5 mol/l concentration of $HClO_4$. Above this concentration desorption degree does not increase. It may be concerned with the arrangement and stability of remaining xelat cycles.
Adsorption and desorption processes have taken place in static condition.

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P-C2

COUPLED SYNTHESIS OF CERAMIC COMPOSITIONS ON THE BASIS OF SILICON NITRIDE

Chukhlomina L.N., Maksimov Yu.M.

Dept. for Structural Macrokinetics, Tomsk Scientific Centre. SB RAS, Tomsk, 634021, Russia
maks@fisman.tomsk.ru, liudnik@yandex.ru

It is commonly known that the use of the SHS method for material synthesis is considerably limited to exothermicity of reactions. It is possible to expand essentially technical application of the method by means of autowave modes for low-exothermal processes by organizing the coupled processes. The idea of coupled combustion process organizing belongs to A.G. Merzhanov. According to the terminology offered by A.G. Merzhanov [1], the processes are called pure thermally coupled (PTC) if donor and acceptor reactions proceed independently. Pure chemical coupling is conducted in isothermal conditions, when the chemical energy transfer from the reaction giving this energy to the reaction accepting it, is possible only in the presence of a common intermediate product. Both thermal and chemical coupling is most often realized during SHS of composite materials, when a green mixture is multicomponent.

This work represents the results of SHS for a number of composite materials based on nitride of silicon with the use of ferrosilicon and natural oxide raw materials, and carbon and ferroboron as well. Nitriding of ferrosilicon in nitrogen in the SHS mode is considered to be an inducing (initial) process:

$$4\ Si + FeSi_2 + 4N_2 \rightarrow 2\ Si_3N_4 + Fe + Q \qquad (1)$$

SHS of the Si_3N_4-SiC composition is conducted according to the scheme (1) with the addition of carbon to a green mixture. When in the presence of carbon the temperature reaches the melting point of eutectic, carbon is melted in a melt in a combustion mode by forming intermediate compound of variable composition:

$$[Fe\text{-}Si]_{melt} + C + N_2 \rightarrow FeSi_xC_yN_z \qquad (2)$$

Here, the exothermal processes of nitride formation are induced by the low-exothermal process of carbide formation (thermal coupling) and formation of the $FeSi_xC_yN_z$ intermediate compound (chemical coupling). Ferrum-silicon carbonitride is a channel between two complicated processes of nitriding and carbonisation [3].

The creation of conditions that provide with the balance between the rates of nitride and carbide formation allows the Si_3N_4-SiC-Fe composition to be synthesized. To produce pure ceramic compositions, ferrum is removed by acid enrichment.

Synthesis of composites based on $Si_3N_4 - ZrO_2$ is conducted with the use of a zirconium concentrate that is one of the hardest minerals. Under conditions of SHS, nitriding of ferrosilicon in the presence of zircon needed to obtain the highest degree of nitriding can be represented by a gross-reaction as follows:

$$FeSi_2 + 4\ Si + ZrSiO_4 + 4\ N_2 \rightarrow Si_3N_4 + ZrO_2 + 2\ Si_2N_2O + Fe \qquad (3)$$

Thus, the exothermal process of nitride formation induces and supports the endothermic process of zircon dissociation; as a result ZrO_2 and SiO_2 are formed. SiO_2 is an intermediate product and participates in subsequent thermostimulated structural chemical transformations. The initiation and development of an induced process convert an astable combustion mode, typical for nitriding of pure ferrosilicon, into a surface mode, and the combustion products acquire an anisotropic structure.

Synthesis of the composition based on Si_3N_4 - TiN is conducted with the use of an ilmenite concentrate. The manufacturing technology of ilmenite opening (sulfuric acid method and chlorination) is complicated, multistage, power-consuming, and environmentally unsafe. In the SHS mode, the ilmenite opening and composition formation on the basis of Si_3N_4 - TiN take place for one stage according to the scheme:

$$FeSi_2 + 13\ Si + 2\ FeTiO_3 + 9\ N_2 \rightarrow Si_3N_4 + 2\ TiN + 6\ Si_2N_2O + 3\ Fe \qquad (4)$$

Thus, the Si_3N_4 formation induces physical and chemical processes with the participation of ilmenite: its melting (1365°C), reduction of titanium and ferrum oxides with the formation of the FeTi intermediate compound, and its nitriding to TiN and Fe.

Synthesis of the Si-Al-O-N and Si_3N_4 + BN compositions is conducted with the use of alumina and ferroboron that is not nitrated by itself in a mode of SHS because of the low boron content in an alloy.

The analysis of the received experimental data and revealed regularities has shown that the organization of chemical and/or thermal coupling of processes can expand manifold a spectrum of produced composite materials.

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P-C3

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS REACTIONS FOR ISRU AND ISFR APPLICATIONS

Corrias G., Licheri R., Orrù R., Cao G.*

Dipartimento di Ingegneria Chimica e Materiali, Centro Studi sulle Reazioni Autopropaganti (CESRA), Unità di Ricerca del Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Unità di Ricerca del Consiglio Nazionale delle Ricerche (CNR) – Dipartimento di Energia e Trasporti, Università degli Studi di Cagliari, Piazza D'Armi, 09123 Cagliari, Italy
* cao@dicm.unica.it

The goal of this work is the development of new processes useful for future manned space missions, in the framework of the so-called ISRU (In-Situ Resource Utilization) and ISFR (In-Situ Fabrication and Repair) concepts. Specifically, the approach to ISRU will focus on technologies necessary to extract consumables for human life-support system replenishment while ISFR is aimed to satisfy other human needs particularly related to the Fabrication Technologies, the Repair & Non Destructive Evaluation Technologies and the Habitat Structures. The final purpose is to allow manned space missions to extract and utilize in-situ resources necessary for human survival without being equipped with huge amount of supplies and to utilize specific technologies to repair Lunar and/or Martian platforms also using in-situ materials, otherwise transported from the Earth.

The possibility to increase mission-time and economic aspects represents the main direct consequences.
Along these lines, the Self-propagating High temperature Synthesis (SHS) process represents a promising tool because of its low consumption energy and relatively-simple configuration equipments required.
In this work, the mixtures to be reacted by SHS are prepared taking advantage of the composition of lunar and martian regoliths. Lunar regolith simulant JSC-1A (R_L), Martian regolith JSC-1A (R_M), and Mojave martian regolith simulant (R_{Moj}) are considered. In addition, Aluminum is used as reducing agent for all systems examined, whereas ilmenite ($FeTiO_3$) and iron oxides, namely ematite (Fe_2O_3), are added to the initial mixtures to be reacted in order to increase their exothermicity. It should be noted that both ilmenite and iron oxides are anyhow present in significant quantities on Moon and Mars, respectively.

Thus, the general stoichiometries of the SHS systems investigated in this work are the following:

$$xR_L + yFeTiO_3 + zAl \rightarrow Products$$
$$xR_M + yFe_2O_3 + zAl \rightarrow Products$$
$$xR_{Moj} + yFe_2O_3 + zAl \rightarrow Products$$

The effect of starting mixture compositions on the self-propagating behaviour is examined under different gas pressures of the environment (atmospheric or vacuum) and gravity level (terrestrial or microgravity) and the optimal experimental conditions are identified for each system investigated. The obtained products are characterized in view of their possible utilization as building materials.

P-C4

RECEPTION FERROTUNGSTEN FROM RAW MATERIALS WITH LOW CONTENT OF TUNGSTEN AND TUNGSTEN SCRAP UNDER PRESSURE

Golovchenko N.*[1], Bayrakova O.[2], Ksandopulo G.I.[2], Aknazarov S.Kh.[2]

[1] Kazakh National University named Al-Farabi
[2] Institute problem of combustion
*teya86@mail.ru

One important practical and theoretical issue is the effect of temperature and external pressure on the extraction of recoverable items in the ingot. Due to the aluminothermic combustion oxides when the combustion temperature exceeds the boiling point of aluminum, the explosive process thus there is a variation of the reacting mixture and the metal loss due to evaporation of oxides. Increased pressure in the system leads to an increase in the rate of reaction, which is important in obtaining ferrotungsten from raw materials with low content of tungsten oxide. Upon receipt of ferrotungsten under pressure as a secondary raw material used tungsten scrap of different origin: the production of waste electric lamps (a mixture of tungsten and molybdenum wire) ferrotungsten scrap and pure tungsten scrap. For selection of optimum process conditions were different versions of experiments. Varied the number of downloads of charge to vary the pressure and process time. Excessive pressure during combustion to a certain magnitude of its value leads to an acceleration of the combustion process, in our case the maximum pressure leads to an acceleration of 7 atm. At a pressure of 9 atm the burning rate begins to decline. For best results when the alloy is obtained by a uniform at a pressure of 11-13 atm, the burning rate 50-72 seconds. The scaling factor having an impact on the course metallothermic process. As the ever increasing burden and isothermal, so you can reduce the amount of warming up supplements. The experiments were conducted in a sealed crucible. Ignition was performed by electro impulse. System pressure 8.7 atm, the burning time of 120-150 seconds. It was found that the increase in grain size tungstate reduces the yield of the alloy by reducing the surface of the reactants and the increase in heat loss. Perfected compositions of the charge for ferrotungsten the desired composition of the raw materials with low content of tungsten alloys are obtained.

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P-C5

MECHANICAL ACTIVATION AND SHS DIFFICULT TO REMOVE METALS

Golovchenko O.Yu., Aknazarov S.Kh.

Institute Problems of Combustion, Almaty, Kazakhstan
teya65@mail.ru

Subjected to machining the sample was placed in a preheated oven to a temperature of 850-9000°C. When heated, mixture ignites spontaneously. For all compositions characterized by pronounced endothermic process due to the allotropic change of oxide of arsenic. The temperature profiles of combustion of the same system but activated in a planetary mill for 30 min. No area of endothermic reactions, because all these processes have been during the mechanochemical activation.

The temperature profile of the combustion system with carbon content of 10% a pronounced biphasic mode of combustion. For both options mixtures (activated and not activated) is characterized by occurrence of phase transitions in the temperature range from 330 to 7000 C. Further heating the mixture does not lead to any changes in the structure of the wave is smooth heating system to the furnace temperature.

The second addition to arsenopyrite as a reducing agent used aluminum. Samples were prepared in two versions - not activated and activated. By analyzing the temperature profiles of combustion mixture of arsenopyrite with aluminum is not activated we can conclude that only a mixture of arsenopyrite with 10 % aluminum burned in two-wave mode.

According to the profiles of the combustion wave during the induction of co- doped samples compared to non- activated considerably shorter and the onset temperature of exothermic reaction is shifted to lower temperatures associated with removing the diffusion barriers due to bond formation Al - O - Me .

The experimental results showed that mechanical activation influences the macrokinetic characteristics of the combustion process. Changing characteristics of process such as the induction period of ignition, ignition temperature, maximum temperature and combustion time.

Was carried out another series of experiments, when as a reducing agent injected aluminum and carbon. One part of the prepared samples was activated, the second was used without treatment.

Activated samples containing 20 % coal and alumina after activation, when you open the drum cover spontaneous combustion. Activated mixture containing 15 % aluminum and coal when you try to compress and ignite spontaneously.

Hold SHS process was possible only with the sample containing 10 % coal and 10 % aluminum. The activated sample was burning in single-wave mode (Fig. 1), the combustion temperature 9000°C.

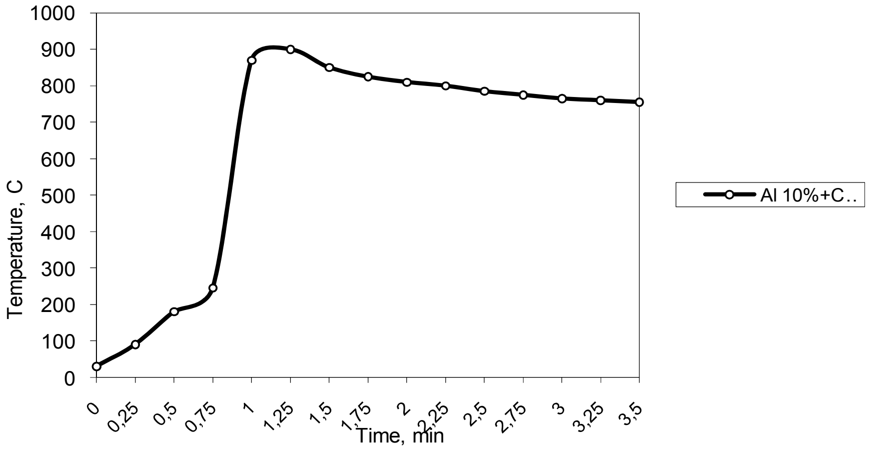

Fig. 1. The temperature profile of the combustion wave system FeAsS - Al - C,after activation

On the basis of the experiments we can conclude that the system FeAsS - C is not checked off in the low two- wave regime. The temperature profile of the combustion wave of each of the present endothermic areas, but they are present for each composition at different temperatures. Temperature profiles of combustion wave activated samples of the same composition have a different look. They do not have endothermic areas. Compositions containing 10% and 15 % of the coal burning in the two wave mode, the sample was 80% arsenopyrite and 20 % of the coal burns in a single wave mode. The maximum combustion temperature lies within of 600- 650 C. Combustion temperature in comparison with non- activated samples decreased.

P-C6

COMBUSTION OF TERMITE TYPE SYSTEMS IN THIN LAYERS AND FORMATION OF CAST GRANULES IN-SITU SHS

Ikornikov D.M., Andreev D.E., Sanin V.N., and Yukhvid V.I.

Institute of Structural Macrokinetics and Materials Science Russian Academy of Science
Institutskaya street 8, Chernogolovka, Moscow region, 142432, Russia
den@ism.ac.ru

SHS reactions in metallothermic systems, also termed as SHS metallurgy [1,2], are known to proceed at temperatures (up to 4500 K) well above the melting points of reaction products. In this case, melted reaction products contain an oxide of metalredactant (such as Al_2O_3) and target product (intermetallics, carbides, borides, silicides). At a sufficiently long melt lifetime, a lighter oxide phase and heavier product phase can undergo partial phase segregation in the field of gravity forces (flotation).

Intense splashing of SHS products caused by high temperatures and formation of gaseous intermediates was always regarded as a negative effect that required suppression by taking some special measures such as elevated pressure [3], centrifugal forces [4], dilution with an end product or their combinations. In this work, we attempted to take advantage of the above 'drawback' and to apply metallothermic SHS reactions to production of cast granules of combustion products with a required size.

Table. Reactive mixtures under study

	Reaction scheme	T_{ad}, K
Mix **I**	$3NiO + 3Al \rightarrow Ni_3Al + Al_2O_3$	3000
Mix **II**	$3NiO + 5Al \rightarrow 3NiAl + Al_2O_3$	2999
Mix **III**	$3NiO + 11Al \rightarrow 3NiAl_3 + Al_2O_3$	2326

The powders of NiO and Al were intermixed in a planetary mixer and thin green layer was deposited onto a graphite substrate and ignited with coil. In experiments, layer thickness *h* was varied between 0.25 and 4.0 mm. The amount of inert diluent (α-Al2O3) added to green compositions was varied within the range 0–20 wt %.

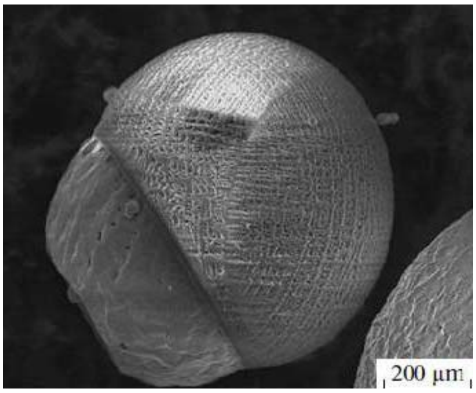

Fig. 1. Overview of dispersed product granules formed in the reaction $3NiO + 3Al \rightarrow Ni_3Al + Al_2O_3$.

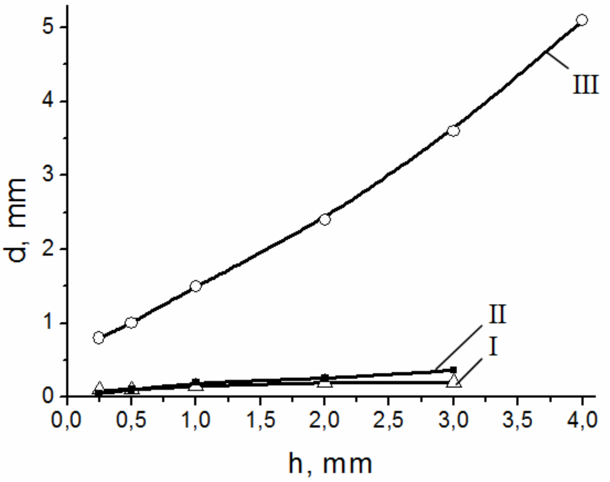

Fig. 2. Effect of *h* on diameter *d* of the granules formed from mixtures I–III.

Combustion of mixtures I and II was found to give a 95-% splash of combustion products, irrespective of *h*. The propagation of combustion wave for the mixtures is accompanied by heaving a two-phase flux of hot gases and product granules ahead of the moving combustion wave. Figure 1 shows the micrographs of dispersed product granules formed upon combustion of mix I and mix II. The granules were found to comprise of metallic and oxide phases.

Figure 2 shows the effect of *h* on diameter *d* of the granules formed from mixtures I–III. The effect is seen to be well pronounced for mixtures III—a 6-fold increase in *d*—and insignificant for highly caloric mixtures I and II.

Another factor affecting the size/structure of combustion-produced granules can be expected to be dilution with inert additives. It was reaveld that dilution with Al_2O_3 leads to increasing of diameter *d* of the granules for mix **I**: a 5-fold increase in *d*.

It was shown that the thermit-type SHS reactions in thin layers at atmospheric pressure can be used for fabrication of cast granules with a particle size of 0.2–4.0 mm. The structure/size of SHS-produced granules can be affected by variation in layer thickness *h* and the amount of added neutral diluent. The results of our study can expectedly make a basis for elaboration of a one-stage and energy-saving process for production of cast granules with unique properties.

This work was supported by the Russian Foundation for Basic Research (project nos. 10-03-00316 and 10-03-91219).

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P-C7

SHS SURFACING: EFFECT OF ALUMINUM PARTICLE SIZE AND BRAND

Kachin A.R.*, Yukhvid V.I., Yashin V.A.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
*kachin@ism.ac.ru

As is known [1, 2], the speed of casting process is of key importance. In these experiments, we used the aluminum powder of ASD-1 brand. In this work, we investigated reducers of various brands and particle sizes and their influence on the peak pressure in the reactor. Aluminum of different brands was added to the mixtures of chromium, titanium, iron, and carbon oxides. A charge was placed onto a steel substrate (diameter 39 mm, thickness 10 mm) and put into a reactor. Surfacing was carried out under an Ar pressure of 50 atm and the pressure change was registered. We used following brands of Al powders: AKP (coarse), AMD (Al/Mg_{bound} = 47/47%, Al/Mg_{free} = 3/3%), PA-1, ASD-4, and mixture of Al and Mg.

A correlation between a growth in the particle size and a decrease in a maximum pressure in the reactor was established. Polydispersed ASD-1 and fractionated MgAl alloy (AMD) with a particle size of 1–40 μm gave almost the same pressure increase (37–40 atm) while AMD powder (315–630 μm fraction), a smaller pressure jump. In the case of AKP aluminum (<40 μm) the pressure was about 19 atm. Aluminum PA-1 gave the lowest pressure surge ~9 atm and the pressure practically does not change with increasing particle size.

Thus, the study shows the possibility of use reducers mentioned above for SHS casting under low pressure.

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P-C8

ELECTROCHEMISTRY AND DYNAMIC IONOGRAPHY OF SHS: NEW METHODS OF HETEROGENEOUS COMBUSTION DIAGNOSTICS

Morozov Yu.G.*, Kuznetsov M.V.

Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences (ISMAN), Institutskaya Street 8, Chernogolovka, Moscow region, 142432 Russia
*morozov@ism.ac.ru

Heterogeneous combustion (or self-propagating high-temperature synthesis (SHS)) widely used for making inorganic materials. SHS in such systems accompanied by generation of electric potentials, which appear between the combustion wave front and condensed products of combustion as a result of chemical ionization of starting materials and intermediate products (so-called Electro Motive Force of combustion – EMF). Maximal registered EMF signals in SHS now having amplitude more than 2.5 Volts. Experiments were carried out for both ions of the starting reagents as well as ions of intermediate and final products. Control of the processes may be carried out by using external electric and magnetic fields. During SHS-process, intermediate reaction products arise in an ionic form. In condensed media, SHS processes involve an electrochemical stage, which can be considered to be a concentration cell that moves together with the combustion wave front and result in origin of EMF of combustion. As a result of that, the full ion-diagrams of combustion processes has been constructed for many complex oxide systems with the elements of I-VIII groups of Periodic Table. It is opening a wide horizons for the diagnostics of heterogeneous combustion processes at nano-level. Besides that, as a result of our experiments, preconditions for the new directions in combustion science has been formed such as ionic chemistry of heterogeneous combustion and dynamic iconography of heterogeneous combustion processes. External electrical and magnetic fields modify combustion parameters of the SHS systems (including EMF). All the produced results have promoted the prerequisites of new directions in combustion and materials science – electrochemistry of combustion, ionic chemistry of combustion, and dynamic ionography of heterogeneous combustion processes.

P-C9

OBTAINING AND REGULATION OF THE PHOSPHATE MATERIALS STRUCTURE IN THE MODE OF THE SELF-PROPAGATING EXOTHERMAL REACTION

Pak Ch.G., Batrashov V.M.

Penza State University, Penza, Krasnaya street, 40
metal@pnzgu.ru

Self-propagating high-temperature synthesis (SHS) is widely used for obtaining high-refractory compounds [1]. The given method is based on forming the final products at the expense of using the energy of the source components interaction, expenditure of heat and electric energy being eliminated. The synthesis of the material runs for a short period of time with the predetermined characteristics.

In UralNIIstromproekt an aerated phosphate material in the mode of self-propagating synthesis was obtained at the expense of using a new system of a binding agent: the phosphate binder-powders of active metals [2].
With certain quantitative and qualitative components proportions, the reaction of the interaction of the active metal with the binder runs with heat-, gas-emission. If fillers of different chemical nature are added to the given system, a porous refractory material solidifying during several minutes is formed.

The technology manufacturing products from the aerated phosphate material consists of the following stages: rationally selected mixture – panning - short local exposure to the heat pulse - self-propagating synthesis. Since the phosphate aerated refractory material synthesis runs under the maximum temperature not exceeding 200^{0}C, a special reactor is not required. The given technology allows getting the heat-resistant phosphate materials on the basis of many active metals, located in the electric series to the left of hydrogen (aluminum, magnesium, chromium, nickel, titanium and others.). The research carried out with using disperse aluminum stems the commercial availability of the given product and high heat evolution of the reaction of the interaction of the phosphate binder and disperse aluminum. The temperature of using the designed materials reaches 2000^{0}C. Physico-chemical studies of the processes, running while solodifying and heating composition phosphate materials have determined that after solidification they consist of amorphous aluminum hydrophosphates, monosubstituted aluminophosphate and unreacted metallic aluminum. When heating the processes of recrystallization and dehydration of aluminum phosphates are running. The final phases after heating above 1000^{0}C are high-refractory compounds: -Al_2O_3 and $AlPO_4$ in the cristobalite form [3].

The methods to control the process of synthesis to obtain the given materials have been developed. The main of them are:

- using phosphate binders of different fractional substututionality;
- using mixed phosphate binders (OFK+AHFS, OFK+ABFK, etc.);
- using the controlled amount of powder aluminum;
- using the controlled temperature of source components before the beginning of the synthesis;

  shaping the material using layerwise synthesis.

The given work analysed a possibility to undertake the controlled synthesis of phosphate composition materials in the mode of self-propagating synthesis with the use of powder aluminum POS-15 and PA-4 instead of disperse of powder aluminum PAP-1 and PAP-2.

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P-C10

EFFECT OF MICROSTRUCTURAL CHANGES DURING MECHANICAL ACTIVATION ON THE COMBUSTION PROCESS IN Fe-Al POWDER MIXTURES

Talako T.L.*, Letsko A.I.

Powder Metallurgy Institute, Minsk, 41,Platonov str., 220005, Belarus
* talako@tut.by

Results of an investigation of the combustion process in Fe-25 wt.% Al and Fe-55wt. % Al powder mixtures mechanoactivated in an attritor A-2 and planetary ball mill Fritsch PULVERISETTE 6 are presented. Single reaction $2Fe+5Al = Fe_2Al_5$ with sufficiently high thermal effect (187.71 кJ/mole) goes to completion in Fe-55wt % Al system. Except some deficiency in aluminium content as compared with stoichiometric composition (32.57 wt.% Al For FeAl) and low thermal effect of iron monoaluminide formation from elements (50.28 kJ/mole), two concurrent reactions: $0{,}6Fe+0{,}4Al \rightarrow Fe_2Al_5\ (FeAl_3) + Fe$ or $0{,}6Fe+0{,}4Al=Fe_{0,6}Al_{0,4}$ can take place in Fe-25 wt% Al system, resulting in multiphase composition of the combustion product.

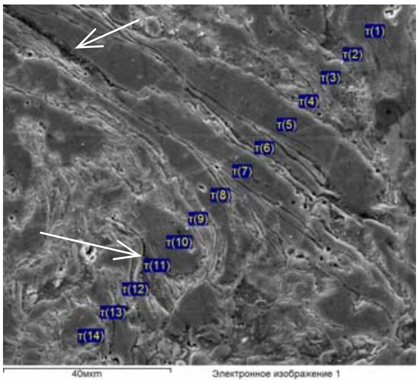
At the first step we determined the minimum preheating temperature at which unsteady combustion is realized in the non-activated Fe-55 wt. % Al powder mixture – 390 ˚C. No combustion was observed in the non-activated Fe-25 wt% Al system at the same conditions.

After that, identical mechanical activation followed by combustion trials have been performed in both systems. Short-term treatment of both compositions in the attritor, resulting in formation of composite particles with uniform reactant distribution, improve their combustion ability. Steady-state combustion with adiabatic temperature 1150 ˚C and combustion velocity ≈0.4 mm/s is observed in Fe-55 wt. % Al system activated for 30 minutes. Unsteady combustion with predominating reaction $0{,}6Fe+0{,}4Al=Fe_{0,6}Al_{0,4}$ takes place in the similarly mechanoactivated Fe-25 wt.% Al system. Combustion temperature and velocity are 817 ˚C and ≈0.22 mm/s.

Increase in MA duration in attritor up to 90 min results in significant increase in combustion velocities in both powder mixtures (1.05 mm/s for Fe-55wt. % Al and 0.74 mm/s for Fe-25 wt.% Al). Combustion temperatures also increase (up to 1204 and 892 ˚C, respectively). Single-phase composition of the both combustion products, correspondent to the equilibrium phase diagram (Fe_2Al_5 and FeAl), is identified.

Mechanical activation in a planetary ball mill for 10 minutes makes it possible to decrease significantly preheating temperature T_p. At T_p=319 ˚C combustion temperature T_c is 1150 ˚C for Fe-55wt. % Al and 1097 ˚C for Fe-25 wt.% Al, and combustion velocities are 2.5 and 2.3 mm/s, respectively. Combustion products are also single-phased.

Similar changes in combustion velocity and temperature with time and mode of mechanical activation for both compositions, in spite of significant difference in thermal effects and chemical routes, testify their similar reasons. As composite particle size does not essentially change with increasing MA duration in attritor from 30 up to 90 min, sharp increase in combustion velocity for 90 minute activation can be attributed to changes in their internal structure. Significant structure refinement is not typical for this MA duration. Detailed structural investigation of the particles cross sections reveals some short-range interdiffusion at the grain boundaries and formation of a small amount of non-equilibrium intermetallic inclusions (marked with white arrows, Fig.1). It is formation of so-called active centres promoting crystallization of new phases during the SHS seems to be the main reason for rising heat evolution rate and combustion velocity in the as-activated powder mixtures. Critical role of potential nucleus of crystallization on the conversion completeness in FeAl based systems was previously shown in [1-2]. It should be noted that strong structure refinement typical for MA in a planetary ball mill is responsible for the significant decrease in temperature of beginning of chemical interaction in both systems.



Spectrum	Al	Fe
p(1)	0.00	100.00
p (2)	17.48	82.52
p (3)	3.06	96.94
p (4)	5.04	94.96
p (5)	0.00	100.00
p (6)	0.00	100.00
p (7)	1.27	98.73
p (8)	0.00	100.00
p (9)	2.45	97.55
p (10)	0.00	100.00
p (11)	48.39	51.61
p (12)	22.69	77.31
p (13)	6.93	93.07
p (14)	28.14	71.86

Fig. 1. Cross-section and point EDX data of Fe-25 wt% Al powder mixture after MA in attritor for 90 min

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P-C11

MECHANISM FOR SHS-REDUCTION OF Na_2WO_4 BY MAGNESIUM

Voskanyan A.A.[a*], Niazyan O.M.[b], Manukyan Kh.V.[a,b], Kharatyan S.L.[a,b],
Mnatsakanyan R.A.[c], Mukasyan A.S.[d]

[a] Department of Inorganic Chemistry, Yerevan State University, 1 A. Manoogian str., Yerevan, 0025, Armenia
[b] Laboratory of Kinetics of SHS processes, A.B. Nalbandyan Institute of Chemical Physics NAS of Armenia, 5/2 P. Sevak str., Yerevan, 0014, Armenia
[c] Laboratory of Kinetics and Catalysis, A.B. Nalbandyan Institute of Chemical Physics NAS of Armenia, 5/2 P. Sevak str., Yerevan, 0014, Armenia
[d] Dept. Chemical and Biomolecular Eng. University of Notre Dame Notre Dame, IN 46556, USA
*Voskanyan-Albert1990@rambler.ru

The self-sustaining reduction of sodium tungstate (Na_2WO_4) by magnesium is investigated. Due to the relatively low but sufficient combustion temperature this process may become a promising way to produce fine tungsten powder. However, the evolved sodium oxide and gaseous sodium during the reduction complicates the process and makes it not safe. For *in situ* binding of the formed sodium-based phases special additives, including various fluoride salts, are proposed. For example, it was shown that addition of CaF_2 may effectively bind evolved sodium oxide and sodium during the process. The mechanism of SHS-reaction in such Na_2WO_4 – Mg based systems was also investigated. Analysis of combustion temperature profiles, as well as, DTA/DTG, XRD and SEM investigations showed that on early stage of the process (at about 550°C) CaF_2 reacts with sodium tungstate:

$$CaF_2 + Na_2WO_4 = 2NaF + CaWO_4$$

After melting of Mg (650 °C) the following reactions simultaneously occur:

$$CaWO_4 + 3Mg = W + CaO + 3MgO$$

$$Na_2WO_4 + 3Mg = W + Na_2O\ (Na) + 3MgO$$

$$Na_2O\ (Na) + CaF_2 = 2NaF + CaO$$

Further experiments showed that all oxides formed during the combustion can be easily eliminated by leaching the products using 10% solution of hydrochloride acid at room temperature for 1hr. XRD pattern of powder obtained after such acid treatment reveals only diffraction lines of metallic tungsten (Fig. 1). It may be also seen from the insert in Fig. 1 that particle size of tungsten powder is in the range from 0.1 to 1 μm.

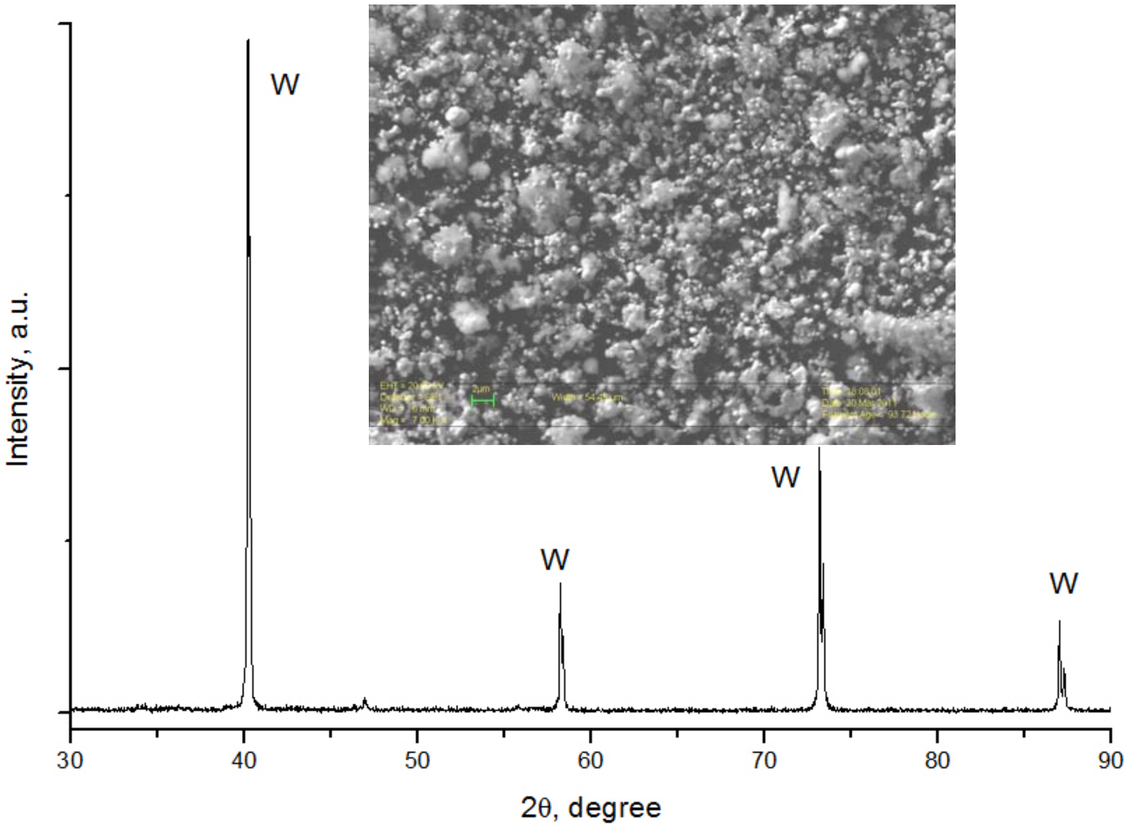

Fig.1 X-ray diffraction pattern and SEM micrograph for the tungsten powder after acid treatment

The results of this work demonstrate that suggested approach for controlling SHS reduction of sodium tungstate by magnesium in presence of fluoride additives is a promising route for synthesis of pure sub-micron tungsten powder.

Acknowledgement
Another are acknowledge the financial support of State Committee of Science of the Republic of Armenia (Project no. 11-1d167).

POSTER PRESENTATIONS

D: SHS of advanced materials: nanomaterials, metals, ceramics, intermetallics, composites, etc.

P-D1

SUBMICRONE SIZE SINGLE CRYSTAL CrB_2 FIBERS

Abdulkarimova D.S.*[1], Vongai I.M.[1], Gubarevich A.V.[2], Wu W.W.[2], Odawara O.[2], Mansurov Z.A. [1]

[1] al-Farabi Kazakh National Institute, Combustion Problems Institute , Bogenbai batyra str., 172, Kazakhstan
[2]Tokyo Institute of Technology, 4259 Nagatsuta-cho Midori-ku, Yokohama, Kanagawa 226-8502, Japan
*abd.danara@mail.ru

A considerable amount of information has been accumulated over the years about metal carbides, nitrides and silicides. In contrast to silicides and carbides, the borides have not been studied adequately due to lack of processing techniques. Specifically, the diborides of the group IVB to VIB transition metals has not been studied adequately in single crystal form and is the subject of this investigation. The analysis of physical, mechanical and chemical properties of the group IVB – VIB diborides has shown that they may well be one of the most advanced materials [1]. For instance, the chromium diboride CrB_2 is highly resistant to the action of dilute/concentrated nitric acid and concentrated hydrochloric, sulfuric, and hydrofluoric acids [2] in combination with high heat resistance and high-temperature strength. In chromium-boron system, Cr_2B, Cr_5B_3, CrB, Cr_3B_4, Cr_2B_3, CrB_2 and CrB_4 have been reported [3]. Among these, CrB_2 is the most stable compound with a melting point of 2200 °C [3].

The presented study investigated the microstructural properties of submicron fibers of CrB_2 produced by Self-propagating high temperature synthesis (SHS). The single crystals were grown in a CrB_2 matrix and this approach is related to solution growth of metal diboride crystals using metal solutionmelts (Fig. 1).

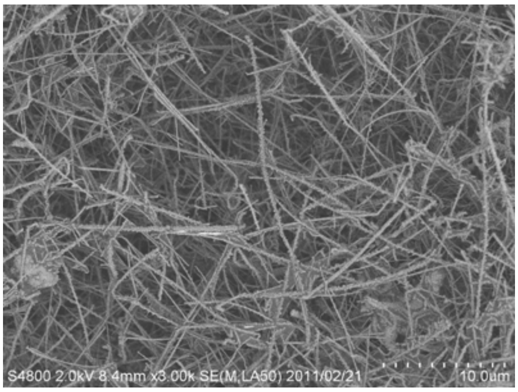

Fig. 1. The chromium diboride threadlike crystals

In our previous work [4], we performed the synthesis of chromium diboride, where the composition of the charge and the amount of the necesssary reducer (aluminium) were calculated according to the reactions:

$6Al + 2B_2O_3 + Cr_2O_3 = 2CrB_2 + 3Al_2O_3$

Characterization of the fibers was done by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The typical representative SEM micrograph of CrB_2 fiber is shown in Fig. 1.

Crystals have direct, contorted and curly form. The diameter of the CrB_2 was around 200 nm respectively. The length of such crystals was usually determined by distribution of strain field distortions during crystallization that causes the branching of the phases.

CrB_2 is an itinerant antiferromagnet with TN=88 K. The crystal structure of CrB_2, in which triangular Cr layers and honeycomb B layers are stacked alternately. A sketch of transferred hyperfine fields at a boron site from nearest neighbor six chromium ions. A boron atom locates at the center of a trigonal prism, which consists of six Cr ions [5]. This stacking results in the preferred growth of CrB_2 along the direction of (001).

The formation of the chromium diboride CrB_2 was confirmed also by the X-ray phase analysis of the material. According to the data of X-ray phase analysis products containing chromium diboride, aluminium oxide and some modifications were obtained [4].

Superior thermal and chemical stability of MeB_2 compounds and narrow fiber diameter distribution offer unique opportunity to fabricate porous structures that may find applications in thermal protection systems, transpiration, filtration of corrosive melts and possible as reinforcement of structural composites.

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P-D2

SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS OF COMPOSITION MATERIALS USING MINERAL RAW MATERIALS

Abdulkarimova R.G., Suleimenova A.S., Abdulkarimova D.S., Mansurov Z.A.

al-Farabi Kazakh National University, Institute of Combustion Problems, 72, Bogenbai batyr str.,
050012, Almaty, Kazakhstan
Roza.Abdulkarimova@kaznu.kz

Carbon containing refractory materials are widely used in different fields of engineering and industry due to the combination of their unigue properties, such as resistance to attack by corrosion media and abrasion, high hardness and heat conduction and others. At present, SH-synthesis allowed to obtain a wide range of such materials [1-2].

One of the problems in production of carbon containing composition systems is the use of different carbon additives which are able to substitute expensive carbon. So, when producing materials by SHS technology, soot of different types, graphite powder are often used as a carbon component [2-3]. The search for new promising substitutes of carbon for production of carbide containing composition materials remains to be actual. An active form of a carbon additive and its uniform distribution in the volume of SHS mixture were obtained due to preliminary thermal carbonization of quartz particles composing the charge mixture of the components. Thermal carbonization gives the possibility of creating nanosized fibrous forms of carbon on the surface of mechanically activated quartz, this contributing to the improvement of physico-mechanical indexes in the course of SH-synthesis of carbon containing refractories [4]. The use of a cheap available raw material in production is of great interest. So, at present, utilization of rice husk, apricot stones is an actual problem which is most widely solved by thermal treatment (carbonization).

When producing materials under SHS conditions, an important role played by preliminary mechanochrmical activation (MA) which allows to achieve a high degree of particle dimensions, to change the structure, power consumption and, hence, to provide high reactivity of the material. Mechanical dispersion of qartz which results in formation of a non-equilibrium fresh surface with a high concentration of broken bonds is one of the striking examples of mechanical activation [4, 5].

Quartz of «Aktas» deposit was used as an oxide component of a charge mixture, aluminium powder of the brand PA-4 was used as a reducer in SHS processes. In the course of mechanochemical activation of quartz, carbon containing modifying additives: carbonized rice husk (CRH), carbonized apricot stones, shungit, graphite (scraps of graphite electrodes) were used.

Mechanochemical treatment of the mixtures under study was carried out in a planetary-centrifugal mill of dynamic action with the speed of the platform rotation 700 r/min and the speed of rotation of milling vessels 1200 r/min. The value of acceleration in a centrifugal planetary mill made up 20g. The process of carbonization of rice husk and apricot stones was carried out under isothermal conditions in a rotating reactor in an inert media at 300-900 ˚C, the rate of argon supply 50 cm^3/min, the time of contact 30-60 minutes. SH-synthesis of samples was carried out in a muffle furnace at the temperature of 800-900˚C.

Having taken quartz containing systems as an example, this work shows the prospective of a complex use of preliminary mechanochemical activation and modification with carbon containing additives for solution of the task on creation of new carbon containing composition SHS materials.

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P-D3

INVESTIGATION OF COMBUSTION IN Ti-Nb-W-C-H SYSTEM AND SYNTHESIS OF COMPLEX CARBOHYDRIDES

Aghajanyan N.N., Dolukhanyan S.K.*

A.B. Nalbandyan Institute of Chemical Physics of Armenian NAS, 5/2 P.Sevak Str., Yerevan 0014, Armenia
*seda@ichph.sci.am

The research of formation of complex carbohydrides based on refractory metals expands the possibility of obtaining of new metal-ceramic materials, prospective in nuclear power as composite solid alloys and constructional materials.

The goal of the present work was to study the interaction with hydrogen of composites of variable composition containing Ti, Nb, W and C in combustion mode, to synthesize the new easily grindable complex carbohydrides, then to compact and dehydrogenate them to receive the carbide ceramics.

Synthesis of complex carbohydrides based on Ti, Nb, W and C was implemented in one technological stage: xTi + (1-x)(Nb + W) + yC mixture ($0.6 \leq x \leq 0.8$; $0.4 \leq y \leq 0.8$) was pressed to a cylindrical tablet (P=100κN) and ignited in hydrogen (P=2atm). The results are presented in Table 1. According to x-ray analysis in all range of changes of metals and carbon ratios in SHS mode, multiphase products formed, the main phase being a titanium carbide with FCC structure. In some cases depending on the ratio of metals, a small phase of Nb_2C was found. In the conditions of our experiments, the tungsten carbide was not revealed. At all concentrations of tungsten (0.2-0.03 at. parts) free tungsten was seen in the diffraction patterns. The investigated compositions were ignited in hydrogen atmosphere to activate the participating reagents, provide the mutual dissolution of synthesized in combustion front carbides, and the formation of carbohydrides.

The concentration of carbon in the charge was specially taken in non-stochiometric quantity to provide the hydrogen insertion into the unoccupied okta - and tetrapores [1].

According to the chemical analysis, the hydrogen content depended on the carbon concentration and on the metals ratio. Hence, in the course of SHS at cooling in hydrogen atmosphere, easily grindable carbohydrides formed. Earlier, we observed the homogenizing role of hydrogen in the multicomponent systems in SHS mode [2]. Apparently, similar homogenization (but not complete) occurred also in the present experiments.

Table 1

Initial charge	T°C	[H_2] wt.%	[C] wt.%	Param. TiC_x Å	Phase
0.6Ti+0.2Nb+0.2W+0.6C	1580	0.35	5.84	4.318	W +TiC
0.6Ti+0.2Nb+0.2W+0.7C	1630	0.15	7.87	4.320	TiC+W
0.6Ti+0.3Nb+0.1W+0.6C	1870	0.63	6.05	4.322	TiC+W
0.6Ti+0.3Nb+0.1W+0.7C	1920	0.2	8.88	4.315	TiC+W
0.7Ti+0.2Nb+0.1W+0.5C	1876	0.69	6.46	4.337	$TiC+W+Nb_2C$
0.7Ti+0.2Nb+0.1W+0.6C	1978	0.54	7.97	4.335	TiC+W
0.7Ti+0.1Nb+0.2W+0.4C	1560	0.78	4.18	4.317	W +TiC
0.7Ti+0.1Nb+0.2W+0.7C	1890	0.33	9.51	4.322	TiC+W
0.7Ti+0.25Nb+0.05W+0.5C	1670	0.89	6.96	4.332	TiC+W
0.7Ti+0.25Nb+0.05W+0.6C	1910	0.67	7.76	4.333	TiC+W
0.7Ti+0.25Nb+0.05W+0.7C	2035	0.33	11.2	4.332	$TiC+ Nb_2C +W$
0.7Ti+0.25Nb+0.05W+0.8C	2180	0.22	9.34	4.332	TiC+W
0.8Ti+0.15Nb+0.05W+0.5C	1820	0.84	7.94	4.497	TiC+W
0.8Ti+0.15Nb+0.05W+0.6C	2025	0.67	9.36	4.332	TiC+W
0.8Ti+0.15Nb+0.05W+0.7C	2370	0.4	11.5	4.334	TiC+W
0.8Ti+0.17Nb+0.03W+0.5C	1875	0.93	8.04	4.332	TiC+W
0.8Ti+0.17Nb+0.03W+0.6C	2180	0.68	10.1	4.342	TiC+W
0.8Ti+0.17Nb+0.03W+0.7C	2435	0.43	11.9	4.337	TiC+W

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P-D4

DENSE Ni-TiC COMPOSITES PRODUCED THROUGH UNDER-PRESSURE COMBUSTION SYNTHESIS

Amel-Farzad H.*, Ghavimi A.H.

Bu-Ali Sina University, Hamadan, Iran
hh_amel@yahoo.com

Ni-TiC is widely studied composite which can be used as cutting tool, and has initially proposed as an alternative for the classic WC-Co composites [1]. Despite WC-Co, this composite can be easily produced through a combustion reaction. Many attempts have been carried out to perform the combustion reactions under pressure and achieve dense ceramics or ceramic composites. In this work, Ni-TiC composites of almost 100% relative density are produced through liquid phase densification obtained in under-pressure CS. In other reports of under pressure SHS, ignition has been carried out using SPS [2] induction coil [3] preheating [4], etc. In this work, simple electric arc has been performed for this purpose. The products were studied using light and electron microscope, XRD and microhardness testing. Comparative evaluation of the effect of nano-scale and micro-scale initial particle sizes and consequent final grain sizes on the densification behavior and hardness were also studied.

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P-D5

PRODUCTION OF Ti NANOPARTICLES VIA COMBUSTION SYNTHESIS

Amel-Farzad H.*, Nazari Sh., Emam F.

Bu-Ali Sina University, Hamadan, Iran
hh_amel@yahoo.com

Metallic nanoparticles are of significant interest during the recent years [1]. Especially, Ti nanoparticles are attractive because of various applications of its alloys. In this work, Ti nanoparticles are produced through the following combustion synthesis.

TiO_2+Mg+xMgO=>Ti +(1+x)MgO

MgO is added to the initial mixture in order to reduce the combustion temperature and keep Ti particles from melting at about 1950K. TiO_2 and MgO particles of nanometer and Mg particles of micrometer scale were mixed and compacted and ignited using electric arc. Finally, the MgO particles were leached using light HCl and the Ti nanoparticles were simply gathered. The products were studied using SEM, TEM, and analyzed using and XRD.

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P-D6

NANOPOROUS Cu PARTS PRODUCTION VIA COMBUSTION SYNTHESIS

Amel-Farzad H.*, Jahangir V., Vakilpur S.

Bu-Ali Sina University, Hamadan, Iran
hh_amel@yahoo.com

Porous structures are of significant interests, especially in recent years, because of various possible applications [1]. Particularly, nanoporous structures, either metallic or ceramic ones, are more attractive. Porous Structures with porosities of mictrometer to millimeter in size are producible through combustion synthesis. Nanoporous structures have not been produced through this method. Cu porous structures are of special interest because of their possible use in heat sinks. Especially, nanoporous Cu particles will be ideal heat sinks. In this work nanoporous Cu particles are produced via combustion synthesis. The following reaction is designed for this purpose.

$CuO+Mg+xMgO=>Cu+ (1+x)MgO$

Since the reducing CuO be means of Mg is too exothermic (T_{ad}>5000K), additional MgO particles are added to the initial mixture so that the combustion temperature is reduced. Theoretically, the combustion temperature must be less than CuO melting point (@@@) and higher than the melting point of Ti (1948K). Cu particles melt at the combustion temperature and the join to each other among the MgO particles, which leads to a complete matrix of cellular Cupper.

Finally, the MgO particles were leached by means of light HCl. The Cellular Cu matrix remained away [2]. The products were studied using SEM. The open porosities of submicron size were formed through this method.

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P-D7

FORMATION OF THE NANOCRYSTALLINE NiAl PHASE BY MECHANICALLY ACTIVATED SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS REACTION

Arroussi S.[1,*], Ali Rachedi M.[1], Benaldjia A.[1], Andasmas M.[2], Guerioune M.[1], Vrel D.[2]

[1]Laboratoire d'Étude et de Recherche des États Condensés (LEREC).Département de physique, Faculté des Sciences, Université d'Annaba, B. P. 12 (23000) Annaba-Algérie
[2]LIMHP, CNRS, Av. J.B. Clément, F-93430 Villetaneuse, France
*soum_phys@yahoo.fr

Nanotechnology, involves the production of a diverse array of nanomaterials (NM), which include nano-objects and nanoparticles (NP). Nanomaterials are generally defined as having one or more external dimensions or an internal or surface structure on the nanoscale (about 1–100 nm) [1]. Recently, mechanical activation of elemental powders prior to self-propagating high temperature synthesis (SHS) (mechanically activated SHS (MASHS)) has also been conducted [3–4]. MASHS has a number of advantages including the production of a nanostructured product phase; however, the resulting product is reported to contain high levels of porosity (40–50%) [5]. This process results from the combination of two steps: a short duration ball-milling of a pure elemental Ni+Al powder mixture followed by a self-propagating high-temperature synthesis (SHS) reaction induced by the Ni+Al reaction exothermicity.

To identify the mechanically activated powders and MASHS end-products, and to determine their microstructural characteristics, X-ray diffraction (XRD) analyses were performed. The characterization of the constituent phases was quantitatively evaluated using Rietveld whole profile fitting method adopting the most developed software MAUD well adopted to fit accurately the whole X-ray patterns [6].

Structural analysis deduced from the Rietveld refinement of X-ray diffraction patterns of NiAl compounds milled for 6 h+ SHS show the formation of single phase β-NiAl($a=0.2848\pm1.3.10^{-4}$) nm. Microstructural analysis has revealed the nanocrystalline character of MASHS. The average crystallite sizes are of about (41.4651 ± 0.218) nm and the microstrains values are closed to those of metallic alloys ($0.3255 \pm 1.2\ .10^{-4}$ %).

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P-D8

X-RAYS AND MÖSSBAUER STUDY OF $Ti_{2-x}Fe_xO_3$ SYNTHESIS BY THE SHS METHOD

Benaldjia A.[1*], Sehab N.[1*], Otmani A.[2], Amara A.[1], Arroussi S.[1], Vrel D.[3], Grénèche J.M.[4]

[1] Laboratoire d'Etude et de Recherche de l'Etat Condensé, Faculté des Sciences – Université Badji Mokhtar – Annaba B.P.12 Annaba- Algérie 23 000.
[2] Laboratoire de Magnétisme et de Spectroscopie des Solides , Faculté des Sciences, Université Badji Mokhtar B.P. 12 Annaba -Algérie 23000
[3] Laboratoire LIMHP, CNRS, av. J-B clément F93 430 Villetaneuse, Paris 13, France
[4] Laboratoire de Physique de l'Etat Condensé, UMR CNRS 6087 Université du Maine Faculté des Sciences 72085 LEMANS Cedex 9 –France
[1*] abbenaldjia2000@yahoo.fr
[2*] sehab_nadjette@yahoo.fr

The necessity to develop new materials with better properties oriented research verses other methods of synthesis. Among these the self–propagation high-temperature synthesis SHS that permits to elaborate some variety of materials as ceramics, intermetallics and their composites and nanostructured alloys [1-3]. The method is based on the use of the heat released during exothermic reactions in order to preheat raw materials and to obtain a self sustained system. Reaction is started by the use of an electric or chemical system and after ignition the reactions proceed as a reaction front with linear speeds of 1–100 mm/s through the compacted raw materials in powder form. The procedure has low energy consumption and has large potentials for industrial applications due to the high productivity and the very simple equipment involved.

For synthesizing the $Ti_{2-x}Fe_xO_3$, by SHS method, firstly, we have milled mixture powders of Fe_2O_3, Al and TiO_2 for various concentrations. Secondly, the powders of a nanocrystalline alloy produced by mechanical alloying were consolidated to form a bulk nanocrystalline sample under an uniaxial pressure. Mechanical alloying was performed with a planetary ball mill type Fritsch-Pulverisette 6. The green density reached is 70% of the theoretical density. With the additives Al_2O_3, the final products remain relatively dense with a relative density up to 90 %.

Characterizations of obtained products were carried by usual techniques X-rays diffraction and Mössbauer spectroscopy. Careful evaluations of the crystallite size, crystalline parameters and percentage of the phases have been made using the Rietveld analysis method [4]. This method was successfully applied for determination of the quantitative phase abundances of the mixture powders.

The crystalline size of the final products is in the order of 100 nm and the cell parameter of final product of $Ti_{2-x}Fe_xO_3$ is about 0.476(5) nm**.** The change of magnetic properties is observed by Mössbauer spectrometry and related to environment of the atoms of iron and their sites.

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P-D9

EFFECT OF MIXING AND SAMPLE PREPARATION CONDITIONS ON IGNITION AND COMBUSTION CHARACTERISTICS OF Ni – Al MIXTURES

Boyarchenko O.D., Shkodich N.F.*, Sachkova N.V., Vadchenko S.G., Rogachev A.S., Sytschev A.E.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
* n.f.shkodich@mail.ru

Synthesis of new chemical compounds is one of the main problems of chemical physics so new physical methods for reaction acceleration have been applied. Mechanical activation (MA) is one of the effective ways to controlling the green structure, synthesis parameters, and the processes of phase structure formation and reactions.

In this work, we investigated the influence of activation on the particles structure and ignition/combustion parameters in Ni – Al mixture. Powders of Al (ASD-4 brand, 99.1 % pure, <40 μm) and Ni (PNE-1 brand, 99.8 %, <70 μm) were used as a starting materials
Activation was carried out in two-stages: preliminary “dry” MA followed by “wet” MA. The technique allows one to obtain fine active powders from ductile metals.

We studied the evolution in the microstructure of activated particles as a function of activation conditions. At the initial stage, Al particles (ductile component) were flattened as a result of clashing with balls and walls of a mill while Ni particles (fragile component) were crashed. Prolongation of MA results in thorough mixing and forming composites with alternating layers of Al and Ni. The thickness of layers depends on the time (the longer MA, the less thickness) [1, 2]. In the case of dispersion in liquids we observed Ni – Al layers splitting caused by disjoining stress. As a result flat particles with developed lamellar cellular microstructure formed.

Ignition temperature was measured for small amounts of activated mixtures in the form of activated particles, pressed pellets, and rolled foils. For comparison, the ignition temperatures were determined under the same conditions also for non-activated mixtures and nanofoils obtained by alternate magnetron deposition.

It was shown that the ignition temperature could be diminished by 300–400 degrees and approach the ignition point for nanofilms. Combustion velocity for foils rolled from the activated powders was 4–5 times higher and depends on MA conditions.

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This work was supported by the Russian Foundation for Basic Research (project no. 10-03-00217-a) and the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (grant no. NSh-6497.2010.3).

P-D10

COMBUSTION OF IRON-VANADIUM ALLOY IN FLOW OF NITROGEN CONTAINING GAS

Braverman B.Sh., Tsibulnik Yu.V., Maksimov Yu.M.

Department for Structural Macrokinetics, Tomsk Scientific Center of SB RAS.

bbraverman@yandex.ru

Nitrided ferrovanadium is extensively used in metallurgy. At the present time one of the most effective method for nitrided ferrovanadium obtaining is combustion of the ferrovanadium powder in nitrogen (SHS-method) developed by Yu.M. Maksimov and M.Kh. Ziatdinov [1]. This technology is applied at nitrogen pressure 5-10 MPa. High pressure makes the technological process complicated and dangerous. It is known a variation of SHS – combustion with forced filtration of an active gas, when the flow of reagent gas to the reaction zone is generated by external devices [2-4]. The gas flow, in addition to the reagent transfer, takes part in heat exchange between hot products and a cold green mixture. If the gas flow is opposite to the combustion zone propagation (counter flow regime), then temperature of the combustion zone decreases. If the gas flow coincides with the direction of combustion zone propagation (co-flow regime), then gas enters the combustion zone through the hot products of reaction transfering the heat energy. It results in the increase in temperature of the combustion zone and increase in reaction rate. Combustion in a co-flow regime can reduce the acceptable pressure of nitrided ferrovanadium synthesis.

An objective of this work is to investigate the possible production of nitrided ferrovanadium by SHS in the flow of nitrogen at pressure close to atmospheric. Direction of gas flow coincides with direction of combustion zone propagation.

The preparation of a green mixture has difference. The first case, the powder obtained by of the alloy containing 50% of vanadium and 50% of iron was placed in reactor. In the second case the powder was preliminary granulated similarly to [5]. Colophony was used as a binder.

In first case, SHS was conducted only for powder with a dispersity less then $80*10^{-6}$ m at gas rates more then 0.6 m/sec and only in the flow of pure nitrogen.

In second case, it is possible to use coarse powder (up to $100*10^{-6}$ m). The flow rate can be reduced to 0.1 m/sec and combustion is observed when the gas mixture contains 50% nitrogen and 50% argon.

These results show that the main problem of ferrovanadium nitriding by SHS with forced filtration is gas permeability of reaction materials.

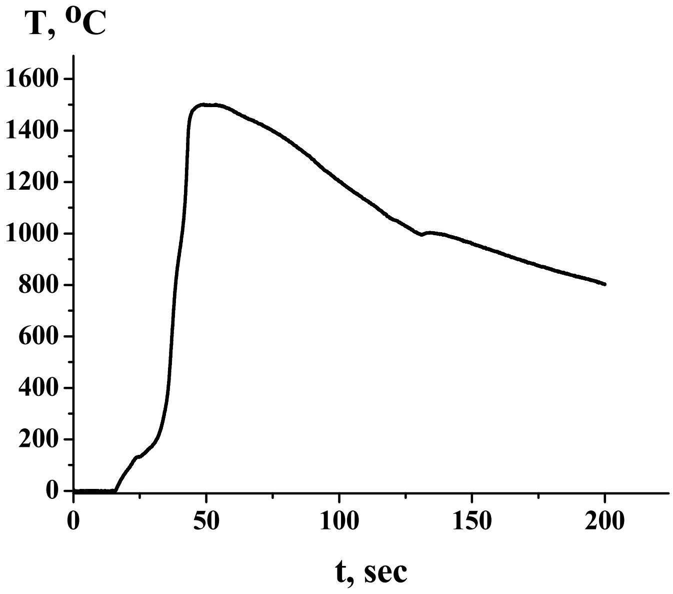

Fig. 1. Typical thermogram of ferrovanadium powder combustion in nitrogen flow

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P-D11

SYNTHESIS OF HIGH DENSITY POLYETHYLENE CARBON NANOTUBE COMPOSITES BY SHS

Chouit F.[1], Guerioune M.[1], Boukhezar S.[1], Guellati O.[1,2,3]

[1]Laboratoire d'Etude et de Recherche des Etats Condensés (LEREC), Université Badji Mokhtar,
BP. 12, Annaba, Algeria
[2] Centre Universitaire de Souk Ahras, Algeria
[3] Laboratoire de Chimie et d'Electrochimie des surfaces (CES), FUNDP rue de Bruxelles 61,
B-5000 Namur, Belgium
chouit1fairouz@yahoo.fr

High density density polyethylene (HDPE) multiwalled carbon nanotubes (MWCNTs) with weight fractions ranging from 0.1 to 10wt% were prepared by self-propagating high-temperature synthesis (SHS). The morphology and the dispersion of the MWCNTs in HDPE matrix was investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

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P-D12

COMBUSTION SYNTHESIS OF Ni-Ti COMPOSITES REINFORCED BY CARBON NANOTUBES

Chouit F.[1], Boukhezar S.[1], Guellati O.[1,2,3], Guerioune M.[1]

[1]Laboratoire d'Etude et de Recherche des Etats Condensés (LEREC), Université Badji Mokhtar,
BP. 12, Annaba, Algeria
[2] Centre Universitaire de Souk Ahras, Algeria
[3] Laboratoire de Chimie et d'Electrochimie des surfaces (CES), FUNDP rue de Bruxelles 61,
B-5000 Namur, Belgium
chouit1fairouz@yahoo.fr

Two important materials are employed in this study, the carbon nanotubes(CNTs) and Ni-Ti shape memory alloy which have many interesting properties finding their application in different fields such as nanoelectronic devices. The production of Ni-Ti/CNTs nanocomposites from elemental powders compact was conducted by self-propagating high-temperature synthesis (SHS) in this work.

Effect of the stœchiometry of the starting mixture, the initial sample density and the initial sample temperature on the composition of final products was studied. The nanocomposites were comprehensively characterized by X-Ray diffraction (XRD) and scanning electronic microscopy (SEM).

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P-D13

MICROWAVE COMBUSTION SYNTHESIS OF LANI$_{1-X}$FE$_X$O$_3$ NANOPOWDERS

Del Nero de Freitas M.A.F.[1], Silva T. de F.[2], Assaf J.M.[2] and
Kiminami R.H.G.A[1]

[1]Federal University of São Carlos, Dept. of Materials Engineering, 13565-905 São Carlos, SP, Brazil
[2]Federal University of São Carlos, Dept. of Chemicals Engineering, 13565-905 São Carlos, SP, Brazil
ruth@ufscar.br

Rare-earth perovskite-type oxide catalysts have been researched exhaustively due to their unique properties, which have led to applications in numerous reactions. These applications include various oxidation reactions (e.g., CO, NH_3), hydrogenation, hydrogenolysis, catalytic combustion, etc. However, more recent research has focused on studies of these catalysts in the methane oxidation process of gas turbines. The use of a catalyst for natural gas combustion presents several advantages. By controlling the reaction rate, the release of heat produced by total oxidation of natural gas is more progressive than in a flame. The catalytic reaction is very efficient in completely converting methane to carbon dioxide and water, even with a lean methane mixture, reducing the emission of unburned hydrocarbons to traces [1]. However, the characterization and comparison of the catalytic performances of various catalysts in conditions similar to reaction conditions is always a difficult problem due to the exothermicity of the reaction and to the transfer limitations (heat and mass) occurring in the reaction conditions. To overcome this problem, in this work we used methane dry reforming to characterize the catalytic performance. Most of the catalysts used in modern industrial applications are based on noble metals such as Ru and Rh in the position of alkaline metals. Although these metals are excellent catalysts, they involve high production costs. Studies have shown that noble metals can be replaced by Ni, which has the same catalytic effect [2]. The only disadvantage of this replacement is that the system is inactive during its use as a catalyst due to the formation of an amorphous carbon phase on its surface. Fe and other metals were added to the mixture to stabilize the perovskite-type catalyst containing Ni. Fe-based materials quickly became popular because of their increased stability under adverse conditions. Despite the excellent catalytic properties of perovskites, the conventional method to synthesize them requires conductive heating for extended periods at high temperatures with intermittent grinding. Therefore, there is a growing demand for new synthesis methods to overcome these limitations. A number of synthesization methods for oxide and non-oxide ceramic powders, starting from precursor solutions, have been developed over the last few decades. The "Auto Ignition" process or "Combustion Synthesis" is one of such process to synthesize crystalline ceramic nanopowders using the precursor route. In these synthesization methods, an intermediate amorphous solid is formed from the liquid precursor. The desired crystalline phase is formed directly from an amorphous solid by local rearrangement of the ions with no interdiffusion of species. The process is based on the principle that, once initiated by an external source, an exothermic reaction occurs, becoming self-sustained and resulting in the end product within a short period of time. The technique is usually an easy, safe and fast way to produce ceramic powders, and its potential advantages are that it requires less energy than conventional ceramic synthesis processes and that the processing time is reduced to a few minutes [3]. It has been demonstrated that this quick, straightforward process can be used to produce homogeneous, high-purity, crystalline oxide nanopowder ceramic powders. The method uses an exothermic, usually rapid and self-sustaining, chemical reaction between the desired metal salt and a suitable organic fuel.

The purpose of this investigation was to study the microwave combustion synthesis of $LaNi_{1-x}Fe_xO_3$ nanopowders. Samples of the $LaNi_{1-x}Fe_xO_3$ system, with values of x = 0 and 0.5, were prepared and synthesized in a microwave oven (MW) and on a hot plate (HP) for comparison. The compositions were dubbed MWF0, MWF0.5 and HPF0, HPF0.5, respectively. The resulting powders were characterized by X-ray diffraction, nitrogen absorption by BET, and scanning electron microscopy measurements, and tested for their activity towards the catalytic combustion of methane. The XRD results show highly crystalline and quasi-monophasic phases formed during the microwave combustion reaction. The results obtained in this study show that microwave assisted combustion synthesis is reliable for producing pure $LaNi_{1-x}Fe_xO_3$ perovskites with x=0 and x=0.5. The rapid internal heating with microwaves reduces the synthesis time from 12 min (HP) to 2 min (MW), preventing excessive particle growth and the formation of large agglomerates. The particles were on the nanometric scale, with an average size of about 200 nm. In addition to characterizing the powder, a catalytic activity test was performed to examine and confirm the catalytic effect of the perovskites, and an analysis was made of the influence of the addition of iron in the mixture. The method is simple and does not involve intermittent grinding and calcination at high temperatures. The time spent on the preparation of perovskites was reduced by approximately 99.5% compared to other methods of catalyst synthesis. Moreover, the particles and agglomerates obtained by microwave combustion synthesis are smaller than powders prepared by conventional combustion reaction. The fast internal heating by microwaves reduces the synthesis time from 12 min (HP) to 2 min (MW), preventing excessive particle growth and the formation of large agglomerates. Another advantage of microwave combustion synthesis is that heating in a microwave oven favors the uniform emission of gases and rapid heat dissipation, promoting the formation of more aerated foams and less agglomerates powders than those produced conventionally.

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P-D14

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF ELECTROCONDUCTIVE CERAMICS BASED ON $MoSi_2$

Efremov V.L.

Combustion Problems Institute 172, Bogenbay batyr st., Almaty, Kazakhstan, 050012
vlaefremov@mail.ru

The use of self-propagating high-temperature synthesis (SHS) to prepare functional materials ranks high among those areas in ceramic science and technology. SHS is recognized as an attractive process for producing high-temperature, hard materials that difficult and/or expensive to produce by conventional methods

The molybdenum disilicide ($MoSi_2$) owing to its excellent oxidation resistance, reasonable strength, good thermal- and electroconductivity at high temperatures, is applied for manufacturing various constructional ceramics and high-temperature heaters. Such materials are usually obtained by roasting at temperatures 1300-1500 °C in hydrogen medium; however their obtaining is possible with a self-propagating high-temperature synthesis (SHS) [1-3]. The obtaining of MoSi2 and TiSi2 is possible either by direct synthesis from the elements, or by reducing of oxides by various active metals (Al, Mg). In the second case the final product is a composite material. In present report the main features of obtaining of the ceramics based on MoSi2 and as a result of the SHS-process are considering. The cardinal goal of these investigations was production of the dense compact samples which could be used directly as electric heaters.

On heating the mixture of MoSi2 with Al and Si take place redox processes with large heat release according to the following total schemes:

$MoO_3 + 2A1 + 2Si \rightarrow MoSi_2 + A1_2O_3$ (1)

With respect to this reaction that energy release in this system constitutes 1061 kJ/mole, and adiabatic temperature exceeds 3000 °C. At this the components of the mixture melt, gas release is intensive, and so, it's practically impossible to obtain non-deformed products. That's why the initial mixture should be by relating inert compounds, which decreasing the temperature in the combustion wave, provides a more stable synthesis regime, and thus, obtaining of dense compact products.

Among a wide range of appropriate compounds we limited ourselves silicon carbide, carbon, magnesium, aluminium oxide, silicon. The choice was defined, first of all, by high melting temperatures, and also their ability to form complex oxides with aluminium oxide which is obtained according reaction (1).

Dense compact materials are formed in conditions when SHS wave along the samples is propagating in a stable and steady regime. Maximal temperature, estimated by optical pyrometer, is 1700 - 1800 °C. Velocity of the combustion wave in such conditions is 3-4 mm/sec.
It was established that there exist upper and lower limits of stable combustion depended on the ratio of components in the initial mixture. At low energetic power of the initial mixture (at the concentration of inert compounds more then 55%) the combustion wave stopped in several

seconds after ignition. At concentration these components less 35% the SHS was too intensive, and was accompanied by strong gasification. The structure of the finite materials had large pores and profound separation of metallic and ceramic phases.

Samples of the heating elements are dense compact materials with density 1.9-2.3 g/cm3. Bending strength call reaches 90-100 MPa, if all the technological operations of synthesis are strictly followed. The temperature expansion coefficient within 20-1200 °C constitutes $2\text{-}3\text{-}10^{-6}$ cm^{-1}. Materials could stand multiple heating up to 900 °C and sharp cooling in water without visible destruction.

Specific electric resistance of obtained ceramic heaters constitutes $10^{-4} - 10^{-2}$ ohm m, which allows both their switching to low-voltage sources of power and directly to the 220 V circuit.

It was determined that at continuous work of ceramic heaters, there practically doesn't occur any increase of the resistance. However, a heating - cooling regime sharply changes, - within 50 cycles electric resistance increases practically twice. This is an undesirable property, as, to preserve given specific heat release is necessary to increase voltage of the power source.

Although at present SHS-ceramic heaters on the basis of molybdenum disilicide less stable at high temperatures them conventional $MoSi_2$-heaters there are real possibility for improvement of their properties by means of alloying of various reinforcing additives.

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P-D15

ON THE MECHANISM OF CHEMICAL CONVERSIONS IN THE COMBUSTION WAVE OF THE MoO_3 / TiO_2 / Al / Si SYSTEM

Gorshkov V.A., Miloserdov P.A., Yukhvid V.I., and Sachkova N.V.

Institute of Structural Macrokinetics and Materials Science,
Russian Academy of Sciences, 142 432 Chernogolovka, Russia
[*] gorsh@ism.ac.ru

INTRODUCTION

Transition metal silicides are commonly used in the production of high-temperature heating elements of electrical furnaces operating in oxidative media as well as of construction ceramics. In the industrial practice the purpose is gained by the use of molybdenum disilicide and its compositions with silicides of the IV-VI group metals of the Mendeleev Table [1]. One of the promising methods of such materials production is SHS metallurgy employing high-temperature systems of thermite type as the initial reagents [2, 3]. The specific features and mechanism of chemical conversions during pressurized liquid-phase combustion of the system MoO_3 / TiO_2 / Al / Si were studied in the present investigation.

RESULTS

Powder mixtures of analytically pure oxides of molybdenum (6) and titanium (4), ASD-1 aluminum, and KR-0 silicon were used in the synthesis. The mixtures were placed into quartz glasses (50/20 mm). Synthesis was performed in a 3-liter constant-pressure bomb at the initial pressure of argon $P_0 = 4$ MPa. The following systems were used in the experiments:

$$MoO_3 + 2Al + 2Si \rightarrow MoSi_2 + Al_2O_3 \qquad (T = 2934\ K) \qquad (1)$$

$$4TiO_2 + 4Al + 6Si \rightarrow 3TiSi_2 + 2Al_2O_3 \qquad (T = 1522\ K) \qquad (2)$$

Dilution of ‘hot’ mixture (1) with ‘cold’ one (2) was successfully used to quench the combustion front at the mixture weight ratio (1)/(2) = 0.65/0.35. The sample investigation showed that the lower and upper regions of the sample were respectively occupied with an unreacted powder mixture and final cast product, the intermediate zone residing between them (see Fig. 1). The obtained reaction cell was studied with the method of local X-ray analysis. As follows from the analysis of the microstructure and local composition of its constituents, the near-boundary zone is a cermet sintered layer. The matrix in the layer is formed of the oxide solution Al_2O_3 - SiO_2, with particles of the metallic product (Mo-Ti-Si), residues of the initial reagents (Si, TiO_2, and MoO_3), and intermediate products (MoO, Al-Si, Mo-Ti-O-Si, Si-O) distributed within it. The obtained results show that liquid-phase chemical conversion during combustion in the initial mixture of $MoO_3/TiO_2/Al/Si$ is of a step-wise character. The scheme of the chemical processes proceeding in the combustion wave can be qualitatively presented as

$$MoO_3 + Al \rightarrow Mo\text{-}Al\text{-}O_x + Mo\text{-}Al, \qquad (1)$$
$$TiO_2 + Al \rightarrow Ti\text{-}Al\text{-}O_x + Ti\text{-}Al \qquad (2)$$
$$MoO_3 + Si \rightarrow Mo\text{-}Si\text{-}O_x + Mo\text{-}Si, \qquad (3)$$
$$Mo\text{-}Al\text{-}O_x + Ti\text{-}Al\text{-}O_x + Mo\text{-}Si\text{-}O_x \rightarrow Mo\text{-}Ti\text{-}Al\text{-}Si\text{-}O_x, \qquad (4)$$
$$Mo\text{-}Al + Ti\text{-}Al + Si\text{-}Al \rightarrow Mo\text{-}Ti\text{-}Si\text{-}Al, \qquad (5)$$
$$Mo\text{-}Ti\text{-}Si\text{-}Al + Mo\text{-}Ti\text{-}Al\text{-}Si\text{-}O_x \rightarrow (MoTi)Si_x + Al_2O_3xSiO_2 \qquad (6)$$

At the beginning, reductive processes (1), (2), (3) proceed at the boundary of the molybdenum oxide with aluminum and silicon. They yield intermediate oxide (4) and metallic (5) solutions. Reaction (6) takes place after the matrix solution Mo-Ti-Al-Si-O_x, has been formed (as a consequence of diffusion dissolution).

CONCLUSION

The obtained results provide the possibility of creating the scientific basis of the control over SHS technologies of cast $MoSi_2$, $(MoTi)Si_2$ and production of $MoSi_2$,-, $(MoTi)Si_2$-based powders for sintering of ceramic articles.

Investigation was financially supported with PFI P RAN P-7.

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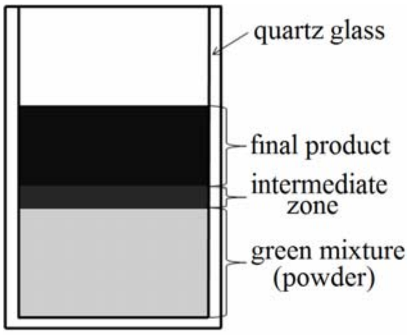


Fig. 1.

P-D16

ULTRAFINE AND NANOSIZED $MoSi_2$ POWDERS: SYNTHESIS AND SEPARATION

Ignat'eva T.I., Borovinskaya I.P., Semenova V.N., Kovalev D.Yu., and Barinov Yu.N.

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka,
Moscow, 142432 Russia
itian@ism.ac.ru

Molybdenum disilicide, $MoSi_2$, is known for its low density (6.3 g/cm^3), high melting point (2020°C), and good oxidation resistance up to 1900°C due to formation of protective SiO_2 film on its surface. An important drawback of powdered $MoSi_2$ and related composites is the agglomeration of particles, which diminishes the mechanical strength of resultant composites (cracking at the interface with coarse grains). The problem can be overcome by using ultrafine and nanosized starting $MoSi_2$ powders.

Previously we have demonstrated [1-3] that an optimized mechanical diminution in combination with subsequent chemical dispersion (hot etching) of raw SHS products can be used in order to obtain fine powders with a uniform distribution of particles over their size.

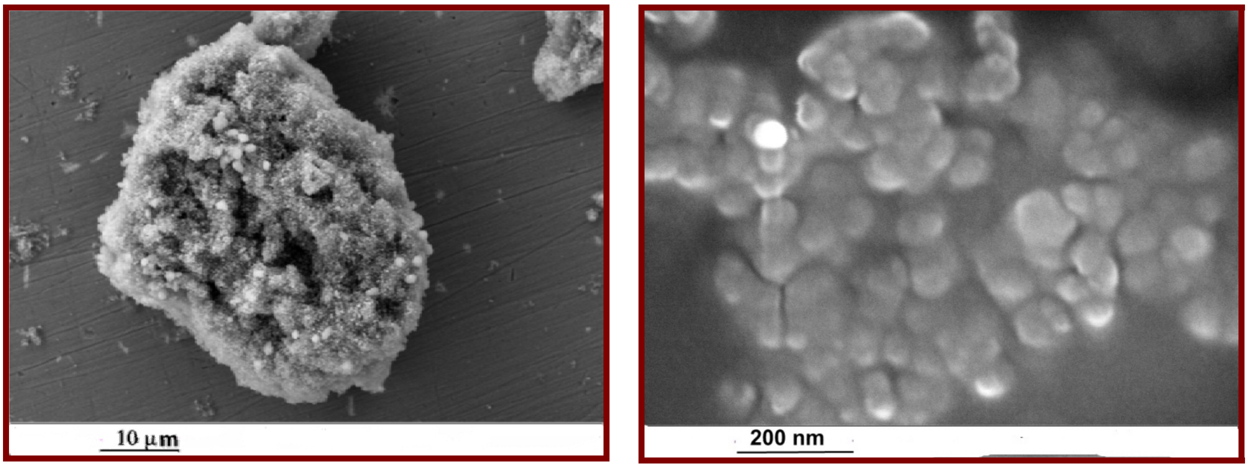
Ultrafine $MoSi_2$ powders were prepared by SHS reaction from the elements (under an Ar pressure of 5 atm) followed by optimized diminution process and chemical dispersion (hot alkali etching). It was detected molybdenum oxides in the gaseous-phase of reaction. Raw SHS products (cakes) were found to contain tetragonal $MoSi_2$ and an admixture of $Mo_{4.8}Si_3C_{0.6}$.
The inhomogeneous and partially sintered powder is seen to contain agglomerated thin particulates and bound large ones.

After subsequent processing in the planetary mill, the sintered agglomerates destroyed alongside the interfaces. This was accompanied by a 2-fold increase in the HWHM of diffraction peaks, which is indicative of decreasing particle size.

The surface of $MoSi_2$ particles becomes covered with a SiO_2 + MoO_3 layer. Amorphous SiO_2 and $MoSi_2$ can be readily dissolved upon hot alkali etching of SHS-produced powder (chemical dispersion).

Chemically dispersed powders contain porous agglomerates formed by ultrafine and nanosized fragments. The amount of pores (several nm in size) was found to increase with increasing processing time in the planetary mill, duration of alkali etching, and concentration of etching solution.

The precipitates extracted from etching solutions (upon drying) represented soft agglomerates formed by spherical nanoparticles (<100 nm) of $MoSi_2$, K_2MoO_4 particles and amorphous SiO_2 film (Fig.). It was also confirmed by XRD data and chemical analysis.



(a) **(b)**

Fig. Agglomerate of $MoSi_2$, K_2MoO_4, and SiO_2 particles (a) and $MoSi_2$ nanoparticles extracted from etching solution (b).

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P-D17

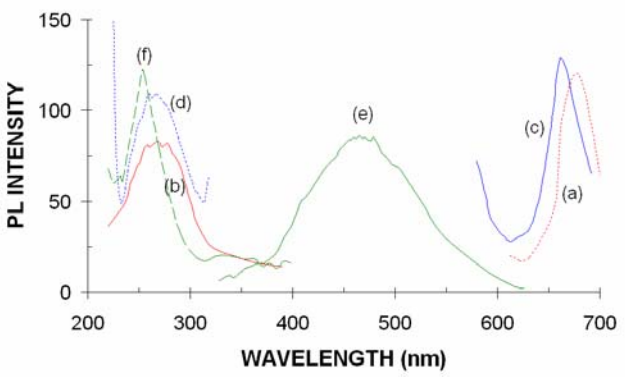
COMBUSTION SYNTHESIS OF SOME COMPOUNDS IN Li_2O-Al_2O_3 SYSTEM

Kale M.A.[1], Joshi C.P.*[2], Moharil S.V.[3]

1 Physics Department, SVSS College of Engineering, and Research, Nagpur, India
2 Applied Physic Department, R. K.N Engineering College, Katol Road, Nagpur 440 013, India
3 Physics Department, RTM Nagpur University, Nagpur 440 010, India
*joshicp@rknec.edu, charusheela_4253@yahoo.co.in

At least four compounds in Li_2O-Al_2O_3 system viz. $LiAlO_2$, $LiAl_5O_8$, Li_5AlO_4 and $Li_2Al_4O_7$ are known. These are important for several technological applications [1, 2]. Combustion synthesis of these compounds using urea as a fuel was attempted. $LiAlO_2$ and $LiAl_5O_8$ could be successfully prepared by choosing the starting materials in required stoichiometric ratios [3]. $Li_2Al_4O_7$ was not obtained as a pure phase; gamma $LiAlO_2$ was formed as an impurity phase. Li_5AlO_4 could not be prepared by combustion process. Some phosphors based on these aluminates could also be prepared.

Activation of these aluminates with Fe^{3+}, Mn^{4+}, Cu^{+}, etc. was successfully achieved. Figure shows PL excitation and emission spectra in $LiAl_5O_8$:Fe^{3+} (a, b) and $LiAl_5O_8$:Mn^{2+} (c, d). PL in $Li_2Al_4O_7$:Cu^{+} (e, f) is reported for the first time.



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P-D18

ON THE MECHANISM OF MOLTEN-SALT-CONTROLLED THERMITE REACTIONS

Kirakosyan Kh.G.[1*], Grigoryan Y.G.[1], Niazyan O.M.[1], Yeghishyan A.V.[1], Kirakosyan A.G.[1], Manukyan Kh.V.[1,2], Kharatyan S.L.[1,2]

[1]Laboratory of Kinetics of SHS Processes, A.B. Nalbandyan Institute of Chemical Physics NAS RA, 5/2, P. Sevak str., Yerevan, 0014, Armenia
[2]Department of Inorganic chemistry, Yerevan State University, 1, A. Manoogian str., Yerevan, 0025, Armenia
* mkhachatur@gmail.com

It is well known that in thermite-type reactions intensive gas evolution coupled with high reaction temperatures make it difficult to control the microstructure of the obtained products. One of the most recognized methods for softening violent reaction conditions and tune the morphology of products is the application of so called inert diluents. A modified process of thermite reactions with halide salt additives (mainly NaCl) have known as molten salt-controlled combustion synthesis [1,2]. Due to the heat generated by self-sustaining reaction, salt melts at about 800°C and further nucleation of product particles occurs in the molten salt environment, which protects them from agglomeration and grain growth. In all published works, however, the effect of sodium chloride on chemistry of combustion process was not studied and salt was always considered as only an inert diluent. The present work is devoted to studying the effect of sodium chloride on the chemistry and phase formation mechanism of salt-controlled combustion reaction in the MoO_3+Mg system.

The obtained results in this study suggest that reaction parameters in the MoO_3+Mg+NaCl system depend on the salt content. The process temperature may be reduced from 2200 down to 800°C upon growing the salt content in the reacting mixture. Temperature profile analysis, DTA/TG investigations, XRD and SEM analyses helped clearly identify phase formation mechanism in the reaction front. According which at 450-650°C molybdenum oxide exothermically reacts with salt by the following reaction:

$$2MoO_{3(s)} + 2NaCl_{(s)} = MoO_2Cl_{2(g)} + Na_2MoO_{4(s,l)} \qquad (1)$$

Investigations suggest that the following reaction starts just after the Mg melting (650°C):

$$MoO_{3(s)} + 3Mg_{(l)} = Mo_{(s)} + 3MgO_{(s)} \qquad (2)$$

Microstructure analysis shows that at salt-poor conditions nucleation of products particles mainly takes place in the molten magnesium (Fig.1a). Meanwhile in the salt-reach mixtures nucleation of product particles mainly takes place at molten NaCl media (Fig.1b). Whiskers formed (Fig. 1c) by vapour-liquid-solid mechanism indicate that the following reaction may occur in the flame propagation:

$$Na_2MoO_{4(s,l)} + MoO_2Cl_{2(g)} + 6Mg_{(l,g)} = 2Mo_{(s)} + 6MgO_{(s)} + 2NaCl_{(g,l)} \qquad (3)$$

The calculated low activation energy (50kJ/mol) of combustion reaction may be additional proof of high role of gaseous (liquid) intermediates at the phase formation processes.

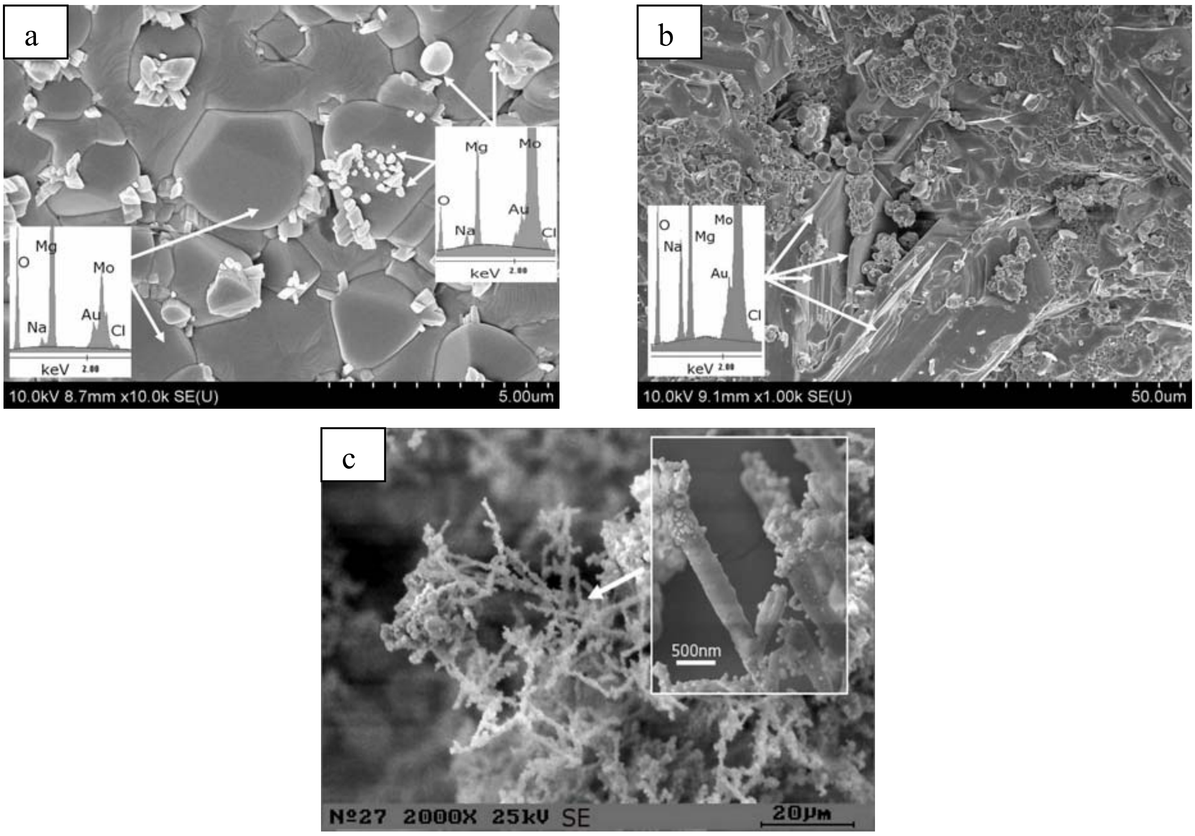

Fig.1 Microstructure of products obtained from the mixtures: MoO_3+3Mg+2NaCl (a), MoO_3+3Mg+4NaCl (b) and whiskers formed at product for the MoO_3+3Mg+2NaCl mixture (c)

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P-D19

DISPERSION HARDENING OF CERMET Al_2O_3/TiC WITH IRON-TITANIUM BOND

Kobyakov V.P., Novikov I.V., Sichinava M.A., Ratnikov V.I., Bokov A.V., Sachkova N.V.

Institute of Structural Macrokinetics and Materials Science
Chernogolovka, Institutskaya str., 8, Moscow Region, 143432, Russia.
koba@ism.ac.ru

Previously, it was shown promising for use of materials based on the composition Al_2O_3/TiC as a ceramic matrix for the immobilization of carbon-containing radioactive waste. It pay attention to the high strength of these materials. In this paper we study the fine structure, and also measured the mechanical properties of materials based cermet Al_2O_3/TiC. The main experimental results were obtained using raw powder compacts of stoichiometric composition in accordance with the overall reaction:

$$Fe_2O_3 + 3TiO_2 + 6Al + 3C = 2\ Fe + 3Al_2O_3 + 3TiC.$$

Cylindrical compacts with a diameter of 28 mm, height 35 - 40 mm, weight 45 - 50 g were pressed on a hydraulic press under a load of 80 MPa. When the apparent density of the compacts 1.7 g/cm^3 and the calculated charge density 3.4 g / cm^3, porosity of the initial compacts averaged 50%.

The combustion process in all cases was carried out under atmospheric conditions. Workpiece mounted on a ceramic insulating stand as without shrouding the shell, and when using different kinds of shells. To initiate the combustion of used spark - arc generator GID-01 type, providing a pulse output arc of about 1 kJ / c. Igniter compositions were not used, studied the stoichiometric mixture is ignited immediately.

Results of the study of the microstructure shown in Fig. 1-3 and in Table 1.

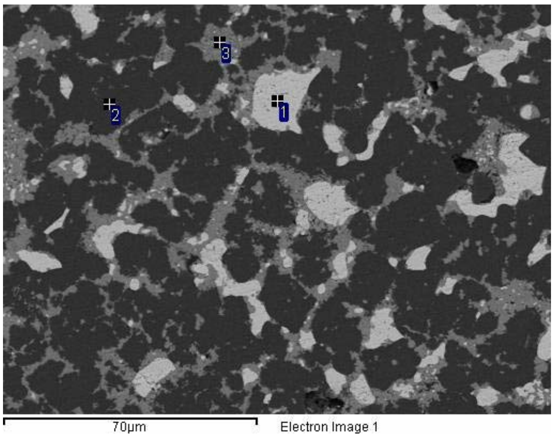

Fig.1.

According to Fig.1 and Table 1 shows that the main components of the structure are: Al_2O_3 (dark grains), the iron-titanium alloy (bright areas), gray highlight TiC. It is seen that the first two components are mutually well-distributed and dispersed carbide selection fill the space between dark and white grains. Previously, focuses on the microstructure of iron-titanium bonds and nanostructured titanium carbide precipitates within a bonds [1]. In this case, we came upon the existence of the fine microstructure in an Al_2O_3 grains. Figure 2 is visible at high magnification the unusual shape of the microstructure - filamentary and ring formation. Transverse size of the filaments 170-250 nm and diameter of the ring structures of 1-2 microns. It is evident that the fine microstructure formed phase TiC, which, as it reinforces the Al_2O_3 grains. This kind of microstructure we have never met.

Table 2 presents the preliminary results of measuring the bending strength and compression strength of the synthesized materials (average porosity of about 2%), which show promise of this research trend.

Table 2.

	σ bend, MPa	σ compr., MPa
Mean:	250	1024

Earlier [1] increased strength cermet Al_2O_3/TiC on iron-titanium bond, resulting in similar circumstances, we attributed to the dispersion hardening of the bonds due to nucleation in bond volume of nanostructured TiC. Based on the data presented above, we can assume that such a high physical and mechanical properties of cermet also due to dispersion hardening of its oxide component.

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P-D20

SHS PRODUCTION OF STRUCTURAL UNITS OF LUNAR REGOLITH SIMULANT

Arvanitis K.[1], Xanthopoulou G.[2], Vekinis G.[2], Zoumpoulakis L.[1], Katsaros T.[3] and Ganetsos T.[4]

[1]Department of Chemical Engineering, National Technical University of Athens, Greece
[2]Institute of Materials Science, NCSR Demokritos, 15310, Agia Paraskevi, Greece
[3]Byzantine Museum, Athens, Greece
[4]Institute of Electronics, Technical Educational Foundation, lamia, Greece
gvekinis@ims.demokritos.gr

Lately there is increased realization that, in order to establish a viable lunar base or another planetary body, we'll have to rely more on locally sourced materials, i.e."In-Situ Resource Utilisation" (ISRU), rather than carry materials from earth, a very costly endeavour.

One area where such an approach is seen as crucial is the development of methods for the utilization of lunar (or Martian etc) regolith (soil) for various structural applications such as construction blocks for protection, especially from dangerous space radiation. Other possible applications of regolith is the construction of large, glassy surfaces which may be used as solar energy traps for electricity and heat generation. Because of the parallel need to keep energy costs to a minimum, the SHS methods appears very well suited for creating such structures in-situ on the moon or other planetary body's surface. The high temperatures possible with SHS, even in the absence of any atmosphere, offers the possibility for producing solid structural blocks and glassy surfaces of low porosity, high reflexion ability, good mechanical properties, with minimum energy and effort.

Earth-based studies therefore require first the development of a simulant regolith material that can be used to test and develop new methods in the lab. Table 1 shows the available knowledge on the constituent minerals of lunar regolith as obtained by the Apollo missions. We have developed a range of lunar regolith simulants based on this information and have used it to study its behaviour under SHS using Al powder as reducer. The concentration of aluminium used varied from 8 – 16 %. Aluminium was used because it may be recycled in-situ from abandoned articles of space missions and is a typical reducer in the SHS exothermic mixtures.

Table 1. Lunar minerals

FELDSPARS	PYROXENES	
Anorthite $CaAl_2Si_2O_8$	Diopside $MgCaSi_2O_6$	Hedenbergarite $FeCaSi_2O_6$
Albite $NaAlSi_3O_8$	Enstatite $Mg_2Si_2O_6$	Ferrosilite $Fe_2Si_2O_6$
K-Feldspar $KAlSi_3O_8$	Wollastonite $Ca_2Si_2O_6$ (not a true pyroxene)	
OLIVINES	**OXIDES**	
Forsterite Mg_2SiO_4	Ilmenite $FeTiO_3$	
Fayalite Fe_2SiO_4	Chromite $FeCr_2O_4$	

The composition of the various lunar regoliths around the moon is not constant, so it was logical to start with each mineral shown in Table 1 separately and produce materials on their basis. It will be very useful for future exploration to have database for each mineral and calculate composition and condition of SH synthesis for any composition of regolith of lunar surface. It is very useful that lunar regolith has fine particle size so it does not need to be ground down. This gives the SHS method an added advantage. SHS was carried out at pre-heating temperatures from 400° C to 1000° C. The first goal was to reduce the SHS temperature to reduce the energy needs on the lunar surface. No other materials were used apart from the regolith simulant (and Al powder).

Most lunar regolith has significant amounts of mineral ilmenite and this was the main starting material we studied at the start of the work. The ilmenite mineral we used was obtained from the Greek island of Milos and has the following composition: $FeTiO_3$, $Fe_2Ti_3O_9$, Fe_2O_3, Fe_3O_4, SiO_2, CaO Al_2O_3 SiO_2. The initial composition for the production of solid bodies using SHS was 89% ilmenite and 11% aluminium. The mixture was preheated at temperatures of 400^{o}C-700^{o}C, and the temperature during combustion was estimated at 1400–1600^{o}C. The velocity of combustion measured varied in the range 0,05 – 0,1 cm/s. The physical and mechanical properties of the produced blocks were determined. The ceramic with final composition a mixture of $FeAl_2Ti_3O_{10}$, a-Fe, a-SiO_2, TiO_2, Fe_2O_3/Al_2O_3 were produced successfully and its characteristics were: porosity of 40 – 50 %, gas permeability 0,1/ m^2, density 2.4-3.0 g/cm^3 and compressive strength 8 – 11 MPa.

Another ore in lunar regolith is chromite and we carried out SHS studies on a chromite-base regolith simulant. Chromite mineral was also obtained from Greece and had an initial composition Mg, Fe, $(CrAl)_2O_4$ and amorphous phase ~ 10%. The composition for the production of SHS blocks was 85% chromite and 15% aluminium. The preheating temperature range was 800 – 1300^o C and the combustion temperature around 1200^{o}C with a velocity of combustion pf about 0,12 – 0,15 cm/s. The final compositions obtained contains $MgFe(Al_{0,75}Cr_{0,75})O_4$ or $MgFe(CrAl)_2O_4$ and ~ 10% of amorphous phase. Porosity of the SHS product was about 30 – 36%, gas permeability 0,010 – 0,013 m^2, density 3.0-3.5 g/cm^3 . It was found that with the rising preheating temperature, the density is increasing and reaches 3,5 g/cm^3. Finally the surface area varies from 0,02 to 0,05 m^2 and the compressive strength of 10 – 15 MPa.

The microstructure and morphology of the SHS products were examined by SEM/EDX (figure 1) and they show crystallites of mixed oxides of Fe, Al, Ti and O. It was clear that SHS enabled the reaction of aluminium with ilmenite even at relatively low pre-heating temperatures. To reduce the pre-heating temperature even further, olivine (also found in the lunar regolith samples) was used as additive enhancing eutectic reactions offering stronger materials due to partial melting and allowing automated shaping in a mould.

The work is continuing but in general it has shown conclusively that SHS can be used to produce blocks that are appropriate as structural units. Both chromite and ilmenite (with or without olevine) appear to be usable to produce lunar structural blocks by SHS.

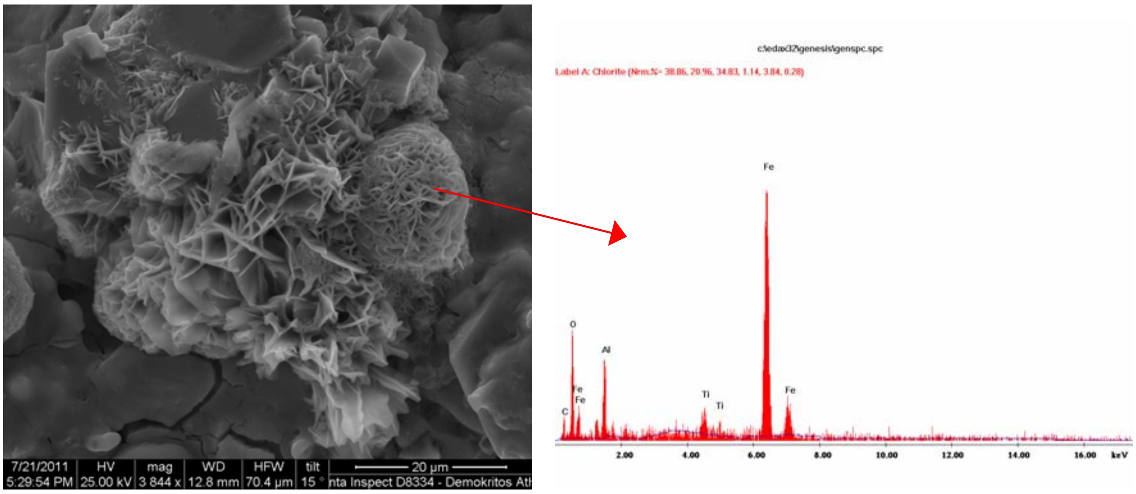

Fig.1 SEM /EDX photograph of ilmenite-Al SHS ceramic product

P-D21

SHS OF COMPLEX OXIDES

Kuznetsov M.V.

Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences (ISMAN), Institutskaya Street 8, Chernogolovka, Moscow region, 142432 Russia
maxim1968@mail.ru

SHS of complex oxide materials (COM), as an independent and perspective direction in materials and combustion science were formed in earlier seventies. The modern state and future perspectives of the problem are discussed. The biggest success in SHS of complex oxides were to date achieved in elaboration of pure and doped HTSC (all known yttrium, bismuth, thallium and rare-earth based compounds), all types of ferrites (including continued technologies of its producing), refractory materials, pigments, segnetoelectrics etc.

By using SHS method and chemical products market development, the most perspective directions were chosenб such as SOFC structures and other functional perovskite-like compounds, including alkaline and alkaline-earth substituted $LnMO_3$ compounds; components of rechargeable lithium batteries and its analogs; functional ceramics (including magnetic materials synthesis under conditions of external physico-chemical affects); useful chemical products producing by using natural ore resources, industrial wastes and dumps; radioactive and high-active wastes (RAW and HAW) neutralization etc.

The new experimental methods for investigations of complex oxides phase formation during SHS was established. The first experiments using of penetrating synchrotron radiation and energy dispersive detectors for the different classes of complex inorganic materials was carried out during last years in ESRF (Grenoble, France) and Daresbury (UK). A new and very sensitive thermal imaging method (Thermal Imaging Technique (TIT)) is based on the continuous registration of the whole combustion process by using a highly-sensitive IR-camera and software developed by MIKRON Instrument Co. (USA) was also used for precise registration of the combustion parameters during SHS COM. SHS were performed using different types of pure and doped COMs in pellet and powder form in a range of magnetic field strengths up to 20 T and dc electric field up to ±220 kV/m. Constant magnetic field was applied during the reaction, supplied either by a permanent magnet (1.1 T) or by an electromagnet (up to 20 T) and dc electric field were applied to along a direction of the combustion wave front propagation. The combine process of SHS and Selective Laser Sintering (SLS) of 3D articles for the different powdered compositions was realized with the optimal parameters of a laser influence, under which the SHS reaction carries under control regime.

During SHS-process of COM, intermediate reaction products arise in an ionic form. In condensed media, SHS processes involve an electrochemical stage, which can be considered to be a concentration cell that moves together with the combustion wave front and result in origin of EMF of combustion. As a result of that, the full ion-diagrams of combustion processes has been constructed for many complex oxide systems with the elements of I-VIII groups of Periodic Table. It is opening new horizons for the alternative diagnostics of heterogeneous combustion processes at nano-level. Besides that, as a result of our experiments, preconditions for the new directions in combustion science has been formed such as ionic chemistry of heterogeneous combustion and dynamic iconography of heterogeneous combustion processes were established. External electrical and magnetic fields modify combustion parameters of the SHS systems (including EMF) and may be, via the transformation and displacement of the concentration cell, relative to zone of maximal heat evolution by virtue of changes in the concentration of active ions and the heat loss. It was experimentally established that in the processes of heterogeneous combustion of the reacting powdered oxide systems, the maximum EMF of combustion for the whole process may exceed 2.5 V. A continuous heterogeneous combustion process in which feed material is continually added may provide the possibility of a permanent EMF source. This could provide both an external power supply at the same time as forming new materials for use in industry.

Last tendencies in materials science are leading to the formation of new directions in SHS of complex functionalized materials for different applications. The main interest of researchers is focused on the following groups of them: multifunctional materials such as multiferroics, magnetielectrics, ferromagnetic semicinductors as well as mixed composite ceramics; luminescence and optical materials; gas-sensing materials for detection of potentially toxic, explosive and other hazard substances.

P-D22

FRICTIONAL PROPERTIES AGAINST Cu of Ti-Al-C PREPARED BY COMBUSTION SYNTHESIS AND SIMULTANEOUS DENSIFICATION

Li C., He X., Li Y., Wu M.

Center for Composite Materials, Harbin Institute of Technology, Harbin, 150001, China
liye-147@163.com

Titanium-Aluminum-Carbide (Ti_3AlC_2) is one of the most interesting new layered materials because it combines many of the merits of both ceramics and metals. Like ceramics, it displays high mechanical properties. Like metals, it has good electrical conductivities and excellent machinability. The unique advantages make it a promising material that will be widely used in many industrial fields. Up to now, the bulk Ti_3AlC_2 has been synthesized via solid-liquid reaction/in-situ hot pressing, pressureless sintering, spark plasma sintering, hot isostatic pressing or hot pressing. However, the bulk Ti_3AlC_2 material prepared by different methods has different properties.

The combustion synthesis and simultaneous densification (combustion synthesis/densification) process takes use of the extreme heat generated by the exothermic reaction during the formation of some materials. The main advantages of this technique include low energy requirement, the relative simplicity of the process and equipment, higher purity of products and low cost. A Φ150mm Ti_3AlC_2 bulk material prepared by combustion synthesis/densification method was obtained by our research group. The purpose of this paper is to report on compressive damage mechanism of the bulk Ti_3AlC_2 prepared by combustion synthesis/densification method.

In this work, frictional properties against Cu of Ti_3AlC_2 were measured by ball-disk method. The surfaces of samples after tests were examined by SEM for understanding the frictional mechanism of Ti_3AlC_2. Results showed Ti_3AlC_2 prepared by combustion synthesis/densification method diplayed excellent frictional properties. It was found that the friction coefficient of Ti_3AlC_2 was lower than 0.2, and dependent on the presence of a frictional film on the frictional surface. Due to the existence of this film, the friction coefficient decreased gradually with the extension of running time.

P-D23

INVESTIGATION OF SHS α-Si_3N_4, α-, β-SiAlON SINTERING AND THEIR PHASE FORMATION REGULARITIES

Loryan V.E.*[1], Borovinskaya I.P.[1], Titov S.G.[2]

[1]ISMAN, 8 Institutskaya ul., Chernogolovka, Moscow region, 142432 Russia
[2]VNIIMETMASH, 8-a Ryazansky prt., Moscow, Russia.
*loryan@ism.ac.ru

The terms of sintering of SHS powders of α-silicon nitride and α`- and β`-SiAlON-s were studied. SHS-SiAlON-s and SHS- polytypoids 15R and 21R were used as sintering additives as well as oxides. Strength characteristics of the sintered samples were measured. Characteristics of initial powders and compositions of some mixtures for sintering are given in Tables 1, 2. The powders were modified by the method of chemical dispersion [1]. They were sintered at T=1650 - 1800ºC and P_N= 2 MPa during 1 h. Additional HIP was applied at T=1750ºC and P_N=100 MPa during 1 h.

Table 1.
Characteristics of initial powders

No.	SHS Powders	Chemical composition, mass %			
		Si_{free}	N	O	Fe
1.	α-Si_3N_4 (79%)	0.23	35.3	0.5	0.67
2.	β`-SiAlON (Z=4)	0.7	-	-	0.3
3.	15R	0.3	-	-	0.5
4.	21R	0.3	-	-	0.5
5.	α-Si_3N_4 (82%) modified	0.21	35.6	0.5	0.1
6.	β`-SiAlON (Z=4) modified	0.5	-	-	0.3

Table 2.
Mixture compositions and characteristics

No.	Content, mass %			Average diameter, µm
	α-Si_3N_4	SiAlON (Z=4)	Y_2O_3	
1.	-	100	-	3.5 - 4
2.	-	95	5	
3.	70	25	5	0.9 – 1.0
4.	80	15	5	
5.	85	10	5	
6.	90	5	5	
7*.	85	10	5	
8*.	80	15	5	

*Modified powders $S_{sp.}$ ~ 10 m^2/g

The investigation proves:

1. SiAlON (z=4) obtained by the SHS method can be sintered unlike SiAlON obtained by the method of powder metallurgy. After sintering at 1800ºC its density is 2.59 g/cm^3.
2. Introduction of 5 % yttrium oxide allows sintering SiAlON at T= 1750ºC up to its density close to the theoretical value.

3. Additional introduction of SiAlON or polytypoids 15R, 21R to the powder mixtures of α-Si_3N_4 + 5% Y_2O_3 increases drastically the material sinterability and allows obtaining samples with the density higher than 95 % of the theoretical value after sintering at 1750ºC, the quantity of SiAlON additives being 5 mass %.
4. Additional HIP (1750ºC, 100 MPa, 1 h) increases the sample density and strength ($\sigma_{bend.}$=650 MPa, ρ=3.2 g/cm^3).
5. With an increase in SiAlON content in the initial mixture the sample strength has its maximum at SiAlON content (z=4) being 10 - 15 %.
6. Additional modification of SHS silicon nitride and SiAlON powders by the method of chemical dispersion influences significantly the strength characteristics of the samples ($\sigma_{bend.}$=620 MPa, ρ=3.1 g/cm^3).
7. α→β phase transition of silicon nitride in the case of SiAlON and yttrium oxide introduction as sintering additives is completed at T=1650ºC – 1750ºC during 1 hour.
8. At sintering of α`-SiAlON an increase in the quantity of $Al_2O_3$ sintering additive up to 15 % results in practically absolute α`→β` transition.

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P-D24

THE PECULIARITIES OF COMBUSTION AND PHASE FORMATION IN THE COURSE OF SHS OF MECHANOACTIVATED MIXTURES QUARTZ-CALCITE

Mofa N.N.*, Aknazarov S.Kh., Sadykov B.S.

Combustion Problems Institute, Bogenbay Batyr str., 172, Almaty, Kazakhstan
*Nina.Mofa@kaznu.kz

SH-synthesis is a unique technological process of creating composition materials of different purposes, in particular, refractories and heat insulators. The specific character of the properties of SHS-composites is determined by their phase composition and structural peculiarities formed according to the regularities and kinetic parameters of combustion of multicomponent systems. Varying the initial composition and state of reagents one may regulate the process of combustion and form a new material the properties of which are determined by the synthesis products quantitatively and qualitatively. A preliminary mechanochemical treatment (activation and modification) of the charge material components is an effective method of influencing the process of the further technological combustion [1].

A quartz-calcite system is one of the universal ones when producing inorganic materials of a wide range of purposes which, first of all, develop an enhanced thermal, chemical and mechanical stability. We studied the process of combustion and phase formation in the course of SH-synthesis of a quartz-calcite mixture with aluminium in a stoichiometric ratio to each of the components. Quartz and calcite were subjected to mechanochemical treatment (MCT) depending on time and the ratio of the mass powder to the mass of balls (M_p/M_b) and with the use of different carbon- and nitrogen containing modifiers (polyvinyl alcohol, succinic acid, ammonium hydroxide, carbamide and others). Activation and modification of the surface of charge mixture particles result in the change of kinetic parameters of the technological process directed to formation of the structural components of SHS-composites.

Temperature profiles of the system combustion were studied. The presence of calcite in the mixture results in the increase of the induction period and the decrease in combustion rate. This is due to, first of all, decomposition of calcium carbonate and formation of calcium and carbon oxide. The gaseous component can act as a reducer for oxides or, at least, be a medium preventing oxidation of aluminium. Besides, there occurs multiple phase formation in the end of combustion process. The induction period significantly decreases after preliminary MCT of quartz and calcite. The longer is the treatment of the mixture, the quicker is combustion of the sample and the temperature of combustion at the final stage of synthesis considerably decreases.When using preactivated components in the charge mixture (quartz + calcite) in the presence of modifiers, in particular succinic acid, the rate and temperature of combustion increase, especially with the increase in the period of treatment.

In the products of combustion of a non-activated system containing quartz and calcite in a stoihiometric ratio to aluminium there was detected helenite – $Ca_2Al(AlSiO_7)$. After activation of minerals, in the reaction products there appears anorthite – $Ca(Al_2Si_2O_8)$ as well as compound $CaAl_4O_7$, the amount of which is determined by MCT conditions. The presence of different modifiers in the charge increases the rate and temperature of the process causing the formation of different forms of wollastonite the amount of which is determined by the ratio of quartz and calcite contents as well as the type of additive-activator. The greatest amount of wollastonite phase (up to 36%) is formed at the ratio $CaCO_3/SiO_2=50/50$ and in the presence of carbamide. In this case, in the reaction products there were also defected silicon carbide and aluminium nitride, the amount of the latter increases with the increase of carbamide content or when using the mixture of succinic acid with ammonia as an additive. The phase composition of synthesis products determines the properties and exploitation qualities of the material being obtained. MCT of the mixture (SiO_2+CaCO_3) in the presence of modifiers contribute to a considerable change (by an order and more) of strength characteristics of the material being obtained. In all cases, the increase in the strength corresponds to formation of wollastonite, anorthite, aluminium nitride and silicon carbide.

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P-D25

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF A SUPEROXIDE COMPOUND IN NA-FE-Y-O SYSTEM

Morozov Yu.G.*[1], Kuznetsov M.V.[1], Ignat'eva T.I.[1]

[1]Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences (ISMAN), Institutskaya Street 8, Chernogolovka, Moscow region 142432 Russia
* morozov@ism.ac.ru

For the first time a chemical compound in Na-Y-Fe-O system was synthesized. The compound was obtained from powder intermixture of sodium peroxide, iron and yttrium oxide. All combustion processes occurred in a stationary mode of self-propagation with the maximal combustion temperatures ranged from 750 up to 1200 °C and burning velocities – from 1 up to 4 mm/s. By using the dynamic ionography method the characteristic peaks which be attributed to electrical responses from ionic streams of cations of Fe^{3+}, Ye^{3+}, Na^{+}, O^{2-} and their combinations are discovered [1]. The influence of the initial components contents on combustion limits of the mixtures and final products composition was investigated. SEM, EDX, XRD, chemical analysis and vibrating sample magnetometry for studies of microstructure, phase- and chemical composition and magnetic properties of the synthesized materials were used. It was discovered that the single-phase product of $NaFeYO_{7+x}$ composition was obtained with an excess amount of the sodium in the initial mixture. To stabilize the product the water-washing procedure immediately after synthesis was used. The post-synthesized material has a cubic crystal structure with parameter close to one of lattice of the sodium yttrate $NaYO_2$, very weak magnetic properties and superstoichiometric oxygen content. In open air this superoxide is slight-hydrophobic and keeps its thermal stability up to temperature in 450 K. The synthesized product is a new inorganic superoxide and has the good technological perspective as solid-state oxygen-container material.

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P-D26

RARE-EARTH DOPED SILICON NITRIDE BLUE-EMITTING PHOSPHOR

Nersisyan H.H.*, Won H.I., Won C.W.

[1] Rapidly Solidified Materials Research Center (RASOM), Chungnam National University,
220 Kung-Dong, Yuseong-gu, Daejeon, 305-764, Republic of Korea
* nersisyan_hayk@cnu.ac.kr

A blue-emitting phosphor of $SrSi_6N_8:Eu^{2+}$ composition was synthesized by a modified combustion technique. The influence of Eu^{2+} concentration on the luminescence properties of $SrSi_6N_8:Eu^{2+}$ has been investigated. $SrSi_6N_8:Eu^{2+}$ phosphor shows blue-emission with maxima from 440 to 450 nm depending on concentration of europium. $SrSi_6N_8:Eu^{2+}$ demonstrates to be promising blue-emitting phosphor for electronic applications.

The structure of strontium silicon nitride ($SrSi_6N_8$) single crystals was first shown in [1]. It was reported that the framework of $SrSi_6N_8$ contains SiN_4 tetrahedrons and direct Si-Si bonds in N_3Si-SiN_3. In $SrSi_6N_8$ host lattice, Sr^{2+} ions are tenfold coordinated to N^{3-} anions (versus sixfold coordination of in $M_2Si_5N_8$ (M=Ca, Sr, and Ba), sevenfold coordination in Ca-α-SiAlON) at distances of 2.69-3.16 A [2]. Recently Shioi et al. [3] prepared $SrSi_6N_8:Eu^{2+}$ phosphor samples from α-Si_3N_4, $SrSi_2$ and Eu_2O_3 by calcinations of powder mixture at 1900 ^{o}C under 0.9 MPa nitrogen pressure.

In this study powder samples of $SrSi_6N_8:Eu^{2+}$, with europium concentration varying in the range of 1-5 at% with respect to strontium, were prepared from an exothermic mixture containing strontium salt, silicon, silicon nitride and europium oxide. The combustion temperature recorded by W/Re thermocouples was 1900-2000 ^{o}C, and X-ray powder diffraction performed on the resulting powder confirmed that this process led to the formation of $SrSi_6N_8$, but the sample contained small amounts of secondary phases, such as $Sr_2Si_5N_8$ and Si_3N_4. $SrSi_6N_8$ powder has a grey-white color as shown in Fig. 1a. The morphology of powder shown in Fig. 1b demonstrate that it is consisting of well-developed ***crystalline*** shape particles with ***average size*** about 25-100 μm.

This phosphor shows the wide excitation spectrum covering from 250 to 450 nm, and emits pure-blue light at 450 nm. The intense blue emission spectrum upon UV or near-UV excitation consists of a single broad band with a maximum wavelength from 440 to 450 nm depending on Eu^{2+} concentration. This means that $SrSi_6N_8:Eu^{2+}$ phosphor hold a promise to be a good blue phosphor candidate for creating white-light when combined with a UV-LED and other green and red phosphors.

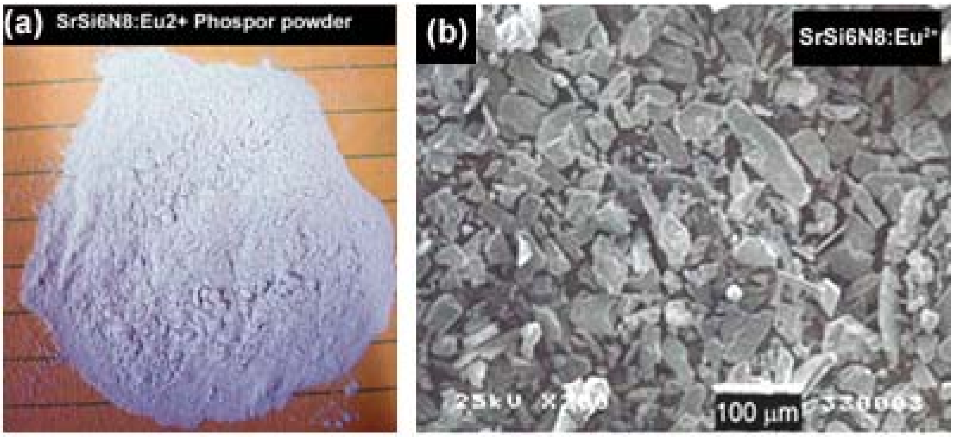

Fig. 1. (a) $SrSi_6N_8:Eu^{2+}$ phosphor powder, and (b) SEM microstructure of as-prepared phosphor particles.

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P-D27

OBTAINING OF RADIATION RESISTANT MATERIALS BY SHS

Oniashvili G.S.*, Aslamazashvili Z.G., Zakharov G.V., Chikhradze M.N.

F. Tavadze Institute of Metallurgy and Materials Science, 15Kazbegi str., Tbilisi 0186, Georgia
* oniash@gtu.ge

Production of materials containing boron isotope ^{10}B is currently restrained because of its high production cost, complicated technology and considerably low quality of the end product.

Preliminary study of this task has shown that using of starting materials containing boron isotope ^{10}B provides production of multifunctional material, including nanostructure, radiation-resistant, metal-ceramic materials with high resistance to impact blow, and fabrication of components using a Self-Propagating High-Temperature Synthesis (SHS). This means the synthesis of compounds (or materials) in a wave of chemical reaction (combustion) that propagates over starting reactive mixture owing to layer-by-layer heat transfer, so that high technological and economic efficiencies are intrinsic to this (SHS) method. Intensive heat generation during chemical reaction between the initial ingredients, instead of heating from outside source, provides production of the material and the end product in one technological cycle, possessing a desired shape, dimensions, properties and microstructure. The method is considerably low cost and environmentally safe in comparison with the conventional technologies.

At present fabrication and application of ^{10}B containing materials are restricted due to the difficult technologies of their production and high cost price. In order to obtain such materials we use SHS technology.

The main innovation in the work is based on the technological method: to obtain low cost priced materials and product, which contain boron isotope ^{10}B.

We have developed four different technologies to obtain Boron containing materials:

- SHS technology in the high pressure reactor
- SHS technology of moulding in the field of centrifugal forces
- SHS -compaction in combustion and Thermal explosion mode
- SHS technology under atmospheric conditions

After applying each technological direction we obtain different type of materials and product. In particular, powders, moulds, compacts (among them gradient nanostructure), also porous and nonporous composite materials, containing ^{10}B.

The names of the product obtained by those 4 technologies are listed below:

1. A)Powder of boron carbide B_4C B) granules (d<5mm) of Ferro boron (FeB)
2. A) FeB (60%). FeB_2(40%); B) FeB (40%). FeB_2(60%);
   C) $Mg_{2,99}Ni_{7,52}B_6$ D) VB_2;CrB;CrB_2
3. A) TiBx; B) TiC-TiBx; TiAl-TiBx; Ti_3Al-TiBx. Where x=0,4-2,0
4. CrB_2-Al_2O_3

The application of the above SHS technology, using the high-pressure reactor, ensures 90% extraction rate of boron after chemical-thermal treatment of the end product (KBF_4 is used as an initial raw material). In the process of ligature production in the system Fe-B and Ni-B, which are used for alloying of special steels, the end product does not contain any ingot- or edge-to-center segregation, and energy consumption is minimal. In addition, a by-product of the process, KF, is used for production of KBF_4. While using the SHS technology of compacting in the modes of burning, unique nonporous bulk materials and functionally graded boron-containing materials are obtained. This technology ensures production of bulk metal-ceramic materials resistant to impact blow, so that the loss of boron in this technology is less than 1%. The SHS technology under atmospheric conditions provides production of porous, heat-resistant composites. The peculiarities of the suggested technology allow varying the gas permeability of the material from 400 units to 0. Fabrication of components with the shape of cylinder, barrel, cap and plate is possible, and loss of boron is less than 1%.

The advantage of the proposed technology is a possibility of production of boron-containing, multifunctional (including nanostructure), radiation-resistant materials and components made of them, resistant to impact blow. The advantages are also: reduction of loss, increase of boron extraction rate, and fabrication of material and the end product with the specified shape, dimensions, properties and microstructure in a single technological cycle.

The produced materials will be relevant to nuclear reactor's requirements dealing with radiation shielding, and to space technologies dealing with radiation- and meteorite protection.

P-D28

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF TANTALUM POWDER

Orlov V.M.*, Kryzhanov M.V.

A RAS institution, I.V.Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, KSC RAS, Apatity, Academgorodok 26a, 184209, Russia
*orlov@chemy.kolasc.net.ru

Tantalum powders with a large specific surface area can be effectively produced by reducing tantalum pentoxide by magnesium vapors [1].
The disadvantage to this method is its long duration, since the vapors take time to penetrate into the pentoxide layer. The reduction of pentoxide mixture with magnesium has the nature of an explosion, because at the reaction temperature of 1700 - 2000 °C, the pressure of magnesium vapors is 3.0 - 6.5 MPa [2]. An alternative solution may become magnesium-thermal reduction of Ta_2O_5 in a self-propagating high-temperature synthesis regime [3, 4]. The authors have investigated the interaction in Ta_2O_5+5Mg+kA systems, where A is MgO or NaCl, playing the function of heat ballast decreasing the burning temperature at an argon pressure of 0.5 MPa [3]. In work [4], the reduction in Ta_2O_5-Mg system was performed at - 2.5 MPa. Increased pressure has made it possible to raise the magnesium boiling temperature and decreasing the quantity of Mg lost on evaporation. It was of interest to study the parameters of Ta_2O_5-Mg and Ta_2O_5-Mg-NaCl systems burning in argon atmosphere under normal pressure (0.1 MPa).

Thermodynamic studies of the systems were carried out at an ASTRA software complex in the temperature interval of 27-2727 °C. To establish tantalates formation, their standard formation enthalpy ΔH^0_{298} (kJoule/mole) and entropy S^0_{298} (Joule/mole K) were determined. They were for $MgTa_2O_6$ -2650 and 168; $Mg_3Ta_2O_8$ -3853 and 222; $Mg_4Ta_2O_9$ -4455 and 284; $Mg_5Ta_4O_{15}$ -7105 and 418, respectively [5]. In our case, the reaction adiabatic temperature for the Ta_2O_5-Mg-Ar system was found to be 2317 °C; and it was independent of the initial reagents temperature. At excess reducer and sodium chloride addition, the reaction equilibrium temperature is lower. The adiabatic temperature can be decreasing below the magnesium boiling temperature (1107 °C) either via a magnesium excess of 75% of the stoichiometric value, or by adding 7 moles of NaCl per one mole of Ta_2O_5. Analysis of the calculated composition of resulting products has revealed the absence of magnesium tantalates in it.

The initial mixture of tantalum pentoxide and magnesium (and sodium chloride) in required proportions was compacted into pellets of 20 mm in diameter, about 20 mm high, and density of 29-35%. Combustion was initiated with a tantalum wire spiral pressed against the pellet face, to which an 8V voltage was applied. The temperature was measured at the pellet's faces and centre. The reduction products were treated with a 10% hydrochloric acid solution.

It has been determined that at varying the pellets density from 29 % to 35 %, the combustion rate diminishes from 7.2 to 3.9 mm/s. Raising the charge temperature from 20 to 400 °C, increased the combustion rate from 3.9 to 13.2 mm/s. Increasing the magnesium excess from 10% to 50% of its stoichiometric quantity has brought the combustion temperature down from 1705 °C to 1125, the combustion rate grows out in this case from 4.4 mm/s to 5.6 mm/s. The latter is the consequence of increasing thermal conduction of the charge. The combustion rate essentially depends on the reagent size. For the reaction of tantalum pentoxide reduction with a specific surface of 2.2 and 5.6 m^2/g, the combustion rate was 4.1 and 6.1 mm/s, respectively, when using a magnesium powder with particle sizes of 0-0.63 mm. For finer dispersed magnesium with particle sizes of 0.125-0.2 mm, the combustion rate increased to 5.2 and 8.4 mm/s, respectively. The surface of resulting powders, practically unaffected by the reduction conditions, was 1 m^2/g. The powder after the Ta_2O_5-Mg system reduction contained 30% of magnesium tantalate $Mg_4Ta_2O_9$, which was removed by additional heating of the powder in magnesium vapors at 800 °C. The surface of deoxidized powders was 10-11 m^2/g. In the case of charge reduction with 2 moles of NaCl per one Ta_2O_5 mole, the powder did not contain any magnesium tantalate.

It can be assumed that the divergence of the SHS synthesis parameters for tantalum powders, found in this work, with those reported in [3, 4] can be accounted for by the difference in charge preparation and higher argon pressures used in these works.

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P-D29

GROWTH OF SINGLE CRYSTAL TIB$_2$ AND TIC BY PLASMA-ARC MELTING OF SHS PRODUCTS

Ponomarev M.A.

Institute of Structural Macrokinetics RAS, Chernogolovka, Moscow region, 142432 Russia
map@ism.ac.ru

SHS raw material, cleaned from impurities as a result of combustions is suiting for receiving single crystals carbide and boride of metals IV-VI groups with high purity by plasma-arc melting [1,2]. Growing modes were researched in experiment with stabilization parameters of process. They were used systems to stabilizations of the temperature melt (SSTM), system to stabilizations level melt (SSLM) and system of modulation of power (SM).

On fig. 1 are brought data competitive growing of crystal blocks TiB_2 and TiC from polycrystalline SHS-substrates under single crystal growth from SHS-rods and powdered SHS-material in the form of curves $\delta_m=\delta_m(l_m)$, here δ_m - a non-dimensional value of crystalline block of maximum size ("leading" crystalline block), l_m - a distance from begining ingot to given cross-section, ν - a frequency of feeding, v_g - a velocity of growing, m_p - feeding portions. At achievement l_m* "leading" crystalline block fills all cross-section of ingot.. That is possible to select three main stages: 1 - at the beginning initially quick increase the size "leading" block; 2 - at reduction of the number grains and deceleration of the growing "leading" block; 3 - quick increase the size "leading" crystalline block up to diameter of the ingot. The competitive growing of blocks on first stage is characterized by means angle of slopping tangent to curve in point, corresponding to beginning of the ingot: $\varphi_m{}^0$ =arctg(d_m/l_m).

In table 1 and 2 are brought values $l_m{}^*$, $\varphi_m{}^0$, got under single crystal growth TiB_2 from rods and powder under vg=0,35-0,5mm/min. From data on fig.1 and in tabl.1-2, possible follows the conclusion - an using the system SSTM and SSLM positively influences upon growing procedure that reveals itself, in the form of larger values angles $\varphi_m{}^0$ and small length polycrystalline part l_m*. On fig.1,a, curve 4 and fig.1,c, curve 3 show the competitive growing crystalline block under crystal growth TiB_2 and TiC under SSTM. The length polycrystalline part record low: for TiB_2 - l_m*= 17мм, for TiC - l_m*= 18мм.

Under nondeep modulation Wm/W<15% (W - a main power of the arc, W_m -an maximum modulated reduction of power) growth of "leading" block meets difficulties - at length ingot 70-100мм monocrystalline structure is not formed. With increase W_m/W before 20% length polycrystalline area in TiB_2 and TiC decreases to acceptable values (30-35mm).

The growing of crystal TiB_2 occurred toward, close to $< 10\,\bar{1}\,0 >$. The phase analysis has shown the presence of one phase - TiB_2. The parameters of the elementary cell of the crystalline lattice (the structured type AlB_2) were: a=3,025 Å, c=3,227 Å. Under growth crystal TiC (face-centered cubic lattice) growing occurred toward <100> mainly. The two orders blocks substructure exist in single crystall TiB_2 in planes $\{10\,\bar{1}\,0\}$ - 200-250 μm and 15-60 μm. Exists layers in ingot, appearing as a result lay-by-layer its growing at feeding. Vidmanshtettov structure existed in single crystall TiB_2. Cell-structure of single crystall TiB_2 and TiC are displayed. The Typical size cell for TiB_2 forms - 5-10 μm, for TiC - 4 μm. Density of the dimples of the pickling in single crystall TiB_2 forms from $5\cdot10^5$ to $5\cdot10^6$ cm^{-2}.

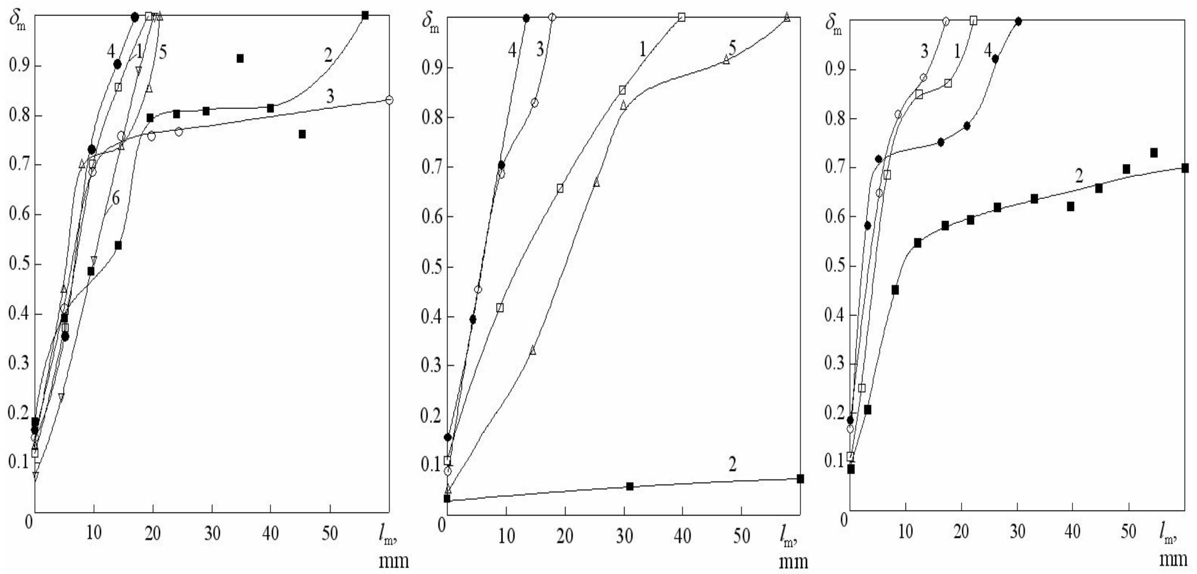

Fig.1. The growing crystals maximum size in ingot TiB_2 from rods (a): 1 - ν=3 min^{-1}, d_c=5,8мм; 2 - ν=15 min^{-1}; 3 - ν=3min^{-1}; 4 – SSTM, ν=3min^{-1}; 5 – SM (ΔW/W=25%), ν=3min^{-1}; 6 - ν=3min^{-1}, d_c=7,7mm; from SHS-powder at ν=20 min^{-1} (b): 1 - v_g=0,5mm/min, m_p=1,8mg,; 2 - v_g=5,5mm/min, mp=9mg, ν=20 min^{-1}; 3 - SSTM (m_p=5mg, ν=20 min^{-1}); 4 - SM (ΔW/W=12%), v_g=0,35mm/min; 5 - SM (ΔW/W=28%), v_g=0,35mm/min . and the growing crystals maximum size in ingot of the carbide of from SHS-rods (c): 1 - ν=3min^{-1}, v_g=0,4mm/min; 2 - ν=8 min^{-1}, v_g=1mm/min; 3 – SSTM, ν=3min^{-1}; 4 - SM (ΔW/W=25%), ν=3min^{-1};

Tab.1. Values φ_m^0 and l_m^* for ingot TiB_2, got under different growing mode from rods.

Mode	SSLM	SSLM	SSLM, SSTM	SSLM, SM (ΔW/W=15%)	SSLM, SM (ΔW/W=25%)
φ_m^0, deg	13	17	13	15	24
l_m^*,mm	20	70	17	>60	35

Tab.2. Values φ_m^0 and l_m^* for ingot TiB_2, got from powder (d=0,5-0,6mm).

Mode	SSLM	SSLM, SSTM	SSLM, SM (ΔW/W=12%)	SSLM и SM (ΔW/W=28%)
φ_m^0, deg	10	29	17	15
l_m^*,mm	40	19	13	58

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P-D30

STRUCTURE FORMATION AT DENSIFICATION OF TITANIUM MONODISPERSED SPHERICAL PARTICLES IN THE MIXTURE WITH BORON

Ponomarev M.A.*, Loryan V.E., Merzhanov A.G.

Institute of Structural Macrokinetics RAS, Chernogolovka, Moscow region, 142432 Russia
*map@ism.ac.ru

The SHS method allows obtaining refractory long-sized items with *l/D* ratio >> 1. Such items are applied widely [1] especially for growing refractory single crystals [2, 3]. The method of consecutive layer-by-layer pressing of small powder portions in long-sized molds is used for obtaining long-sized SHS items [4]. The method allowed discovering the phenomenon of structural ordering in thin layers of powder mixtures [4]. It was also observed at densification of layers of glass spheres [5].

The paper considers the peculiarities of structure formation in the powder mixture of titanium and boron. In model experiments titanium spherical powder of a narrow fraction ~300 µm, black amorphous boron of 0.2 – 6 µm and their mixture Ti+2B were used. Charges of the weight *M*, which can form from one up to six monolayers of titanium particles by the height *H* of the thin layer, were densified. The densification was modeled in a thin layer with a restricted base. Cylindrical molds of 4.3 mm in diameter (D>>H) were used. Impulse densification took place under the action of a punch by the scheme of standard uniaxial compaction, N strikes being made by a dropping load of 684 g in weight from the height of 43 mm.

Dependences of densities of compacted layers for pure boron and titanium powders as well as their mixture were made. Experimental curves were compared with theoretical data on the stacking density of ideal spheres in regular packages [4 – 6]. The dependence of $\rho_0=\rho_0$ (M) for boron is linear at considered M values with a noticeable data scattering (±5 %). The dependence of $\rho_0=\rho_0$ (M) for spherical titanium powder (Fig. 1,a) has some density extremes because of structure formation in the layer at definite values of M. Some density extremes were also observed for the mixture of spherical titanium and boron (Fig. 1,b). The plots of the dependences of $\rho_0=\rho_0$ (M) are curves with alternating growing and decreasing sections with definite maximums and minimums with their coordinates being constant independent on the number of densifying strikes. The intervals of maximum and minimum initiation are stable and close in their values. The observed curves are in accordance with theoretical dependences [4-6]. Tough structure formation from titanium particles in the powder mixture Ti+2B proves the travel of $\rho_0=\rho_0$ (N) curve, where the plots of the structure relative stability to shock loading alternate with the plots of abrupt density change. Such changes are connected with changes in titanium particle packages and transition to more stable state due to the gradual accumulation of the changes in the system. The experimental results prove the conservation of this ordering and therefore, the type of $\rho_0= \rho_0$(M) dependences with increasing *N*.

This work was supported by the Russian Foundation for Basic Research (RFBR) (Grant No. 11-03-00572-a).

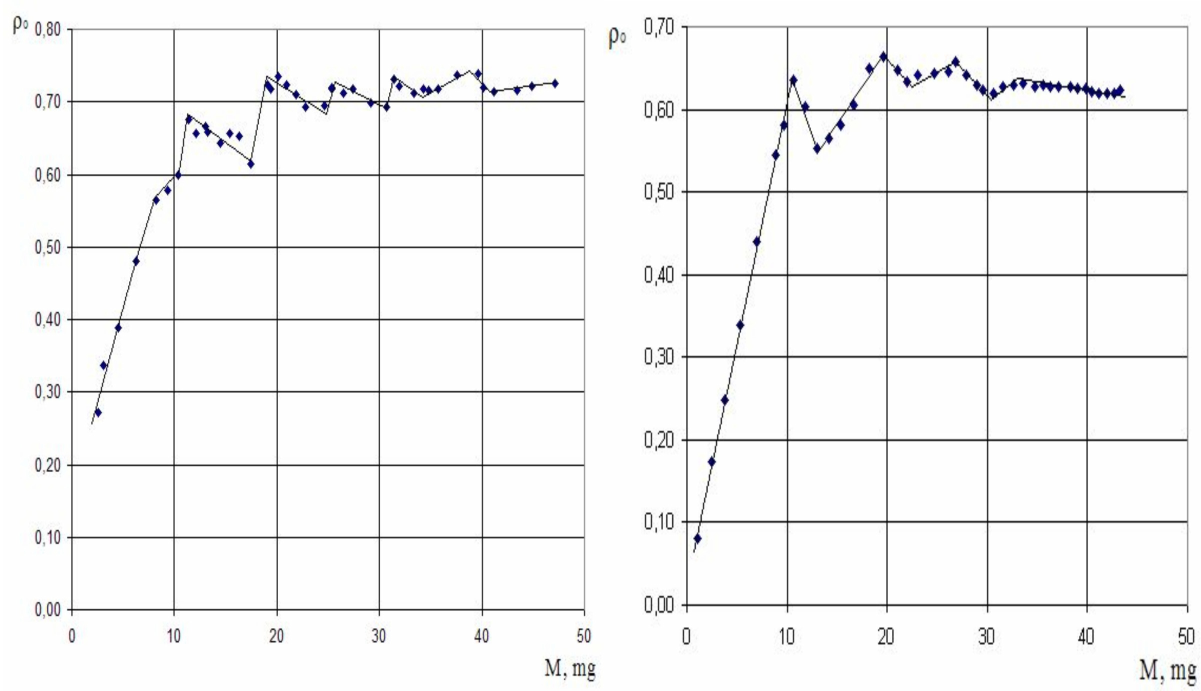

Fig.1. Dependence of relative density layer on loading weight *M* of titanium powder (a), of mixture of spherical titanium and boron (b).

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P-D31

DEHYDRATED TITANIUM POWDER: PROPERTIES AND USE IN SHS-MATERIALS

Prokudina V.K.*, Ratnikov V.I., Borovinskaya I.P., and Sachkova N.V.

RAS Institute of Structural Macrokinetics and Materials Science (ISMAN)
8, Institutskaya str., 142432 Chernogolovka, RUSSIA
* prokud@ism.ac.ru

The presentation concerns the results of investigation of the properties of titanium powders obtained from a titanium sponge hydrated in an SHS reaction [1], crashed and dehydrated (H&D). The synthesis conditions, properties of the H&D titanium powder, and the results of its participation in the design of novel advanced SHS materials are considered. The schemes and samples of the special equipment for SHS hydration and dehydration are regarded and some results of the search for the optimum conditions of the dehydration process are discussed [2]. The H&D titanium powder is compared to the powder analogs produced so far in Russia. It is shown that H&D titanium powder in its chemical composition is more pure than powders produced in Tula and Berezniki. Its dispersity is close to that of Tulskii PTM. The crystal structure is hexagonal with the parameters typical for the titanium of technical purity.

Analysis of the particle surface structure by means of scanning and time-resolved electron microscopies shows that the surface of the H&D titanium powder is different from that of the analogs and can be described as composed of molten and loose fragments. The H&D titanium particles have nano-sized structural elements such as channels, cracks, scabs, and other formations of 100-500 nm in size. Ordered (nanostructured) layers separated by some 70 nm from each other characteristic of hydrides (Fig. 1) as well as conglomerates formed of the nanosize particles (Fig. 2) have been found in the H&D powder structure. The presence of nanostructured elements would assist more effective sintering and provide higher strength of the articles based on the H&D titanium powder. Therefore the results of preliminary testing of the H&D titanium powder when used in the synthesis of the materials synthesized according to the STIM technologies are also considered.

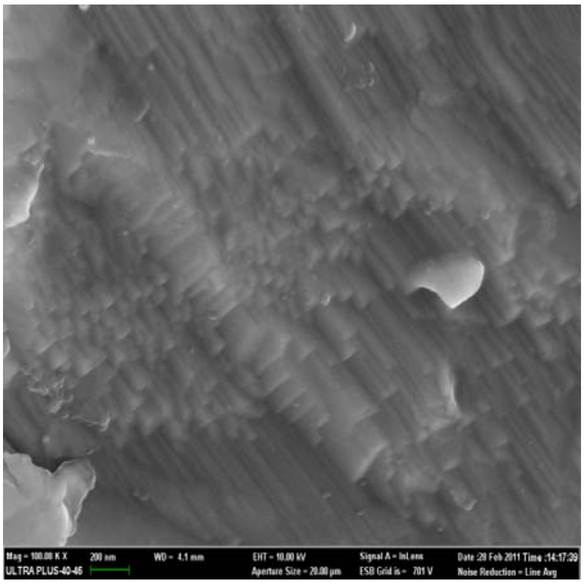

Fig. 1

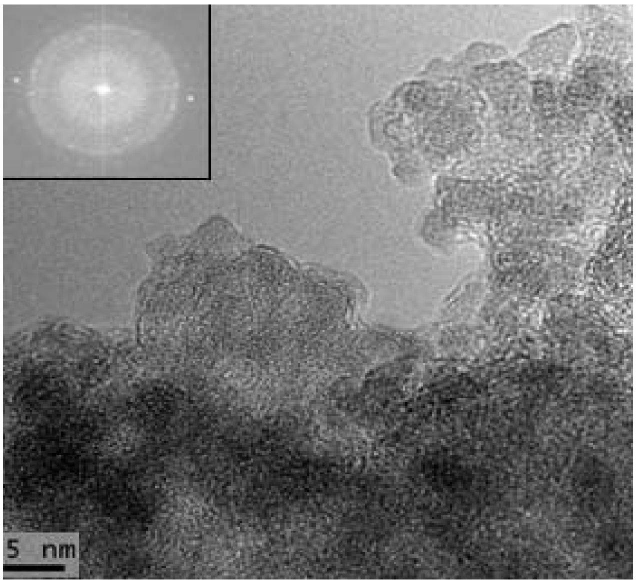

Fig. 2

H&D titanium powder has been used as the main component in the composition of alloys produced by the STIM technology. The method of large-scale SHS compaction has been applied to synthesis of Ti-Al-Nb-Cr alloys for the aerospace techniques as being light, and able to withstand thermal and mechanical impacts. The alloy with H&D titanium exhibits a two time higher resistance to compression as compared to the alloy based on its analog (Tula PTM).

The H&D powder in the Ti-Al-Si_3N_4-C alloy intended for the targets of magnetron spattering used for strengthening various surfaces was tested in the Scientific Educational Center of MISiS-ISMAN. The alloy based on H&D titanium showed a high elasticity modulus like that of the alloy with the Tula PTM powder.

The above preliminary results are the evidence for the challenging horizons of substitution of the conventional titanium powders for that based on H&D entailing 4-5-time reduction of net cost of SHS materials and articles.

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P-D32

COMBUSTION SYNTHESIS OF HIGH POROSITY SiC FOAM

Qiu J.F.[1,2], Li J.T.[1], and Smirnov K.L.*[3]

[1] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
[2] Graduated School of the Chinese Academy of Sciences, Beijing, China
[3] Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia
* kosm@ism.ac.ru

SiC foam has been widely used as diesel particle filters for internal engines, high temperature catalyst carrier and heat insulation materials, due to its unique combination of low thermal-expansion coefficient, good thermal-shock resistance, as well as excellent mechanical and chemical stability at elevated temperature [1-4]. The present work focus on explore fabrication new advanced technique of high porosity SiC foam by associating the gel-casting technique with combustion synthesis. Gel-casting is a new processing route for the fabrication of highly porous ceramics. This method combines the foaming of aqueous slurry of ceramic powder and organic monomers and the in situ polymerization of the foamed slurry.

In this work n-octylamine was used as foaming agent, acrylamide (AM) was used as monomer, difunctional N, N′-methylenebisacrylamide (MBAM) was coupling agent, ammonium persulphate (APS) was initiator, N, N, N′, N′-tetramethylethylenediamine (TEMED) was catalyst, and tetramethylammonium-hydroxide (TMAH) was added into the slurry to control the pH value. The Si/C powder mixtures with a mole ratio of 1:1 were used as raw materials for forming the high porous Si/C foam. The dried Si/C foam was loaded into a porous graphite crucible. The combustion synthesis was carried out under nitrogen pressure 4MPa.

According X-ray diffraction patterns the dominate phase of product was β-SiC and trace amount of Si_2N_2O was also detected. Si_2N_2O may be derived from the reaction between Si_3N_4 and SiO_2. Si_3N_4 is intermediate product in the Si-C-N system [5]. SiO_2 exists on the surface of Si powder and some additional amount of SiO_2 can arise from the chemical reaction of Si powder with oxygen containing polymer binder.

The combustion synthesized SiC foams exhibited high porosity and satisfied strength. The porosity of the SiC foam was from 73 % to 91 %. The strength of the synthetic SiC foam was strongly dependent on its porosity. The maximum flexural strength reached 1,6 Mpa at the porosity level of 73,2 %. When the porosity increased to 91,5 %, the strength decreased to a much lower value 0,1 MPa. It is also noticed that the strength of SiC foam reached 0,8 MPa at the porosity level of 84,3 %, which is high enough for the melt filtering purpose in steel making industry.

SEM images of as-synthesized SiC foam were shown in Fig. 1. It could be observed that the pore size was smaller than 500 μm, and the grain size of SiC particles making up the foam strut ranges from 80 nm to 300 nm. Most of fine grains were tightly bonded to make up the foam struts, which could be attributed to the high sintering degree in the combustion synthesis process. Such dense struts accorded with the relative high strength of the combustion synthesized SiC foam with porosity of 80 %.

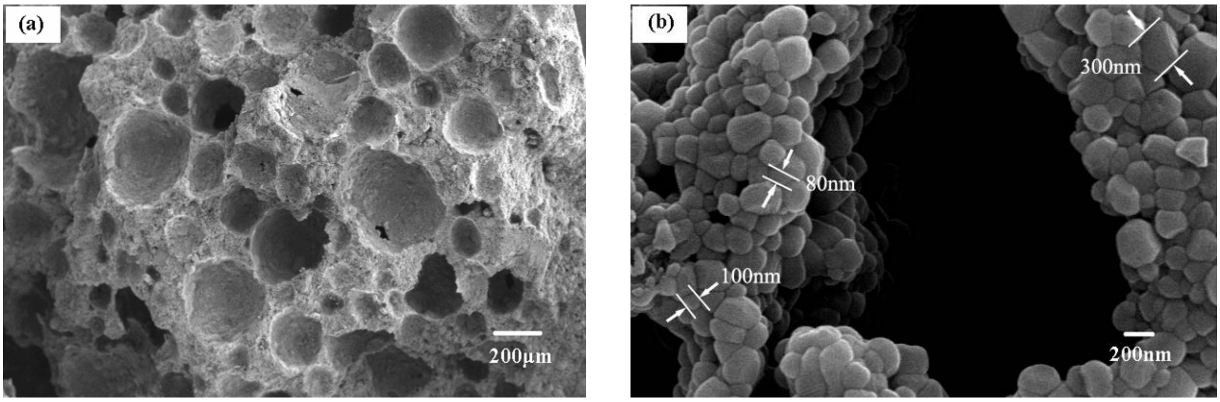

Fig.1. SEM images of the porous structure in the combustion synthesized SiC foam: the fracture surface (a) and the strut of SiC foam (b). Porosity of SiC foam is about 80 %.

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P-D33

COMBUSTION SYNTHESIS OF PZN-10PT NANOPOWDERS

Raigoza C.F.V.[1,3]*, Garcia D.[2], Eiras J.A.[2], Kiminami R.H.G.A.[1]

1 Universidade Federal de São Carlos, Departamento de Engenharia de Materiais – Programa de Pós-Graduação em Ciência e Engenharia de Materiais, São Carlos, SP, Brasil
2 Universidade Federal de São Carlos – Departamento de Física – Grupo de Cerâmicas Ferroelétricas (GCFerr), São Carlos, SP, Brasil
3 Universidad del Cauca- Departamento de Física - Grupo de Ciencia y Tecnología de Materiales Cerámicos - Popayán, Colombia

Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), is a very interesting ferroelectric material because of its excellent dielectric and electrostrictive properties [1]. The solid solution between PZN with rhombohedral symmetry and $PbTiO_3$ (PT) with tetragonal symmetry has a morphotropic phase boundary (MPB) of about 10 mol% PT [2]. Single crystals with a composition near the MPB show extremely large dielectric constants (k~22000) and piezoelectric coefficients (K_p~92%, d_{33} ~1500pC/N) [2]. However, it has been reported that perovskite PZN or 0.90PZN–0.10PT (PZN-10PT) crystals are thermodynamically unstable over a wide range of temperatures (600–1400°C), rapidly yielding a pyrochlore phase in PbO and ZnO as they decompose. It is well known that PZN and PZN-PT (in MPB compositions) ceramics with single-phase perovskite are difficult to obtain by conventional ceramic processes under environmental conditions of pressure and temperature without the application of mechanical pressure. This fact is due to the inherent instability of PZN at different temperatures. In Pb-based complex perovskites, PbO evaporates easily at high temperatures and forms undesirable phases. The presence of an undesirable phase such as cubic pyrochlore, even in small amounts, is detrimental to both the dielectric and piezoelectric properties. Many efforts have focused on eliminating the cubic pyrochlore phase and on stabilizing the perovskite phase in the PZN-PT system. These attempts include various ceramic and chemical processing routes such as oxide mixtures, columbite and sol-gel methods, or even novel ones such as combustion, Pechini, sol-gel and mechanochemical routes. However, the single-crystal growth technique is the only method that has succeeded in producing PZN-PT material with a feasible perovskite phase. Processing routes with polycrystalline forms involve the emergence of pyrochlore phase with or without a minor amount of perovskite phase in the resulting material. This work describes an alternative process to prepare ferroelectric PZN-10PT nanopowders: the combustion synthesis process [4]. The combustion synthesis process is an interesting alternative for its potential advantages: relatively cheap starting reactants (e.g., metal nitrates and carbonates); simple and easily available organic molecules as combustibles; and highly exothermic and self-sustaining reactions. The theory of combustion synthesis is governed by propellant chemistry and thermodynamic calculations. According to both propellant chemistry and thermodynamics, CO_2, H_2O and N_2 are more stable products of the combustion synthesis reaction than other theoretically accepted combinations that might be considered [5]. In this context, carbon and hydrogen are considered reducing elements with valences of +4 and +1, respectively, oxygen is seen as an oxidizer with a valence of -2, and nitrogen is considered to have a valence of 0. In ceramic oxides, metallic cations are considered reducing elements with their corresponding valences (n+ in M^{n+}). The mechanism of the combustion reaction is quite complex, and the parameters that influence the reaction are (a) type of fuel, (b) fuel-to-oxidizer ratio, (c) ignition technique, (d) ignition temperature, (e) type of precursors, and (f) addition of water. This work discuses the influence of the fuel employed in combustion synthesis to obtain single-phase (perovskite) $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ nanopowder with an x=0.10

composition. $Pb(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $(NH_4NbO(C_2O_4)_2)$, and $C_8H_{20}O_4Ti$ were used as cation precursors in the combustion synthesis, and urea, glycine, glycine/urea (50/50 ratio), and tetraformal triazine (TFTA) were used as fuels and two sets of precursors were used with each of these fuels, denoted as set-1 and set-2 precursors and the four different fuels. The results indicated that the highest percentage of perovskite phase in the PZN-10PT nanopowders was obtained by using a mixture of urea/glycine as fuel. When the urea/glycine mixture is added to the solution containing cations precursors, the two fuels form a gel in aqueous solution, this gel contributes not only to obtain homogeneously mixed in the starting material but also aids explosive combustion, leading to a high temperature reaction (~1050^{o}C) within a shorter period of time (~5s), which is a condition that favors the formation of nanopowders PZN-10PT metastable phase. In this work, the method was employed successfully in the preparation of PZN-10PT crystalline nanopowders, proving less time-consuming than other methods and resulting in particles with a narrow size distribution.

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P-D34

β-NiAl COATED γ-TiAl INTERMETALLIC BASED ALLOY BY CONTEMPORARY COMBUSTION SYNTHESIS

Rosa R.*[1], Veronesi P.[1], Colombini E.[1], Leonelli C.[1], Poli G.[1], Casagrande A.[2]

[1] Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università degli Studi di Modena e Reggio Emilia, via Vignolese 905, 41125 Modena, Italy
[2] Dipartimento di Scienza dei Metalli, Elettrochimica e Tecniche Chimiche (SMETEC), Alma Mater Studiorum – Università di Bologna, viale Risorgimento 4, 40136 Bologna, Italy
* roberto.rosa@unimore.it

γ-TiAl based intermetallic alloys are considered ideal candidate materials as potential replacements for heavy steels, Ni- and Co- based superalloys for high temperatures structural applications such as in aerospace, automotive and power generation fields [1,2]. However, γ-TiAl based intermetallic alloys are characterized by poor high temperature oxidation resistance, due to the fact that they do not form long-lasting protective alumina scales.

In order to improve high temperature oxidation behaviour, single phase β-NiAl coated γ-TiAl based alloys were synthesised following a single combustion synthesis (CS) step in a single mode microwaves (MWs) applicator operating at 2.45 GHz under a moderate pressure of 0.8 MPa. Two reactive cylindrical specimens composed respectively of Ti + Al (50:50 at%) and Ni + Al (50:50 at%) powders mixtures were positioned one above the other in the centre of the single mode MW cavity, allowing the load to be exposed to the maximum of the electric field. A disc shaped silicon carbide MW co-absorber was used in some of the experiments conducted, in order to reduce arcing generation phenomena and to enhance the homogeneity of the electric field distribution inside the cavity and on the load itself. The contemporary combustion synthesis of the γ-TiAl based alloy substrate and the phase pure nickel monoaluminide coating was performed for the first time in a single combustion experiment. The high exothermicity of the reactions involved, together with the application of a slight pressure, were enough to synthesise in a self-propagating regime the new intermetallic phases and to promote a good adhesion between the substrate and the coating, due to the formation of complex reaction interface belonging to the system Ni-Al-Ti.

Typical micrograph of the as combustion synthesised complex reaction layer obtained at the interface between NiAl coating and γ-TiAl based alloy substrate is reported in Figure 1.

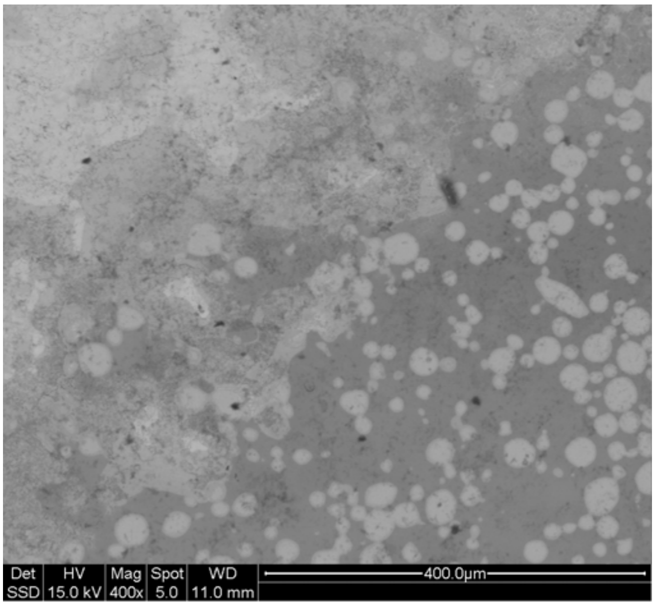

Figure 1. Reaction layer obtained at the interface between NiAl coating (upper left corner) and γ-TiAl intermetallic based alloy substrate (lower corner on the right).

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P-D35

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF THERMOELECTRIC OXIDES

Selig J.[1], Lin S.*[1], Lin H.T.[2], Johnson D.R.[2]

[1] Lamar University, Dan F. Smith Department of Chemical Engineering, P.O. Box 10053, Beaumont, TX 77710, USA
[2] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.
* sidney.lin@lamar.edu

Thermoelectric materials can convert waste heat to electrical energy. One application of these materials is to generate electrical power from automobile exhaust. About two thirds of the energy used in transportation is lost, mainly as waste heat to the environment. Because of the high temperature of the exhaust (~600 ºC), thermoelectric materials that are stable at high temperatures are needed for this application. Also, an ideal thermoelectric material should not contain precious or toxic materials to guarantee wide implementation across the automotive industry. One of the prospective materials for high temperature thermoelectric application is calcium cobaltate (Ca1.24Co1.62O3.86)[1,2].

The performance of thermoelectric materials is characterized by a figure of merit (ZT), which is defined as $ZT\ \alpha^2\sigma/\kappa\ T$, where T is absolute temperature, α is Seebeck coefficient, σ is electrical conductivity, and κ is thermal conductivity. In order to achieve a large ZT value, a material with high Seebeck, high electrical conductivity, and low thermal conductivity is desired. Self-propagating High-temperature Synthesis (SHS) process can reduce the thermal conductivity of products due to the high surface roughness of the particles and small grain size resulting in increased phonon scattering in a consolidated sample.

The main advantage of SHS reaction over other methods is its simplicity. This feature results in a significantly reduced cost of production while the properties of the synthesized materials, such as calcium cobaltate are comparable or better than calcium cobaltate prepared by other more expensive and complex methods [3]. In this presentation, calcium cobaltate was prepared from SHS process using cobalt metal powder and calcium peroxide with sodium perchlorate added as solid oxidizer shown as the following reaction.

1.62Co + 1.24 CaO2 + 0.18 NaClO4 + 0.33 O2 → Ca1.24Co1.62O3.86 + 0.18 NaCl

Prepared calcium cobaltate was characterized by XRD for phase purity. BET and SEM were used to measure the specific surface area and particle size, respectively. Thermoelectric properties were also measured at Oak Ridge National Laboratory. Temperature history data during the SHS reaction were collected by thermocouples inserted into the center of the pellet and by IR thermal imager, which was used to measure the temperature on the pellet's surface.

Calcium cobaltate prepared by SHS has a very large Seebeck coefficient, and a low thermal conductivity. The figure of merit is comparable to compounds prepared by more complex and expensive synthesis methods.

Finite element model of the SHS reaction of calcium cobaltate was generated. The model includes the heat, momentum, and mass transfers. Diffusion of oxygen from the surrounding gas and its effect on the SHS reaction are studied in details. The calculated results of the model correlate very well with experimental temperature measurements. The model can thus be employed to predict the temperature profile during a scale-up from small samples reacted in the lab to industrial application.

Acknowledgement: Research sponsored by the Heavy Vehicle Propulsion Materials Program, DOE Office of FreedomCAR and Vehicle Technology Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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P-D36

MECHANICAL ACTIVATION POWDERS AND ELECTRIC CURRENT MAINTAINING EFFECTS ON THE SYNTHESIS OF Ti_2AlC MAX PHASE BY ETEPC

Sehab N.*[1], Benaldjia A.[1], Amara A.[1], Ali Rachedi M.[1], Langlois P.[2], Vrel D.[2]

[1] Laboratoire LEREC, Faculté des Sciences, Département de Physique, Université Badji-Mokhtar Annaba, BP 12 Annaba 23000, Algérie.
[2] CNRS-LIMHP, UPR 1311, Université Paris 13, Institut Galilée, 99 Av. J.-B. Clément, Villetaneuse, 93430 France
* sehab_nadjette@yahoo.fr

The layered ternary carbides and nitrides with the general formula $M_{n+1}AX_n$, where n= 1, 2, or 3, M is an early transition metal, A is an A-group element (mostly IIIA or IVA), and X is either C or N, represent a new class of solids. These materials have been the subject of many studies because of their unique physical and mechanical properties, such as high melting point, good thermal and electrical conductivity, excellent thermal shock and suitable mechanical characteristics [1–4]. The latter properties are strongly related to their layered crystal structures [5] and make the layered ternary carbides a highly promising candidate for various applications in high-temperature environments. Among the $M_{n+1}AX_n$ compounds, we have the Ti_2AlC as candidate. Jeitschko et al have provided the crystal information connected with layered ternary Ti_2AlC ceramic in 1963. It has an hexagonal phase with lattice constants of a=0.304 nm, c=1.360 nm and low density of 4.11 g / cm^3. Ti_2AlC was synthesized by several methods such as CVD method [6], from the blend of Ti, Al_4C_3 and C powders by reactive hot pressing (RHP) [7], reactive hot isostatic pressing (RHIP) [8] and Self-propagating high-temperature synthesis (SHS), etc. The remarkable disadvantages of both RHP and RHIP processing routes are the use of high-temperature furnaces (up to 1600°C), long processing times (several hours) and the expensive encapsulation procedure (for HIP). SHS method is based on self-sustained exothermic reaction that propagates in a starting reagent blend (combustion wave) or occurs simultaneously in the sample volume (thermal explosion), and represent an energetically efficient means of in situ materials processing [9, 10].

Electro-Thermal Explosion under Pressure with Confinement (ETEPC) is a process permitting simultaneous synthesis and densification: an electric current propagating through a green compact ignites the SHS reaction in a thermal explosion mode. In this work we study the effect of activation powders and electric current maintaining after ignition on the purity of Ti2AlC synthesized materials by ETEPC [11]. The reaction products were characterized by X-ray diffraction, Scanning electronic microscopy (SEM) and differential scanning callometry (DSC).

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P-D37

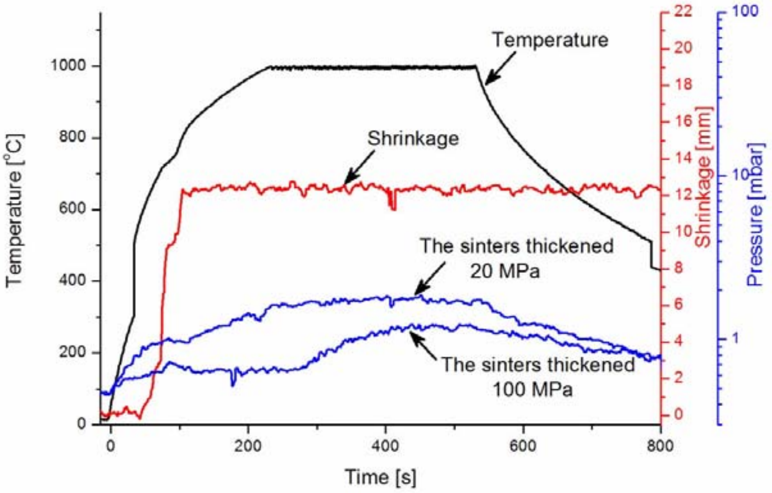
STRUCTURE AND PROPERTIES OF FE40AL INTERMETALLIC SINTERED WITH ADDITIONAL PRESSING DURING SHS REACTION

Siemiaszko D.*, Czarnecki M.

Military University of Technology, Warsaw, S. Kaliskiego 2, Poland
* dsiemiaszko@wat.edu.pl

The Fe-Al phases have very interesting properties like: enhanced resistance to wear, corrosion, high temperature oxidation and sulphidation resistance [1,2]. From this causes iron aluminides are really interesting as replacement of stainless steel for industrial applications. One of the most interesting method to produced Fe-Al alloys is powder metallurgy. During this process between iron and alumina powers occurring strongly exothermic reaction SHS which could be reason for sinters porosity [3,4]. On the other hand high temperature with appear during SHS reaction make the powder more plastic and it is possible to use this time to increase pressing for reduce a porosity in the final product [5].

This work shows structure and mechanical properties of Fe40Al sinters produced with additional pressing during SHS reaction. The processes were make in a special sintering equipment. The material is placed in a graphite die between two graphite punches in a vacuum chamber. The pressed powder was heated by a induction coin with heating speed about 200 K/s to sintering temperature between 700 and 1050°C. The pressing force was increase from 0 to 100 MPa when the SHS reaction was observed. The figure shows typical changes of temperature, shrinkage and pressure in the chamber during sintering process. The phases composition, density, hardness and surface area (BET) of the sinters were determined.



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P-D38

SHS-METALLURGY OF CAST ALUMINIUM OXYNITRIDES

Silyakov S.L.*, Gorshkov V.A., Yukhvid V.I., Sachkova N.V., Ignat'eva T.I.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
* ssl@ism.ac.ru

Among the obvious advantages of oxynitride ceramics are uniqueness of its properties and availability of the green mixture components. The main method of production of oxynitride aluminum ceramics is powder metallurgy of aluminum oxide and aluminum nitride sintered with some special additives. In ISMAN oxynitride ceramics was produced by the method of self-propagating high-temperature synthesis (SHS) based on infiltration combustion of the initial components under the nitrogen pressure [1]. This method provides the possibility of synthesizing a wide range of oxynitride composite materials based on aluminum and silicon nitrides.

In ISMAN investigations of synthesis of cast oxynitride ceramics have been recently performed in the combustion regime via the SHS route [2, 3]. This approach allows production of nitrogen-containing compounds and materials in the liquid (cast) state using highly exothermic mixtures of a thermite type.

In the present investigation two possible versions of synthesis of cast aluminum oxynitrides are considered. In one case, synthesis proceeds along the following scheme:

$$\gamma_1 Fe_2O_3 + \gamma_2 Al + \gamma_3 N_2 \rightarrow \gamma_4 Al_x\text{–}O_y\text{–}N_z + \gamma_5 Fe_a\text{–}Al_b\text{–}N_c\,.$$

The aluminum content in the initial exothermic mixture from 25.2 up to 50.3 wt% and variation of the initial nitrogen pressure within 0.1–10 MPa provide the condition of generating combustion temperature higher than the melting points of the final products and formation of both metallic and ceramic cast products. The combustion velocity of as arranged compositions (u) does not exceed 0.3cm/s and the process is accompanied by slight dissipation of the combustion products. The resultant cast oxynitride ceramics contains up to 2 wt% bound nitrogen. Its presence is determined in the gas-transport reactions.

A specific feature of the other version is the possibility of additional introduction of nitrogen-containing components (aluminum or silicon nitrides, AlN or Si_3N_4) into the green exothermic mixture. The chemical scheme of the process is as follows:

$$\gamma_1 Fe_2O_3 + \gamma_2 Al + \gamma_3 AlN(\,Si_3N_4) + \gamma_4 N_2 \rightarrow \gamma_5 Al_x\text{–}O_y\text{–}N_z + \gamma_6 Fe_a\text{–}Al_b\text{–}N_c$$

The Fe_2O_3/Al compositions added with AlN and Si_3N_4 can burn at the additive content no more than 50 wt%. In this region, after the process initiation a combustion front formed propagates along the mixture. The combustion front velocity is determined by the amount of the additive introduced. In the vicinity of the combustion limit it is equal to 0.1–0.2 cm/s. At the AlN and Si_3N_4 content of no more than 10 wt%, the combustion process yields cast products that form individual metallic and ceramic layers.

At the additive content > 10 wt%, the combustion products are casts formed by a mixture of metallic and oxynitride phases. At the increase in the AlN and Si_3N_4 content an average linear velocity of combustion diminishes from ~1.0 down to ~0.1 cm/s. The relative mass loss is slightly reduced and constitutes 1-2 wt%. A combined scheme of the synthesis run provides the increase in the bound nitrogen portion in the cast oxynitride ceramics up to 7 wt%. Its content in the cast ceramics depends on both the initial nitrogen pressure and the amount of the nitride additive in the green exothermic mixture.

An X-ray analysis of the final cast oxynitride ceramics shows that the following main phases $Al_{2.81}O_{3.56}N_{0.44}$; $Al_8O_3N_6$; $Al_9O_3N_7$; $Al_{2.78}O_{3.65}N_{0.35}$ can be synthesized dependent on the variation of the experimental conditions. Optimization of the synthesis conditions may bring about formation of a cast one-phase aluminum oxynitride of the $Al_{2.78}O_{3.65}N_{0.35}$ phase composition.

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This work was financially supported by Grant RFBR №09-03-00326

P-D39

COMBUSTION SYNTHESIS OF SILICON OXYNITRIDE UNDER AIR PRESSURE

Studenikin I.A.*, Grachev V.V.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Moscow, Russia
* stivan@bk.ru

Due to its excellent mechanical and dielectric properties at elevated temperatures, silicon oxynitride Si_2N_2O is highly promising for use as a structural ceramic material. Compared to silicon nitride, oxynitride exhibits higher heat resistance in oxidative media [1]. Si_2N_2O-based ceramics can be produced by the methods of powder metallurgy, such as reactive sintering [2], hot isostatic pressing [3, 4], and spark plasma sintering [5]. Silicon oxynitride (in combination with MgO, Al_2O_3, Y_2O_3) is also known as a good sintering agent for silicon nitride and silicon carbide.

Refractory inorganic compounds (including silicon nitride, silicon carbide, and SiAlON) can also be produced by SHS. The synthesis of silicon oxynitride from a mixture of Si, SiO_2, and Si_2N_2O (as an additive) by combustion in nitrogen gas at $P(N_2) = 3$ MPa was reported in [5] while that from a mixture of Si and SiO_2 (crystalline, amorphous) at $P(N_2) = 10$ MPa, in [6]. In work [7] was investigated the synthesis of silicon oxynitride Si_2N_2O from a mixture of Si, SiO_2, and Si_3N_4 by infiltration-mediated combustion in nitrogen gas for $P(N_2) = 4–14$ MPa.

In this work, we investigated the synthesis of silicon oxynitride Si_2N_2O from silicon-containing mixtures by infiltration-mediated combustion in air atmosphere under pressure 4 MPa.

In this case, during the burning process silicon interacts with components of the air with the formation of SiO_2 and Si_3N_4, which then react each other to form Si_2N_2O. The chemical/phase composition of product and process parameters (temperature and burning velocity) were studied upon variation in charge composition.

It was shown:

- to increase the amount of target oxynitride in the combustion products it is necessary to introduce the silicon oxide as an additional source of oxygen in the green mixture;
- to prevent coagulation of melted silicon and silicon oxide particles in the combustion wave it is necessary to introduce a refractory diluents in the initial mixture, for this purpose silicon oxynitride is the best candidate;
- besides the role of anticoagulant the added oxynitride acted as crystallization centers for the newly formed phase Si_2N_2O, as result the more homogeneous product with a high content of oxynitride phase was obtained.

Acknowledgments

This work was supported by the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (grant no. NSh - 6497.2010.3).

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P-D40

MEMBRANE-CATALYTIC SYSTEMS FOR VAPOR CONVERSION OF ETHANOL AND ACETIC ACID

Uvarov V.I.*, Borovinskaya I.P., Malevannaya I.G.

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, Moscow region, 142432 Russia.
*uvar@ism.ac.ru

Production of high-temperature corrosion-resistant and mechanically strong nano-porous structures used in efficient membranes for vapor conversion, are under consideration. Studying "gas-kinetic model" of porous structure formation during SHS we applied the Laplace's equation for determining pore size. As known, metals melt in the combustion wave and in the case if pressure of liquid vapor with a touch of dissolved gases is higher than the external pressure, open porosity in the final products (membranes) is formed during fast cooling. In the work conditions for porosity formation and conversion of closed porosity into open one were defined. It allows one to control structure and pores size in the graded nano-porous SHS materials, i.e. membranes. As a result, the catalytically active high-porous ceramic carriers of membrane-catalytic systems based on refractory inorganic compounds Ni-Al-Co/TiO_2/NiO, Ni-Al/NiO were obtained. Their characteristics:

Open porosity, %	45 – 58
Pore size, µm	2.5 – 3.1
Bending strength, MPa	55 – 63
Specific surface, m^2/g	3 – 15
Gas consumption	up to 25 m^3/h.

The catalytic layer of metal oxides was formed inside the membrane channels by sol-gel method where organic solutions of metal-complex precursors in toluene and agents stabilizing the mother liquor were utilized. Pipe-like microporous membranes of 15 mm in diameter and 130 mm in length were used as initial membranes. Mother liquors of metal-complex precursors were pumped through the membrane in order to modify the internal surface of the channels. Then the membrane was blown through with heated moistened air, dried in vacuum (1 Torr), and heated at various modes.

We studied vapor conversion of ethanol and acetic acid as the main products of biomass fermentation in the membrane-catalytic system containing palladium particles as an active component. The initial mixture composition corresponded to that of the fermentation products (substrate/H_2O – 1/12). The specific activity in hydrogen formation was 600 $l/dm^3_{membr}\cdot h$ and 400 $l/dm^3_{membr}\cdot h$ for acetic acid and ethanol, respectively.

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P-D41

MODES OF THERMAL EXPLOSION DEVELOPMENT IN Fe-Al, B-Al SYSTEMS

Vadchenko S.G., Boyarchenko O.D.*

Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, 142432 Russia
*olgaboyarchenko@gmail.com

Thermal explosion or green mixtures heating up to temperature of self-ignition was applied for production of some important intermetallics including aluminides with remarkable properties: wear resistance and high-temperature strength. Due to high fusion heat of aluminum, sometimes preliminary heating is necessary for the reaction initiation. Unlike mechanical activation or thermo treatment in vacuum it is a more easy and efficient technique. Phase transformation with great heat absorption courses various modes of thermal explosion development [1–3]. Thermal explosion in Al–Fe–B system was studied in experiments where rate of sample heating was a main variable.

Green mixture was pressed into cylindrical samples (d=50 mm, l=1–1.5 mm) with relative density 0.4 - 0.5 and then put into the furnace in which the length of the isothermal zone exceeds sample's length 1.5 –2 times. Experiments were carried out in argon under atmosphere pressure. Temperature was detected with four thermocouples.

For the first time, the nonstationary temperature field was studied under thermal explosion of a low caloric system by the example of direct synthesis of iron or boron aluminides from elements. It was shown that in the cases of phase transformation, ignition occurs at the temperatures close to the Al fusing point. In dependence of heating rate, a significant temperature drop before melting can be registered. Melt appearance does not always give rise to a reaction start immediately and liquid aluminum can coexist rather long with a solid refractory reagent.

Besides traditional inflammation and self-ignition regimes, a new temperature oscillation subregime before self-ignition was determined. It can be caused by capillary stir of a melt.

This work was supported by the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (grant no. NSh-6497.2010.3).

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P-D42

EFFECT OF MICROGRAVITY ON STRUCTURE FORMATION IN SHS

Vadchenko S.G., Kamynina O.K., Sytschev A.E.

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,
Chernogolovka, Moscow, 142432 Russia
*kuz@ism.ac.ru

The further study and development of space have been generating intense interest and long-term Programs on planets development have been carrying out recently. Particularities of SHS (low energy consumption, short times, simple and compact technological equipment, possibility of synthesis in vacuum) make the technology promising to be applied in space.

In experiments carried out aboard the International Space Station (ISS) we investigated SHS in the multi-layer samples. Thermal explosion in the layers of low exothermic (Ni-Al, 3Ni+Al, Co+Al, Nb+3Al, Ti+Co+B_4C, Ti+Ni) was possible due to intercalation with pressed layers of high caloric (Ti+xC, 5Ti+3Si, Ti+Si, Ti-Al-C, Ti+Ni+x_1Al+y_1NiO) burning in the wave mode. For example, SHS starting in Ti-Al-C layer propagates to Ni+Al layer when the latter had been heated to the temperature of ignition.

Interaction between the layers of various compositions and joints formation were studed. Besides, foils of different metals (Ni, Ti, Mo, Nb, Ta, Al) were pressed into the initial samples in order to study their interaction with initial components and products melts under microgravitation. Peculiarity of reaction mechanism was investigated.

It was shown that SHS under prolonged microgravity can be a unique technique for obtaining highly porous foam materials and coatings for aerospace industry. The experimental results can be used for organization of welding, surfacing, capsulation, reparation of defects and etc. aboard a space station.

This work was performed jointly with S.P. Korolev Rocket and Space Corporation «Energia».

P-D43

ONE STEP SYNTHESIS AND DENSIFICATION OF TiC-Ni AND Ti_2AlC-Ni COMPOSITES.

Vrel D.[1], Sytschev A.E.[2], Fagnon N.[1], Stolin A.M.[2], Galyshev S.N.[2], Bazhin P.M.[2]

[1] Université Paris 13, CNRS, LSPM – UPR 3407, 99 avenue J.-B. Clément, 93430 Villetaneuse, France
[2] Institute of Structural Macrokinetics and Materials Science, Chernogolovka, 142432 Russia
* dominique.vrel@lspm.cnrs.fr

In order to obtain dense ceramic materials, we previously studied the hot forging of MAX compounds in the Ti-Al-C system [1]. The directing idea of this study was to use the high temperature generated by the SHS reaction in order to facilitate the plastic deformation of the ceramic produced.

However, because the sample was not surrounded by a mould during compaction, the final results displayed a density gradient from the center of the sample to its edge. On the other hand, because hot forging was applied very shortly after the onset of the reaction, and due to large initial reactants grain sizes, the reactions were incomplete, and some intermediate products could be found, such as titanium aluminides.

In this study, titanium and carbon mixtures will be used as reactants to synthesize titanium carbide by SHS or by MASHS, and nickel will be used as a sintering aid. Different shape factors will be used for the moulds, using initials samples with constant dimensions.

In a second time, a similar approach will be used for samples aimed at MAX phases compositions.

Samples will be characterized using x-ray diffraction, scanning electron microscopy, and by measuring the final density obtained for the final products.

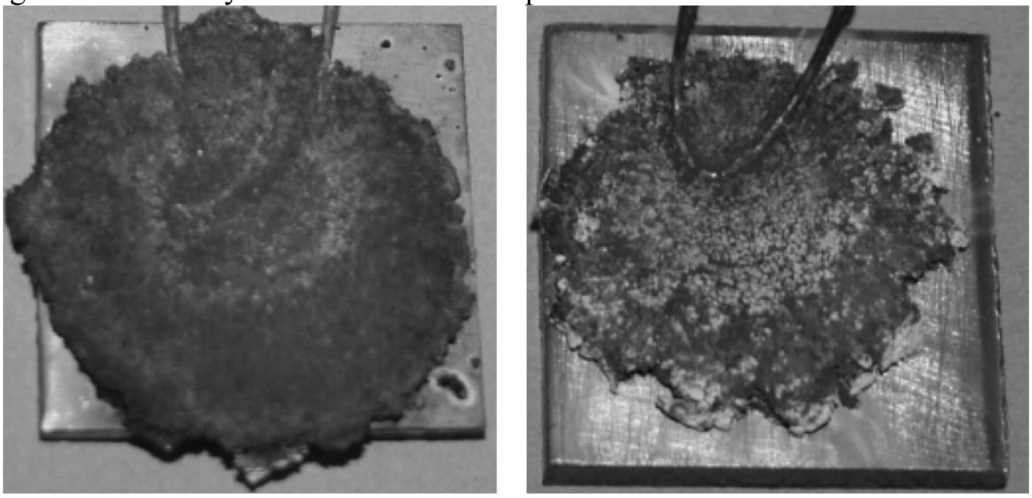

Figure: Influence of delay time on densification of Ti_2AlC sample: (a) pressed at 10 MPa for 30s immediately after synthesis (b) pressed at the same pressure during this same time, but after a delay time of 5 seconds. Note the presence of white material in sample (b) as a result of ceramic oxidation before compaction. After [1].

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P-D44

ALIGNED SINGLE-CRYSTALLINE β-Si_3N_4 WHISKERS PREPARED WITH SELF-PROPAGATING HIGH TEMPERATURE-SYNTHESIS

Xia M.[1], Ge C.[1,2]*, Guo H.[1]

Institute of Powder Metallurgy and Advanced Ceramics, Southwest Jiaotong University, Chengdu 610031, China.
And Institute of Special Ceramics and Powder Metallurgy, University of Science & Technology Beijing,
Beijing 10083, China.
xmdsg@126.com

It is known that controlling microstructural orientation has been used as one of the important ways to improve the flexural strength and the fracture toughness of ceramic composites at the same time. Seed particles with anisotropic shapes were often used for making ceramic composites, and alignment of the seeds determines the degree of microstructural anisotropy and the properties of the composites. However, it is difficult to prepare a highly aligned whisker with high aspect ratio. In this paper, aligned single-crystal β-Si_3N_4 whiskers free from defects with high aspect ratio have been synthesized with SHS process for the first time. The as-synthesized whiskers are very long whiskers, which possess smooth surfaces, uniform diameters about 400 nm, lengths about 200 μm and the same growth [001] direction. Above all, the products show a perfect aligned structure, which is quite different from the reported β-Si_3N_4 whiskers. Results demonstrated that tungsten plays a significant effect on the growth and morphology of β-Si_3N_4 whiskers, and the as-synthesized aligned single-crystalline β-Si_3N_4 whisker with high aspect ratio shows a great potential application in the strength improvement of metal matrix composites (MMC) and ceramic matrix composites (CMC), it can be widely used in high temperature environment without any crystallographic transformation taking place.

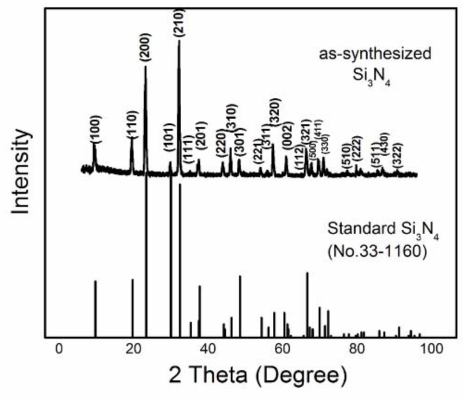


Figure 1. (XRD patterns of the as-synthesized Si_3N_4 whiskers and standard β-Si_3N_4)

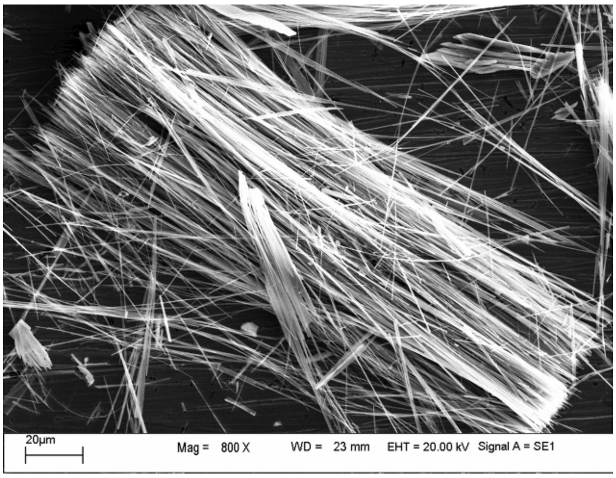


Figure 2a. (Low-magnification image of the original whiskers fabricated by using tungstens as catalyst, showing an aligned structure and an uniform diameter and length.)

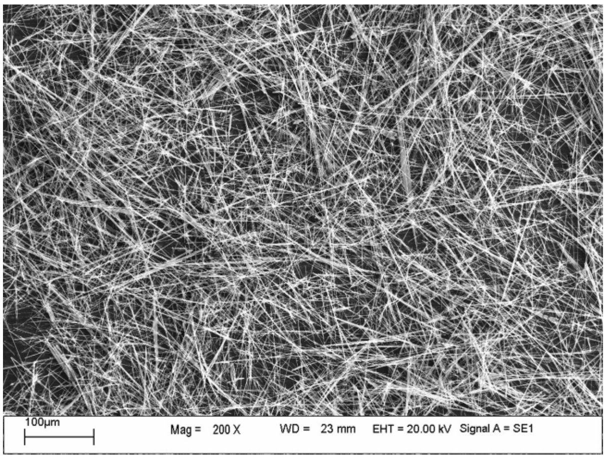


Figure 2b. (Image shows the aligned β-Si_3N_4 whiskers have better dispering ability by using ultrasonic waves in alcohol.)

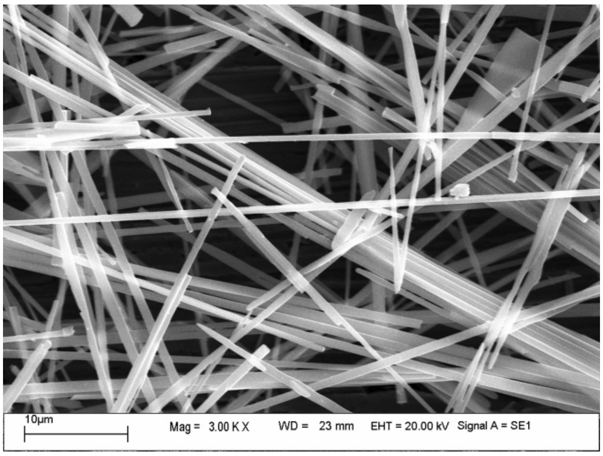


Figure 2c. (High-magnification image clearly demostrates the uniform diameter of the whiskers, with diameters about 400 nm.)

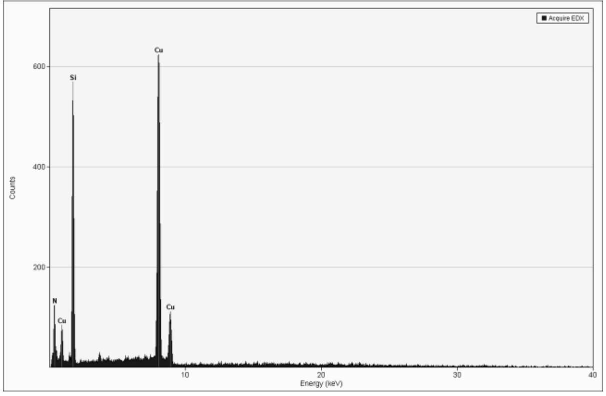


Figure 2d. (EDX spectra of the aligned β-Si_3N_4 whiskers.)

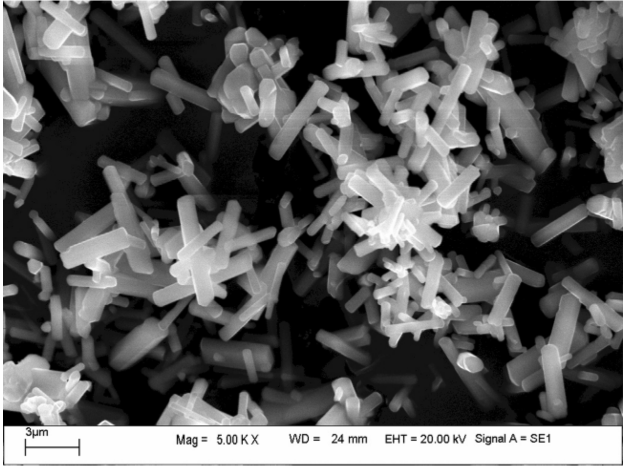


Figure 2e. (Low-magnification image of the β-Si_3N_4 whiskers fabricated under the same reaction conditions of the aligned β-Si_3N_4 whiskers without adding tungstens as catalyst.)

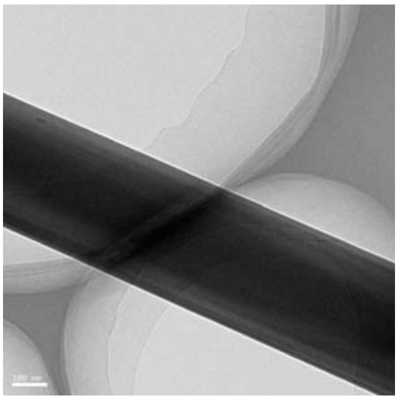


Figure 3a. (An individual β-Si_3N_4whisker with a every smooth and straight surface, no defects are detected.)

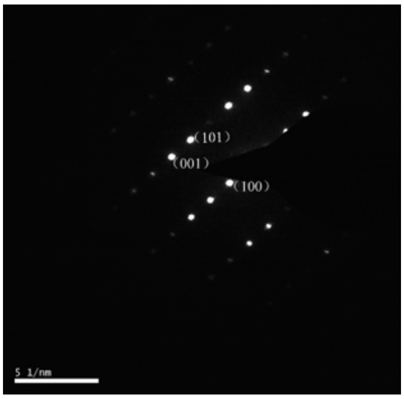


Figure 3b. (High-magnification image shows a highly crystalline β-Si_3N_4 whisker grown with the [001] direction.)

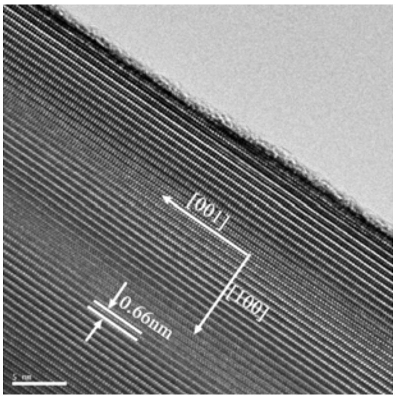


Figure 3c. (SAED image of an individual β-Si_3N_4whisker also demonstrate a perfect single-crystalline structure.)

P-D45

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF H-BN-SIC CERAMIC COMPOSITES PREPARED BY SHS

Zheng Y.T., Li H.B., Zhou T., He X.*

Center for Composite Materials and Structure, Harbin Institute of Technology, Harbin, Heilongjiang, 150001, China
* hexd@hit.edu.cn

Hexagonal boron-nitride (h-BN) ceramic is an excellent solid lubricant because of the similar crystal structure to graphite, and has low thermal expansion coefficient, high thermal conductivity and resistance to thermal shock and corrosion, wherefore h-BN ceramics have been applied to crucibles, jackets of thermalcouples and other components that subjected to high temperature environment.

h-BN is a hard-sintering material owing to its strong covalent bonds and sintering aids added frequently during the preparing process to improve the sinterablity. However the sintering aids, which formed low point phases in the products, deteriorated the elevated temperature properties of h-BN ceramic. Self-propagating High-temperature Synthesis (SHS, also called Combustion Synthesis) provides an effective way to avoiding the weakness above mentioned.

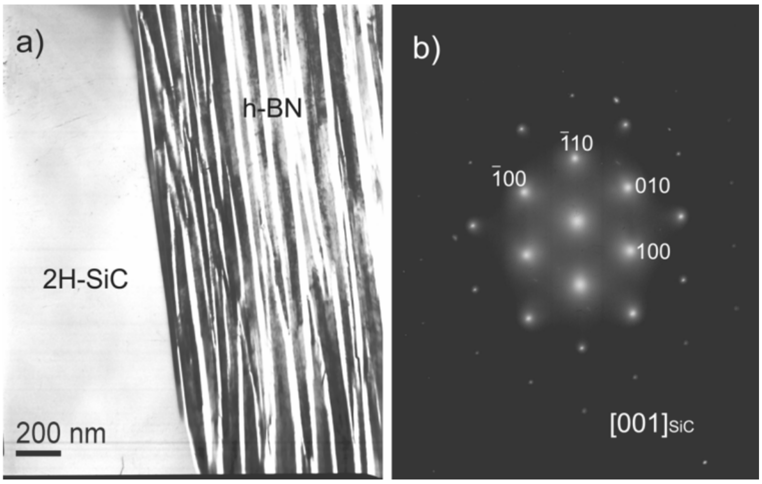
This study reports a cheap approach for synthesizing an h-BN-SiC composite based on the following reaction:

$$B4C+Si+2N2=4BN+SiC$$

The theoretical solid-phase composition of the product in above reaction is 71.23 wt% and 28.77 wt% for BN and SiC, respectively, and respective volume percents are 77.5 % and 22.5 %.
The raw materials used in this experiment were boron carbide (B4C, 5 μm) and silicon powders (Si, 10 μm). The thoroughly mixed powders were cold isostatically pressed under 10 MPa pressure to obtain the cylindrical compacts with diameter of 40 mm and porosity of about 56 %. The SHS reaction was carried out in a super-high pressure container under 60, 80, 100, 120 MPa nitrogen pressure.

The XRD patterns show that the reactants reacted completely to form h-BN and SiC phase, except for the product under nitrogen pressure of 120 MPa, where small content of Si_3N_4 found. This indicated that higher nitrogen pressure above 100 MPa is favour for the formation of Si_3N_4.

Experimental shows that higher reaction nitrogen pressure is favour for the performance improvement of the h-BN-SiC ceramic composites. With the reaction nitrogen pressure increasing from 60 MPa to 120 MPa, the relative density (RD) of the products increased from 68 % to 82 % correspondingly. SEM photos show that equiaxed SiC grains embedded in large mount of plate-like h-BN phases. TEM photos exhibit clearly the plate-like structure of h-BN and good interface between h-BN and SiC. Mechanical performance testing shows that h-BN-SiC ceramic composites prepared by in-situ combustion synthesis have good mechanical properties, and the bending strength and fracture toughness reach 82 MPa and 1.9 $MPa\cdot m^{1/2}$, respectively.



TEM images of h-BN-SiC ceramic composites: a) Interface between BN and SiC and b) SAED of SiC phase.

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P-D46

POROUS EQUIATOMIC NiTi ALLOY PRODUCED BY SHS

Zanotti C.*[1], Giuliani P.[1], Bassani P.[2]

[1] Institute for Energetics and Interphases, Via R. Cozzi, 53 20125 Milano, Italy
[2] Institute for Energetics and Interphases, Corso Promessi Sposi, 29 Lecco, Italy
*zanotti@ieni.cnr.it

Experimental and numerical studies, finalized to product porous NiTi alloys by SHS technique and to define thermo-mechanical properties are presented. Samples have been prepared starting from elemental powders of Ni and Ti, homogeneously dry mixed in the stoichiometric ratio 1:1 and then pressed to obtain samples having different initial density. Sample sizes were chosen on the basis of the analyzed phenomena namely heating, ignition and reaction processes. Tests aimed to obtain volumetric heating of sample (diameter 8 mm, length 1-2 mm) was carried out to investigate the effect of the heating rate on the ignition parameters. A numerical model was developed to simulate the heating transients for estimating the energy necessary to ignite the sample [1]. Self-propagating high-temperature synthesis phenomenon was investigated to define the dependence of reaction front velocity and reaction temperature on the pre-heating conditions (sample diameter 8-10 mm and length 10-20 mm) [2]. Porous products were characterized mainly from a morphological point of view. Total porosity, as well as pore size, shape and distribution, was analyzed. Sample microstructure was also investigated indicating that the main phase produced during the self-propagating high-temperature synthesis reaction is Ti rich NiTi phase. Compression tests were carried out at room temperature and also above Af in order to highlight the influence of pore shape and distribution on mechanical behavior of the sample. Dilatometric tests were also performed and the results well indicated the martensite to austenite transformation at the same temperature showed by the DSC analyses. Thermal analysis was completed defining the thermal conductivity dependence on temperature and porosity from 300 K up to 1400 K. Samples featured by porosity levels of 30%, 48%, 68% have been produced and tested [3] and the obtained results compared with the fully dense alloy. Figure 1 points out that thermal conductivity increases with the temperature while it decreases with porosity increase. Moreover, in the temperature range (dashed lines) where the phase transformation from Martensite to Austenite occurs, thermal conductivity presents a discontinuity. Finally, preliminar results concerning the capability to react NiTi powder mixture, prepared by ball milling, at low temperature are reported too.

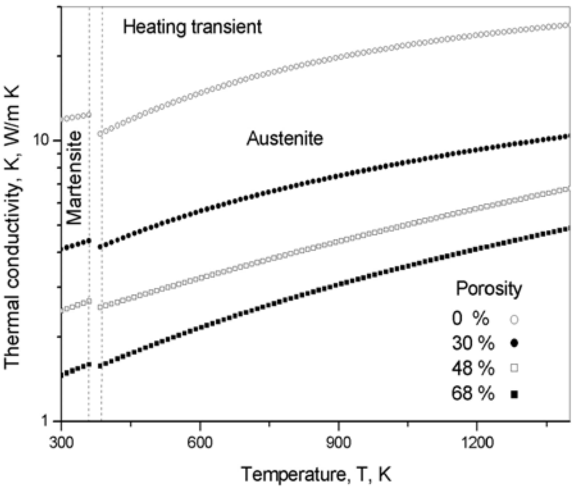

Fig. 1 Dependence of thermal conductivity on temperature and sample porosity

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P-D47

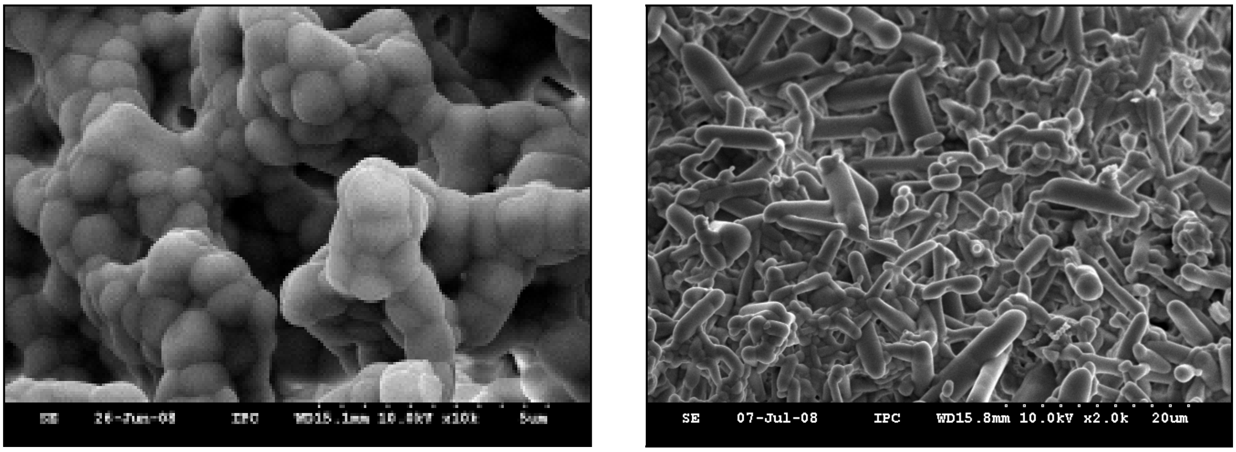
MICROSTRUCTURE FORMATION OF Y-α-SiAlON UNDER INFILTRATION ASSISTED COMBUSTION SYNTHESIS

Zhao Y.S.[1], Yang Y.[1], Li J.T.[1], Borovinskaya I.P.[2], and Smirnov K.L.*[2]

[1] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
[2] Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia
* kosm@ism.ac.ru

α-SiAlON, as a solution of α-Si_3N_4, is an ideal structural ceramic material due to its high hardness, wear resistance, and outstanding high-temperature performances [1]. Despite a high hardness, the poor toughness of α-SiAlON caused by the usual equiaxed grains is the bottleneck of its further applications. Chen et al. [2] prepared a tough α-SiAlON ceramic with whisker-like microstructure and pointed out the importance of controlling the nuclei and grain growth during the sintering process. Their further work demonstrated that it was effective to control the nuclei and grain growth by adding α-SiAlON seeds, especially elongated ones [3]. Thus, the study on how to fabricate elongated α-SiAlON seed microcrystals is currently a hot subject of research. So far, two methods for preparing α-SiAlON seed microcrystals have been reported. One is sintering of small seed microcrystals by liquid-phase growth [4], and the other is combustion synthesis (CS) of seed microcrystal powders [5], which appears to be more attractive for its low cost and short process time.

In this work, Y-α-SiAlON represented by the formula $Y_{0.33}Si_{9.8}Al_{2.2}O_{1.2}N_{14.8}$ was selected for investigation. Starting reaction mixers with different content of Si was initiated under nitrogen pressure 2 MPa. A modified method of CS was also developed to prepare rod-like Y-α-SiAlON powders when the combustion reaction was carried out in a chemical oven. The composition of the chemical oven was 60 wt % of Si powder and 40 wt % of β-Si_3N_4 powder.



a) b)

Fig.1. The morphology of the combustion products of samples synthesized by simple (a) and chemical oven assisted (b) method. Content of Si in green mixers is 44 wt. %.

The final phase assemblages of samples with high content of Si in green mixers contain some residual Si, which indicates that it can not get a complete nitridation during the short time of the combustion reaction, when the content of Si is more than 50 wt. %. The final phase assemblages of samples with low content of Si in green mixers don't contain residual Si, but contain some β-

SiAlON. This phase usually formed during the earlier step of sintering the Y-α-SiAlON ceramics then changed to Y-α-SiAlON at temperature higher than 1650°C. According to temperature profile during the combustion reaction of samples with low content of Si in green mixers the dwell time at temperatures above 1650°C is so short that the β-SiAlON don't change to Y-α-SiAlON and remains in the products.

Rod-like microcrystals predominate in the products synthesized by simple CS method from green mixers with very high content of Si (more than 60 wt. %) and coexist with high content of residual Si. In the products of samples with lower content of Si in green mixers only equiaxed grains are observed. When content of Si in green mixers is less than 40 wt. % secondary grains are observed. The size of secondary grains is less than 0.5 μm, which is the same as that of starting α-Si_3N_4 powders. This corresponds with the XRD result of these samples that contain some residual α-Si_3N_4. Compared to samples synthesized by simple method, the grains of samples synthesized by chemical oven assisted method are much larger and many rod-like microcrystals are observed (Figure 1). The reaction temperature profiles for these samples show that the maximum temperatures have a difference over 400°C. The bigger grain size of sample synthesized by chemical oven assisted method is attributed to the much higher reaction temperature.

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POSTER PRESENTATIONS

E: Non–conventional SHS processes: New methods and applications

P-E1

FORMATION OF ALLOYS IN THE Ti-Nb SYSTEM BY HYDRIDE CYCLE METHOD AND $Ti_XNb_{1-X}H_Y$ HYDRIDES SYNTHESIS IN COMBUSTION REGIME

Aleksanyan A.G.*[1], Dolukhanyan S.K.[1], Ter-Galstyan O.P.[1], Martirosyan M.V.[2]

[1]A.B. Nalbandyan Institute of Chemical Physics of Armenian NAS;
[2]State Engeeniring University of Armenia
a.g.aleks_yan@mail.ru

The method of synthesis of alloys in hydride cycle, developed in the Laboratory of high-temperature synthesis of A.B. Nalbandyan Institute of Chemical Physics of Armenian NAS [1], gives the possibility to synthesize refractory alloys even those, components of which have high fusion temperatures. The alloys in system **Ti-Nb** belong to such alloys (the fusion temperature of Ti is 1668°C, and of Nb – 2500°C. The receiving of these alloys by traditional methods is rather difficult. Search of new ways of synthesis the titan-niobium alloys is an enough actual problem. The increasing interest to the titan-niobium alloys is caused by combination of their unique properties – thermal stability, superconductivity, corrosion firmness, unique properties, low electron work function, etc. Besides, these alloys can exhibit unique hydrogen absorbing properties and serve as a matrix for hydrogen storage.

In this work the results are presented received at study of regularities of formation in ‘hydride cycle’ of refractory alloys based on Ti and Nb and of synthesis of hydrides of these alloys by SHS method [1,3] The mechanisms of formation and phase structure of alloys depending on the ratio of reagents $\mathbf{TiH_2/NbH_x}$ and the parameters of process: density of the sample, dynamics of change of temperature at dehydrogenation-sintering and at cooling, also on the kinetic of hydrogen removing from the initial hydrides, etc. are studied.

The essence of hydride cycle consists in consecutive use of processes of synthesis of hydrides of transition metals by SHS method[1,2], compaction of given composition of Are measured also microhardness of some samples of alloys of system Ti-Nb depending on a ratio of componentsmixture of these hydrides or of their mixture with powders of III, V, VI group metals, and dehydogenation-sintering of compacted sample As a result of interaction between the hydrides of transition metals, or between a hydride of transition metal and metal powder, alloys with α , ω, or β phases depending on a ratio of initial components and other parameters of proceeding processes are formed [3]

The process of formation of alloys proceeds in accordance with the reactions:

$$\mathbf{xMe'H_2+(1-x)\,Me''H_2 \rightarrow Me'_xMe''_{(1-x)} + H_2\uparrow} \text{ or } \mathbf{xMe'H_2 + (1-x)Me'' \rightarrow Me'_x\,Me''_{(1-x)} + H_2\uparrow}$$

The formation of alloy in the given scheme includes a number physical and chemical processes: phase transitions, formation of defects accelerating mutual diffusion, a strong activation of metals takes place at the expense of destruction of Me-H link, clarification of a metal powder surfaces at hydrogen leaving, re-crystallization, etc. These processes facilitate the alloy formation at temperature, at least, lower by 600-800°C in comparison with the traditional methods of formation of alloys of the same metals (induction, arc fusion, diffusion sinering). In our experiments, as a result of interaction of hydrides of Nb and Ti, Ti_xNb_{1-x} alloys formed, in which, according to X-ray analysis, a phase with **BCC** structure prevailed.

Thus, the combination of two independent methods - SHS [1] and "hydride cycle" the titanium-niobium alloys had been successfully synthesized. The superconducting properties of synthesized alloys were measured. The highest superconducting properties were obtained for $Ti_{0.4}Nb_{0.6}$ and TiNb alloys. The critical temperature for transition of received in hydride cycle TiNb alloy to the superconducting condition, 10.3K, is similar to that known from the literature, while the critical temperature for no one of these metals reach 10K. Are measured also microhardness of some samples of alloys of system Ti-Nb depending on a ratio of components. In work also the possibility of interaction of the synthesized alloys with hydrogen in the combustion mode was studied. It was shown that the received compact Ti/Nb alloys without crushing interact with hydrogen in SHS mode, forming hydrogen rich hydrides of alloys, $Ti_xNb_{1-x}H_{1.2-1.9}$. In the Table, the characteristics of received alloys are shown. The thermal characteristics of synthesized hydrides were determined; using DTA method, the dissociation temperatures of $Ti_xNb_{1-x}H_{1.2-1.9}$ hydrides were established.

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P-E2

HAFNIUM INTERMETALLIDES AND THEIR HYDRIDES OBTAINED IN SHS REGIME AND "HYDRIDE CYCLE"

Hakobyan H.G.*[1], Aleksanyan A.G.[1], Dolukhanyan S.K.*[1], Shekhtman V.Sh.[2] and Mnatsakanyan N.L.[1]

[1]A.B. Nalbandyan Institute of Chemical Physics of Armenian NAS, 5/2 P.Sevak Str., Yerevan, 0014 Republic of Armenia
[2]Institute of Solid State Physics, RAS, Chernogolovka, Moscow District, 142432
* seda@ichph.sci.am, ayrum@ichph.sci.am

The intermetallic compounds (IMCs) based on IV and VIII group metals and their hydrides remain to be in a center of attention of material science. The interest to these compounds is connected with the actuality of metallic matrixes creation for storage and transportation of hydrogen, catalysts, materials of nano- and super-dispersion structure, bio-implants (basis for surface-active ceramics), etc.

In the present work, the results of experiments on obtaining binary IMCs in system Hf-Ni(Co) are presented. The conducted investigations have shown the possibility of formation of IMCs and their hydrides in modes of self-propagating high-temperature synthesis (SHS) and of so called "hydride cycle" [1,2]. The total scheme of "hydride cycle" for IMC and alloys receiving is: $HfH_2 + Ni(Co) \rightarrow HfNi(Co) + H_2\uparrow$.In "hydride cycle" regime, where hafnium hydride is used as a source reagent, the reaction of dehydrogenation/annealing of initial charge and formation of IMC proceeds in solid phase. It was established, that the obtained samples of IMCs interacted with hydrogen and deuterium (5-10 atm) in combustion (SHS) regime without grinding. This interaction resulted in formation of corresponding hydrides and deuterides of IMCs (H/Me= 2.5-2.7).

In our experiments, the powders of HfH_2 (the hydrogen content 1.11 wt.%) synthesized in SHS regime and powders of nickel (99.6 wt %), and cobalt (99.33 wt %) were used. Dehydrogenation/annealing was curried out in hermetic quartz reactor at temperatures 900-1150°C. The obtained samples were subjected to chemical, X-ray (diffractometer DRON-0.5 using CuK_α radiation) and DTA (Derivatograph Q-1500, Hungary) analyses. The chemical analysis of hydrogen content was carried out by pyrolysis method at temperatures 350-1000°C.

The influence of pressing pressure, dispersion of source reagents, temperature of hydrogenation-annealing on the process of IMCs formation (completeness and depth of reaction) and the phase composition etc. have been studied.

Experiments, carried out for different compositions have shown that in the rather wide interval of ratio of ingredients in the initial mixture (HfH_2/Ni(Co) result in formation of phases, corresponding to the phases of state diagram of the respective systems Hf-Co, Hf-Ni: intermetallides NiHf, $NiHf_2$, HfCo; Hf_2Co and hydride of hafnium intermetallics were received.

Compared to the known methods of obtaining the IMCs (induction/arc melting, powder metallurgy and combustion synthesis the elaborated method allows receiving of IMCs at temperatures not exceeding 1050°C; in solid-phase mechanism without melting; in short time interval (no more than 2 hours); resulting formation of strong samples of given shape and composition.

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P-E3

PIGMENTS ON THE BASIS OF Cr-, Mn- AND Co-MODIFIED WOLLASTONITE FOR INDUSTRIAL APPLICATIONS

Athanasakou N.S.[1,2], Xanthopoulou G.[2], Vekinis G.[2] and Zoumpoulakis L.[1]

[1]Department of Chemical Engineering, National Technical University of Athens, Athens, 15780, Greece
[2] Institute of Materials Science, NCSR Demokritos, Ag. Paraskevi Attikis, 15310, Greece
gxantho@ims.demokritos.gr

The traditional production of pigments is a time-consuming and energy consuming process. In many cases, especially when bright, stable colors are needed for use in ceramic glazes or porcelain, synthesis by calcination of powder mixtures takes place over many hours, even days, at high temperatures that can top 1450-1500°C to ensure completed reactions between the powders. In addition to such synthesis by calcination, production may also include extended milling (300 h wet milling is not unusual) and fine grinding to obtain the necessary grain size and distribution. The conditions under which these operations are carried out are decisive in determining the final quality and cost of the pigments, which can vary by almost an order of magnitude [1].

The development of less expensive raw materials and non-traditional methods for the synthesis and production of pigments may reduce their production cost and many attempts appear in the literature. In this work, the use of special additives during calcination and SHS, are shown to be effective in synthesising a wide range of ceramic pigments from minerals or even wastes [1] to reduce the cost of production are reported herein.

The production of inorganic pigments using wollastonite minerals, found in Northern Greece [4] and other areas and the influence of the initial batch composition, firing time and temperature of the pigments on the mechanical properties of plastic and ceramic materials, in which the pigments were added, were studied and are presented herein. Specifically, pigments based on the calcination of mineral wollastonite $CaSiO_3$, in which Ca^{2+} is the effective cation, were studied. The pigments obtained are relatively low-melting but sufficiently resistant to the dissolving effect of glazes and can be used to obtain overglaze paints and colored glazes [2, 3].

To reduce the calcination temperature and time, three recipes based on wollastonite, sodium carbonate and three kinds of oxides and salts ($K_2Cr_2O_7$, Co_3O and $KMnO_4$) one for each recipe, were produced. Each of the salts or oxides gave a different colour to the sintered product. For each colour, pill-shaped powder mixture samples were first produced containing different ratios of wollastonite and sodium carbonate as well as 10% of one of the oxides or salts. The Cr-containing samples were heated at three different temperatures [(800, 900, 1000) °C] for 30 minutes and those containing Co were heated at four different temperatures (800, 900, 950, 1000) °C for 30 minutes. Those at 1000 °C were fired for 20, 30, 40 and 60 minutes. The calcined pigments were then milled to the required grain size. XRD and SEM/EDX were used to analyse the influence of the initial composition and the conditions of synthesis of the pigments on their chemical and physical properties, such as grain size and resulting chemical structure. Covering power and oil absorption were also examined. In addition, the pigments produced were examined regarding colouring capability in various paints, on the fracture strength (Hertzian loading) of pigmented glass and ceramic glaze, on the effective hardness (Hertzian ball loading) of pigmented epoxy resin and on bending strength and shear strength of pigmented polyethylene and polypropylene.

Oil absorption analysis of the above calcined pigments, showed that increasing the quantity of Na_2CO_3 in the calcined mixtures resulted in decreasing the capacity of absorbing oil of the final pigment as shown in Figure1. It was also found that the covering power of the pigments produced was stable and did not depend on the sintering temperature, time or composition of the pigments.

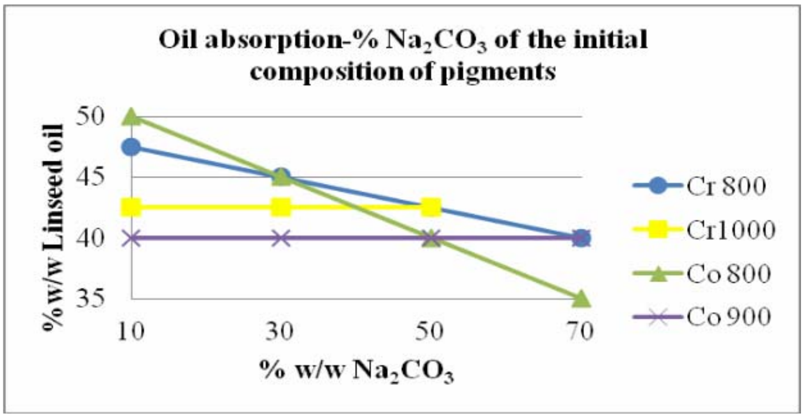

Fig. 1: Influence of temperature and Na_2CO_3 content of the pigments in the initial batch on their oil absorption.

Pigments were also synthesized using the SHS method, on the base of wollastonite modified by the addition of Co^+, $C^{r+,}$ Mn^+, Fe^+ - containing oxide and salts. Colouring ions were added to different lattices structures of spinel and mixed oxides: Ca-Si-O, Al-Ca-O, Ca-Mg-O, Ca-Ti-O, Al-Mg-O and Mg-Ca-O. The synthesized SHS pigments were milled and added to polypropylene, glass and epoxy resin and the effective hardness was studied and compared to the calcined pigments discussed above, as shown in Figure 2.

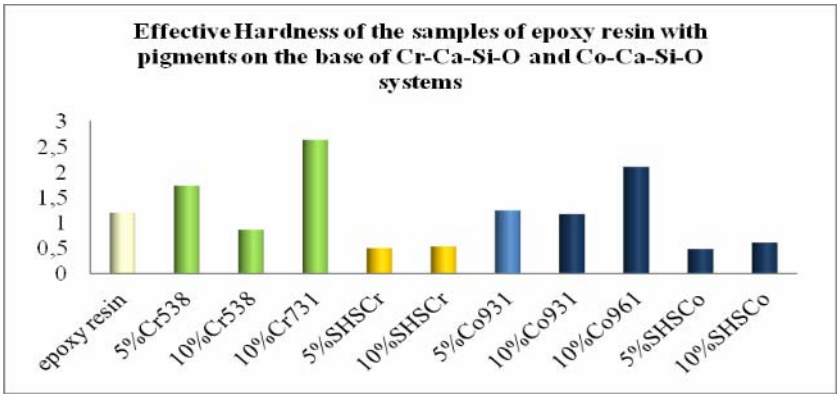

Fig.2: Influence of type of pigments and content of pigments on the effective hardness of pigmented epoxy resin samples.

The results show that wollastonite pigments produced by low-temperature calcination and by SHS are suitable for industrial application in glass, in opaque and transparent ceramic glazes, in epoxy resin, in PP and PE and water-based paints and oil-based paints.

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P-E4

FRONTAL POLYMERIZATION OF HYDROGEL

Feng Q., Ge C., Yan Q.

Institute of Special Ceramics and Powder Metallurgy, University of Science & Technology Beijing,
Beijing 10083, China

The synthesis of a series of starch-graft super absorbent hydrogels and polyacrylamide hydrogels was explored with the frontal copolymerization is first reported in the world. The effects of ambient temperature and tube size on the propagating front and the characteristic properties of starch-graft-poly (acrylic acid) hydrogels were systematically studied. The preparation of porous polymers by frontal polymerization combined with foaming process was investigated in detail.

Poly (N-isopropylacrylamide) (PNIPAM) is a typically thermo-sensitive smart material. The PNIPAM and its derivatives have potential applications for controlled drug delivery, chemical separation and sensors. The conventional batch polymerization (CBP) suffers from the long-time preparation and the poor mechanical strength as well as the slow response. To overcome above-mentioned problems, frontal polymerization (FP) process was first explored to prepare a series of PNIPAM-based hydrogels, including copolymer, interpenetrating networks and composite polymer. The fast response hydrogel and the reinforced hydrogel with compressive strength of 53.6 KPa were obtained. Compared with the product prepared by CBP route, the polymer produced by FP shows better response rate and higer compressive strength. Frontal copolymerization provides new approach to fabrication new materials. This innovative work on frontal copolymerization of our group provides new approach for making new smart materials.

P-E5

CONDENSATION, LIGHT AND ELECTRICAL DETONATIONS

Fortov V.*[1], Efremov V.L.[1], Dianov E.[2], Bufetov I.[2], Frolov A.[2], Krasnoperov E.[3], Dorofeev G.[3], Kuroedov Yu.[3], Bespalov E.[1], Eremin A.[1], Emelianov A.[1], Jander H.[4], Wagner H.Gg.[4]

[1] JIHT RAS, Izhorskaya 13/19, Moscow, 125412, Russia
[2] Fiber Optics Research Center RAS , Moscow, Vavilova 38, 119991, Russia
[3] RRC "Kurchatov Institute" Moscow, 123182, Russia
[4] Institute für Physicalische Chemie, Universität Gőttingen, D- 37077 Gőttingen, Germany
*fortov@ihed.ras.ru

It is reported experimental observation of influence of condensation of the supersaturated carbon vapor formed behind reflected shock waves on the process of propagation of a shock wave and formation of a detonation wave of condensation. Highly supersaturated carbon vapor was formed at the thermal decay of unstable carbon suboxide $C_3O_2 \rightarrow C + 2CO$ behind a shock wave in the mixtures containing 10 ÷ 30 % C_3O_2 in Ar. This reaction was followed by a fast growth of condensed carbon particles, accompanied by essential heat release. Experiments have shown the considerable temperature and pressure increase in a narrow zone behind the wave front, resulting in the amplification of a shock wave and its transition to a detonation-like regime. The analysis of kinetics of heat release in the given conditions and the calculations by one-dimensional detonation theory have shown that in the mixture 10 % C_3O_2+Ar the insufficient heat release resulted in regime of the "overdriven detonation". In the mixture 20 % C_3O_2+Ar a very good coincidence of measured values of pressure and wave velocity with calculated Chapman-Jouguet parameters has been attained. In a more rich mixture 30 % C_3O_2+Ar an excess heat release caused the slowing down of the effective condensation rate and the regime of the "underdriven detonation" has been observed.

Laser-induced optical fibers core damage remains a limiting factor of laser energy transport by optical fiber. Damages propagation as function of carried energy density has two distinguished mode (burning and detonation). The fast and most catastrophic mode is the laser driven detonation. Destruction wave propagating with high velocities (~3 km/s) through the core of silica-based fiber under intensive laser radiation has been investigated. Such regimes were detected at all investigated core diameters of silica-based fibers (D_c ~1.5-10 um). Plasma and destruction waves in optical fiber were recorded at laser beam intensity up to ~40 W/um^2 with camera exposition time 2ns for the first time. Dense plasma propagation takes place together with movement of cracks zone at investigated energy densities in core. Measurements of temperatures for both "start-stop" points and process of propagation were carried out. The measured radiating temperature for "start-stop" points was ~11000K and for detonation-like regime "observed" temperature was ~ 9400K. Maximal local pressure in core of the fiber has been estimated as ~ 50- 100kbar using a suggested equation of state.

Superconductive electric lines can demonstrate fast propagation of the normal (resistive) phase under definite conditions. These conditions (carried electric current, external magnetic field) and propagation velocities had been investigated for alone superconducting wires consisting of Nb-Ti and Nb-Zr.

P-E6

EXAMINATION OF SILICON PRODUCTION FROM QUARZ BY ALUMINIUM WITH THE HELP OF VACUUM ELECTRIC ARC

Grishin Yu.M., Kozlov N.P.[1], Skriabin A.S.[1]*, Kovalev D.Yu.[2], Mukhina N.I.[2],
Shukin A.S.[2], and Sytschev A.E.[2]

[1] Moscow State Technical University named after Bauman (MSTU), Moscow, Russia
[2]Institute of Structural Macrokinetics and Materials Science (ISMAN), Chernogolovka, Russia
* terra107@yandex.ru

The results of examination of silicon reduction from quartz by aluminum with the help of vacuum electric arc are presented. XRD research indicated that the main phases in the product are Si, SiO_2, Al_2O_3 and Al. Electron microscopy and EDS investigation demonstrated that silicon purity is 90-98 in weight %. It's showed that the optimum process duration time is about 10 min at 20 Torr of pressure in a chamber and 7 kW of discharge power.

The using of electric discharge as an energy source for realization of pure silicon production (or its refinement) is a very perspective trend [1]. This is caused by intensification of diffusion and evaporation of low-melt admixtures from the product. At present MSTU and ISMAN examine and develop of silicon production method using a vacuum arc-heated plasma furnace.

Experimental research of silicon production was made with the help of the vacuum furnace in argon atmosphere [2]. A sample for the research presented a molded mixture from fine quartz and aluminum with the use of butyral resin for improvement of material adhesion. Stoichiometry of the sample corresponded to next reaction: $4Al + 3SiO_2 = 2Al_2O_3 + 3Si$. Initial samples had cylindrical shape with diameter 4 cm and length 1 cm. Theoretical density of the samples was about 2.67 g/cm^3. Process parameters had next meanings: discharge current was 200 A, discharge voltage was 35 V, and pressure in the chamber was 20 Torr and process duration time was being varied from 1 to 15 min.

It was experimentally shown that samples mass loss was 2-30 % at changing of the process duration time from 1 to 15 min. Phase analysis of the product was made with the use of XRD research. It was demonstrated that the main phases in the product are Si, SiO_2, Al and Al_2O_3. Existence of non-interacted SiO_2 and Al in the product can be explained by low heat efficiency owing to poor thermal conduction of this molded sample. Based on electron microscopy and EDS investigation it was proved that main elements in the silicon from the product are C (7 in weight %), Al (1 in weight %) and O (1 in weight %). Existence of carbon in the product can be explained by using of an organic coupling medium at the sample fabrication. There is an electron image of a slice for sample produced at process duration time 10 min at fig. 1. More light color corresponds to more heavy phase (with dominance of Si), but dark color corresponds to light phase (with dominance of Al or O). It was installed that optimum process duration time is about 10 min. At process duration 1-10 min time it's not enough for effective reaction leaking and at process duration 10-15 min evaporation of silicon from the sample become essential effect.

At further investigations we'll continue to research discussed silicon production mode and refinement of obtained silicon.

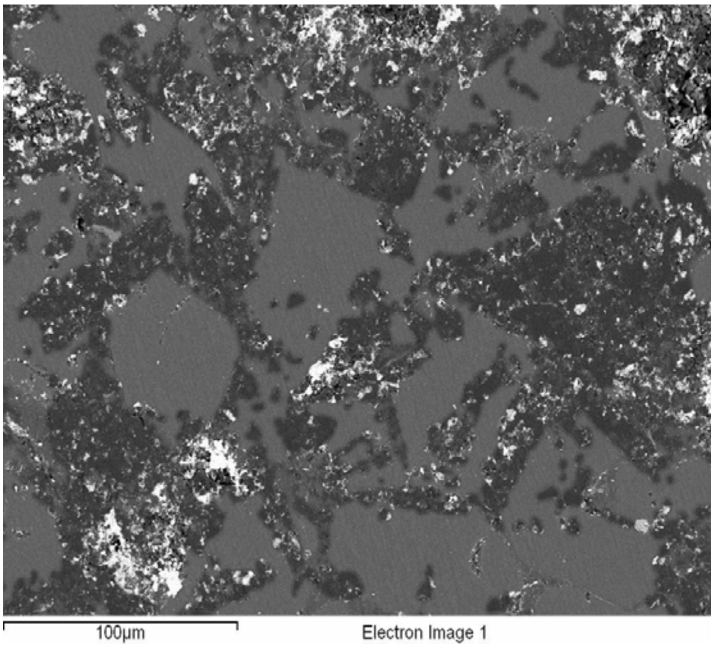

Fig.1. Electron image of a sample slice.

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P-E7

APPLICATION OF SHS-TARGETS FOR DEPOSITION OF NANOSTRUCTURED FILMS USING PULSED MAGNETRON SPUTTERING AND PULSED ARC EVAPORATION

Kiryukhantsev-Korneev Ph.V.[1*], Levashov E.A.[1], Sheveiko A.N.[1], Kuptsov K.A.[1], Pogozhev Yu.S.[1], Kurbatkina V.V.[1], Paternoster C.[2], Delplancke-Ogletree M.P.[2], Shtansky D.V.[1]

[1]National University of Science and Technology "MISIS", Moscow, Russia
[2]Université Libre de Bruxelles, Brussels, Belgium
* kiryukhantsev-korneev@yandex.ru

The synthesis of advanced multifunctional nanostructured films by physical vapor deposition (PVD) requires the development of new composite targets. Self-propagating high-temperature synthesis (SHS) provides a highly dense, uniform structure that exhibits required mechanical, thermal, and electrical properties needed for such composite target materials [1]. The control of chemical composition of the composite targets facilitates the deposition of multifunctional films with required composition. The principal difference between sputtering of composite targets and metallic or intermetallic targets is that, in the first case, the uniform flow of both metal and non metal atoms and ions is realized from the target to substrate. SHS composite targets can be especially benefit for the deposition of multifunctional nanostructured films in which both metallic (Ti,Al,Mo,Cr,Ca) and nonmetallic (Si,B,C,P,O,N) elements are present. The process of sputtering of composite targets can be even more complicated than sputtering from single element targets due to either the preferential sputtering effect or target poisoning.

The d.c. magnetron sputtering and d.c. arc evaporation are widely used technologies for production of hard multifunctional nanostructured films [2]. It's well known that the properties of the two-component films (TiN, CrN, TiO_2, etc.) deposited by pulsed magnetron sputtering can be improved by changing the frequency [3]. However the investigation of pulsed magnetron sputtering and pulsed arc evaporation method is still limited by area of two-component films, reactively deposited from elemental targets. The present work is dedicated to the investigation of the multifunctional nanostructured films produced by sputtering of composite targets using pulsed PVD technologies.

The MeB and MeC based targets alloyed with additional elements (Al,Cr,Ca,Si,P,O) were manufactured by SHS-synthesis. The targets with different geometry (disk, plate, ring, and rod) were produced using electro-erosion cutting. The pulsed magnetron sputtering was performed using either single or dual magnetron systems. The close-field unbalanced magnetron sputtering system was also used. Arc evaporation was performed using static ring or rotated rod cathodes. The deposition experiments were fulfilled under various parameters, such as frequency, power supply, substrate temperature, and nitrogen partial pressure. The targets and films were investigated by means of X-ray diffraction, scanning and transmission electron microscopy, glow discharge optical emission spectroscopy, and mechanical testing. Composite SHS-targets were successfully used under different energetic regimes. It was shown that the structure and properties of the films can be significantly improved by using pulsed power supply. The optimal values of frequency which provide best mechanical or tribological properties for each film composition and sputtering system were established (Fig. 1).

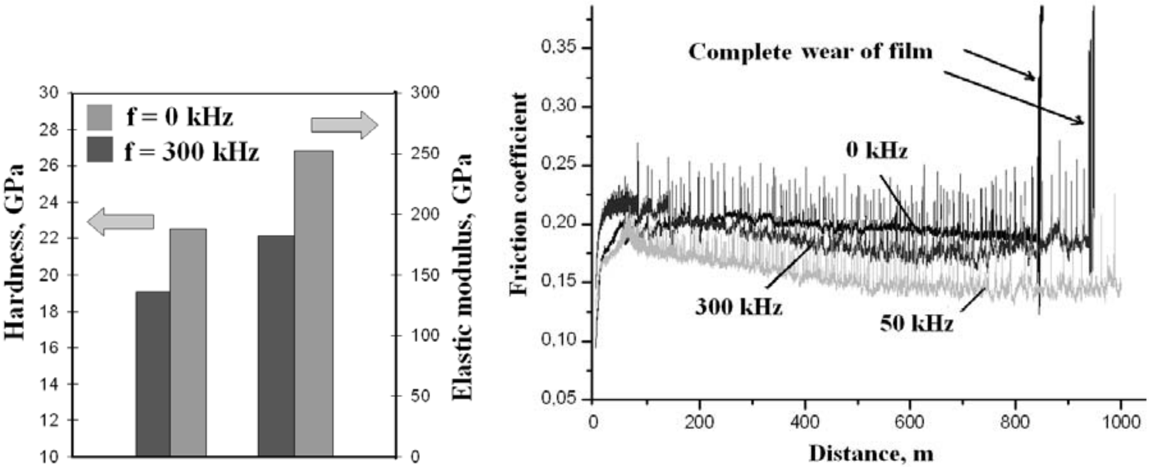

Fig. 1. Properties of films deposited from TiCCaOP target vs. frequency of power supply

The work was financially supported by П1248 project of Ministry of Education and Science of Russian Federation. The research also was performed as part of the “Interuniversity Attraction Poles” IAP-PAI program financed by the Belgian government.

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P-E8

COMBINED SHS/ARGON-ARC DEPOSITION OF PROTECTIVE COATINGS

Kvanin V.L.*[1], Balikhina N.T.[1], Karabakhin V.G.[2] and Merzhanov A.G.[1]

[1]Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow, 142432 Russia
[2] Kaluga Turbine Plant, ul. Moskovskaya 241, Kaluga, 248010 Russia
*kvanin@ism.ac.ru

Titanium alloys are being widely used as structural materials in numerous areas of modern engineering in view of their good mechanical strength and heat/corrosion resistance. Since titanium alloys exhibit poor friction behavior, relatively high reactivity, and proneness to seizure, adhering, and scuffing, the surface of titanium machine parts is normally strengthened by protective coatings deposited by using galvanic, chemical, thermochemical, plasmochemical, electrospark, etc. methods.

In this communication, we report on a new method [1, 2] for deposition of protective coatings onto machine components made of titanium alloys. The method combines the SHS of adding material and its argon-arc deposition onto a Ti substrate for use as friction pairs operating under heavy and high-velocity.

Surfacing was carried out as schematically shown SHS electrode is inserted into the electric arc ignited between substrate *1* and non-melting electrode, which gives rise to SHS reaction in electrode . Hot combustion products are remelted in the arc to form protective coating.

In a search for proper electrode materials, we tested the mixtures of different metals (Ni–Al, Ni–Ti, Ti–Al, Ti–Al–Nb–Mo, Ti–Al–Nb–Cr), metals with carbides (TiC–Ni–Mo, TiC–Ni, TiC–steel), and metals with borides/carbides (TiB–Ti, TiB–Ti–Cu, TiC–TiB–Ti). The best results were obtained with the two TiB–TiC–Ti coatings characterized in the Table.

Table. Some characteristics of deposited coatings

	Composition	d, g/cm^3	HRA	σ_b, MPa	σ_c, MPa
Coating 1	20% (TiB, TiC), rest Ti alloy	4.58	76.0–78.0	650–700	2440–2620
Coating 2	30% (TiB, TiC), rest Ti alloy	4.56	79.5–80.0	550–600	2480–2700

The diffraction pattern of coatings clearly showed the presence of the TiB, TiC, and Ti phases. The deposited material is represented a Ti-based matrix doped with TiC grains and TiB whiskers oriented largely along the direction of item motion. The microhardness of TiB whiskers was found to have a value of 1100–1350 HμV.

The ring pieces were tested for corrosion resistance: their holding in sea water at normal conditions for 720 h gave no visible changes in the quality of deposited surface. Tests in intense water flux for 200 h gave the coefficient of material erosion $K_{er} \approx 4.3 \times 10^{-12}$ m/h, which is six orders of magnitude lower that that of existing cermet prototype ($2.7–3.0 \times 10^{-6}$ m/h).

Tribological testing (ring-on-ring rotation in water) showed that the critical load applied to our rings was higher by a factor 1.5–2.0 compared to existing prototype.

A new method for combined SHS/argon-arc deposition of protective coatings 2–10 mm thick onto Ti alloys has been tested on a pilot-scale level using specially designed electrode materials based on reactive SHS-type mixtures. The service parameters of thus deposited TiB–TiC–Ti coatings were found to exceed those of existing materials. The method can be recommended for practical implementation.

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P-E9

HYDROGEN PRODUCTION BY HYDROLYSIS OF MAGNESIUM BASED HYDRIDES PREPARED BY HYDRIDING COMBUSTION SYNTHESIS AND MECHANICAL MILLING

Li L.*, Zhu Y.

College of Materials Science and Engineering, Nanjing University of Technology
5 Xinmofan Road, Nanjing, 210009, PR China
* lilq@njut.edu.cn

Hydrogen production by the hydrolysis of magnesium-based hydrides has been regarded as a promising solution for on-board vehicle hydrogen storage because of the high gravimetric density of 7.6 wt.% (MgH_2), as well as, the ability to produce twice as much hydrogen during hydrolysis. This paper presents an investigation on the hydrogen production by the hydrolysis of magnesium-based hydrides which are prepared by the material processing of HCS+MM, that is hydriding combustion synthesis (HCS) followed by mechanical milling (MM). Specifically, the effects of the HCS condition (e.g., the Mg/Ni ratio, the holding time at 613 K), the different milling times (0.5 h, 5 h, 10 h), the process control agents (graphite) of MM and the hydrolysis temperatures on the microstructures of HCS+MM products, as well as, the hydrolysis properties were investigated. The results showed that the HCS+MM products with Mg:Ni=99:1, holding time at 613 K for 20 h, and after 5 h MM were mainly comprised of MgH_2, Mg_2NiH_4 and Mg. Graphite addition in ball milling process inhibits the agglomerates and cold welding of magnesium hydrides particles. $Mg_{99}Ni$ hydrides prepared by the process of HCS+MM could produce 850 ml/g hydrogen (7.6 wt.%, 50% in conversion) within 60 min at room temperature. The kinetic analyses of hydrolysis indicated that hydrolysis process divided into two parts: part one is the surface control reaction before the formation of $Mg(OH)_2$ layer and part two is the diffusion control reaction after the formation of $Mg(OH)_2$ layer. The ball milling process could be used to prepare the fine particles to increase the specific surface area and to extend the rapid reaction time of the formation of $Mg(OH)_2$. The results showed that both the hydrogen amount and reaction rate were all increased by increasing temperature (Fig. 1). In the 333 K water, $Mg_{99}Ni$ hydrides could produce 1350 ml/g hydrogen (12.1 wt.%, 79.5 % in conversion) within 60 min. It was concluded that temperature and time are key factors for controlling the hydrolysis reaction and the HCS+MM process shows great promise for on-board vehicle hydrogen storage.

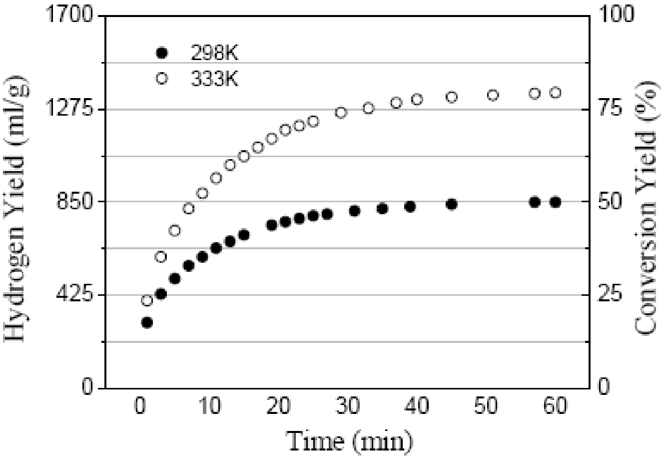

Fig. 1 Kinetics of hydrogen generation at 298 K and 333 K by hydrolysis of $Mg_{99}Ni$ hydrides prepared by the process of HCS+MM.

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P-E10

HIGHLY ACTIVE Cu–Cr–O MIXED SPINEL SHS CATALYST FOR THE OXIDATION OF CO

Marinou A., Xanthopoulou G., Vekinis G.

Institute of Materials Science "Demokritos" National Center for Scientific Research, Aghia Paraskevi,
15310 Athens, Greece
gxantho@ims.demokritos.gr

The best industrial catalysts for low temperature CO oxidation are noble metals but their high cost has prompted a search for cheaper systems. Various mixed oxides of transition metals, copper and chromium among them, show substantial promise in this regard. Catalysts containing copper oxide are well known to be active in catalytic oxidation of carbon monoxide and SHS versions of such catalysts have been reported in the past [1,2]. In this work, materials were synthesized using Self-Propagating High-Temperature Synthesis (SHS) of powder mixtures based on Cu-Cr-O, compacted under a pressure of 20±5 MPa in the form of rods of diameter 2 cm and tested for catalytic oxidation of CO. The materials that were produced consisted of mixtures of $CuCr_2O_4$ and $CuCrO_2$ spinels as well as mixed oxides of various ratios.

The catalysts were synthesized at different preheating temperatures (650-850^oC) for a few minutes prior to initiation of SHS. Combustion temperature and the final properties of the catalyst depended on the properties of the starting raw materials and the conditions during SHS, especially the grain size and distribution, the purity as well as the synthesis parameters. All these parameters were systematically investigated in order to maximize the catalytic properties of the materials. During SHS and later thermal treatments, the oxides partially react to form various types of spinel-like materials depending on the SHS combustion and later calcination temperature. These spinels have different effect on the catalytic activity. The ratio of $CuCr_2O_4$ to $CuCrO_2$ was regulated by additional thermal treatment at different temperatures and duration of thermal treatment. All samples were analyzed and characterized using XRD, SEM and measurements of mechanical strength, porosity and surface area.

The catalytic activity for CO oxidation was measured at temperatures between 30 and 400 °C. for coarsely crushed SHS material of average pellet size 2-3 mm. Catalytic activity was carried out using flowing CO of concentration 1000ppm in air, similar to what is the maximum that would be expected in car exhausts under normal operating conditions, at a flow rate of about 11000 hr^{-1}.

It was found that samples which contained maximum concentration of SHS $CuCr_2O_4$ in the catalyst had maximum catalytic activity, with such catalytic activity starting at a temperature as low as 30 ^oC and reaching 100% conversion at a temperature as low as 210 ^oC (Fig.1). Such highly active catalysts containing SHS $CuCr_2O_4$ are thus very good alternatives to precious metals such as platinum for promoting the oxidation of CO (compare with state-of-the-art Pd/Al_2O_3 catalysts in Fig.2) in exhausts from incomplete combustion in internal combustion engines during the early stages of their operations and other similar situations.

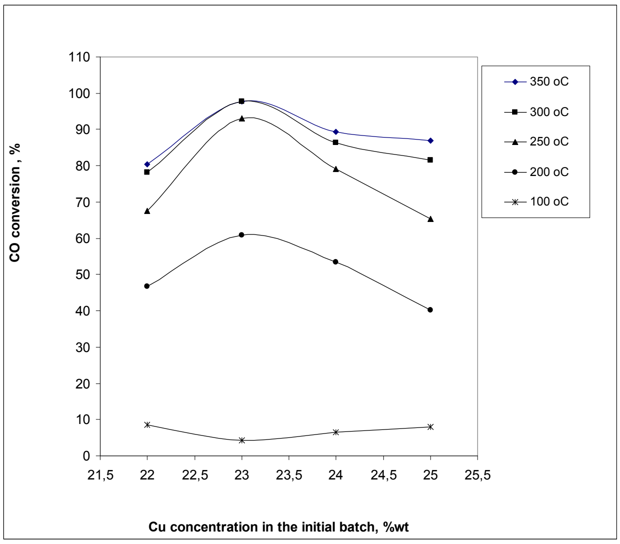

Fig.1 CO catalytic oxidation activity of SHS Cu-Cr-O catalyst

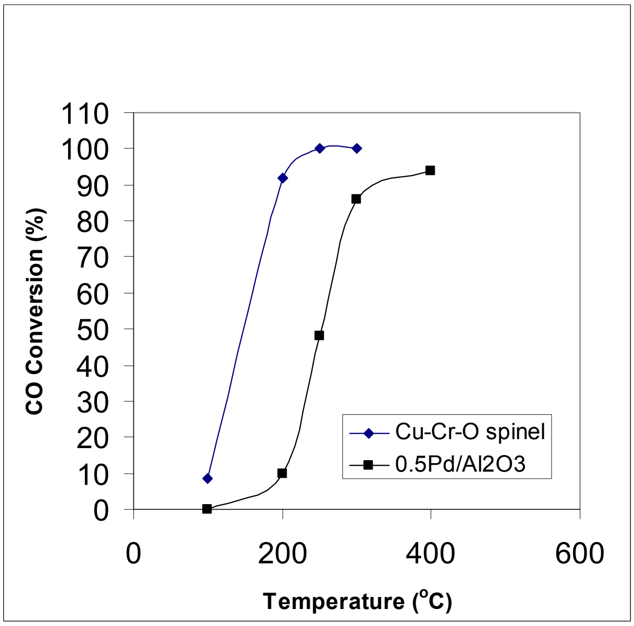

Fig.2 Comparison of Cu-Cr-O and Pd/Al_2O_3 catalytic activity in CO oxidation process

Significantly, the $CuCr_2O_4$ samples exhibited the above-presented catalytic activity for the oxidation of CO, even though they had no micropores and a surface area of only about $1m^2/g$, 2 orders of magnitude lower than what is needed by Pd/Al_2O_3 for the above result. This means that the new SHS catalysts would not be. Further work is being carried out to improve the surface area and the conversion efficiency.

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P-E11

METHODS FOR DETERMINATION OF PORE SIZE DISTRIDUTION IN THE VOLUME OF POROUS MATERIALS

Maznoy A.S.*[1], Kirdyashkin A.I.[2], Maksimov Yu.M.[2], Kazazaev N.Yu.[1]

[1] Tomsk State University, 36 Lenin Avenue, Tomsk, 634050, Russian Federation
[2] Department of Structural Macrokinetics of Tomsk Scientific Center SB RAS, 10/3 Akademicheskii Avenue, Tomsk, 634021, Russian Federation.
* maznoy_a@mail.ru

INTRODUCTION

The experimental pore size is shown [1] to be the function of the method for their determination and the volumetric and continuous-flow methods to be sensitive to the pore shape. Such techniques are inapplicable to the materials with the bimodal, gradient, or periodical structure of porosity. Since the metallographical methods can be used for an effective porosity analysis, automatic image analyzers (AIA) are widespread for metallographic analysis. Despite their capability to determine up to 40 geometrical parameters, AIA cannot process statistical data on porous material morphology using the methods of stereometric metallography. The stereometric metallography calculations allow 3-dimensional characteristics of a material to be determined, while conventional analyzers give only 2-dimensional characteristics of the objects under study.

Definition of the number of spherical particles in the volume of the studied material and the particle size distribution parameters in terms of geometric series. There are «the array» and «the framework» structures of porosity which are in turn classified into «regular» and «nonregular» [2]. It is obvious that porous SHS materials belong to the nonregular structures. The nonregular structures can be both isotropic and anisotropic. A special class among the nonregular heterophase systems is the so-called statistically isotropic mixtures where all phases are presented similar building blocks. In real porous SHS-materials, the statistically isotropic mixtures are the framework material, where framework porosity is formed by closed pores. In this case, the characteristic geometrical parameters of nonregular building blocks (pore sizes) become random quantities and undergo some kind of distribution. We modified the method for definition of the number of spherical particles in the volume of porous materials and size distribution parameters (diameters) in terms of geometric series (Saltykov method (SM) [3]). The modified SM allows us to use any number of dimensional groups in reconstruction of pore size distribution and to vary the value of the denominator of geometric series of diameters. Let i be the number of dimensional groups, ni – the amount of pore cross-sections of respective dimensional groups per 1 mm^2 of a metallographic section, D_1 – the size of the first dimensional group equal to the diameter of a maximal pore section, D_i – the diameter of an «i-th» dimensional group, Z – the denominator of a geometrical progression of a decreasing series, the number of pores in the «i-th» dimensional group in the volume of framework material, in this case, N_i , is calculated as:

$$N_i = \frac{1}{D_i} \sum_{j=1}^{i} \theta_j \cdot n_{i-j+1}$$

$$D_i = K_i \cdot D_1; \; K_i = (10^{-Z})^{i-1},$$

$$\alpha_i = \left|\sqrt{1-K_i^2} - \sqrt{1-K_{i+1}^2}\right| \cdot 100,$$

$$\theta_1 = \frac{100}{\alpha_1}, \quad \theta_2 = -\frac{\alpha_2 \cdot \theta_1}{\alpha_1}, \quad i \geq 3 \quad \Rightarrow \quad \theta_i = -\frac{\alpha_i \cdot \theta_1}{\alpha_1} - \sum_{j=3}^{i} \frac{\alpha_{i-j+2} \cdot \theta_{j-1}}{\alpha_1}.$$

If the pore number in the «*i*-th» dimensional group is negative, it is necessary to stop the calculation and, for reconstruction, use the data up to «(*i-1*)-th» dimensional group inclusive. The developed method can also be used for the materials whose pores are spheroids in the form but only for the case where the pores are ellipsoids, and their spinning axes are codirectional to a certain direction and the studied plane is perpendicular or parallel to the given direction. The obtained data characterize the pore size distribution in the volume of framework material, the total number of «closed pores» in the volume of framework, and characterize framework porosity of a porous material.

CONCLUSION

We upgraded the method for definition of the number of spherical pores in the material volume (3D) and size distribution parameters (diameters) in terms of geometric series. The method is based on analysis of the data on pore cross sections (2D) and allows us to consider any number of dimensional groups and to vary the denominator of the progression. The data obtained characterize the pore size distribution in the volume of framework material, the total number of pores, and characterize material porosity. The method was tested on a model porous sample and on porous SHS-materials. The results of tests show that the procedures can be used for analysis of porous materials of various origin and porosity structure.

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P-E12

INVESTIGATION OF HYDROGEN INTERACTION WITH TITANIUM BASED HIGH-DENSITY ALLOYS IN THE SHS MODE

Mayilyan D.G.*, Dolukhanyan S.K.

A.B. Nalbandyan Institute of Chemical Physics of NAS, 5/2 P. Sevak Str., 0014, Yerevan, Armenia
* davitmayilyan@gmail.com

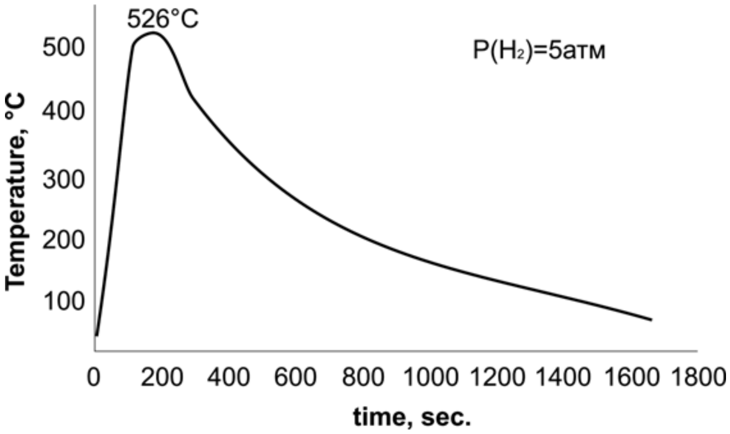
In this work, we investigated the processes of combustion of Ti-Hf, Zr-Hf, Ti-Zr-Hf alloys in hydrogen in Self-propagating High-temperature Synthesis (SHS) mode. Alloys of different compositions have been synthesized in these systems by “hydride cycle” method, which is developed at the laboratory of technology of SHS processes of IChPh [1, 2].

The study of Ti-Hf, Zr-Hf, Ti-Zr-Hf alloys interaction with hydrogen has shown that the compact alloys without crushing are capable to interact with hydrogen, forming the hydrogen-rich hydrides (H/Me = 2-2.28).

Process of hydrogen interaction with alloys can be presented by the following reaction:

$$Ti_xHf_{1-x} + H_2 \leftrightarrow Ti_xHf_{1-x}H_y.$$

These reactions are reversible – important characteristic for cycling and usage of the hydrides in the quality of hydrogen accumulators.



Thermogram of combustion of $Ti_{0.66}Hf_{0.34}$ alloy in SHS mode at hydrogen pressure 5 atm.

Combustion temperature of an alloy of any composition was between 500-650°C. It was shown, that at interaction of alloy with hydrogen, the developed combustion temperature is rather low in comparison with the pure metal (Ti, Zr, Hf) combustion temperatures [3, 4].

The influence of hydrogen pressure on the process of alloy combustion was investigated on a sample of $Ti_{0.66}Hf_{0.34}$ alloy. With the increase of hydrogen pressure in the interval 1-50 atm, the combustion temperature grew from 450°C to 750°C. Combustion temperature increases, since with increase of pressure hydrogen concentration in reactionary space grows, and it is strongly influence on the temperature of exothermal reaction, due to which are realized SHS processes in

Me-H system. The study had shown that the density of compact sample and hydrogen pressure (1-50 atm) had not influence on the hydrogen content in the synthesized hydride. The details of investigations of SHS processes in Me-H system cited in earlier published work [5].

It was shown that the crystal structure of the synthesized hydrides depends on the composition of an initial alloy. At some compositions, the interaction of an alloy with hydrogen results in hydrides with cubic structure of fluorite (CaF_2), at other compositions – the hydrides with tetragonal structure of thorium dihydride (ThH_2) are formed. X-ray analysis data show, that the values of lattice parameters, **a** and **c,** depend on the structure of an initial alloy and decrease with the reducing of the titanium concentration.

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P-E13

INVESTIGATION OF Pd/FIBER GLASS AND Pd/γ-Al_2O_3/FIBER GLASS CATALYSTS PREPARED BY SURFACE SELF-PROPAGATING THERMOSYNTHESIS (SSTS).

Mironenko O.O.[1], Goncharov V.B.[2*], Tsyrul'nikov P.G.[1]

[1]Institute of hydrocarbon processing Siberian Brunch RAS, Omsk, Neftezavodskaya st. 54, 644040, Russia
[2]Boreskov Institute of catalysis Siberian Division RAS, Novosibirsk, Lavrentieva prospect 5, 630090, Russia
* shishkina_oo@ihcp.oscsbras.ru

The combustion methods: self-propagating high-temperature synthesis (SHS), various modifications of solution combustion synthesis (SCS) and some others are widely used for catalysts preparation. The surface self-propagating thermosynthesis (SSTS) is a variant of the SHS method. The SSTS is used to obtain metal and oxide catalysts on chemically and geometrically different supports [1-2]. The preparation technique consists of: 1) impregnation of various carriers (fiberglass, for example) by the solution of active component precursors and fuel additives which can be oxidized (burned) with oxygen (air); 2) drying the sample, and 3) initiating by the heat pulse the surface flameless combustion. This method allows to prepare the catalysts for minutes, and to control the synthesis temperature in the range of 300 - 1000^0C. In many cases the SSTS allows to exclude the hydrogen reduction step in metal catalysts preparation.

We prepared two sets of samples by SSTS method: a) 1wt%Pd/ZrFG and b) 1wt%Pd/γ-Al_2O_3/ZrFG catalysts, where ZrFG is the Zr containing fiberglass and γ-Al_2O_3/ZrFG is the support with a secondary carrier (5-20% γ-Al_2O_3 by mass.). $Pd(NO_3)_2$ solution and fuel additives: citric acid (CA) or D - glucose (GL) were used as precursors. For comparison we also prepared the catalysts by conventional method (impregnation, drying, H_2 reduction) with the same composition as for the samples a) and b). Catalytic characteristics of prepared samples were determined in the reaction of liquid-phase selective hydrogenation of acetylene to ethylene in the CO presence in the shacked gradient less flow reactor under the following conditions: reaction temperature 90ºC, V gas mixture 100 ml/min. N-methylpyrrolidone was used as the solvent. The composition of reaction gas mixture is: 4 vol. % C_2H_2, 90 vol. % H_2, 2 vol. % CO and 4 vol. % He. The inlet and outlet gas composition was analyzed by chromatography analysis.

It was found that samples on fiberglass support 1wt% Pd/ZrFG prepared by the SSTS and by the conventional method have low activities in the investigated reaction because of low samples S_{BET}. For the SSTS samples (1% Pd/γ-Al_2O_3/ZrFG) high values of conversion and selectivity to ethylene were observed comparable with data for catalysts prepared by conventional method.

The SSTS catalysts were investigated by XPS, EXAFS, TEM and by XRD on synchrotron irradiation with time resolution (XRD SI) [3]. The data obtained by XRD SI method, allowed to detemine the lengthes of different zones of the heat front, the changes in phase composition and the sizes of coherent-scattering regions (CSR) of forming active component along zones. It is shown that the amount of fuel additive (CA) for samples 1% Pd/ZrFG and 1% Pd/5%γ-Al_2O_3/ZrFG affects on transformation of Pd $(NO_3)_2$ into Pd and PdO phases. In this case the formation of the active phase was found takes place after the temperature maximum of the combustion front. The formation of Pd^0 and PdO was observed just before the combustion front for samples 1% Pd/ZrFG and 1%Pd/5% γ-Al_2O_3/ZrFG, if the D-glucose was taken as a fuel additive. It should be noted that the final particles of Pd and PdO of all samples have similar sizes of CSR.

The data obtained allowed to suggest that the large palladium particles were formed on the fiber glass surface, while palladium oxide was stabilized in the secondary carrier γ-Al_2O_3. Note that the dynamics of acetylene hydrogenation conversion for all catalysts tested had a tendency to increase. This is probably due to the rapid reduction of palladium oxide presented in the active layer. The nature and amount of fuel additive affects on the state of the precursors, and the dynamics of the Pd and PdO phases formation and, consequently, on the catalytic characteristics of catalysts. It was found by physical methods that the catalysts contain Pd^0 and PdO in various ratios.

The authors gratefully acknowledge the financial support from the RFBR (Grants 08-03-00335a, 10-03-90727, 10-03-90729, 10-03-00451a).

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P-E14

SOLAR ENERGY/SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS - NEW APPROACH FOR INCREASE OF TECHNOLOGICAL ENERGY EFFICIENCY

Okrostsvaridze O.Sh.*, Tavadze G.F., Aslamazashvili Z.G., Zakharov G.V., Badzoshvili T.V.

LEPL – Ferdinand Tavadze Institute of Metallurgy and Materials Science, 15, Al. Kazbegi av.,
0160, Tbilisi, Georgia
* otari_ok@yahoo.com

The main criteria for obtaining by the SHS-process the construction materials upon the basis of ultra-dispersion powders (nano powders) are meeting the two conditions:

1. lowering the combustion temperature through diluting original components with different produce;
2. heating of the reaction charge and raising its starting temperature, which in our case was implemented by means of the solar system.

The solar system consists of the two modules, a short-focused solar heat-collector and a reception facility, the SHS-reactor itself СЭ-0,27. In the figure is demonstrated the scheme of the solar system modules layout.

Fig. The scheme of the solar system modules layout

For the SHS-process the original mixture is placed into the reaction zone of the SHS-reactor, the initiated spiral and a thermocouple are carried into contact with the original mixture. The body of the SHS-reactor is pressurized and the gas, for instance 10 atm., is pumped in through the socket. The SHS-reactor is positioned in the focus of the solar heat-collector and is representing a camera with lightproof window, which can be vacuum-pumped inside, create the inert-gas atmosphere, etc.

In the metal water-cooling camera there is placed a thermally isolated graphite crucible, into which there is disposed the original mixture. The closed system of the SHS-reactor case is installed in the zone of solar energy supply, while the sunbeams pass through the protective lightproof glass. After heating up the original mixture to the temperature 550-650°, the original mixture is initiated, in the synthesizing process the excess gas is diverted through the socket by means of a protective shutter. After the synthesis the excess gas is withdrawn through the socket, while the synthesized material is extracted from the reactor. The camera serves for the cooling of the SHS-reactor. The whole process of the materials synthesis is carried out distantly [1].

The solar system is functioning so, as to principally raise the coefficient of efficiency and economic efficiency of the process of helio-conversion at the expense of constructive modules, short-focus solar heat-collector and receiving apparatus.

The modules are disposed so that the sunbeams penetrate through them in the most energy amount into the SHS-reactor, maximally heating the technology material placed there. For providing maximally possible limitation of the heat loss, through the transparent material lowering heat-isolation characteristics of the reactor, in the reaction camera are applied the technological materials with increased beam-consuming characteristics, specific heat capacities and heat accumulating properties. Besides, the heat losses are limited at the expense of the heat isolation of the reaction form from the contact with the metal case of the SHS-reactor. This facilitates the accumulation of the heat energy in the technological materials of the SHS-reactor. Thus, subject to the assigned task, on the one hand, in the process of the materials synthesis the heat losses are maximally lowered and the "persistence" of the final product as regards the temperature is high, while on the other hand, when the chilling of the synthesized product is required, the cooled gas is supplied to the reaction zone. All these technological and constructive peculiarities of the solar system allow obtaining super-dispersion and nano-dimension composite powders in low-calorie systems.

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P-E15

SHS OF Mo-BASED HYDROGENATION CATALYSTS

Pagonis N.[1,2], Xanthopoulou G.[2], Vekinis G.[2], Polymenis S.[1]

[1] *Department of Chemical Engineering, National Technological University of Athens, Greece*
[2] *Institute of Materials Science, NCSR "Demokritos", 15310, Athens, Greece*
gxantho@ims.demokritos.gr

This paper presents the results of an investigation in producing SHS catalysts for hydrogenation. The systems Al-NiO-MoO_3-Al_2O_3 and Al-Ni-Mo were studied and the research was focused on their materials characteristics that affect their catalytic activity. The catalysts were produced at various pr-heating temperatures between 700°C and 950°C. Properties measured included compressive strength, microstructure and morphology (SEM), atomic structure (XRD), their porosity and their surface area before and after chemical leeching (with 20% NaOH solution).

The possible reactions that take place at the system Al-Ni-MoO_3- Al_2O_3 during the SHS process are the following:

1. $Al + 3NiO \rightarrow 3Ni + Al_2O_3$
2. $3Al + Ni \rightarrow NiAl_3$
3. $MoO_3 + NiO \rightarrow NiMoO_4$
4. $MoO_3 + 2Al \rightarrow Mo + Al_2O_3$
5. $3Mo + Al \rightarrow AlMo_3$

These were confirmed by XRD as shown in the typical XRD spectrum in Figure 1.

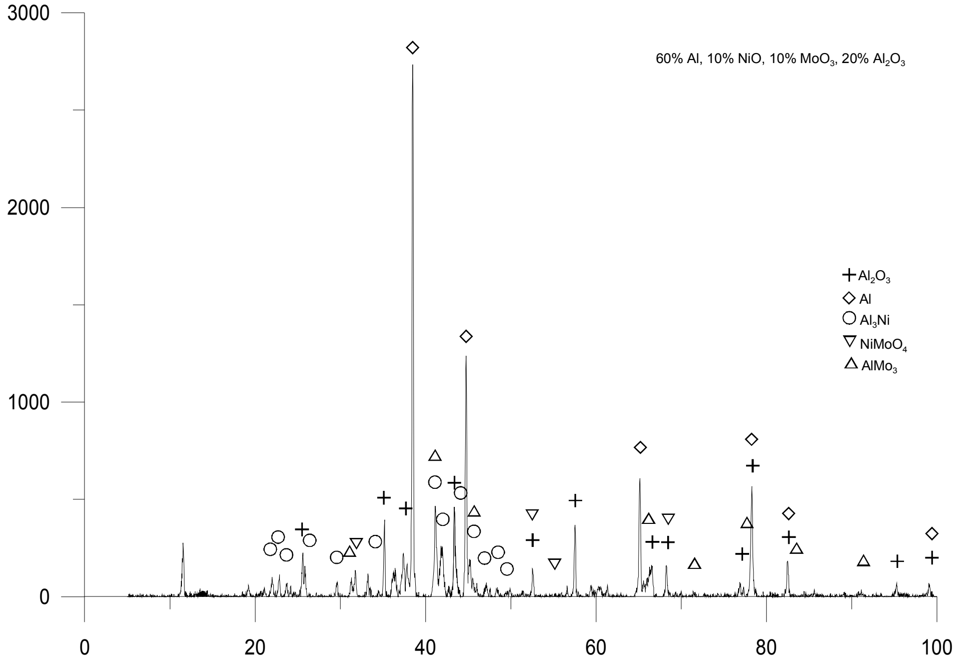
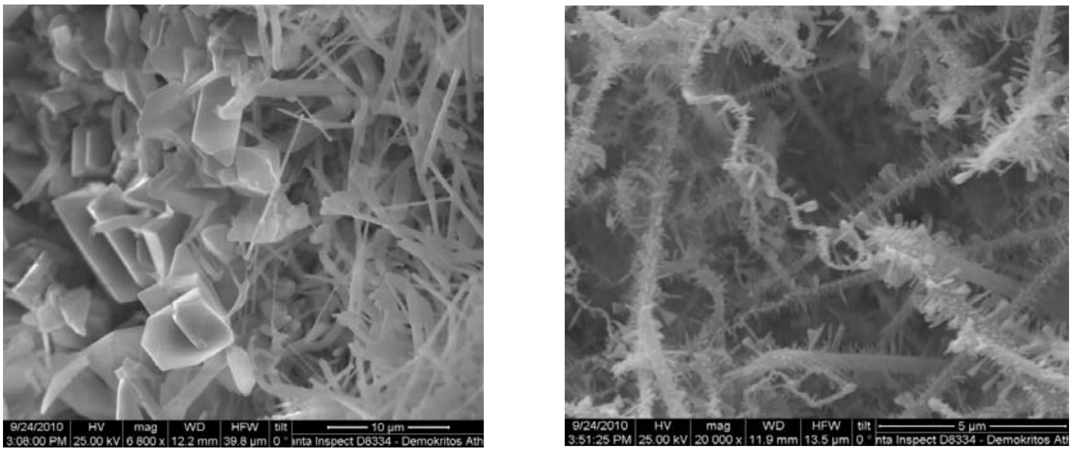


Fig.1.Typical XRD spectrum of the system Al-NiO-MoO_3-Al_2O_3 showing the presence of $AlMo_3$

Structural differences were found in the SHS products that correspond the starting composition used (0% MoO_3, 5% MoO_3, 10% MoO_3 and 20% MoO_3).

Typical property values of the system Al-NiO-MoO_3-Al_2O_3 are: Porosity:50% - 70%, surface area:1.5 - 3m^2/g, density:1.6 – 2.1 g/cm^3.

In the presence of $AlMo_3$ significant quantity of AlN were found as shown in the SEM micrographs in Figure.2



a b

Fig 2.SEM photos of AlN whiskers (without MoO_3 (a) and with 5% of MoO_3(b) in the initial batch)

Compressive strength of the catalysts on the basis of system $Al-NiO-MoO_3-Al_2O_3$ increased with increasing of MoO_3 concentration in the initial batch, because of increasing of quantity of intermetallic compounds, but it was lower than in the system $Al-NiO-Al_2O_3$ because of the development of $NiMoO_4$ in the presence of MoO_3 as shown in Figure 3.

To increase their specific surface area, the catalysts were leeched with 20% NaOH solution at 60°C for an hour and then washed with water. The hydrogenation of butindyol-1,4 was done in standard installation for liquid phase hydrogenation at temperatures from 20°C to 90°C. Water was used as solvent. In every experiment, 1ml butindyol-1,4 was used, calculated to absorb 140ml of hydrogen. The quantity of the catalyst varied from 0.5g to 10g. Before every experiment, the catalyst was saturated with hydrogen for 2 hours. The hydrogenation kinetic curve contains 2 maxima that correspond to the conversion of butyndiol to butendiol and that of butendiol to butandiol respectively (Figure 4).

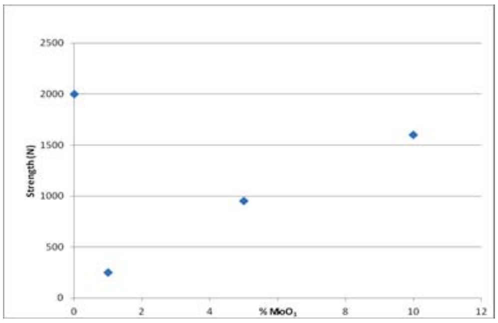


Fig3.dependence of the compression strength of the catalysts from the concentration of MoO_3 in the initial batch

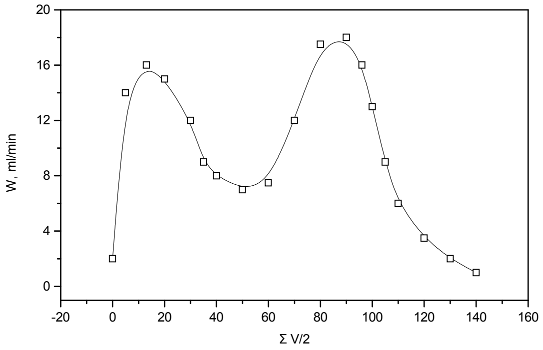


Fig.4 Butyndiol hydrogenation kinetic curve

P-E16

METHOD FOR APPLICATION OF SHS-COMPACTING IN VACUUM

Sakhvadze D.V.*[1], Tavadze G.F.[1], Shteinberg A.S.[2], Khantadze J.V.[1], Jandieri G.V.[1]

[1] Ferdinand Tavadze Institute of Metallurgy and Materials Science, AS of Georgia;
[2] ALOFT, Chem. Eng. and Mater. Sci. Consulting Inc., Berkeley, California, 94708, US
*david.sakhvadze@yahoo.com

SHS-compaction is a promising method for obtaining hard-alloy materials. SHS-compaction based technology including SHS-pressing and SHS-extrusion allows one to synthesize required material and to obtain end product by using an installation described in [1].

Due to high temperatures the process is characterized by high rates and conversion degrees, on the one hand, and high ductility of the end synthesis product on the other hand. That allows one to apply pressure to still hot combustion product to shape in desired manner thus in most cases directly obtaining end product. One of the main features of the process is that both reagents and final products are in condensed state. Under real conditions, even at SH-synthesis in mixtures of quite pure powders, combustion is always accompanied by emission of relatively small amounts of gases. This phenomenon may be related to such processes as desorption of gases from surface of the powders during their heating, evaporation of volatile impurities, de-oxidation of the oxide films, etc. [2].

The emission of gases breaks contacts between the reagent particles, causes shattering of the reaction mass and may finally cause decreasing of the target material conversion degree. It is also noteworthy that due to high rates of the combustion product cooling, some amount of gas fails to escape from the target material prior to the pressing stage beginning. This gas forms the closed pores in the compacted material.

According to the literature data [3], at SHS-pressing of the TiC-TiB_2 system the increase in impurity-related gas emission in the range of 30-60 cm^3/g causes significant growth of the target material porosity. M. Ponomaryov [4 , 5] showed experimentally that gas evolution takes place in the preheat zone that is before the chemical reaction responsible for SHS. The evolving gas separates surfaces of the reagents causing worsening diffusion conditions and slowing down macrokinetic processes. This mechanism is indicated by an unusual dependence of the combustion rate on the sample thickness (for a wide range of this parameter): the SHS front propagation velocity decreases as the sample thickness grows.

Emission of gas due to impurities during SHS-compaction is also responsible for distortion of desired shapes of even porous final products (items). Thus development of method ensuring gas removal from SHS hot product prior to the stage of its pressing would be of significant importance. This matter of interest is related to the fundamental study of the SHS-compaction theory. The study of capabilities and aspects of SHS-compaction involving forced (vacuum-assisted) extraction of impurity-born gas from still non-compressed mixture burning in a press-form is of great interest.

A new method of SHS-compaction by using a specifically developed vacuum press-form (Fig. 1) [6] is considered. Some experimental results are presented. It is demonstrated that application of the press-form facilitates gas escape from the SHS product which allows one to make a serious step towards solution of many practical SHS-compaction problems.

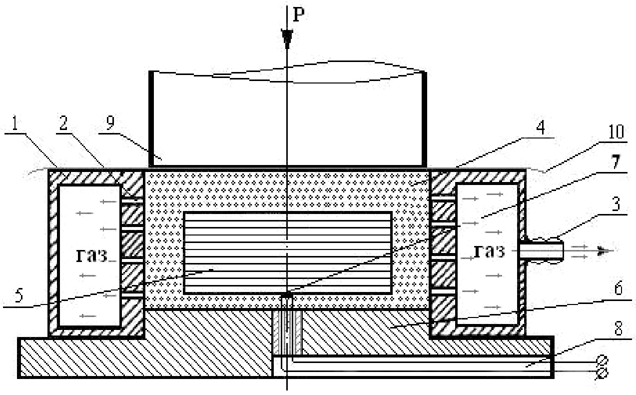


Fig. 1. Press-form for SHS-compaction in vacuum

1 – matrix with vacuum chamber, 2 –breeching holes, 3 – connecting pipe for gas pump-down,
4 – heat-insulating mass, 5 – reaction system, 6 – the press-form base,
7 – initiating spiral, 8 – porcelain two-way system for spiral, 9 – die,
10 – polyethylene film.

This study leads to increasing the process reliability and the quality of the end products with respect to their desired shape and size as well as the synthesized material characteristics.

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P-E17

3D CERAMIC FABRICATION VIA SELECTIVE LASER SINTERING (SLS) AND COMBINED SLS – SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS)

Shishkovsky I.V.[1], Kuznetsov M.V.*[b,c], Morozov Yu.G.[b]

[1] Lebedev Physics Institute, Samara branch, Russian Academy of Sciences, 443011 Samara, Russia.
[2] Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences (ISMAN), Institutskaya Street 8, Chernogolovka, Moscow region, 142432 Russia
[3] Mordovian State University, Bolshevistskaya Street 68, Saransk, 430005 Mordovia
*maxim1968@mail.ru

Three dimensional shapes with a wide range of electro-physical characteristics were synthesized via a Selective Laser Sintering process from different oxide powder mixtures: ceramic-plastics (PZT+ PVDF or SiO_2 additives); magnetic systems Ba+M and Li+M (M ~ Fe, Cr) for $Li_{0.5}Fe_{2.52x}Cr_xO_4$ and $BaFe_{12-2x}Cr_xO_{19}$ ferrites and high temperature superconductive ceramics $YBa_2Cu_3O_7$, $SrFe_{12}O_{19}$. Such materials have promising applications in smart micro devices (Micro Electro Mechanical Systems, or MEMS devices): sensors; filters; piezoelectric detectors and pumps. The concept of connectivity can be used to describe the arrangement of the component phases within a composite. The physical properties of 3D parts can be tailored by changing the phase–structure connectivity, volume fraction, phases distribution and pores within the composite. The optimum regime for laser synthesis of 3D parts and some of their associated electro-physical properties were determined by changing the laser parameters and by conducting the SHS-SLS reactions in applied electric and magnetic fields. An external field applied during SHS alters the interaction mechanism and the product structure by influencing the generation and motion of electrons and chemically ionized particles formed in the reaction front in the transient liquid phase. The mechanical properties and the ability to influence the Shape Memory Effect (SME) in porous nitinol synthesized by means of laser-controlled combination of SLS and SHS was also studied. The strain-stress curves, X-ray, SEM and temperature dependency of electrical resistivity on laser influence parameters are presented. The optimum laser energy input range 100-300 J/cm^2, the limit of elasticity (0.04 - 0.06 MPa) and bending tensile strength (0.06-0.12 MPa) of 3D NiTi porous products were determined. Measurements of the temperature dependence of specific electrical resistivity on surface laser energy indicate, that in some regimes of synthesis (in the range of ~ 180-240 J/cm^2) such temperature regions can be found where it is possible to observe a shape memory effect. A comparative study of bone-integration of porous-surfaced NiTi implants with control samples (porous SL-Sintered and commercial used casting Ti) was conducted.

P-E18

MECHANO-SYNTHESIS OF W-C ALLOYS BY PLANETARY BALL MILLING

Vrel D., Redolfi M., Brinza O., Delacqua L.C., Lombardi G. and Bonnin X.

Université Paris 13, CNRS, LSPM – UPR 3407, 99 avenue J.-B. Clément, 93430 Villetaneuse, France
* dominique.vrel@lspm.cnrs.fr

The synthesis of tungsten carbide is usually considered to be not exothermic enough to be performed by self-sustained reactions. All the while, several studies have shown that SHS reactions would be eased if the reactant powders would be mechanically activated, e.g. by vibratory milling or by planetary ball milling.

In the present context of a very high scientific interest for nanomaterials, we chose to study the milling of tungsten and graphite in order to reproduce possible ITER dust compositions. Indeed, considering the tungsten and carbon walls which would be present in the divertor section of the reactor, erosion from plasma contact could occur and generate dust of, so far, unpredictable compositions. Within this framework, mechanosynthesis could be of a great help for the production of tailored powder compositions, to better understand the chemical and physical behaviour of these dusts, before the first runs of the ITER tokamak.

Finally, as a good understanding of the plasma-wall interaction is necessary for optimal functioning of this reactor, powders produced will be exposed to hydrogen plasma, using the CASIMIR II device [1].

Powders produced have been characterized by X-ray diffraction to determine the lattice parameter and the mean crystallite size using Rietveld analysis, BET measurement to determine Specific Surface Areas, Scanning and Transmission Electronic Microscopies, Figure 1.

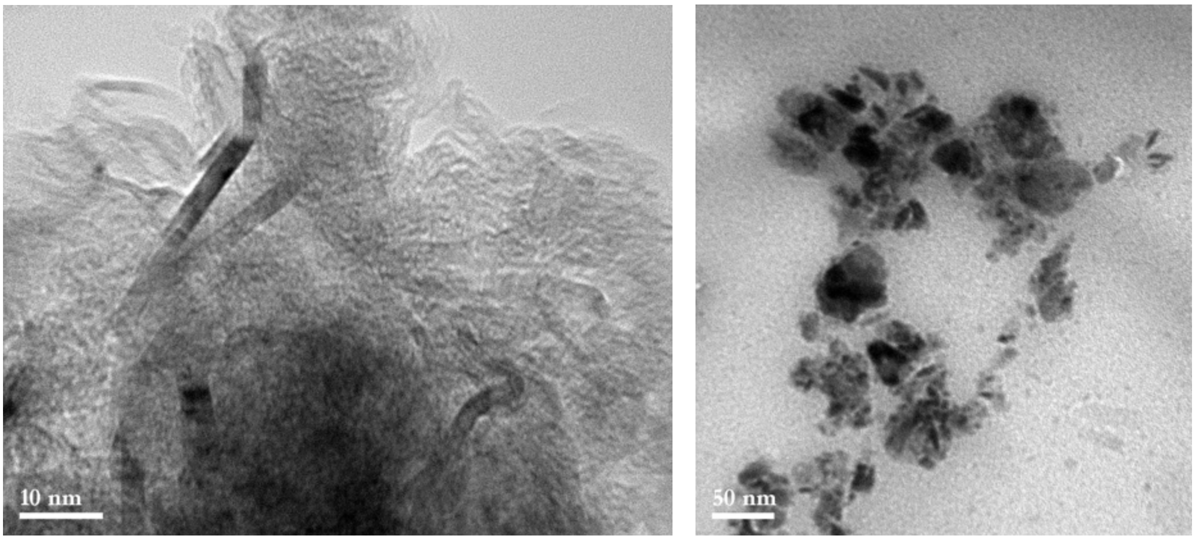

Figure 1 : Transmission Electronic micrographs of graphite (left) and tungsten (right) milled in a planetary ball mill at 350 RPM, using tungsten carbide milling media and a Ball to Powder Ratio of 40:1.

This study was supported by the Agence Nationale de la Recherche, under the ANR-09-BLAN-0070-01 grant number.

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P-E19

SOLUTION COMBUSTION SYNTHESIS OF COBALT PIGMENTS

Thoda O. [1,2], Xanthopoulou G.[1], Vekinis G.[1], Zoumpoulakis L.[2], Boukos N.[1]

[1] Institute of Materials Science, NCSR “Demokritos”, Ag. Paraskevi, Athens, 153 10, Greece
[2] School of Chemical Engineering, National Technical University of Athens, Zografos, Athens, 157 80, Greece
gxantho@ims.demokritos.gr

Cobalt-based pigments are of great importance in ceramic industry due to their spectacular variety of colours, high tinting strength and remarkable stability under chemical, thermal and reducing conditions. The colours of cobalt compounds are stereochemically specific depending upon the atomic co-ordination site and number. While the octahedral cobalt compounds are generally pink to violet, the tetrahedral ones are blue. The conventional method for the preparation of these pigments is by solid state reaction in furnaces (calcination) using appropriate metal salts such as oxides, carbonates, etc. This requires high temperature treatments (1000–1400°C are typical temperatures) and long processing times (several hours to days). The end products require further processing such as wet or dry milling to produce fine powders. Addition of mineralizers is often necessary to facilitate the solid state reaction in the fluid state. The overall result is a long process with high cost.

SHS has been shown in the past to be an excellent alternative to such long and costly production methods for pigments. We have now extended this by the development of the solution combustion synthesis method for the production and study of Co-based pigments. Nanosize oxides and spinels were successfully synthesized by the combustion of aqueous solution containing stoichiometric and non-stoichiometric amounts of metal nitrates $Co(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$, $Zn(NO_3)_2$, $Bi(NO_3)_2$, $Ba(NO_3)_2$, $Ca(NO_3)_2$ with urea as a reducer. The aqueous solution with the redox mixture is placed in a Pyrex beaker which is then introduced in a muffle furnace preheated to 350-650 ^oC. When the liquid reaches combustion ignition temperature, it starts boiling and foams to a solid producing the corresponding oxides and spinels. XRD and SEM analyses showed that, in the Co-Al-O system, we received blue cobalt aluminate ($CoAl_2O_4$) and in the presence of boric acid, purple pyroborate $Co_2B_2O_5$. The heat of combustion of 1 mole of $(NH_2)_2Co$ is -632.2KJ.

The equation of the formation of the cobalt pigments can be presented as:

$$Co(NO_3)_2.6H_2O + 2Al(NO_3)_3.6H_2O + (NH_2)_2CO \rightarrow CoAl_2O_4 + CO_2 + N_2 + H_2O + NO + NO_2$$

When $Mg(NO_3)_2$ was included in the (aq) initial batch, the pigments received had a light pink or blue colour depending on the percentage of the reactors in the mixture. Improvements to the colour of the produced pigment were made by changing the amount on $Mg(NO_3)_2$.

The Ba-containing pigments gave pink and purple colour. The percentage of boric acid and urea were kept steady and the preheating temperature was 350 ^oC.

When the content of $Co(NO_3)_2$ in the initial batch was changed from 5% to 70%, it produced changes of content of colouring components $Co_2B_2O_4$ and $BaCoO_4$ spinels in the product (Figure 1) and a large range of different shades of purple pigments were obtained. It was found that origination of CoB_2O_4 is a preferable route in comparison with $BaCoO_4$. Structure of those spinels were found out by SEM/EDX and TEM analysis (Figure 2 and 3) where nano-sized grains are visible.

In conclusion, considering the low processing temperature and the ease of production, and the good quality pigments produced, solution combustion synthesis seems to be a very economical and environmentally friendly method for industrial production of pigments in comparison with traditional methods.

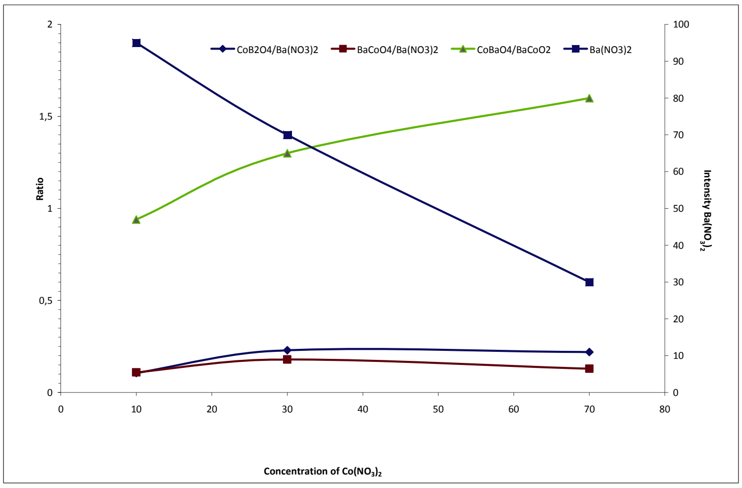

Figure 1.Dependence of final composition of Co-Ba-B-O based pigment on concentration of $Co(NO_3)_2$ in the initial batch

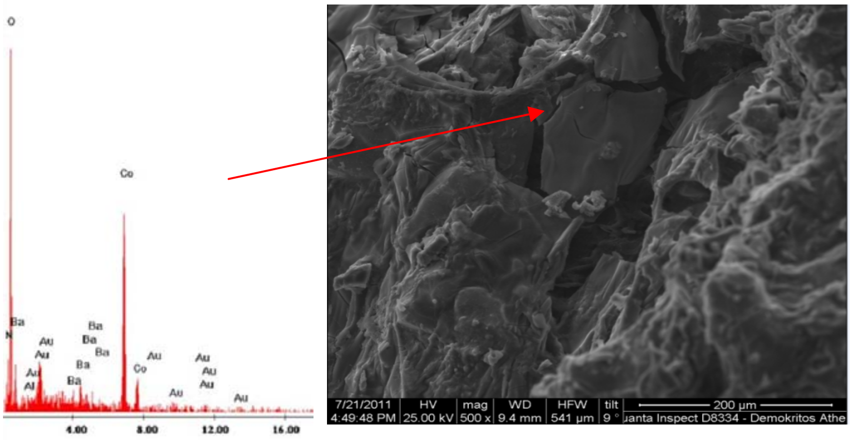

Fig2. SEM /EDX photograph of Co-Ba-B-O based pigment

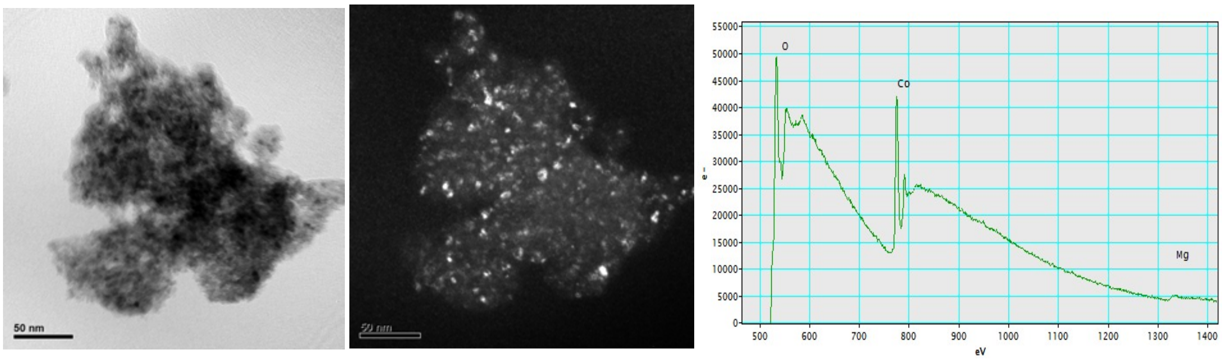

Fig.3: TEM Bright field (a), corresponding dark field (b) micrograph and electron energy loss spectroscopy spectrum (c) of a nanocrystalline $MgCo_2O_4$ agglomerated pigment. The crystallite size varies in the range 3-10nm.

P-E20

JOINING OF SiC, MgO, $MgAl_2O_4$ AND FERROUS METALS USING SHS

Xanthopoulou G. and Vekinis G.

Institute of Materials Science, NCSR Demokritos, Aghia Paraskevi, 15310 Athens, Greece
gvekinis@ims.demokritos.gr

The bonding of advanced ceramics and composites such as SiC, $MgO/MgAl_2O_4$ with metals is an enabling technology for the broader engineering application of these materials. Many different approaches have been reported to join dissimilar materials such as SiC and metals, such as the use of polymer precursors, glass bonding, melt infiltration and metal diffusion bonding. They can all be performed at practical processing temperatures and these methods can be used to produce joints with high-temperature strength but require special conditions to avoid damaging the SiC.

We have adapted the SHS process to combine the high temperatures generated with sufficient diffusion to enable bonding of such dissimilar materials. The process is relatively simple and rapid and we have succeeded in bonding silicon carbide and other ceramics with metals by solid-state conversion of joint alloys into spinels and other mixed oxides that enable reactive bonding. SHS diffusion bonding tests were performed using thin layers of thermites that were lapped flat prior to bonding. The influence of bonding temperature, bonding pressure and thickness of bonding layer on bond quality was determined by metallographic inspection of the bonds. The microstructure and phases in the joint region of the diffusion bonds were evaluated using SEM/EDX. Bonding pressure appeared to have little influence on bond quality.

Joining SiC and SiC/SiC for the Fusion reactor

Effective joining of SiC_f/SiC (fiber composite) for potential use on the plasma-face blanket of a fusion reactor must satisfy a number of criteria: the joint material must be chemically and physically compatible with SiC_f/SiC, the joints must have adequate mechanical and physical properties and no open porosity, the method used must not adversely affect the properties of the materials being joined, the method used must enable joining of relatively large areas both between segments of SiC_f/SiC and with the backing material. In joining, the wave is allowed to proceed between the two surfaces to be joined, which can be held in place under pressure. The resulting SiC joint is fully compatible with the materials joined.

The advantages of SHS method for joining are: a)Very high wave propagation velocities – mm to cm per second. This eliminates possible damage to the surrounding materials. b) Possibility to tailor the composition of the joint to that needed for the application. c) The SHS wave, once initiated, can cover a large area effectively joining the two surfaces

Experiments were carried out with a range of pre-cursors and initiation conditions and the synthesised materials were characterised by a X-ray diffraction, measurement of their density and porosity and by SEM. A promising system with very good SiC wetting properties (with no microscopical evidence of reaction with SiC) are the Ti -C –Ni, Al-Ni, Al-Fe systems with different additives. Joining experiments were also carried out using the Si-C SHS synthesis system (34.5% SiC) for joining monolithic and composite SiC_f/SiC materials at temperatures 700-1000^{o}C. Pressure was exerted by simply using a dead weight on the pieces to be bonded with a pressure of about 10MPa. The joined materials display good integrity, good wetting and good strength. SEM micrographs of SiC joined with SiC_f/SiC by the SHS method are shown in Figure 1. Good crystallisation and morphology are evident. The relatively large amount of porosity can be minimised by the use of pressure during combustion. Grain size can be controlled by controlling the initial parameters and the processing conditions used.

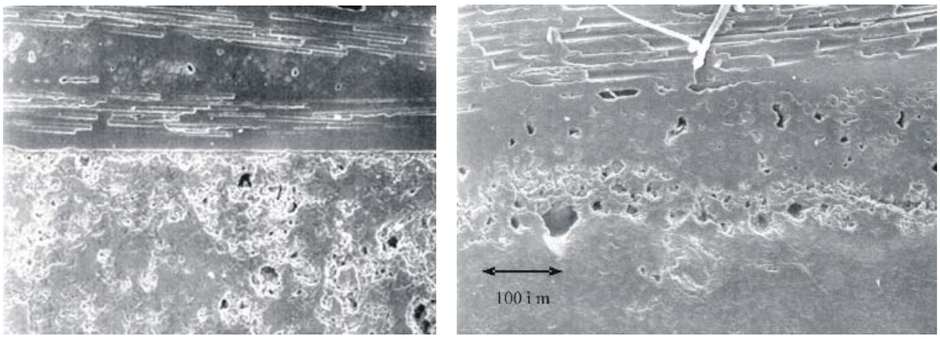

Figure 1. Microstructure of Ni-Al(left) and Al-Fe (right) joint with SiC monolithic material (below). Wetting is good, SiC/SiC fibers are visible (SEM)

Bonding refractories based on MgO and $MgAl_2O_4$ High temperature refractories on the basis of MgO/ $MgAl_2O_4$ mixtures display great difficulty to be joined to other materials or to themselves (in tile form) to make a thermal protective shield (TPS) for spacecraft. The eventual development of the HybridTPS system [1], for use in spacecraft will also depend on the capability for bonding the tiles together to make a seamless shield or other protective layer. In fact, one of the main weaknesses of any TPS made of tiles is the usually weak interface between the tiles. During atmospheric entry these interfaces tend to become overheated and degrade, allowing penetration of hot gases leading to failure.

A number of approaches were tried to bond these refractory tiles together, such as:

- The use of a refractory slip (aqueous suspension of mixtures of MgO and Al_2O_3) to bond SHS-fired tiles together – these attempts were discontinued due to large thermal expansion mismatch stresses between the materials giving destructive cracking on SHS.
- Bonding pre-fired tiles using SHS in a sandwich arrangement. Although initial bonding was present, on cooling all attempts ended in debonding due to CTE mismatch between the pre-fired tiles and the fresh SHS material.
- Co-firing under SHS of a "sandwich" system made up of a thin layer of 50%MgO-50%spinel between two High-MgO tiles which proved successful.

Co-firing gave excellent bonding and sufficient through-thickness porosity of the structure as shown in Figure 2 and the fact that fracture in bending goes through both the joint layer as well as the High-MgO tiles.

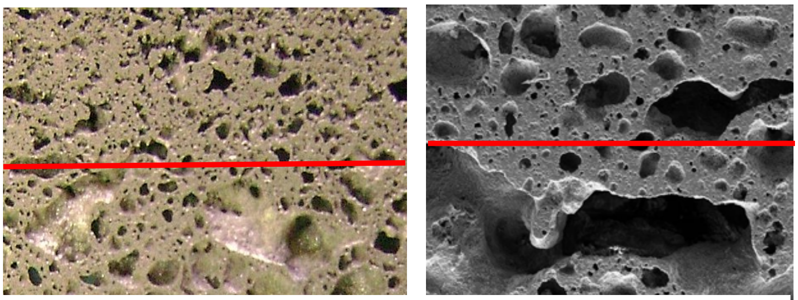

Figure 2. Photo of joints (approx. shown by red lines) between a high-MgO tile (above) and the joint material (below), made by co-firing under SHS, showing excellent adhesion (width of field: left: 3mm, right: 1mm)

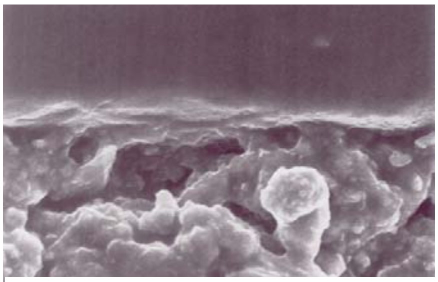

Figure 3. Photo of a joint between ferrous metal and the joint material Ni-

Ferrous metals

Very good results of joining (Figure 3) were received for bonding of metals at different temperatures (700-1000^{o}C). Influence of temperature, composition and additives on the minimum thickness of the layer for systems Al-Ni, Al-Ni-O,Al-Fe-O, Al-Cr-O, Al-Co-O was studied.

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P-E21

INITIAL ACTIVATION BEHAVIOR OF $LaNi_5$ PRODUCED BY SELF-IGNITION COMBUSTION SYNTHESIS USING HYDROGENATION HEAT OF CALCIUM

Yasuda N.*[1], Tsuchiya T.[1], Sasaki S.[1], Okinaka N.[1], Akiyama T.[1]

[1]Center for Advanced Research of Energy & Materials, Faculty of Engineering, Hokkaido University,
Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan
* yasuda_7010@eng.hokudai.ac.jp

INTRODUCTION

Nickel rare-earth metal compounds, so-called AB_5-type hydrogen storage alloys, are conventionally produced using a *melting method* that requires several time- and energy-consuming processes, such as heat treatment, pulverization, and activation treatment. In general, the activation treatment requires more hydrogen pressure than the equilibrium hydrogen pressure of hydrogen storage alloys. The newly developed alloy is strongly required to store as much hydrogen as possible at pressures closer to the equilibrium pressure. To overcome these problems, we proposed that *Self-ignition combustion synthesis* (SICS) utilizing the hydrogenation heat of metallic calcium for the production of nickel rare-earth-based alloys such as $LaNi_5$. The purpose of this study is to synthesize a $LaNi_5$ by SICS at different hydrogen pressures and to evaluate the hydrogenation properties, in which initial activation behavior at less than 1.0 MPa in hydrogen pressure was mainly examined.

EXPERIMENTAL

In the experiments, 40 g of the reagents were first mixed in a molar ratio of La_2O_3:Ni:Ca = 1:10:6, and then heated at 0.1, 0.5, and 1.0 MPa of hydrogen pressure until ignition due to the hydrogenation of calcium. The products were recovered after natural cooling for 2 h. The product powders obtained were washed with an aqueous solution of 5 mass% acetic acid in order to remove the residue of calcium and the by-product of calcium oxide and were finally dried in a desiccator in air at 353 K for 12 h. The hydrogenation properties were evaluated using Sieverts' method.

RESULTS AND DISCUSSION

The ignition point decreased with the hydrogen pressure, because the hydrogenation rate of calcium increased with the higher hydrogen pressure. The products changed from bulk to powder with hydrogen pressure. This was probably caused by volume expansion due to hydrogenation at higher pressure.

Figure 1 shows the hydriding curves of the SICSed $LaNi_5$ at a temperature of 298 K and an initial hydrogen pressure of 0.95 MPa, together with the pure $LaNi_5$ reagent as a reference. The reagent, with a diameter of 250-500 μm, did not absorb any hydrogen under the experimental conditions. The product obtained at 1.0 MPa showed the highest hydrogen storage capacity, even under less than 1.0 MPa. The difference of initial activity in our experiments can be explained by the formation of severe cracks and the introduction of lattice defects. The results of this research can be applied as an innovative production route for $LaNi_5$ without the conventional melting of La and Ni.

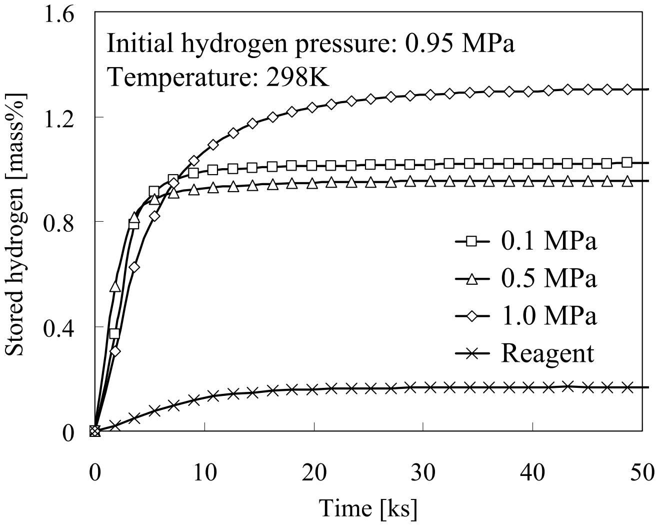

Fig. 1 Hydriding curves of reagent and SICSed $LaNi_5$ at 298K in temperature and 0.95MPa in initial hydrogen pressure.

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P-E22

COMBUSTION SYNTHESIS AND THERMAL STABILITY OF TI_3ALC_2

Zhu C.*[1], He X. [2], Qian X.[2], Ying G.[2]

[1] College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150001, China
[2]Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China
*zhuccshs@yahoo.com.cn

High purity Ti_3AlC_2 has been successfully fabricated by self-propagating high-temperature synthesis with the pseudo–hot isostatic pressing (SHS/PHIP). And the thermal stability of the Ti_3AlC_2 in Ar atmosphere is investigated. The XRD results and the analysis of inductively coupled plasma-atomic emission spectrometry (ICP-AES) show that there are 96.7% Ti_3AlC_2 together with the TiC and Ti-Al intermetallics. Typical nano-laminated structure is observed. Thermodynamic stability with the oxidation of the Ti_3AlC_2 is found, and decomposition temperature of 1370 ºC is determined by thermal gravimetric-differential thermal analysis.

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POSTER PRESENTATIONS

F: Industrialization of SHS

P-F1

ELECTRIC CONDUCTIVITY OF CARBON CONTAINING SHS-REFRACTORY MATERIALS

Dilmukhambetov E.E.*, Mansurov Z.A., Fomenko S.M.

Combustion Problems Institute, 172, Bogenbai Batyr Street, Almaty, 050012, Republic of Kazakhstan
* esen.dil@yandex.ru

Earlier, principles of sol-gel- and SHS-technologies were successfully combined to produce carbon containing refractory materials and composites [1, 2] as applied to induction furnace. An important characteristics of carbonaceous and graphite refractories being used in melting induction furnace is their electric conductance. The aim of this work is optimization of electrophysical characteristics of SHS products in maximum proximity to the conditions of induction furnace operation.

The objects of investigation were SHS products of exothermal mixtures containing aluminium, silicon and titanium powders as reducers and silicon and titanium oxides as oxidants in the presence of carbon and aluminosilicate mortar. Dry mixtures were mixed with silica sol. The obtained mass was used to prepare samples of cylindrical and cubic forms. Heterocoagulation of silica sols provided the necessary initial mechanical strength of the products. After being dried, the samples were subjected to heating in electric furnace to initiate SHS at temperatures 850 – 950 °C.

Measurements of electric resistivity nave snown that all synthesized materials possess significant electric conductance. For two series of SHS products from exothermal mixtures with the use of silicon and titanium oxides as the main oxidants, the values of electric resistivity at 298 K made up $2 \cdot 10^{-4} – 5 \cdot 10^{-4}$ Ω·m and $3 \cdot 10^{-5} – 4 \cdot 10^{-3}$ Ω·m, respectively.

The temperature dependence of electric resistivity indicates the semiconducting character of conduction for silicon containing composites and the metallic character – for titanium containing ones. In the first case, according the results of X-ray phase analysis, the main electric conducting phases are silicon, carbon, silicon carbide and in the second case – titanium and titanium silicides. A considerable difference in resistivities of SHS-composites and crucible graphite is eliminated when introducing silicon powder into the initial titanium containing exothermal system (Figure 1).

With the content of silicon in the initial aluminothermal mixture 6 – 8 %, resistivities of SHS-composite and crucible graphite get equal. Resistance of metals to attack by corrosive media is characterized by the loss of mass not more than 3 % in the course of standard treatment in the melt of bronze at 1450 °C.

The obtained results show the possibility of producing refractory carbon containing composition products which are able to replace graphite elements of induction furnaces of ferrous and non-ferrous metallurgy without changing significantly the electric regime of their operation.

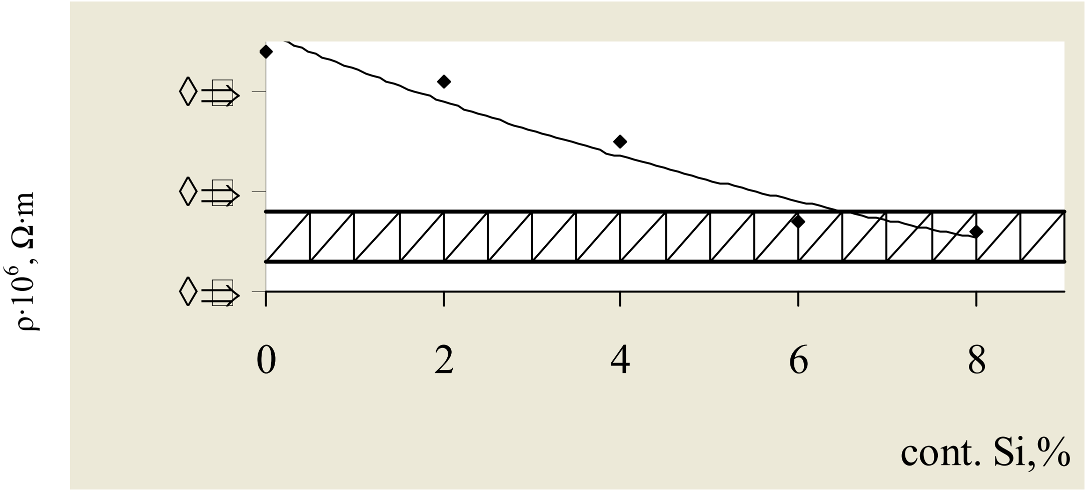

Figure 1 – Electric resistivity of a highly carbonaceous composite (the hatched region corresponds to resistivity of crucible graphite)

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P-F2

PULSED ELECTROSPARK STRENGTHENING OF STAMP RIGGING USING ADVANCED NANOSTRUCTURED ELECTRODE MATERIALS

Kudryashov A.E.*[1], Levashov E.A.[1], Pogozhev Yu.S.[1], Kurbatkin I.I.[2]

[1] National University of Science and Technology MISIS, Leninskii pr. 4, Moscow, 119049 Russia
[2] A.Yu. Ishlinsky Institute for Problems in Mechanics, R A S, Vernadskogo pr. 101 k.1, Moscow, 119526, Russia
* aekudr@rambler.ru

High adhesion of coating, feasibility of local processing, low energy requirements, environment friendliness, and moderate requirements to personnel qualification facilitated wide implementation of pulsed electrospark (ES) technology into various industries. However standard WC-based hard alloys of VK and TK brands [1-3] not always meet requirements to ES electrode materials because of their high erosion resistance, low mass transfer coefficients, low heat resistance of WC, and high cost.

In this work, we explored the ES deposition of coatings onto die steel Kh12MF with new advanced nanostructured hard-alloy electrodes and approbation of a designed process for die processing in conditions of industrial-scale production.

In experiments, we used SHS-produced hard alloys based on titanium carbide, chromium carbide, and titanium diboride. WC-based nanostructured electrodes were fabricated by vacuum sintering (the size of WC particles <100 nm).

SHS-produced electrodes were doped (during their preparation) with nanopowders of ZrO_2, Al_2O_3, W, WC, (WC–Co), NbC, (Mo–0.5% Al_2O_3), and Mo in amounts of 3.5–7.0 vol %. ES deposition of coatings was carried out in air using an ALIER-METAL facility upon variation in the overall power of discharge pulses within the range 0.27–43.2 kJ/min. For each group of electrode materials, process conditions were optimized as for a best relationship between deposition rate, satisfactory surface finish, and minimal content of oxide phases of coatings.

Deposited coatings have been characterized for their microhardness, thickness, continuity, wear resistance, heat resistance and surface roughness. Investigated was the influence of process parameters on the phase composition of deposited coatings. The coatings deposited with nanostructured electrodes exhibited high continuity (up to 100%) and elevated hardness (up to 12.5 GPa), wear resistance (by a factor of seven), and heat resistance. Characterized was the distribution of the elements over the coating depth. Deposited coatings were found to have a fine-grained structure with a grain size of below 100 nm. Lowest oxidation rates at 500°C were exhibited by the coatings deposited with STIM-9/20A (TiB_2–TiAl) and STIM-40NA (TiC–NiAl) electrode materials.

Secondary ES processing of deposited coatings with carbon-containing electrodes or deposition of solid lubricants lowered friction coefficients and elevated wear resistance of such coatings. Heat resistance of the coatings deposited with nanostructured WC-based electrodes was improved upon secondary ES processing with Ni electrodes. Implementation of our technology to strengthening dies for hot pressing was found to increase the service life of ES strengthened dies by a factor of 2.7.

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This work was supported by the Program on Development of Research Potential of Higher Education System in 2009–2011 (project No. 2.1.2/2970).

P-F3

THE EFFECTS OF ELECTROSPARK ALLOYING ON CONTACT SURFACES IN SLIDING PAIRS

Kurbatkin I.I.*[1], Kudryashov A.E.[2]

[1] Institute for Problems in Mechanics of the Russian Academy of Sciences.
[2] National University of Science and Technology "MISIS"
*iikurbatkin@mail.ru

Solving problems related to the compatibility of contact surfaces is an important scientific and engineering task. In our project, we used the method of electrospark alloying (ESA) to create an anti-friction contact layer. As electrodes used as traditional materials, and SHS-materials We studied its tribological characteristics and the structure and makeup of its surface. The first stage included a galling test. The second stage involved surface treatment and tribological testing. To perform the study, a contact pair of aluminum anti-friction alloy and high-strength cast iron (counterpart) was chosen.

These materials were used in friction knots of heavily loaded friction bearings [1-2]. The contact layer was applied to the surface of the counterpart. An ALIER-METAL 2002 facility was used to apply the coverings. Dispersive nickel and graphite dust was used as the base material for the coatings. Testing was conducted using a T-05 tribometer using a shaft—pad scheme. The load was 400-900 N. Motor oil was used for lubrication under conditions of interfacial friction. The structure and makeup of the surface was studied using optical and electronic microscopes. The experiments established an increase in the friction coefficient from 0.006→0.038 during galling. The load equaled 1750 N.

After testing, we performed electrospark alloying of the contact surface of the axle. The layer thickness was 15-20 microns. The ES-coating showed a coarse typography for a nickel layer: R_a 2.7 – 3.3 microns, and for a nickel-graphite layer, R_a 1.6 – 2.9 microns. Tribological testing showed that galling began under loads of 500-550 N. Surface treatment by grinding and polishing decreased the coarseness by R_a = 0.4 – 0.6 microns for the nickel covering and by R_a = 0.2 – 0.5 for the two-layer nickel-graphite. Tribological testing for galling showed that the friction coefficient had fallen, and that galling resistance had risen.

Study of the structure and makeup of the surface using SEM and x-ray microprobe revealed the primary zones. The contact zone, where furrows and traces from the interaction of the two surfaces are visible. The zones with no contact due to the discreteness of contact. The zones of intense mass transfer. The project included a study of processes for restoring the tribological characteristics of the contact surface using electrospark doping and grinding and polishing operations. The structure, makeup and characteristics of the contact zone were established. At the third stage are studied tribological properties of electrospark coating on titanic and nickel-based alloys, steel substraties. As electrodes used SHS-produced materials of mark STIM. Tribological tests were carried out with using ball on disk scheme. When a material of counterpart is WC-based hard alloys, loading – 1-5 N, environment air. In order to reduce friction coefficient (K_{fr}) and increase wear resistance of ES – coating, the latter ones were subjected to additional ES treatment with carbon-containing electrode materials.

The project was completed with the support of grants from the RFFI 09-08-00901-a; 09-08-01148; and a Grant from the President of the RF to support Russia's leading scientific schools (draft NSh-3288.2010.1).

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P-F4

SHS METALLURGY OF HEAT-RESISTANT NONFERROUS ALLOYS UNDER HIGH GRAVITY

Sanin V.N., Andreev D.E., Ikornikov D.M. and Yukhvid V.I.

Institute of Structural Macrokinetics and Materials Science Russian Academy of Science
Institutskaya street 8, Chernogolovka, Moscow region, 142432, Russia
svn@ism.ac.ru

Heat-resistant alloys are extensively used for applications involving service temperatures in excess of 650°C. Today, cast heat-resistant alloys play an important role in the performance of aero- and land-based gas turbines [1]. The majority of cast nickel alloys predominate are being used as superalloys in the hot sections of modern aero turbine engines, while cast cobalt alloys are routinely specified for particularly demanding applications such as fuel nozzles, vanes for industrial gas turbines and specific heat-resistant coatings [2],

In this work we examined a scientific and engineering background for high energy efficient, fast and low-cost production manufacturing technology for some new cast nickel, cobalt and niobium based alloys via SHS-metallurgy. SHS metallurgy technique is a combination of Self-propagating High-temperature Synthesis (SHS) and metallothermy [3].

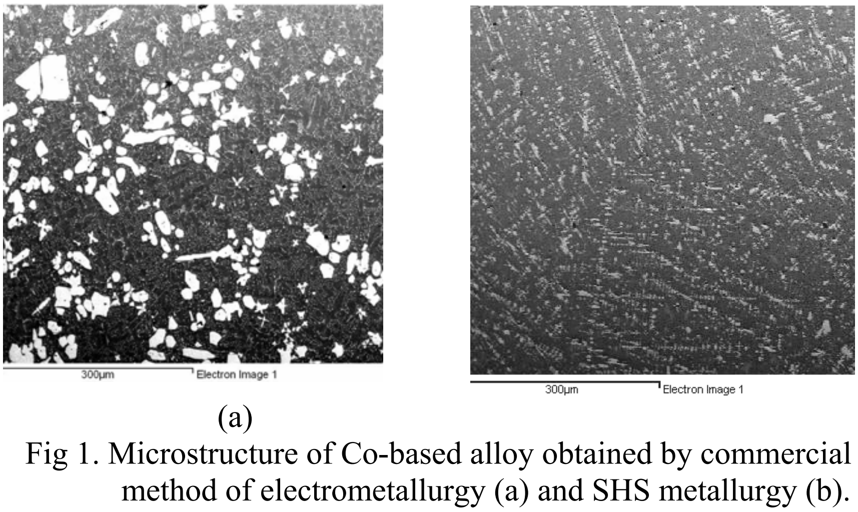
The overall scheme of thermit-like SHS reactions can be represented as follows:

$(M_1 + M_2 + M_3 + \dots M_n) + (N_1 + N_2 + \dots N_n) + R + F_{add} \rightarrow$[Heat resistent alloy] $+Al_2O_3+Q$,

where: M_n – stands for the oxides of Ni, Co, Ti, Cr, Nb, Mo, W, V, Mn, etc., N_n – nonmetal Si, C, etc., R – reducing metal (Al), F_{add} – functional additions and Q the reaction heat.

Since the combustion temperatures are extremely high (2000–3500 K), the combustion products (alloys and oxides) appear in the their liquid state. It leds to splashing of final products during combustion. To suppress it the combustion was carried out in the centrifugal machine under high gravity up to 1000*g*, where *g* is free fall acceleration. Realization of high temperatures without using any additional power sources is the basic difference of the approach from the conventional vacuum electrometallurgy.

The microstructure of the obtained alloys was investigated. It was revealed that the alloys obtained by SHS have fine distribution each element over ingot. The microstructure of cobalt-based superalloys obtained by the industrial vacuum technology *(a)* and SHS metallurgy *(b)* is presented in Fig.1. It can be seen that SHS alloy has not phase segregation and has higher heterogeneity. The size of structural components is 10 times lower and has nano-size inclusions.



(a) (b)

Fig 1. Microstructure of Co-based alloy obtained by commercial method of electrometallurgy (a) and SHS metallurgy (b).

A decrease in grain size is caused by SHS conditions: first of all, it is high synthesis temperatures *(about 2500^0C in comparison with 1800^0C realized in electric furnaces)* and higher cooling rate. The effect of high gravity leads to the uniformity of chemical composition in the ingots and a decrease in structural components size.

Pilot-scale series of cast Co-Cr-Nb-W-Mo-Al-C, Ni-Cr-Ti–Co-W-Al-C, Nb-Hf-Ti–Si-Al alloys were produced by thermit-type SHS under high gravity. Using the available laboratory equipment, we obtained more than 400 kg of the alloys. However, for increasing the production scale, it is necessary to make centrifugal installations with higher output.

The energy efficient SHS technology provides better economic parameters in comparison with the commercial analogues from the viewpoint of price/quality, price/output criteria, and as to the final product (heat resistant items) a price/resource one. It will allow extending an application area of the alloys.

The work was carried out under the financial support of RFBR, grant № 10-03-91219 and the Program of basic research of chemical department of RAS (program № 7) nanotechnology and nanomaterials.

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P-F5

COMPARATIVE MICROSTRUCTURAL ANALYSES AND HISTOMORPHOLOGICAL STUDIES OF TISSUE REACTIONS TO POROUS TITANIUM AND NITINOL IMPLANTS PRODUCED BY SHS-SLS

Shishkovsky I.V.*[1], Kuznetsov M.V.[2], Morozov Yu.G.[2]

[1] P.N. Lebedev Physics Institute /LPI/, Samara branch, Russian Academy of Sciences, 221 Novo-Sadovaya Street, Samara, 443011 Russia
[2]Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow, 142432 Russia
* shiv@fian.smr.ru

Comparative microstructural analyses and histomorphological studies of tissue reactions to porous titanium and nitinol implants synthesized by Selective Laser Sintering (SLS) are presented for bone implants using a rat model. Surface of porous pegs made from titanium and nitinol by combined SHS-SLS process has significantly favorable structure for the fixation of living tissues. Histological analysis shows that around the implant spongiform osteal tissue in the form of trabecules and lacunas are formed. Among the connective tissue the following cells: macrophages, fibroblasts, adipocytes and lymphocytes are discernible. It was shown, that nitinol synthesized by combined SHS and SLS, has more developed and ordered submicron structure than commercial one.

In the combined SHS-SLS process SHS reaction is required to be limited by laser radiation input mode because, in the other case, the process would lose 3D shape control of implant and starting to be potentially hazard. Hence SHS component is chosen to be weakly exothermic and ideal for intermetallic synthesis where reaction enthalpies of combination tend to be smaller than for metal oxides. Comparative study of the ebullition conditions for living tissues in porous implants synthesized by SLS and commercially available implants is presented by using morphological and histological analysis by scanning electron microscopy, EDX and light microscopy. Comparison was made between the porous sintered implant produced by layer-by-layer SLS from the pure titanium powder; nitinol implant obtained by SHS-SLS from Ni and Ti powder mix, and implant produced from the commercial cast titanium “rematitan® M-(Ti4)”. This study showed advantages for porous titanium and nitinol prepared implants compared to the commercial ones in terms of biointegration. Furthermore the nitinol showed no adverse effects compared to the porous titanium. As our results have shown, porous implants have three-monthly successful tests (researches for longer term period are not provided by “Before Clinical Tests” procedure). No signs of dying off tissue around the implants were observed. Moreover, ebullition of connecting (muscular) tissue and young bone testifies to high biocompatibility. Implants after dredging from the organic environment had no corrosion traces on the surface which also is a positive factor. Comparative morphological and histological analysis of implants made from the porous Ti, porous nitinol and commercial titanium within a rat model for up to three months allowed to make the following conclusions:

1. Nitinol, synthesized by using combined SHS-SLS reactions, has developed and ordered submicron structure. Surfaces of porous titanium and nitinol have more favorable conditions for the attachment and infiltration of living tissues than mechanically processed ones.

2. After implant extraction from scapula, the scapula defect had cylindrical form with accurately outlined edges. Implant’s color was not changed after prolonged implantation, which indicates an absence of corrosion. Neutrophilic-exudative component was not seen. Osteal tissue, surrounding the defect zone, had an organotypical structure. Periosteum was not changed. Its thickness was little different from the normal values and consisted of two layers: cellular and fibrous.

3. Histological analysis showed that internal space around the spongiform osteal tissue defect had connecting tissue in the form of trabecules and lacunas, which were filled in by osteal brain and spongy material. From the medullar spaces of an osteal bed it was possible to observe trabecules, consisting of reticulofibrous osteal tissue. Osteal beams were wide with considerable quantities of osteocytes, which were densely packed relative to each other and were surrounded by dense rows of osteoblasts. Around the trabecules considerable quantities of osteoblasts were observed.

4. Among the connective tissue the following cells: macrophages, fibroblasts, adipocytes and lymphocytes were distinguishable. Macrophages had an extended shape and borders of cells were outlined with rough edges. Fibroblasts on the histological specimens had appendix shapes with oval extended nuclei.

5. Summarizing the whole experimental results, it is possible to draw the conclusion that there were no essential differences in the porous implants made from either titanium or nitinol use. Both materials possess high biocompatibility and may be recommended for implantation. These materials are suitable for use as plastics for soft and hard tissues defects.

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