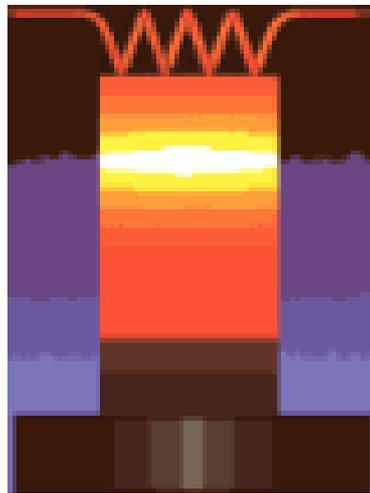# 2nd French-Russian Workshop on SHS
Villetaneuse, France
August 28-29, 2006

SCIENTIFIC PROGRAMME
AND ABSTRACTS

HISTORY

The 1ˢᵗ bilateral French-Russian workshop on SHS was held at ISMAN (Chernogolovka, Russia) on October 6–8, 2003. It was co-organized by ISMAN and Groupe Francais d'Autocombustion, GDR 2391 CNRS, under the aegis of the World Academy of Ceramics, International SHS Association and French Embassy in Moscow. The French delegation comprised of 12 representatives from the French Universities united into a team for SHS research.

The Russian delegation involved the representatives of ISMAN, Institute of Problems of Chemical Physics (Chernogolovka), Institute of Steel and Alloys (Moscow), Bauman Technical University (Moscow), Tomsk Research Center (Tomsk), Institute of Solid-State Chemistry and Mechanochemistry (Novosibirsk). 34 presentations made during the workshop have clarified the areas of mutual interests: effect of external influences on SHS, mechano-activation, time-resolved XRD of SHS, combustion of thin films, deposition of coatings, and controlled structuring of SHS products. It was decided to the held of the next bilateral workshop in France.

As a result of joint collaboration between French and Russian researchers and several exchange visits during last years, the mutual scientific program was created under support of the Centre National de la Recherche Scientifique - CNRS and Russian Foundation for Basic Research - RFBR.

TOPICS

The general challenge of this PICS is design and production of advanced materials (e.g. nanomaterials, ceramics, multilayered films etc. required for aerospace, transport, environment, and other applications) using the promising method of Self-propagating High-temperature Synthesis (SHS). For this purpose, three topics will be studied:

TOPIC 1 *"Advanced Ceramics by SHS under High Gas Pressure".*
TOPIC 2 *"Advanced multilayers and coatings by nano-scale SHS".*
TOPIC 3 *"Advanced alloys by Mechanically Activated SHS (MASHS)"*

ORGANIZING COMMITTEE

Co-Chairmen
Prof. Alexander G.Merzhanov (Russia)
Prof. Jean-Claude Niepce (France)

Members
Prof. Frédéric Bernard (France)
Prof. Alexander S. Rogachev (Russia)
Dr. Alexander E. Sytschev (Russia)
Dr. Dominique Vrel (France)

ORGANIZED BY

LIMHP UPR 1311 CNRS / Université Paris XIII
LRRS UMR 5613 CNRS / Université de Bourgogne
Groupe Français d'Autocombustion
Institute of Structural Macrokinetics and Materials Science RAS

SUPPORTED BY

SCIENTIFIC PROGRAMME

August 28, Monday:

10h00 – Welcome of participants
10h30 – Welcome speech – A.G. Merzhanov / A.Sytschev / F.Bernard

Session 1 relative to the TOPIC 1.

10h45 – <u>V.V.Grachev</u>, R.V. Soloviev : "Filtration combustion under high gas pressure"

11h25 – <u>R.M. Ayral</u> : "Studies of solid-gas reactions under high pressure : Application to the synthesis of AlN, TiN and Si_3N_4 ceramics"

11h45 – <u>M.C Record,</u> N.Pradeilles, R.M. Marin-Ayral, A.V. Linde, I.A. Studenikin, V.V. Grachev. "Influence of thermal conditions on high pressure combustion synthesis of Si_2N_2O ceramics"

12h05 – <u>A.V.Linde</u>, D.Y.Kovalev, I.P. Borovinskaya, A.G.Merzhanov, V.V.Grachev. : "The combustion synthesis of niobium nitride under high pressure of gaseous nitrogen"

12h25 – <u>F. Nardou</u> "SHS processing of ceramics by solid/gas reaction"

12h45 – Lunch

Session 2 relative to the TOPIC 2.

14h30 – <u>A.S. Rogachev</u>, J.C.Gachon, H.E. Grigoryan, E.Illekova, F.N.Nosyrev, J.C.Schuster, M.R. Sharafutdinov, B.P.Tolochko, P.A.Tsygankov, I.Yagubova: "Study of heterogeneous reaction in nanosystems (nanofilms)"

15h10 – <u>J.C.Gachon</u>, E.Illekova. "Thermodynamics of Reactive NanoMultilayers"

15h50 – <u>H.E. Grigoryan,</u> A.S. Rogachev, I.U.Yagubova, J.C.Gachon, P.A. Tsygankov, A.N.Nosyrev. : "Peculiarities of multilayered nanofilms combustion"

16h10 – <u>C. Curfs,</u> A.E. terry, G.B.M. Vaughan, E.H.kisi, M.A. Rodriguez, A. Kvick. "Time-resolved diffraction studies of combustion syntheses: application to the quaternary system Al-Ni-Ti-C »

16h30 – Coffee break

17h00 – Social Program and Dinner.

Session 3 relative to the TOPIC 3.

9h00 – <u>A.M.Stolin</u>, L.S. Stelmakh : "Influence of mechanical effect on SHS processes"

9h40 – <u>E.Gaffet</u>, F. Bernard, D. Vrel "Nanostructured Materials by Mechanically Activated SHS"

10h20 – <u>L.S. Stelmakh</u>, A.M.Stolin, R.N.Ponoramev : "About a competition of a different sintering mechanisms at SHS disintegration".

10h40 - Coffee Break

11h10 – <u>F.Baras</u> "A multilayer model for SHS of intermetallic compounds"

11h30– <u>N.A.Kochetov</u>, A.S. Rogachev, N.Shkodich. "Some peculiarities of mechanical activation influence on SHS process and particles structure in the Ni-Al and Ti-Al systems"

11h50 – <u>V. Gauthier</u>, A.V.Khitev, V.A. Shcherbakov, S. Dubois. "Synthesis of nanocrystalline TiC-Al$_2$O$_3$ composites by mechanically-activated pressure-assisted SHS technique".

12h10 – <u>A.Lemarchand</u>, JP.Bonnet. "Modelling SiC formation during a temperature ramp"..

12h30 – Lunch

Round Tables .

14h00 – Round Table – Topic 1, Topic 2 and Topic 3 in parallel

15h30 – Synthesis and prospective – presentation by coordinators of each Topic

16h00 – Conclusion

16h15 – Coffee break

LIST OF PARTICIPANTS

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Dear Colleagues,

Accept my sincere congratulations on the beginning of the work of the 2nd French-Russian Workshop on the processes of self-propagating high-temperature synthesis. There were various ways which have led the partners to this workshop.

The Russian partners have got almost 40-year experience in R&D of SHS - from the scientific discovery of the solid flame phenomenon and the development of the SHS method to the creation of pilot production of inorganic powders and materials. While proceeding along this way, they had to solve different tasks, i.e.:
•   to carry out the research in kinetics and thermal dynamics of high-temperature material-forming reactions,
•   to use widely experimental methods for studying SHS process mechanisms in various media and systems,
•   to create and study mathematical models Describing SHS processes,
•   to develop the methods of dynamic material science which allowed us to investigate structure formation dynamics of SHS products,
•   to use up-to-date methods of physical material science for studying the peculiarities of structure and properties of inorganic materials and items.

The work within these directions laid the foundation of the new scientific and technical direction of structural macrokinetics.

In 1980 the SHS entered the world arena. The scientists in 49 countries began studying SHS. At first, the USA, Japan and Poland, then Korea and China and later many other countries began to support the projects of their scientists in this field. The cooperation of various countries has become possible. We have already held eight international symposia in SHS, begun publishing the international journal, and organized the international association (SHS-AS).

One of the most important ways of the cooperation is organization of bilateral meetings (mini symposia). The initiators of these meetings appeared to be Russian scientists. Some meetings have already been carried out: Russia-USA, Russia-Italy, Russia-Japan, Russia-China, Armenia-Israel etc. Now our Chinese colleagues are very active in the development of the international links.

Today we are greeting the beginning of the 2nd French-Russian Workshop. The French scientists showed their interest to SHS processes later than others. They were looking attentively to this problem for a long time. But then they began working very actively and the results appeared to be remarkable. Due to the initiative of the Russian researchers, the joint development of some directions has started. Three problems have been chosen for cooperation and are being solved successfully by both partners, i.e.
•   SHS under high nitrogen pressure in gasostats (combustion mechanism and synthesis of nitride ceramics)
•   phase and structure formation in the combustion products using synchrotron radiation
•   mechanochemical SHS processes.

These directions chosen for cooperation were supported by CNRS, French Embassy in Moscow, and International Association of SHS-AS.
From the Russian side many scientists took part in the joint work. Among them are Professors I.Borovinskaya, A. Rogachev, H.Grigoryan, A.Stolin, Dr. V. Grachev, and others. They are ready to share their research experience gained during many years and in the same time they are glad to learn about the achievements of the French colleagues.

The Russian partners treat their French colleagues with respect and value the efforts of Professors J.C. Niepce, F. Bernard, J.C. Bonnet and others in organization of our cooperation.

Let me express the assurance that the cooperation results will become a real business interesting not only for the program participants but also for all the specialists who can value innovation.

I wish all the participants of the cooperation program great success.

Alexander Merzhanov

President of the International Association SHS-AS

Chief Scientific Consultant of the Institute of Structural Macrokinetics And Materials Science Problems, Russian Academy of Sciences

Dear Colleagues,

My dear Russian Colleagues of ISMAN,
My dear French Colleagues of GFA.

You have just heard the "Best Wishes" of Academician Alexander MERZHANOV, best wishes for our 2nd French-Russian Workshop on SHS. It has been also difficult for me to be among you during these two days in Paris.
However, let me tell you, through the care of Professor Frederic BERNARD, few words before the beginning of your scientific discussions.

As Alexander MERZHANOV told you, the French scientists showed their interest to SHS processes later than other non-Russian researchers. The French Group on SHS "GFA" is relatively young, less than 10 years; the first meeting of the French Group on SHS occurred in Poitiers, on March 19, 1998. Then, I had the pleasure to manage GFA, as GDR 2391 of CNRS, from January 2001 until December 2004.
It was a great honor for us, to have quickly fruitful contacts with ISMAN scientists whose SHS abilities was world-famous. Then, you all remember our so nice first ISMAN-GFA workshop in Chernogolovka in October 2003. We would like to go deeper in SHS together; so we signed a "Memorandum". We decided to apply for an international common administrative structure. The best would have been an International Open Laboratory. Nevertheless, we all enjoyed the creation, from 2006 to 2008, of the PICS *"Advanced Materials with Controllable Microstructure and Properties via SHS"* thank to the French CNRS and the Russian RFBR. So, now we have to go on!

Our 2nd French-Russian Workshop on SHS is our first workshop within the PICS. It will have to intensify our cooperation program that would have to generate a lot of good common papers. Have a very nice and fruitful workshop.

I am very grateful to Academician Alexander MERZHANOV, for his confidence to the young French GFA, for his so nice welcome in Chernogolovka. Alex, I will be very pleased to welcome you in Dijon, on July 2007.
We have also, all together, to be very grateful to the French Embassy in Moscow and particularly to Dr. Georges RYSCHENKOW who helped our young cooperation a lot.

I would now express my best friendly wishes to both, Doctor Alexander SYTSCHEV, Sasha for me, and Professor Frederic BERNARD, Fred for me. I am sure they will successfully manage the PICS.

See all of you next year in Dijon, for SHS 2007.

Jean-Claude NIEPCE
Head of CNRS GDR 2391 "GFA"
January 2001-December 2004

FILTRATION COMBUSTION UNDER HIGH GAS PRESSURE

V.V. GRACHEV, R.V. SOLOVIEV

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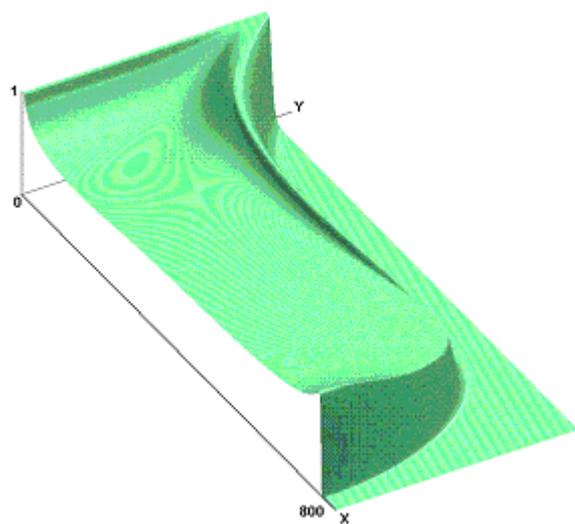
INTRODUCTION

Filtration combustion is widely applied in processes of self-propagating high-temperature synthesis. In this case an exothermic reaction takes place in porous medium between the solid reagent and gaseous oxidant which is consumed and a solid product is formed. The gas consumption in the reaction front causes a pressure gradient which drives natural filtration of oxidant through a porous substance towards the reaction front. The process of oxidant filtration plays the important role in mechanism of gas-solid combustion. The development of the theory of filtration combustion was started in the paper of Aldushin, Merzhanov and Khaikin [1]. It was the first theory and it was the first time when such type of combustion was called filtration combustion. The authors considered one-dimensional problem, when all boundaries are closed to the gas penetration except one, which is open to exchange with a large bath of gas so that the pressure is that of the bath at that end. The initial blend composed of a solid reagent and diluent powders is ignited at the opposite end of the sample by a short-term thermal pulse, which initiates the combustion wave propagation due to the heat released during the exothermic gas - solid reaction yielding a solid product. The initial gas content in pores was not taken into account, it corresponds to low gas pressure. This assumption simplified solution of the problem. It was shown, two modes are possible: with complete and incomplete conversion. Approximate theoretical analysis allowed them to obtain the criterion which defined the combustion mode. The aim of the present work is to consider this problem in frames of two-dimensional model with side heat losses for case of high gas pressure.
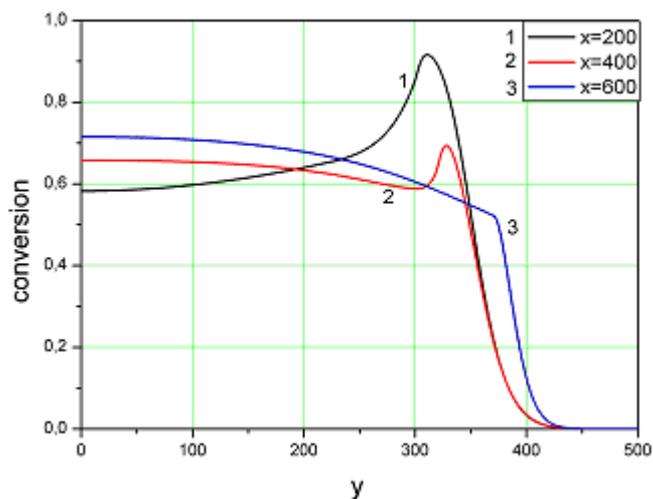
RESULTS

For describing the processes of heat-mass transfer, proceeding in the sample during the filtration combustion, the time-dependent two-dimensional system of equations is used [2], which reflects the laws of the conservation of masses for solid and gaseous reagents, energy, the equation of state of perfect gas and Darcy's law. Initial conditions correspond to uniform distribution of temperature and pressure in the sample. Boundary conditions reflect the absence of gas exchange through sample surface and take into account the heat losses. Approximate analytical and numerical methods were used for analysis of the system.

Besides the known modes with complete and incomplete conversion, a new intermediate mode with incomplete conversion in the middle of the sample has been predicted. Using approximate analytical methods, new criteria for defining the combustion mode for arbitrary initial gas pressures was obtained. Numerical calculation showed that heat losses result in curvature of the combustion front, appearance of an unreacted solid reagent and a peak on the conversion degree profile. In fig.1a the conversion profile at the moment when the combustion wave reaches the open end is shown. The peak height changes with the length. What is the reason of the peak formation? It is a mode of incomplete conversion, in the center the gas is consumed completely, the pressure equals to 0. Close to the wall the temperature is low, the reaction does not occur, the gas is not consumed, the pressure differs from 0. Due to the difference in pressures the gas began flowing from the wall to the center where there is no gas but there is enough

<div align="center">a)</div> <div align="center">b)</div>

<div align="center">Fig.1. The conversion profiles at the moment when the combustion wave reaches the open end</div>

unreacted solid component. As soon as it reaches the zone of a high temperature it starts the reaction. In the result, the peak of conversion degree appears in this zone. So, the peak appears due to the transversal gas supply. Though the lateral faces are gas-impermeable, heat losses result in two-dimensional flow field.

In fig.1b the profiles of the conversion degree in cross sections for various values of a longitudinal coordinate are shown. These values equal to a quarter of a length, half a length and three fourth a length. It is obvious that the farther the cross section from the open end, the longer the cross wave propagation and the higher the maximum value of the conversion degree in the peak. Besides, we can notice that in the center where heat losses are insignificant, the conversion degree in the counter-flow wave front grows with the length according to one-dimensional theory [1]. The profiles obtained conform to the experimental data [3].

CONCLUSION

Using approximate analytical methods, new criteria for defining the combustion mode for arbitrary initial gas pressures was obtained. A new intermediate mode has been predicted. It separates the aria of combustion modes with complete and incomplete conversion under high gas pressures. Two-dimensional combustion modes with gas supply only through the open end have been analyzed. It is shown that due to heat losses the field of gas flow in the sample is essentially two-dimensional. It results in obtaining the maximum conversion degree in the cross-section near the lateral face. Theoretical profiles coincide with experimental ones.

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STUDIES OF SOLID-GAS REACTIONS UNDER HIGH PRESSURE: APPLICATION TO THE SYNTHESIS OF ALN, TIN AND SI$_3$N$_4$ CERAMICS

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INTRODUCTION

Ceramics nitrides can be obtained from the corresponding metal and nitrogen owing to the high heat of reaction via combustion synthesis. A variety of nitrides, including aluminium nitride, titanium nitride and silicon nitride have been synthesized by reacting porous powder metals in gaseous nitrogen. The conversion achieved during the combustion process as well as the composition and structure of the products, is significantly influenced by the gas pressure.

In our experiments, nitrogen pressure varies from 1 to 650 MPa and combustion synthesis is realized by means of a graphite furnace with a thermal gradient which allows ignition of the reaction. Materials are characterized by X-ray diffraction and scanning electron microscopy.

RESULTS

a- High pressure combustion synthesis of aluminium nitride [1]

In this presentation, we will report the results of the combustion synthesis of aluminium nitride, from bulk Al as the starting material under high pressure of nitrogen and nitrogen/argon mixtures. The use of bulk aluminium reduces the oxygen content of our raw material due to its low surface area. The reaction occurs at temperatures higher than 1273K and at pressures of 10-630 MPa. Under low pressure (up to 100 MPa) increasing N$_2$ pressure leads to an increase nitrogen density and amount of nitrogen gas at the interface. The heat of reaction and maximal temperature go up and the degree of conversion increases as a function of N$_2$ pressure. Under high pressures (> 100 MPa) the reaction is controlled mainly by the thermal conductivity of nitrogen. At high pressures, the thermal conductivity of N$_2$ increases and the heat losses become significant. The heat removal from the sample can be rapid. This leads to a decrease in the combustion temperature and conversion degree. At pressures higher than 510 MPa we observe complete extinction of the reaction.

b- High pressure combustion synthesis of titanium nitride [2,3]

A fixed mass of titanium powder is cold pressed uniaxially into parallelepiped compacts in order to obtain relative green densities from 45 to 58%. Two types of behaviour were evidenced when different heating rates in the furnace are used. For low heating rates (30°C/min) during the thermal treatment, SHS reaction is not ignited and a temperature of 1200°C is maintained during 1 h to ensure a conventional nitridation. For high heating rates (90°C/min) a sudden rise in temperature occurs corresponding to the exothermic reaction between titanium powder and nitrogen gas. The first step in the Ti(s) + N$_2$ has been shown to be the Ti(α)$\rightarrow$ Ti (β) transition, simultaneous with TiN$_x$ formation. In our study, different nitrogen pressures were used in order to study the influence of gas pressure on the degree of conversion.Ti/TiN. Increasing nitrogen pressure up to 200 MPa leads to increase the conversion to TiN up to 46.5% of nitrogen. In this

case, the permeation of gaseous nitrogen through the pores maintains the local availability of nitrogen. Then, the degree of conversion decreases and for pressures beyond 300 MPa, SHS reaction is no more ignited.

c- High pressure combustion synthesis of silicon nitride [4-5]

The aim of this work was to re-investigate the combustion synthesis of Si_3N_4 under high nitrogen pressure in order to understand the role of additives components on its mechanism of formation. Indeed, according to the literature, the elaboration of Si_3N_4 by SHS requires the presence of Si_3N_4 as diluent. Furthermore, a liquid phase is needed to ignite the reaction.

Whatever the experimental conditions and the studied mixture, the S.H.S. reaction is ignited at a temperature corresponding to the melting point of silicon (T = 1687K) In this case, ignition and total propagation were observed. The propagation could be allowed because of the thermal conductivity of α-Si_3N_4 which is lower than that of silicon. Indeed, instead of being released, the heat is kept into the sample and the reaction can be ignited.

All reaction products have similar morphology and all contain α-Si_3N_4, β-Si_3N_4 and unreacted silicon. Two different regions were clearly spotted: internal and outer zones: grains in the core of the material have a typical shape of β-Si_3N_4 (whiskers). Thus the α-Si_3N_4 phase should be mainly at the rim of the material.

In further experiments, in order to study the influence of nitrogen pressure, the dilution level was fixed at 40 wt% of α-Si_3N_4. Even for the lowest pressure, the nitrogen content is enough to perform the reaction. When the reaction takes place, the weight fraction of the different phases doesn't change with pressure.

CONCLUSION

These studies showed the influence of high nitrogen pressures on combustion synthesis of ceramics nitrides in HPSHS device. This device is relatively different from usual SHS devices: In this case the heating rates are lower and allows a better diffusion of nitrogen in the metal compact, giving rise to special structures. In the future, thanks to a French Russian collaboration, we will be able to study the differences in these devices and the thermal conditions responsible to the appearance of extra phases in the synthesized material. An extent to the phase NbN is also scheduled.

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INFLUENCE OF THE THERMAL CONDITIONS ON HIGH PRESSURE COMBUSTION SYNTHESIS OF SI$_2$N$_2$O CERAMICS

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INTRODUCTION

Si$_2$N$_2$O is a refractory material which is usually synthesized by reaction sintering of a Si$_3$N$_4$ and SiO$_2$ mixture in the presence of a liquid phase, obtained by the addition of Al$_2$O$_3$ or Y$_2$O$_3$ [1,2]. Nevertheless, because the additives are still present in the product of this reaction, other routes have been investigated: Self-propagating High-Temperature Synthesis is one of them. Two papers have been published so far [3,4] on the SHS of Si$_2$N$_2$O but their results are not in agreement. Therefore we decided to understand the reasons of these differences by studying in details the combustion synthesis of Si$_2$N$_2$O in similar conditions. Two kinds of apparatus were used and the influence of the SHS device or more generally of the thermal conditions on the formation of Si$_2$N$_2$O was studied.

The SHS samples were characterized by X-ray diffraction and SEM analysis. Their quantitative composition was determined by Rietveld refinement.

RESULTS

The results of this study clearly show that the thermal conditions are determining in the ignition and consequently the propagation of the SHS reaction. When the reactant powders are placed in graphite foam which has a high thermal conductivity, a major part of the provided heat is quickly released and the remained energy is not enough to ignite the reaction. The addition of α−Si$_3$N$_4$ which is a refractory compound allows to reduce heat losses. The boron nitride container plays the same part.

These results also show that the percentage of Si$_2$N$_2$O, the speed of combustion, the ignition and the maximum temperature depend on the device. Therefore, we can reasonably assume that the mechanism of reaction differs from one apparatus to another.

The mechanism of formation of Si$_2$N$_2$O by SHS has never been studied so far. The literature results only concern the elaboration of Si$_3$N$_4$ in a conventional SHS device. Two kinds of mechanism have been suggested: according to Ge et al. [5], nitrogen reacts with gaseous silicon ; according to Mukasyan et al. [6], nitrogen reacts with melted silicon.

The mechanism suggested in this work combines these two kinds of reaction. As it is shown in figure 1, the thermal profiles can be considered as the superposition of two phenomena: the first one (a) corresponding to a high exothermic reaction between nitrogen and gaseous silicon, and the second one (b) corresponding to the reaction between nitrogen and melted silicon.

The previous reported results on the combustion synthesis of Si$_2$N$_2$O [3] can be explained by our suggestion.
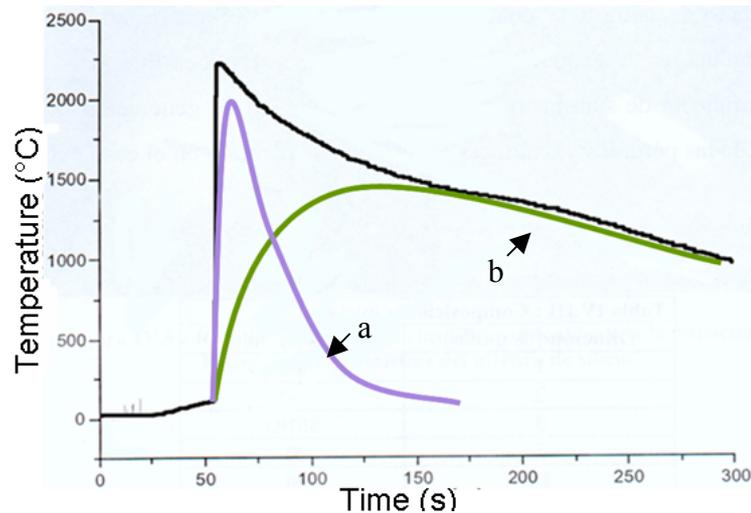
Figure 1 : Decomposition of a thermal profile . a-curve: reaction between N_2 and $Si(g)$, b-curve: reaction between N_2 and $Si(l)$.

CONCLUSION

The objective of this work was to explain the differences observed between previously reported results [3,4] on combustion synthesis of Si_2N_2O. Because these differences seemed to be due to the experimental conditions, an international collaboration between the LPMC laboratory (France) and the ISMAN institute (Russia) has been established in order to carry out comparatives investigations by using two kinds of SHS device. These apparatus mainly differ by the ignition system and the thermal conditions.

The whole of our results allowed us to understand the reactions which take place in the combustion synthesis of Si_2N_2O which each kind of apparatus. Furthermore, the results previously reported in literature could also be understood in the light of this work.

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THE COMBUSTION SYNTHESIS OF NIOBIUM NITRIDE UNDER HIGH PRESSURE OF GASEOUS NITROGEN.

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INTRODUCTION

Transition metal nitrides can be obtained from the corresponding metal and nitrogen via self-propagating high temperature synthesis (SHS) owing to the high heat of the reaction. A variety of nitrides can be obtained by reacting porous powder metal compacts in gaseous nitrogen [1]. The conversion achieved during combustion process, as well as the composition and structure of the products, is significantly influenced by the gas pressure. Among the nitrides of transition metals NbN posses the highest superconducting transition temperature. Many studies report about critical temperature in the range 15-17,3 K. Owing to the relatively high critical temperature NbN has potential applications in superconducting devices. Critical temperature strongly depends on stoichiometry. High pressures are required to attain the stoichiometric composition. Many authors reported about the combustion synthesis of niobium nitride [2-6] under the nitrogen pressure below 100 atm, but the full conversion was not obtained in this pressure range. Paper [7] presents some information about the process at pressure values up to 70 MPa. It is shown that when the pressure grows, the ratio of N/Nb increases too and achieves 1.02. In this case a maximum is observed on the plot of NbN lattice parameter as a function of nitrogen pressure. It corresponds to the transition from the lattice with a lack of nitrogen (N/Nb < 1) to that with a lack of niobium (N/Nb > 1). The aim of this work is to study the influence of higher values of nitrogen pressure on stoichiometry (N/Nb ratio) and parameters of crystal lattice of the obtained nitride.

RESULTS

The synthesis of NbN was carried out in the high pressure reactor in the pressure range 40-230 MPa. Cylindrical pellets of 10 and 15 mm in diameter and 40 mm in height were made of the niobium powder. The initial porosity of the samples ranged from 0.36 to 0.55. After the synthesis the sample was unloaded from the reactor, weighed and analyzed. The product phase composition was determined using an X-ray diffractometer DRON-3, the morphology was studied on the scanning electron microscope Jeol JCXA-733 which was equipped with an X-ray microanalyzer Oxford INCA-300, it allowed defining the elemental composition of the samples under study simultaneously. Chemical analysis of nitrogen and oxygen content was carried out.

The dependence of the reaction products composition and lattice parameter of obtained compound NbN_x on initial nitrogen pressure and thermal experimental conditions was studied. It was shown these values can change in rather a wide range. In Fig.1 we can see a dependence of nitrogen content in the combustion products on the initial nitrogen pressure. It is based on the data of the weight gain and chemical analysis. It is obvious that the data agree with each other. The stoichiometric nitrogen content in NbN is 13.1 %wt and it is achieved in the pressure range from 120 to 210 MPa. Besides some samples with super-stoichiometric nitrogen content were obtained. As it was mentioned above, when pure niobium powder without any dilution with the final product is burnt under low nitrogen pressures (<10 MPa), it is impossible to achieve the complete conversion of niobium into niobium nitride [2-6].
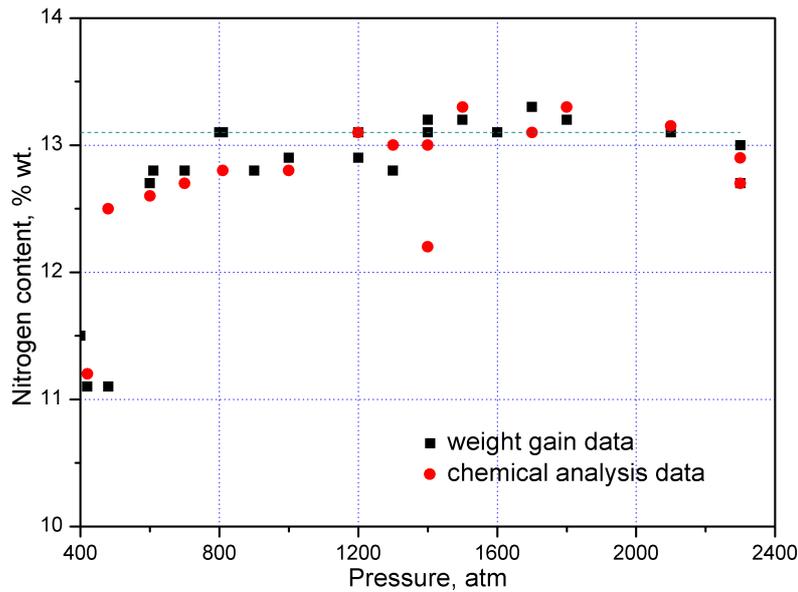
Fig.1. Nitrogen content in the combustion products as a function of initial nitrogen pressure.

X-ray phase analysis of the internal part of the sample shows the existence of the only phase of δ-NbN$_x$ in the combustion products, other phases were not detected. It was shown, that with nitrogen pressure increase a general tendency of nitrogen content growth in the combustion products is observed with a simultaneous decrease in the lattice parameter. According to the literature [8], such behavior is characteristic of niobium nitride which has a lack of niobium atoms in its lattice. In other words, it testifies that in this pressure range we succeeded to obtain nitride with super-stoichiometric nitrogen content (N/Nb>1). That agrees with the data of the chemical analysis and weight gain. This conclusion is also confirmed by the results of local X-ray spectral microanalysis according to which the ratio of N/Nb varied about 1.08 in different points of the sample cross section.

CONCLUSION

Niobium nitrides with various N/Nb ratios which can be both lower and higher than one were synthesized by combustion reaction of nitriding niobium powder in the range of high nitrogen pressures of 40-230 MPa. Nitrogen content in niobium nitride can be regulated by the value of the initial nitrogen pressure.

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SHS CERAMIC PROCESSING USING A GAS / SOLID REACTION

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INTRODUCTION

Self propagating high temperature synthesis (SHS) is an attractive technology for synthesize many advanced materials as ceramics. If a solid /gas SHS processing is used to elaborate dense material some morphological parameters as porosity or thickness have to be considered with attention contrary to a solid/solid SHS processing. Indeed they are directly in correlation with the gaseous reactive.

Nevertheless the mechanism of the combustion synthesis of the metal Zirconium has been studied under various conditions but no attempt has been made to monitor the reaction kinetic. In this work some results obtained for the combustion of Zr-ZrO_2 pellets in oxygen atmosphere will be presented.

Pellets were obtained by applying uniaxial pressure to a 30%Zr and 70%ZrO_2 mixture what leads to a green density ranging between 60 and 70 %.

RESULTS

First results concern the influence of green density and sample size on both temperature and pressure profiles. The combustion synthesis reaction was characterized by the following parameters:

-        an ignition temperature following by a sharp increase in temperature whose slope varies with green density,

-        an after burn which was observed as the reaction continues. The new increase in temperature was more or less important and slows down or up according to the green density,

-        a decrease in temperature to ambient.

The after burn reaction was strongly affected by a modification of the pellet thickness.

Pressure profiles allowed to estimate the number of mole of oxygen reacted at any time of the reaction.

Based on the obtained results, a reactive model has been established. The zirconia's self combustion synthesis develops in two steps (i) a linear consumption of oxygen during front propagation (ii) an after burn reaction in the sample's core.

CONCLUSION

It can be concluded that the two kinetic steps of the zirconia's combustion synthesis in pure oxygen are dependent on porosity and thickness of the initial sample:

- a lower green density will favour oxygen permeability and the surface reaction corresponding to the front propagation reaction that is the first kinetic step of the SHS reaction,

- a larger thickness will control the reaction by diffusion in the sample's core that is the second step of the SHS reaction.

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STUDY OF HETEROGENEOUS REACTION IN NANOSYSTEMS (NANOFILMS)

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INTRODUCTION

Physical and chemical properties of solid matter undergo significant transformations at the nanometer-scale level. It may be expected, that routes of heterogeneous solid-state reactions alter with decreasing size of reaction. Study of this phenomenon has a great importance for progress in nano-technology. The present work reports some results of experimental study of the heterogeneous reactions in Ti-Al multilayer samples as a fruitful model for investigation of reaction mechanisms in nano-systems.

RESULTS

Multilayer samples with the layer thickness from 4 nm to 1000 nm and the total amount of layers up to 5000 were prepared by magnetron deposition technique [1]. Thin rectangular plates about 1x2 cm were cut out of the rolled or deposited bands and used for the Time-Resolved Synchrotron Radiation Diffraction analysis (TRSRD). These plates were put at the heating holder inside the water-cooling reaction chamber made of stainless steel, with beryllium window (0,3 mm thick) for input and output of radiation. The reaction chamber was filled with helium at 1 bar, inner volume of the chamber was 1000 cm^3. The samples were heated by Nichrome electrical resistance furnace at a constant rate 12 K/min up to 190-1000K, then cooled down in the helium atmosphere, temperature was controlled by chromel-allimel thermocouple. Well-monochromized synchrotron beam with wavelength 1,5215 Å ($\Delta\lambda/\lambda\sim10^{-4}$) illuminated area 1x2 mm on the sample's surface. Powder diffraction patterns were detected by one-
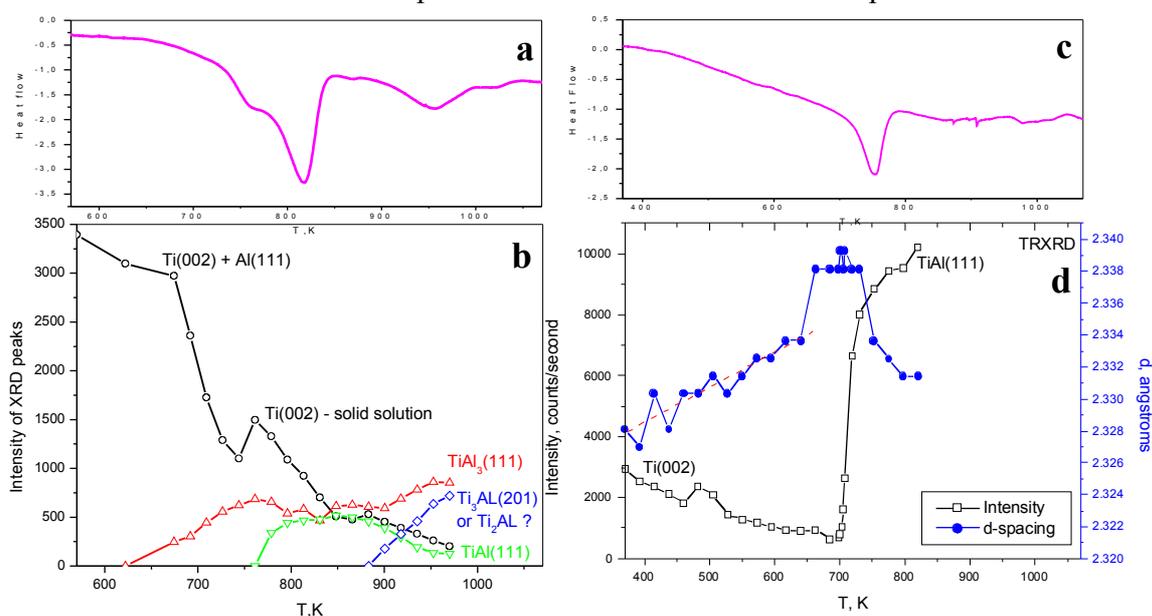

Figure 1 : Results of DSC (a, c) and TRSRD (b,d) for the multilayer Ti/Al samples heated at 12 K/s: (a) ans (b) correspond to the sample with layer thickness 390 nm, (c) and (d) – to the sample with layer thickness 4 nm.

dimensional linear gas-filled detector OD-3, with focus distance 350 mm, angle range 30 degrees, angle resolution 0,01 degree, and loading rate 10 MHz (see for more details [10]). Commonly, rate of recording was chosen as 1 SRD pattern every 10 seconds (corresponds to the temperature range about 2 K). The TRSRD method was combined with Differential Scanning Calorimetry (DSC) carried up at the same heating conditions as the TRSRD experiments. This approach allowed establishing direct correlations between exothermic stages of heterogeneous reaction and phases formation. Additionally, methods of TEM, SEM, Scanning Tunnelling and Atomic Force Microscopy were used for control micro(nano)-structure of the initial samples and products.

The results show that reaction mechanism changes with decreasing thickness of the layer. For example, Figure 1, a,b demonstrates that reaction between relatively thick layers (390 nm) involves 3 exothermic stages, which correspond to different products. When the layer thickness decreases down to 4 nm (Figure 1, c,d), the reaction occurs in 1 stage and starts at lower temperature.

CONCLUSION

Thus, combination of controllable heating during TRSRD analysis with DSC and other methods clears the way for direct *in situ* study of intrinsic reaction mechanisms in micro-lamellar systems by means of monitoring phase evolution during the process. It can be used for better understanding mechanisms of SHS reactions, influence of mechanical activation and nano-scale sizes of reactants on the reaction routes and intermediates.

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THERMODYNAMICS OF REACTIVE NANOMULTILAYERS

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INTRODUCTION

Nanomultilayers are obtained by deposition of alternative layers of two different metals. For an overall thickness of a few microns, the number of individual metal layers ranges from a few tens to several thousands, so individual layer thicknesses are in the range of nanometers. The special features of SHS in such objects is the subject of the INTAS contract 03 51 4103 between 3 laboratories in Russia, one in Austria, 1 in Slovakia and the LCSM in Nancy. We will focus on the thermodynamic part of the study.

RESULTS

Two different points are addressed: the enthalpy of formation of the intermetallic compounds in the films, compared to the same reaction in non "nano" materials, and the kinetics of reaction as a function of the individual layer thicknesses. Two different types of calorimeters are used for this purpose: a DSC 111 from SETARAM in Nancy, and a DSC 7 from PERKIN ELMER in Slovakia. The two calorimeters have very different sensors and they are complementary.

The main results are that the enthalpy of formation is less energetic for the multilayers than for the "bulk" materials (roughly 50%) in TiAl for instance and that the activation energy is dependent of the layer thickness, but this dependence is not linear. In addition reactions are relatively complicated and cannot be understood without help of TRXRD.

A possible explanation for the enthalpy of formation is partial alloying during deposition of the layers. TEM experiments have shown that grain boundaries are very thick and very probably amorphous. Amorphous pure metals are far from likely, and the hypothesis of partial alloying, at least in the grain boundaries, cannot be ruled out.
New experiments will try to fix this point.

PECULIARITIES OF MULTILAYERED NANOFILMS COMBUSTION

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INTRODUCTION

Gasless combustion in multilayer foils with nano-scale thickness of the layer represents a novel class of SHS processes which can be used for the production of nano-crystalline materials, foils and coatings [1].

But characteristics of the combustion process for the multilayer nano-foils have not been adequately studied. In this work some new experimental data concerning the propagation of the reaction front in the Ti/Al multilayer foils will be shown.

These nano-films (fig.1) were obtained by plasma-assisted sputtering technique. Thickness of the alternate layers was varied from 4 to 500 nm, and total number of the layers was varied from 20 to 5660.
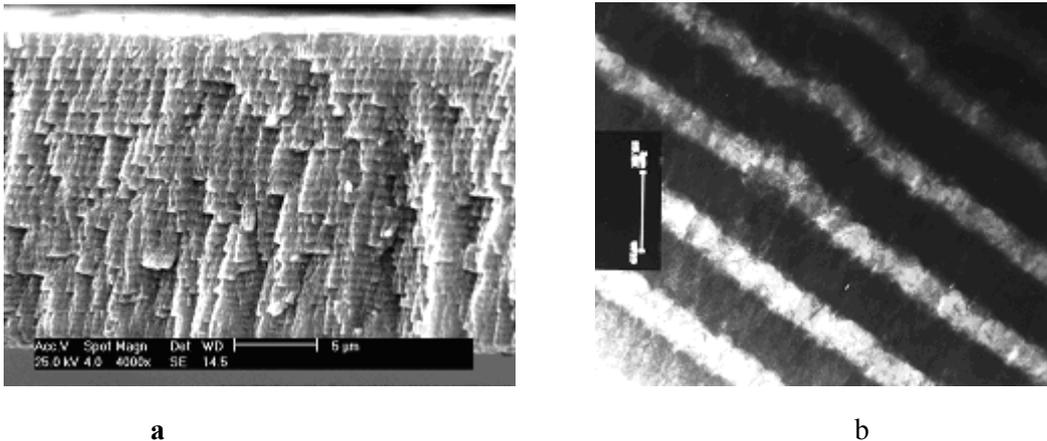

a   b

Figure.1 Microstructure of Initial foils

RESULTS

Definition of position of the combustion wave as a function of time for different experimental positions shows that in all cases, the position of the front coordinate changes linearly with time. Propagation velocity increases by increasing the initial temperature and decreasing the thickness of the layer.

Distributions of local instant velocieties shows that the instant value of the combustion velocity in multilayer foils never drop down to zero, as it frequently happens in powder mixtures. Different kinds of combustion waves were observed.

It was shown for Ni/Al foils, that reaction is so fast and exothermic that it is possible to ignite and observe reaction on the multilayer nano-foils without separation from the substrate i.e. on the substrate. Temperature profiles and combustion velocity were measured [2, 3].

CONCLUSION
The SHS process in the Ti/Al, Ti/3Al, Ni/Al multilayer foils shows an example of the quasi-homogeneous gasless combustion. Deviations of instant velocity probably relate to thermal factors, such as heat evolution/heat losses and do not correlate with the fine microstructure of the foil.

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TIME-RESOLVED DIFFRACTION STUDIES OF COMBUSTION SYNTHESES: APPLICATION TO THE QUATERNARY SYSTEM AL-NI-TI-C

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INTRODUCTION

Combustion synthesis is an extremely rapid, easy and low cost method to fabricate a large range of materials. However, because of the high reaction and heating rates involved, the composition and the physico-chemical properties of the final products are difficult to predict. Thus, in order to control the process, synthesis mechanisms need to be understood. Traditionally, static techniques, such as Optical and Scanning Electron Microscopy of quenched samples, are used. However, the information deduced does not give precise indication of the phases evolution as a function of time and artefacts can be introduced. The only technique actually available to follow the reaction in-situ without perturbing the evolution of the reaction is time-resolved diffraction. In this study, the self-propagating and the thermal explosion modes have been studied for an equi-atomic mixture of Al, Ni, Ti and C using this technique. Synchrotron X-rays were used to determine the phase evolution during the SHS and neutrons during the TES.

RESULTS

To study the self-propagating mode, Time-Resolved X-ray diffraction has been performed on the ID11 beam line at the ESRF, France, using a 45 keV beam with a size of 200 x 200 microns. The sample, under the form of a pellet with a density of 55 %, was placed perpendicular to the beam, which enabled diffraction in transmission geometry, and was ignited from the bottom. 2D diffraction patterns were acquired every 135 ms (25 ms of acquisition and 110 ms of readout time) using a FreloN CCD camera connected to an image intensifier. The synthesis of more than 10 samples of the same composition synthesized under the same conditions has been followed. The results are illustrated in figure 1.a. Based on these data and on a temperature profile, a possible synthesis mechanism has been suggested: In the preheating zone, the temperature of the zone increases due to heat transfer from the already reacted zone. As the temperature reaches 660°C, Al melts. When the temperature reaches 882°C, the phase transition of Ti from its hexagonal to its cubic phase occurs. At the contact point between Al liquid and Ni solid, NiAl forms. This formation generates heat, which allows the temperature to increase further. Al liquid spreads around the solid particles and the NiAl grains grow to touch the titanium particles. At this contact point, the $AlNi_2Ti$ forms and, at the same time, TiC forms at the contact point between the C and the Ti particles. The formation of NiAl and TiC are exothermic, which enables the temperature to increase up to the melting temperature of Ni (1455°C). TiC formation continues at the surface of the C particles until the total disappearance of Ti. It generates enough energy for the temperature to reach the melting temperature of the ternary phase $AlNi_2Ti$ (about 1480°C), which melts. The temperature goes up to1638°C, and the NiAl particles melt. Thanks to the surrounding liquid, which increases the contact surface area and, consequently, the material transfer, the TiC particles continue to grow. The temperature reaches the melting temperature of Ti (1670°C) and a complete liquid solubility of Al, Ni and Ti occurs. Then a TiC layer forms around the C particles, enabling the dissolution of C into the liquid through a dissolution/crystallisation process of this layer. When the liquid starts to saturate in C, TiC precipitates. Once all the titanium carbide has formed, no more exothermic reactions occur and the temperature goes down. When it reaches 1638°C, NiAl crystallizes by a reaction-coalescence process. Finally, during the cooling period, the rutile phase of titanium oxide forms at the surface of the sample.
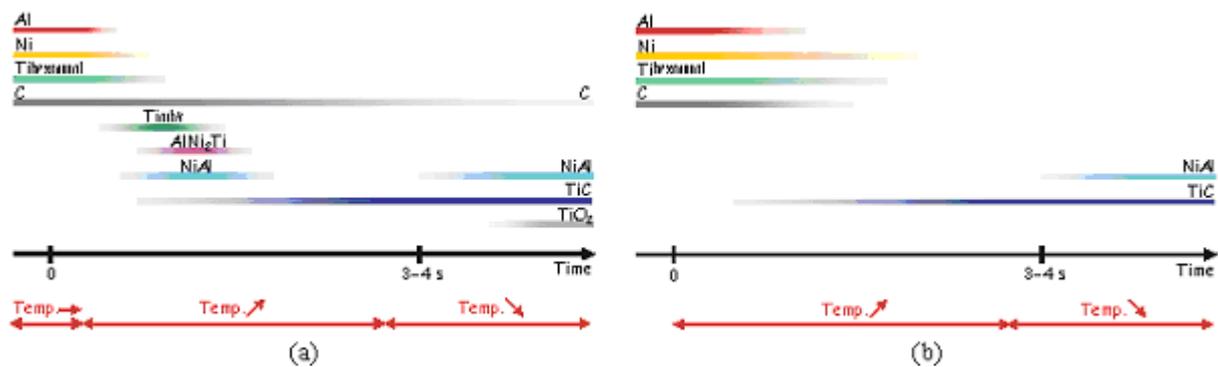
FIGURE 1: CS OF THE AL-NI-TI-C (1:1:1:1) COMPOSITION:

TRXRD results of the SHS mode (a) and TRND of the TES mode (b).

Time-Resolved Neutrons Diffraction has been used to follow in-situ the thermal explosion mode. these experiments have been performed on D20 at ILL, France, using a neutron beam with a wavelength of 1.3Å. The sample was made of 3 thick pellets (7 mm) pilled up with a density of 85 %. 1D patterns covering a 2θ range of 150º were taken every 800 ms (400 ms of acquisition). The results obtained are illustrated in fig. 1.b. They show that the titanium carbide should form by a solid-solid reaction between the hexagonal phase of Ti and the carbon. This reaction occurs at a temperature lower than the melting temperature of the aluminium 660ºC. Being exothermic, the formation of TiC starts the self-sustained reaction and, at that time, the heat released by the furnace is no longer useful. The carbon is completely consumed by the formation of TiC, as well as Ti. The heat supplied by the exothermic reaction is high enough for the temperature to reach the melting temperature of Ni (1455ºC). Finally, when no more TiC forms, there is no more heat generation and the temperature starts to drop. It reaches 1638ºC, temperature at which NiAl crystallises. The heat released by this exothermic reaction is not high enough to increase the temperature of the whole sample and the sample cools down.

CONCLUSION

Time-resolved diffraction has been successfully used to follow in-situ the evolution of crystalline phases during the self-propagating and the thermal explosion modes of the combustion synthesis of an equi-atomic mixture of Al, Ni, Ti and C. Both combustion modes lead to the same final products consisting of small round TiC particles embedded into a matrix of large NiAl grains, which have been formed through the same processes: precipitation for TiC and crystallisation from the melt for NiAl. However, the time-resolved diffraction data have shown that the synthesis mechanisms followed by each mode were different. Thus, during the self-propagating mode, 3 intermediate phases have been observed (Ti^{cub}, NiAl and $AlNi_2Ti$) and none during the thermal explosion one. Moreover, the trigger for the SHS reaction has been determined to be the formation of NiAl and for the TES reaction, the formation of TiC.

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INFLUENCE OF MECHANICAL EFFECTS ON SHS PROCESSES

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INTRODUCTION

Now it is possible to offer on the basis of common views miscellaneous gears of influencing of mechanical effects on processes SHS. More often influencing of mechanical effects (shift deformations) see in stirring and in maintenance of an even distribution of weight and temperature on a volume of a material. Other possible gear is connected with plastic flow of a material and with originating of large shearing stresses. This factor is strong and, in most cases, positive, influential on pattern: the cracks and pores in a deformed material "are healed", there is grinding grains and the large uniformity of texture is reached, the strength and plasticity of materials is augmented.

However mechanical effects can act as the kinetic factor, exerting influence on processes of combustion and gelation: resizing of a grain, its form and positional relationship of grains. As a result of action of pressure on combustion products a picture of phase formation and gelation sharply varies, there are not reacted volumes. Changing mechanical parameters in a broad band, it is possible to change quality of a received dust and its morphology. So, for example, the morphology of titanium carbide obtained in conditions of mechanical effects has characteristic spongy pattern. It qualitatively differs from pieces (splinter) structure of pattern of titanium carbide obtained by a conventional SHS- method (without mechanical effects).

For practice of SHS processes the large concern introduces a problem on effect of deforming at stage of originating finely divided pattern. Trial experiments and the analytical investigations demonstrate, that the deformation parameters, and first of all, speed of deforming, render strong influencing on effect of a hardening of initial morphology, at which one there is no accretion of separate fine grains and formations of a unified chip. Under operating of external forces there is a seal of a material and the process of a sintering is intensified, that results in increase of strength of a structural skeleton of a generatrix material. The product of combustion (at once after completion of auto wave process) is not, strictly speaking, finished product. The chemical processes in it can be finished, but some physicochemical processes (crystallization and recrystallization) prolong to flow past during some time. At increase of time the formation of a material in all volume is completed, however sintering and cooling reduce capacity of a material to plastic deforming. Thus, there are optimal temperature-time frames, in which one the mechanical effects on SHS products are most effective. The boundaries of an optimal time frame depend not only on temperature and depth of completion gross of posts - processes, but also from speed of deforming and pressure.

RESULTS

The mechanical effects result in occurrence of effect texturing of a material encompassing by formation of areas, enriched by flow bundle, or depletion by it. The reason of reallocating of flow bundle is connected, probably, to features of deforming of the burned down bar. If during deforming bar the flow bundle is in a liquid state, under effect of external pressure there is its extrusion in places of a heightened porosity.

Thus, there is a non-uniformity of distribution of flow bundle, and also enrichment by it of initial segments of an article, which one has a heightened porosity.

The capability of formation of deformation textures was studied at SHS extrusion of materials on the basis of hafnium borides and titanium borides with a nickel binder. On this material it is revealed the brightly expressed effects of an texture anisotropy as interleaving bands of light and dark areas prolated along a set of the current of a material. The analysis of all experimental data has allowed suspecting the following gear of formation of light and dark areas. At pressing a porous material through a matrix in the center of deformation there is an orientation of a system of pores along a set of the current. Besides at shift between layers the cracks can be derivated. In these systems of pores and cracks the nickel binder directs, if it is in a liquid state. Thus, as a reason of formation of dark and light areas it is possible to consider shift deformation of a material at presence in it of liquid flow bundle. The dark areas enriched with flow bundle, presumptively are places of a concentration of shift deformation, which one promotes growth of grains and their orientation.

In the present review the different gears of influencing of mechanical effects on SHS processes are reviewed.

NANOSTRUCTURED MATERIALS BY MECHANICALLY ACTIVATED SHS.

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I. Mechanically Activated Processing Review

I.1. Mechanically Activated Annealing Processing (MAP)

In the early 90's years, an alternative synthesis method has been proposed by Malhouroux- Gaffet and Gaffet [1 – 4] to produce silicide powders, the so called Mechanically Activated Annealing Processing (M2AP, so called in french "Elaboration par Recuit Activé Mécaniquement / ERAM).
Such a solid state method, combining short duration mechanical alloying and low temperature annealing has been successfully applied to the synthesis of $FeSi_2$ [1,2], $MoSi_2$ [3] and WSi_2 [4]. Starting from a mixture of elemental powders, the first M2AP step corresponding to the short duration mechanical alloying leads to the formation of micrometer powders in which nanoscale 3 - D polyinterfaces of the elemental components have been formed

The true solid state reaction leading to the end product phases occurred during the annealing. The effect of the milling conditions on the grain sizes as well as the residual stresses have been reported to modify the phase transformation kinetics induced by low temperature isothermal annealing starting from a pre - short duration mechanically alloyed elementary components. Therefore, according to such experimental results, the M2AP is a very suitable powder metallurgy process allowing the direct driving of the solid state reaction occurring for example during the reactive sintering process. More than that, the M2AP has been found to be a very suitable method to produce nanocrystalline $MoSi_2$ phase. Indeed, the first mechanical M2AP step leads to an activation of the three dimension elementary distribution which reacts 400°C below the temperature of the classical processes, i.e. 800°C instead of 1200°C.

I.2. Mechanically Activated Self Heat Sustaining Reaction (MASHS)

Firstly applied by E. Gaffet et al in 1995 [5], the use of such a mechanical activation step as a preparation method of the SHS precursors allows the formation of FeAl nanostructured materials [5]. More recently, new developments have been achieved in the GDR "GFA" n°2391 CNRS, in particular with a strong cooperation between laboratories from the authors., allowing to synthesize a large set of materials by MASHS : the mechanical activation step was found necessary (i) to modify the thermal parameter of the combustion front (i.e. combustion front velocity, thermal heating rate,…) in the cases such as Mo-Si [6,7], Ni-Si [8], Fe-Al [9], Nb-Al [10], Ti-B [11], … (ii) to ignite a combustion front in the case of systems having a low exothermicity such as Fe-Si [12], Cu-Si [13]. Nevertheless, the control of the mechanically activated mixture characteristics and, the understanding of the mechanical activation role on the SHS parameters are essential to produce end-products with expected microstructure. Consequently, real time in-situ investigations of structural changes and chemical dynamics in the combustion area are possible by the use of synchrotron radiation [14].
A review may be found in a recent paper entitled "Mechanical Processing for Nanomaterials" written by E. Gaffet and G. Le Caër [15].

II. Recent Development in mechanical activation.

Specific attention has been paid to improve the knowledge of the effect of mechanical activation to promote SHS precursors. It has been found that depending on mechanical activation modes (i.e. normal or tangential shocks), the induced defects may be selected. In the case of mechanical activated Fe [16], it has been reported that the ratio of the shock energy Es/Et seems to govern the nature of the dislocations (edge or screw), see figure 1.
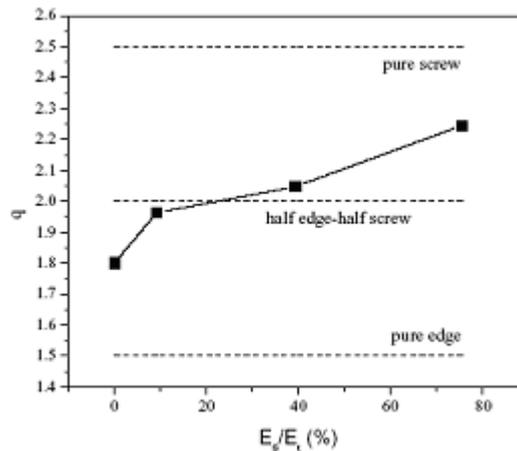

Figure 1 :Nature of the dislocations as a function of the normal to tangential ratio [16].

In a more recent published work [17], such an observation has been confirmed. It is shown that the change of microstructure characteristics of as-milled Cu powder versus the ball milling conditions (under constant time of the ball milling) depend on only some energy parameters of the milling, for example, average size of crystallite is uniquely defined by energy of the shock, whereas the portion of edge and screw components of dislocation structures depend on a ratio between normal and tangential components of shock.

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ABOUT A COMPETITION OF A DIFFERENT SINTERING MECHANISMS AT SHS DISINTEGRATION

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INTRODUCTION

A greate opportunity for creation of new materials is opened with use of SHS process (a self-propagating high-temperature synthesis) in a combination to shift deformation of initial components and formed products during synthesis. Mechanical actions lead to hashing arising structures and suppress development of crystallization processes and recrystallization one. Preliminary experiments allow to draw a conclusion, that deformation parameters, and first of all, speed of deformation, render strong influence on processes of burning and structurization: change of the grain size, its form and a relative positioning of grains [1]. Changing these parameters in a wide range, it is possible to change quality of a received powder and its morphology. Various aspects of influence of mechanical actions on SHS-processes till now are still poorly studied.

One of concrete examples of carrying out SHS process in conditions of mechanical influences are [1-2] new receptions of powders of the refractory oxygen-free connections offered in works technological method, named by SHS-disintegration. The essence of a method (fig.1) consists in crushing the material received in a wave of burning in conditions of shift deformation and enclosed external pressure. Realization of a method is based on ability of hot weight of the synthesized product to macroscopical deformation, therefore a key to understanding of this process is the knowledge behaviour of products SHS in high-temperature area. At carrying out of experiments on SHS-disintegration a number of the interesting phenomena have been found out. It has appeared, that far not always it is possible to crush completely received as a result SHS a material. After the termination of chemical reaction in product SHS various physical and chemical post-processes proceed. The hot porous material is condensed under action of external pressure, the structural skeleton is formed of separate particles, in a material intensively there is a sintering and hardening of products of the burning, connected with cooling. Besides in a material there are crystallization and recrystallization. Adjoining grains of crystal substance at sufficient heating, as a rule, form the general border. Grains contact extends, in other words, process of accretion of grains develops. Development of this process depends on presence of a liquid which divides adjacent grains, and actions of internal and external forces. In conditions of experiment realization of various mechanisms of sintering is possible: sintering in conditions of action only internal forces (operates prior to the beginning of the appendix of external pressure) and sintering in conditions of the enclosed external pressure (from the beginning of crushing up to the end of process). Experimentally it is shown, that the competition of these mechanisms of sintering on a background of cooling of products of burning of it a material causes nonmonotonic character of dependence of the crushed weight of products of M from time of the appendix of mechanical influences. It means, that in optimum conditions a course of post-processes (sintering, condensation, cooling, etc.) Should provide the minimal durability of a material favorable for its crushing. At increase in time of a delay td (an interval of time between initiation of burning and the beginning of the appendix of loading) the material can get such durability, that full crushing will appear impossible. Thus, one of key questions of carrying out of SHS-PROCESS in conditions of mechanical influences is the choice of optimum time of a delay at which with other things being equal there is a maximal output of the crushed powder. Physical sense of optimum time of a delay - time of an output properties of a material on an optimum level for shift deformation.

The purpose of the present work to confirm the stated simple reasons on the basis of the phenomenological description of change of possible mechanisms of sintering and heat exchange at the account of temperature dependence of factors of viscosity and diffusion of a material. On the basis of mathematical model of SHS-CRUSHING theoretical calculation of dependence of durability of a product from time is lead at various mechanisms of process of sintering. We shall enter the geometrical characteristic x - size grain contact. It is qualitatively possible to consider, that this size defines also contact durability between particles at sintering (x it is directly proportional to durability). Formation and development of contact between separate particles can occur on different mechanisms of sintering. In particular, in detail theoretically also features of various mechanisms of sintering of spherical particles - diffusion-viscous current have experimentally been studied; volumetric, superficial and boundary diffusion, evaporation - condensation, dislocations the mechanism. For each of these mechanisms of sintering the kinetic equations defining dependences x (t) are known. In the literature it is marked, that it is necessary to approach to a formulation of quantitative laws and a concrete kind of the kinetic equations with extra care as they have empirical character and describe only certain set of experimental data, instead of are dictated by the general laws of mechanics and thermodynamics. In real conditions growth of interpartial contacts can occur as a result of action of several mechanisms of sintering, course in which time not always is consecutive (one behind another). To differentiate their role not always it is obviously possible. However for the purposes of the present estimated consideration we shall accept simplifying assumptions, that process of sintering occurs in two stages: at the first stage operates the mechanism of sintering due to internal forces, and at the second stage in motive power of sintering external mechanical influences which lead to condensation of a material due to viscous current are. Let's consider each of mechanisms separately.
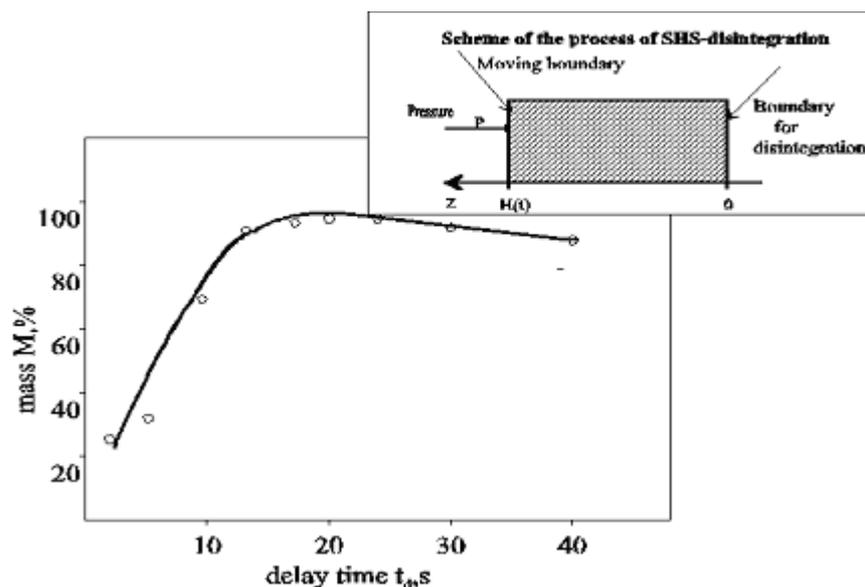

Figure1: Scheme of the process of SHS-disintegration

RESULTS

From the transcendental equation it is possible to receive optimum value of time of the delay, corresponding to the minimal durability got by the sample during process of SHS-CRUSHING, i.e. a maximum quantity of the crushed powder. The scheme of calculation should be following. For given time of crushing, properties of a material and characteristics of process the initial parameter h is counted. From equation it is defined corresponding it h;. The found value defines communication between time of a delay and characteristic time of cooling at which dependence X (td) has a minimum. For example, for time of crushing tdis = 2 with, h=10, time of a delay corresponding the minimal durability - td = 20 with, that will be coordinated with experimentally received results. We shall lead numerical calculation of dependences of x (t) and x (td) for process of the sintering provided by both by mechanisms. The schedule of dependence x (td) is presented to contact durability from time of a delay on mechanisms of sintering due to internal and external forces, and also to dependence of total durability X (td) from time of

a delay. However total contact durability appears nonmonotonic and has a minimum. This feature of sintering at change of its mechanisms can be qualitatively interpreted as consequence of various speed of change of contact durability depending on temperature. Really, according to the kinetic equation, speed of sintering is directly proportional to factor of self-diffusion Da, and according to the kinetic equation it inversely proportional to factor of viscosity.

It is necessary to distinguish dependences of contact durability on current time and on time of a delay. In conditions of experiment time of crushing remains to constants. As general time of experience t = td+tdis at increase in time of a delay, there is an increase and general time of experience. If one mechanism of sintering with increase in time of experience contact durability increased operated only. In our consideration at consecutive action of two mechanisms of sintering the increase in time of a delay leads to increase in an interval of time of sintering due to the first mechanism (from 0 up to td), that causes increase in contact durability. Thus time of sintering due to the second mechanism, equal to time of crushing tdis, remains to constants (conditions of experiments in are those), and general time of experience t = td+tdis increases. However influence of increase in general time of sintering on total contact durability can appear weaker, than influence of change of rate of growth of this durability with cooling products of burning. As a result total durability has appeared non monotonic dependence on time of a delay. The physical sense of this result just also consists that there is optimum time of the appendix of mechanical influences for the SHS-PROCESSES, providing the minimal durability of a material at sintering on a background of cooling of products of burning.

CONCLUSION

Under action of external forces there is a condensation of a material and process of sintering that leads to increase in durability of a structural skeleton of a formed material is intensified. Sintering and cooling of products of burning reduce ability of a material to plastic deformation. Experiments and the theoretical researches lead in the present work have shown existence of an optimum the time interval in which mechanical influences on SHS-PRODUCTS are most effective. Borders of an optimum time interval depend not only on temperature and depth of end gross post-processes, but also from speed of deformation and pressure. For practice of SHS-PROCESSES the big interest represents a question on influence of deformation on a stage arising structures. It is known, that deformation parameters, and first of all, speed of deformation, render strong influence on effect of training of initial morphology at which there is no accretion of separate fine grains and formations of a uniform crystal. From the resulted reasons it is complex to track influence of such parameters, as external pressure and speed of rotation of a rotor. It is expedient to develop models for the theoretical description of influence of these parameters, proceeding from the general consideration of current of a material.

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A MULTILAYER MODEL FOR SHS OF INTERMETTALIC COMPOUNDS.

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INTRODUCTION

The complexity observed in SHS experiments arises from the coupling between the propagation of a thermal wave and the reactive processes at the level of the individual particles. In this talk, we will focus on the behavior of an individual grain when it experiences a temperature rise due to the propagation of the heat front. Using this "mean-field" approach, we investigate the effect of various parameters such as the initial grain size and the heat of the reaction on the development of the global reactive process. This modeling proves to be quite helpful for interpreting the experimental observations and for understanding the micro-structural properties of the final material.

RESULTS

In many situations, the exothermic reaction front propagates in a powder of metallic nanograins (A and B) whenever one of the reactant (B) melts and surrounds the particles of the other (A). Hence it is important to model the reaction of a particle A suspended in a molten phase B. In this case, initially A dissolves in B and, as the liquid B diffuses thorough the solid, layers of intermetallic products can form and propagate inwards converting the solid particles of A into the product [1, 2]. At the same time, the outermost surface may slowly dissolve into the melt. For example, in the Al-Ni system [3], Al melts at 933K and surrounds the Ni particles whose melting point is 1728 K. If the temperature, T, of the reaction does not exceed the melting point of Ni, the formation of the intermetallic compounds is due to liquid solid reaction. Our modeling describes such reactions taking into account details and complexity of the reaction based on the phase diagram of the binary system. As the reaction progresses, various intermetallic compounds of the two metals form in layers. Such layered have been observed in experiments with metal foils [2] and with powders [1]. Our model seeks to describe the dynamics of the growth of these layers and to predict the final multi-layer structure of a typical particle. This structure is, of course, related to the particle size, and the temperature variation it is subjected to during the reaction.

In the model discussed in this talk, we focus on a "typical" single solid particle surrounded by a liquid. The whole system is subjected to a propagating temperature front. The time evolution of the temperature T is assumed to be given; it is the temperature a typical particle in the system experiences (see Fig.1). Our goal is the prediction of the time evolution of the layered structure of the particle for a given temperature front.
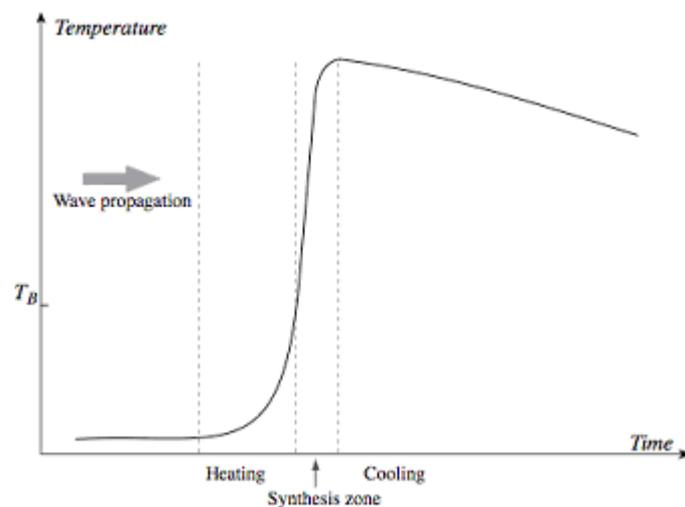

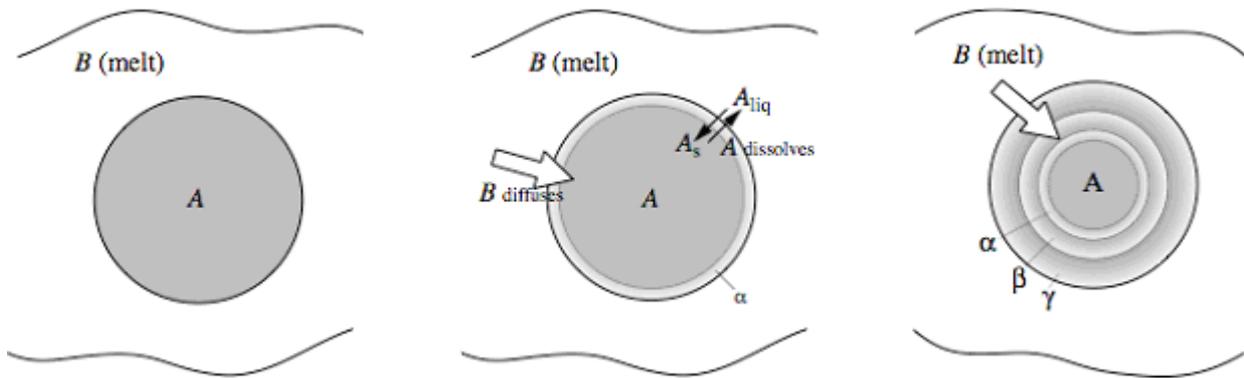**Fig.1 : Temperature evolution versus time inside a combustion front**

Fig.2 : Different stages of the reaction mechanism between two metals *A* and *B*. The highest temperature the system reaches is higher than the melting point of *B* but lower than the melting point of *A*.

The reaction proceeds through the following stages (see Fig.2):

1. First component *B* melts and surrounds particles of *A*, which are assumed to be spherical for simplicity, but other shapes could also be considered.

2. Next, particle *A* begins to dissolve into liquid *B* and, at the same time, *B* diffuses into *A* and forms a layer of intermetallic compound, say α.

3. Since the *A*/ α interface is not in equilibrium, driven by the diffusion of *B* (more accurately, interdiffusion of *A* and *B*) through the α layer, more of *A* converts to α. Thus, the thickness of the α layer grows.

4. At the outer surface of the α layer, *B* may react with the α phase to produce another intermetallic compound β, resulting in the growth of a β layer. Similarly, more layers, γ, δ, etc., could form successively, depending on the number of compounds that the components *A* and *B* can form.

5. The outermost layer dissolves into the melt thus changing the composition of the melt.

During this talk, we will discuss in detail the typical behavior of a two-layer system in different situations.

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SOME PECULIARITIES OF MECHANICAL ACTIVATION INFLUENCE ON SHS-PROCESS AND PARTICLES STRUCTURE IN THE NI-AL AND TI-AL SYSTEMS.

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INTRODUCTION

Gasless combustion of mechanically activated mixtures was investigated in the set of works [1, 2], however microstructure aspects of mechanical activation influence on combustion and particles structure remain insufficiently known.

The present work is devoted to studying influence of mechanical activation (duration and mode) in powder mixes Ni+31.5wt%Al and Ti+wt36% Al on the SHS process and particles structure (here SHS stands for self-propagating high-temperature synthesis). Plastic reagents mixtures mechanical activation (MA) allow to obtain composite particles, composed of intermixed (on micro and sub-micro levels) layers of initial reagents (Fig 1) [3].
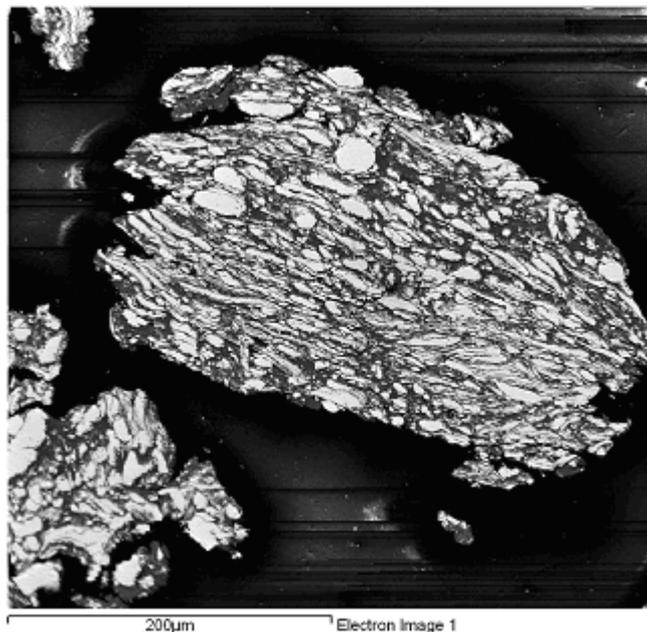

Fig.1. Composite particle Ni+Al, composed of intermixed layers of Ni+Al, obtained by mechanical activation.

Using x-ray diffraction and transmission electron microscopy methods qualitative dynamics of composite particles formation, depending of mechanical activation parameters (duration and mode) is revealed.

In the Ni+Al system mixture after minimum time activation has maximal combustion velocity (exceeds not activated mixture combustion velocity), and then decreased with time of activation, probably because of Al oxide part increasing (Fig. 2 a).

In the Ni+Al system after MA combustion velocity increased with balls acceleration increasing (Fig. 2 b).
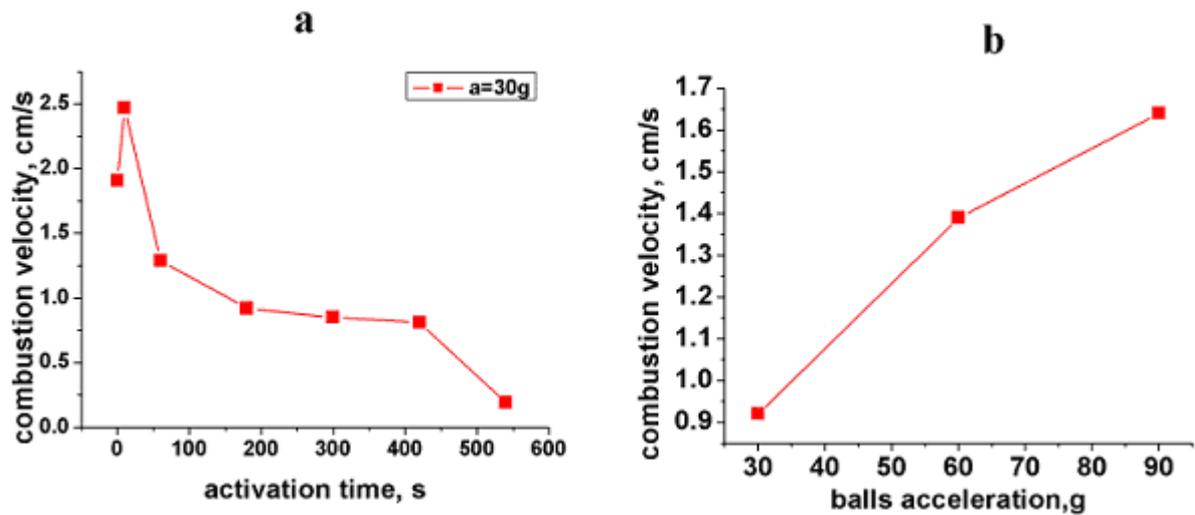
Fig.2. a - combustion velocity dependence from activation time for Ni+Al system (balls acceleration 30 g); b - combustion velocity dependence from balls acceleration for Ni+Al system (activation time 3 min)

After mechanical activation we could initiate gasless combustion wave in the Ti-Al system without preheating, that impossible without mechanical activation.

In combustion products composite particles, obtained by mechanical activation, keep their identity, that allows producing products with unusual structure (for example FGM with graded particle and pore size Fig. 3.
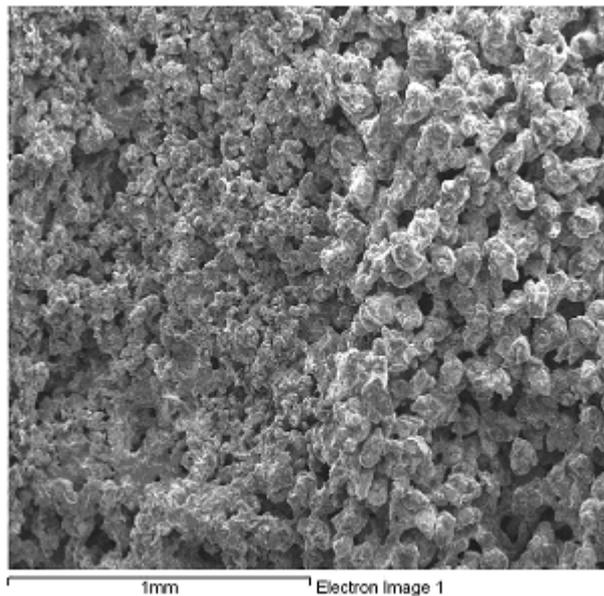

Fig.3. FGM NiAl with graded particle and pore size: boundary between layers

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SYNTHESIS OF NANOCRYSTALLINE TiC-Al$_2$O$_3$ COMPOSITES BY MECHANICALLY-ACTIVATED PRESSURE-ASSISTED SHS TECHNIQUE

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INTRODUCTION

In the last few years, research work has been focused on the morphology (particle size and shape, porosity) and microstructure (grain size, size distribution) control of Self-propagating High-temperature Synthesis (SHS) produced materials. Demand for novel materials with superior properties prompted the research for synthesizing nanocrystalline controlled materials. Indeed, numerous papers have reported many unique properties associated with nanomaterials, such as improved mechanical properties compared with microcrystalline materials. Many different methods, implying a far from equilibrium step to limit grain growth, have been tried to stabilize nanomaterials using SHS technique: the nitrate gel process (citric acid-nitrate, glycine-nitrate, or urea-nitrate) [1], the Mechanically Activated SHS [2], and the use of additives [3].

The aim of this work is to produce dense nanocrystalline TiC-Al$_2$O$_3$ composites in one step by pressure-assisted combustion synthesis. The adiabatic temperature of the (Ti+C) combustion is significantly above the melting point of titanium. As a consequence, TiC grains nucleated in the Ti melt during combustion synthesis can easily grow beyond the nanocrystalline regime. To produce nanocrystalline TiC via SHS, it is thus necessary to simultaneously encourage nucleation and reduce grain growth, two often contradictory requirements. In this study, TiC nucleation is enhanced both by co-milling the reactants in a high-energy vibratory ball-mill creating a large number of Ti/C interfaces, and by introducing nanocrystalline Al$_2$O$_3$ as nucleation sites. Moreover, TiC grain growth is limited due to the decrease of the combustion temperature and the cooling time related to the use of the inert Al$_2$O$_3$ diluent which absorbs one part of the energy given off by the reaction.

RESULTS

Two preparation methods have been used to obtain the initial reactant mixtures with different Al$_2$O$_3$ distributions: the first method consists in performing a mechanical treatment of the (Ti+C+Al$_2$O$_3$) powder mixtures in a high-energy vibratory ball-mill. In the second method, co-milled (Ti+C) powder reactants are mixed with nanocrystalline Al$_2$O$_3$ powders via a liquid way. For both methods, the alumina content is in the range 10-40 vol.%. A special pseudo-isostatic press (P=1100 bars) equipped with an ignition system (graphite plate heated by electrical current) has been used to simultaneously perform the SHS reaction on the (Ti+C+Al$_2$O$_3$) cold-compacted pellets and densify the final products. Reactant powder mixtures and TiC-Al$_2$O$_3$ composites are characterized in terms of microstructure and morphology using X-ray diffraction, scanning and transmission electron microscopy techniques. The composites density is measured by pycnometry methods and their Vickers microhardness is evaluated.

From XRD, TEM and SEM/EDS analyses, it is demonstrated that reactant mixtures consist in aggregates composed of nanocrystalline Ti, nanocrystalline Al$_2$O$_3$, nanocrystalline and amorphous C. For the co-milled (Ti+C+Al$_2$O$_3$) mixtures, alumina distribution is more uniform and larger contact surface areas are formed between reactants (Figure 1).

After combustion synthesis, TiC_x and Al_2O_3 are the only phases detected by XRD analysis, whatever the reactant preparation method. From XRD results, compositions of the TiC_x-Al_2O_3 composites can be determined. For the (Ti + C + 10, 20 and 40 vol.% Al_2O_3) reactant mixtures, compositions of the end-products are respectively (TiC_x - 13.3, 25.5 and 46 vol. % Al_2O_3).

For the (TiC_x- 25.5 and 46 vol.% Al_2O_3) composites, TiC_x XRD peaks are displaced towards larger angles. Such an offset of the TiC_x peaks towards smaller lattice spacing is attributed to a lack of C in the TiC_x end-product. This result clearly indicates that grain growth has been limited [3,4]. From co-milled (Ti+C+Al_2O_3) mixtures, it is moreover demonstrated that TiC_x diffraction coherent domain size depends on the Al_2O_3 volume content. For the largest Al_2O_3 content (40 vol. %), it is possible to stabilize nanocrystalline TiC_x. Submicrocrystalline TiC_x is formed from the 10 and 20 vol.% Al_2O_3 diluted samples (Figure 2).

The relative densities of the TiC_x-Al_2O_3 composites are quite low, in the range 65-95 % of the theoretical density; relative densities of the composites decrease when the Al_2O_3 volume content increases. The TiC-25.5 vol.% Al_2O_3 composites microhardness reaches values of about 4000Hv, higher than those of microcrystalline composites.
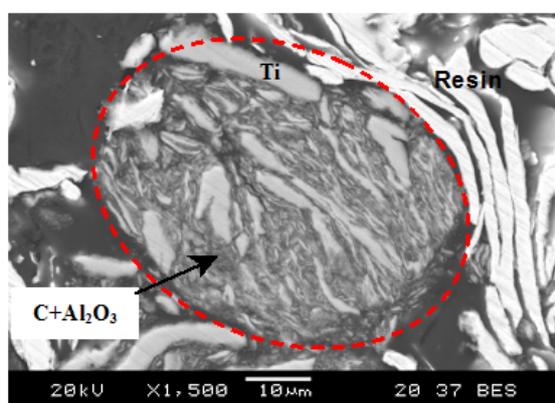

Figure 1: (Ti + C + 10 vol.% Al_2O_3) aggregate formed after mechanical activation (Spex 8000 vibratory ball mill: 3hours, R_{bp}=10).
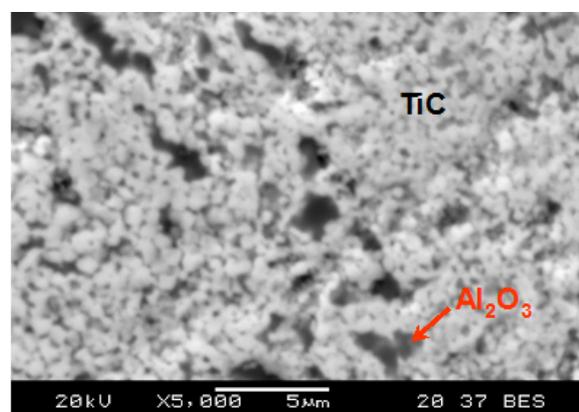

Figure 2: (TiC - 13.3 vol.% Al_2O_3) composite formed after SHS under pressure.

CONCLUSION

In summary, 95 % dense TiC-25.5 vol.% Al_2O_3 composites have been successfully synthesized in one step by pressure-assisted combustion synthesis. The composite performed from (Ti + C + 10 and 20 vol.% Al_2O_3) reactant mixtures consist in submicrocrystalline TiC. When a large alumina content (40 vol. %) is added in the (Ti+C) reactant mixture via a co-milling step, nanocrystallites of TiC_x are stabilized, which indicates that grain growth can be strongly inhibited by using diluent. Finally, preliminary microhardness measurements performed on TiC_x-Al_2O_3 composites with submicronic TiC_x grains show promising results. Larger values of the microhardness may be expected on the TiC_x-Al_2O_3 nanocomposites obtained from co-milled (Ti+C+40 vol.% Al_2O_3) reactant mixtures.

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MODELLING SiC FORMATION DURING HEATING AT CONSTANT RATE

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INTRODUCTION

Our goal is to build a model at a mesoscopic, submicrometric scale that reproduces experimental results[1] observed when mixtures of carbon C and silicon Si are first brought at constant rate up to a maximal temperature ranging from 1325°C to 1400°C and then held at 1400°C. The evolution of the experimental conversion rate in silicon carbide SiC is given in Fig. 1. An intermediate, fast regime is observed between two slow regimes at the beginning and the end of the reaction. The experiments reveal that the speed of the reaction during the fast regime sensitively depends on the size of the silicon grains. We focus on the description of this fast regime.

We conjecture that the number of contact sites between C and Si is one of the factors that control the speed of formation of SiC during the fast regime. The evolution of the reactive system during heating and holding at a temperature smaller than the eutectic temperature is simulated in the period associated with the melting of silicon. The model[2] essentially relies on the following hypotheses. A dissolution-precipitation mechanism is assumed with heterogeneous nucleation of SiC at the interfaces between liquid silicon and a solid. The local heat release accompanying the formation of SiC leads to the melting of silicon in the neighbourhood of the site where reaction took place. Temperature remains constant until solid silicon is present. A 2-d cut of the initial mixture is generated as follows: Si disks and C sticks of sizes sampled according to the experimental distributions are generated without overlap in a square box with periodic boundary conditions. We find that the initial number of contacts between C and Si decreases as the radius of Si disks increases.

RESULTS

Instead of simulating the movements of liquid silicon and following the evolution of solid silicon sites, we determine the total initial number of solid silicon sites and create an identical number of potentially liquid silicon sites around the skeleton of carbon sticks.

To reproduce the formation of SiC, we adopt the following simulation procedure. Starting at time t with N_{Rc} reactive sites of silicon Rc in contact with carbon and N_{Rs} reactive sites of liquid silicon Rs in contact with solid Si or SiC,

(i)   we transform $p_c N_{Rc}$ and $p_s N_{Rs}$ randomly chosen reactive sites into SiC sites, where the reaction probabilities obey $p_c < p_s < 1$,

(ii)   we form 2 or 3 (in average, 2.65) liquid Si sites in the neighborhood of each new SiC site according to the ratio of standard enthalpy of reaction and enthalpy of fusion of Si,

(iii)   we determine the nature (Rc, Rs, or non reactive) of the formed liquid Si sites according to their neighbors and update the values of N_{Rc} and N_{Rs},

(iv)   we increment time by Δt.

At the beginning of the simulation, we observe the formation of large SiC grains by nucleation around the germs located at the initial contacts between solid Si and C. The precipitation of isolated small SiC grains is also observed at the interface between solid and liquid silicon whose role is played by the interface between pores and liquid silicon.
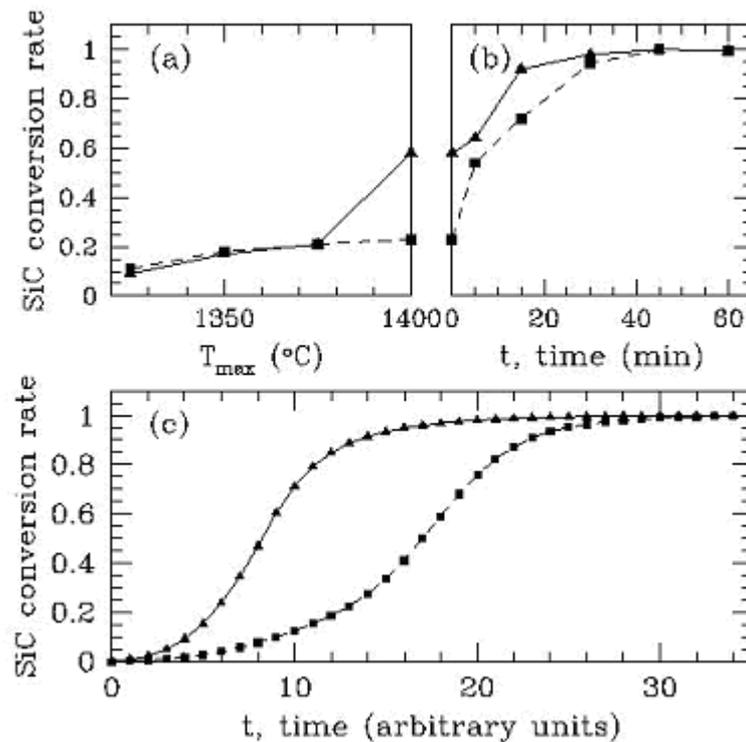
Figure 1 : Top figures: Experimental SiC conversion rate vs. maximal temperature T_{max} reached during heating at constant rate (15°Cmin^{-1}) followed by immediate cooling (a) and vs. time during holding at 1400°C (b). Carbon and silicon were in a molar ratio of 1.1. The porosity of the initial mixture was 50%. The powder of carbon used was natural graphite with d_{50}=10.5μm. The triangles give the results for small silicon grains with d_{50}=5.7μm. The squares are obtained for larger silicon grains with d_{50}=33.9μm. The solid and dashed lines are a guide for the eyes. Bottom figure (c): Simulation results for a probability of reaction of a (solid or liquid) Si site in contact with C, p_C=0.2, a probability of reaction of a liquid Si site in contact with solid Si or SiC, p_S=0.5, and the same other parameters as in (b).

The time evolution of the number of SiC sites in the simulations[2] is compared with the experimental results[1] in Fig. 1. Experiments and simulations are in good qualitative agreement for different sizes of Si grains.

CONCLUSION

The simulations have shown that the number of contacts between carbon and silicon decreases with the diameter of Si grains in the range of diameters used in the experiments. Knowing simply geometrical properties of the initial mixture is sufficient to predict the qualitative behavior of the reaction speed as the size of silicon grains varies: The reaction becomes faster when the diameter of silicon grains decreases, due to the increase of contacts between reagents. The qualitative agreement between the conversion rates obtained in the experiments and the simulations substantiates the hypotheses of the model.

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