

Fluid Mechanics and Its Applications

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Initiation and Flame Propagation in Combustion of Gases and Pyrophoric Metal Nanostructures

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“Man’s quest for knowledge is an expanding series whose limit is infinity, but philosophy seeks to attain that limit at one blow, by a short circuit providing the certainty of complete and inalterable truth. Science meanwhile advances at its gradual pace, often slowing to a crawl, and for periods, it even walks in place, but eventually it reaches the various ultimate trenches dug by philosophical thought, and, quite heedless of the fact that it is not supposed to be able to cross those final barriers to the intellect, goes right on.”

Stanislaw Lem

Preface

The number of publications in various fields of science related to combustion processes has been growing every day. This leads to the occurrence of rather specialized scientists and, therefore, produces particular difficulties for a researcher to access the value of his work. In this book, the issues are examined, which have not been considered in our previous books *The Modes of Gaseous Combustion* (2016, Heat and Mass Transfer, Springer International Publishing) and *Key Factors of Combustion, From Kinetics to Gas Dynamics* (2017, Springer Aerospace technology, Springer International Publishing) where only gaseous combustion was included; the book *Ignition and Wave Processes in Combustion of Solids* (2017, Heat and Mass Transfer, Springer International Publishing), which deals with basic approaches to understanding of solid substances combustion presented in contemporary literature. All these books are intended to allow a reader orientating combustion science confidently. The book is aimed at consideration of the essential problems of combustion science; it is complimentary to previously published ones, mentioned above, and presents the results obtained by the authors in 2017–2020.

This book focuses on the new data on combustion processes having practical applications and includes both fire safety issues in the development of flame arresters and issues in the use of noble metals in hydrogen recombiners for NPP, as well as in catalytically stabilized (CS) combustion technology; the establishment of basic principles of production of metal nanostructures, namely nanopowders of metals and compact products made of them, with the preservation of the unique properties of nanoproducts. This book discusses the effects of gas-dynamic processes and chemical kinetics on the modes of hydrocarbon oxidation processes, including catalytic oxidation on noble metals; catalytic oxidation of hydrogen and deuterium on platinum, palladium, ruthenium and rhodium; new regularities and novel theoretical ideas on combustion of a number of metal nanopowders and compact samples made of them. We wanted also to show how interrelated seemingly different areas of combustion science are.

The book focuses also on the experimental investigation into the interrelation of kinetics and gas dynamics in gas combustion. Some modern problems in the area of gas combustion, as well as the methods allowing calculation and estimation of the

conditions of ignition, and flame propagation on the basis of experimental results obtained by the authors of the book are considered as well as new theoretical grounds of combustion of solid nanostructures.

However, we have recently shown that the concepts of the classical macroscopic theory of a thermal explosion are quite applicable to the massives of nanoobjects. Therefore, the theoretical analysis in this book is carried out from a unified position of the classical combustion theory.

The book focuses on the application of classical combustion theory to the problems on combustion of both gases and solids, stability and preservation of the unique properties of nanopowders and compacts made of nanopowders; the experiments and theory are based on the original works of the authors. The book may be useful for undergraduate and postgraduate students and qualified scientists in the area of experimental studies of combustion processes.

In the book, it has been experimentally found that a flame of dilute natural gas–oxygen mixtures does not penetrate through the central opening of a confuser, but it penetrates only through the central opening of a diffuser, even if there were additional openings on the cone elements. The numerical modeling performed using compressible dimensionless reactive Navier–Stokes equations in a low Mach number approximation made it possible to qualitatively interpret the results. The results obtained by the visualization of flame penetration through orifices of different shape are important for the solution of explosion safety problems for volumes of complex geometry such as production floor areas, combustion chambers and chemical reactors.

It is established that both minimum diameter of a central opening, through which the flame of the diluted methane–oxygen mix can penetrate, and minimum pressure of flame penetration decrease with an increase in the number of openings. It was experimentally shown that the penetration limit by the diameter of the orifice for a single asymmetrical obstacle (<15 mm under our conditions) is less than that of a single symmetrical obstacle (20 mm). It was revealed that the penetration limit increases with an increase in the number of obstacles with asymmetrical openings. It was shown that the penetration limit for two and three asymmetrical obstacles can be lowered by changing the first obstacle toward the direction of flame propagation by the obstacle with a symmetrical opening. The results of the work are important to provide the safe arrangement of the openings between the neighboring technological confinements.

The value of effective activation energy of the dark reaction $2\text{H}_2 + \text{O}_2$ over Pd is evaluated as $E = 4.1 \pm 1$ kcal/mole that is characteristic of a surface process. The value is close to one determined for the dependence of the H_2 fraction at the ignition limit over Pd surface in mixtures with O_2 on temperature: 3.5 ± 1 kcal/mole. Under our conditions, no dark reaction on Pt wire was observed. It was shown that the rate of chain termination determines the value of the critical diameter for flame penetration through Pt or Pd cylinders; the efficiency of Pd surface in the chain termination reaction is much greater than that of Pt.

It is shown that in the presence of Pt catalyst surface, which does not decompose at flame temperature and generates catalytic centers diffusing into volume, heat release and pressure perturbation during the combustion occur out of phase; the catalytic Pt surface eliminates a certain stage of inhibition after the occurrence of the cool flame and NTC phenomenon vanishes. In the presence of the catalytic surface (Pd), which does not decompose at flame temperature and does not generate catalytic centers diffusing into a volume, NTC phenomenon occurs.

It is established that the concentration limit of ignition of a premixed H_2 -air mix in the presence of CF_2Cl_2 at 1 atm. exceeds 10%, whereas the inhibitor limit of ignition of the premixed methane-air mix makes 1% CF_2Cl_2 . It means that CF_2Cl_2 is an effective inhibitor to prevent undesirable ignition of methane-air mixes at atmospheric pressure. It is experimentally shown that the concentration limits of the initiated combustion known from literature are meaningful only for previously prepared mixes. If the mixes are prepared just before the experiment, then the existence or the lack of ignition is determined by both an order of injection of mixture components and the geometry of an installation. Therefore, the inhibition with halons can hardly be used to address the challenges of safety in mines. Thus, the influence of gas-dynamic factors on the efficiency of inhibition is revealed.

It is shown that the active centers of hydrogen and methane combustion determining the development of combustion process have a different chemical nature. Vibrationally excited molecules $\text{HF}(\nu = 3)$ and $\text{HF}(\nu = 2)$ were for the first time detected in the products of combustion of hydrogen and methane in the presence of CF_2Cl_2 . It can be promising phenomenon in laser chemical applications.

It is experimentally shown that the intensity of $\text{HF}(\nu = 3)$ and $\text{HF}(\nu = 2)$ bands in methane combustion in oxygen is higher than in $2\text{H}_2 + \text{O}_2$ combustion in the presence of the same amount of halon. It means that the reaction with CF_2Cl_2 leading to $\text{HF}(\nu = 2, 3)$ formation in methane combustion has to include the active center of methane combustion. Besides, as CF_2Cl_2 is an effective inhibitor of methane combustion, this active center has to participate in the elementary act of chain branching or chain propagation as well as to contain a hydrogen atom to form HF molecule.

It was shown that the Pd catalyst can under certain conditions suppress developing flame propagation in a dilute methane-oxygen mixture, due to the high efficiency of the Pd surface in the termination of active reaction centers. This means that kinetic factors can be important, even under conditions of high turbulence. Numerical simulation using the Navier-Stokes equations for a compressible reaction medium in the low Mach number approximation has shown a qualitative agreement with a number of experimentally observed regularities. The obtained results are of interest for the development of models of turbulent flows in reactive media and in matters relating to explosion safety.

In experiments on $2\text{H}_2 + \text{O}_2$ ignition over Pd and Pt foils at $P_0 = 40\text{--}180$ Torr and $T_0 = 20\text{--}288$ °C, it has been shown that the temperature of the initiated ignition over heated Pd foil is ~ 100 °C lower than that over heated Pt foil; even the minimum temperature is already enough to ignite the mixture. The activity of Pd foil expresses itself both in the dark catalytic reaction and in the occurrence of local ignition centers on the foil, from which combustion wave propagates.

It was experimentally shown that the temperature of the ignition limit over Pd at $P = 1.75$ atm., measured with a bottom-up approach by temperature, of the mixtures 30% methane + 70% hydrogen + air ($\phi = 0.9$, $T = 317$ °C, ($\phi = 1$, equivalence ratio ϕ is a fraction of fuel in the mix with air: $\phi\text{H}_2 + 0.5(\text{O}_2 + 3.76\text{N}_2)$) and 30% propane + 70% H_2 + air ($\phi = 1$, $T = 106$ °C) markedly drops after subsequent ignitions to $T = 270$ °C for H_2 - CH_4 mix and to $T = 32$ °C for the H_2 - C_3H_8 blend. The ignition limit returns to the initial value after treatment of the reactor with O_2 or the air; i.e., a hysteresis phenomenon occurs. The ignition limit of the mixtures 30% (C_2 , C_4 , C_5 , C_6) + 70% H_2 + air ($\phi = 0.6, 1.1, 1.2, 1.2$, correspondingly) over Pd amounts to 25–35 °C at $P = 1.75$ atm.; the hysteresis effect is missing. It was found that the lean 30% C_2H_6 + 70% H_2 + air mix ($\phi = 0.6$) shows the lowest temperature of the ignition limit: 24 °C at 1 atm. The estimate of the effective activation energy of the ignition of the mixes over Pd is $\sim 2.4 \pm 1$ kcal/mole that is characteristic of a surface process. Thus, the usage of Pd catalyst allows igniting H_2 -hydrocarbon mixtures at 1–2 atm. at initial room temperature without external energy sources. It was shown experimentally that the ignition temperature of the 40% H_2 + air mixture over metallic Pd (70 °C, 1 atm.) was ~ 200 °C lower than over the Pt surface (260 °C, 1 atm.). In addition, Pd wire initiates the ignition of the stoichiometric (30–60% H_2 + 70–40% CH_4) + air mixtures (further (30–60% H_2 + 70–40% CH_4)_{stoich} + air mixtures); Pt wire of the same size cannot ignite these mixtures at reactor temperatures below 450 °C. This means that Pd wire is more effective in the initiation of ignition than Pt wire.

The cellular structure of the flame front due to the solid oxide particles formation during ignition in the presence of Pd wire was not observed in contrast to the results obtained on the Pt surface. Therefore, Pd is more suitable than Pt for hydrogen recombiners in nuclear power plants because the catalytic particles do not appear in the gas phase. The experimental value of the effective activation energy of the process was estimated at (3.5 ± 1) kcal/mole, which is characteristic of surface processes. This indicates the significant role of the dark reaction of H_2 and O_2 consumption on the Pd surface observed directly at low pressures. The presence of this reaction reduces the probability of accidental explosion compared to the Pt surface. It was found that in the presence of leucosapphire there was no system of emission bands of H_2O^* in the range 570–650 nm, and a possible explanation of this effect was given. The appearance of an additional source of excited water molecules emitting in the range 900–970 nm was explained.

It was found that the ignition temperatures of hydrogen–oxygen and hydrogen–methane–oxygen mixes at low pressure over heated Pd, Pt, Nichrome and Kanthal wires at 40 Torr increase with a decrease in H_2 concentration; only a heated Pd wire shows the pronounced catalytic action. Numerical calculations allowed to reveal the role of an additional branching step $\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$.

It was shown that at the combustion of (70–40%) hydrogen–(30–60%) propane–air mixtures ($\phi = 1$) over palladium at total pressures 1–2 atm. the ignition delay periods τ first decrease with a decrease in temperature; but then, τ values increase until the ignition limit is achieved; i.e., NTC phenomenon occurs. The effective activation energy of the process is $E = 2.2 \pm 1$ kcal/mole that is characteristic of a

surface process; E values of the surface process, determined by different methods, are practically equal. Thus, NTC phenomenon is strongly associated with the state of Pd surface. It is found out that in the sample treated with ignitions, the defects in the form of openings, which are focused on etching patterns, arise. In the process, PdO particles originate in the process of oxidation of Pd surface at a higher temperature than that of Pt; the particles decompose to Pd and O_2 at the temperature of flame products. This means that Pd is spent in the reaction of chemical etching with active intermediates of combustion. It should limit the applicability of palladium in ignition devices.

It is shown that before ignition, catalytic wire is not heated up uniformly; initial centers of the ignition occur. In addition, in sequential ignitions, clearly observed primary ignition centers change their location on the wire from the first ignition to the next one.

It was shown that Rh is the most effective catalyst of $2H_2 + O_2$ ignition, the lowest ignition temperature over Pd wire coated with Rh (Rh/Pd) makes $210\text{ }^\circ\text{C}$, for Ru/Pd and Pd— $300\text{ }^\circ\text{C}$, for Pt wire— $410\text{ }^\circ\text{C}$ at total pressures < 200 Torr. The hysteresis phenomenon is observed over Ru/Pd, Pt and Pd wires; namely, the ignition limit value measured over the wire, which is not treated with ignitions (a bottom-up approach), is higher than the value measured with a top-down approach. It was shown that Rh is the most effective catalyst of $2D_2 + O_2$ ignition, in this case the lowest ignition temperature over Pd wire coated with Rh (Rh/Pd) makes $100\text{ }^\circ\text{C}$. In all cases, it would be more accurate to speak about ignition over noble metals hydrides/deuterides; thus, the lowest ignition temperature of $2H_2 + O_2$ over Rh hydride makes $210\text{ }^\circ\text{C}$, the lowest ignition limit of $2D_2 + O_2$ over rhodium deuteride makes $100\text{ }^\circ\text{C}$, respectively. The results obtained make it possible to speak about a kinetic inverse isotope effect on the reactivity of MeH and MeD, where Me = Rh, Pd. It was shown that at total pressures up to 200 Torr autoignition areas of $2H_2 + O_2$ mixes over Rh and Pd surfaces are broader than those of $(H_2 + CH_4)_{\text{stoich}} + O_2$ mixtures; the mixtures containing more than 50% CH_4 as well as $(80\% H_2 + 20\% CH_4)_{\text{stoich}} + O_2$ mixtures do not ignite. It is directly related to the formation of carbon-containing film on the noble metal surface. The fuel in the mixtures is consumed in dark reaction. It was shown that the dark reaction in $(80\% H_2 + 20\% C_4H_8)_{\text{stoich}} + O_2$ mixture leads to the formation of carbon nanotubes over the range 10–100 nm mean diameter.

It is experimentally shown that at the temperature lower than $0\text{ }^\circ\text{C}$ Ni nanoparticles do not ignite in dry air; however, passivation (surface preservation) occurs and provides the stability of nanoparticles at room temperature. It is shown that the samples of nickel nanoparticles passivated in dry air contain only nickel. By means of the scanning electronic microscopy and AES method, it is established that passivation at the temperature lower than $0\text{ }^\circ\text{C}$ prevents agglomeration and coalescence of Ni nanoparticles; therefore, the size of nanoparticles after passivation at $-8\text{ }^\circ\text{C}$ is less than for those passivated at $20\text{ }^\circ\text{C}$. Further evidence has been obtained that theoretical approaches of the classical macroscopic theory of thermal explosion can be applied for the description of the phenomena of ignition of macroscopic objects of nanoparticles.

Nickel nanopowders have been synthesized by the chemicometallurgical method under dynamic conditions, when the composition of the gas medium is changed in the process of synthesis with the retention of the overall duration of synthesis, for the first time. It is experimentally shown that the treatment of samples of Ni formate powder during 70 min at 209 °C in Ar flow does not lead to formation of pyrophoric Ni; in this case, the nanopowders have the minimum mean size (30 nm). The method of synthesis of Ni nanoparticles in Ar from Ni formate and further treatment of the obtained particles with H₂ for the different time intervals allows both controlling the mean size of the particles and changing the degree of pyrophoricity of the nanopowder.

A model of the porous sample ignition is proposed, based on an assumption of a limiting role of the oxidizer diffusion in the ignition mechanism. It is shown that the ignition process can have a two-stage character. The duration of the stages is estimated by the methods of combustion theory. The applicability limits of the semi-infinite body model were determined. The role of the finite size of a sample in the ignition process was analyzed.

A model of passivation of a layer of pyrophoric nanopowder was formulated and studied by analytical and numerical methods. Under the assumption that the passivation wave propagation is controlled by the oxidant diffusion, the dependence of the temperature in the heat-release zone on governing parameters was characterized. It was shown that, for the maximum temperature in the nanopowder layer, there is intermediate asymptotic behavior characterized by time-invariant temperature. To decrease the passivation time, while keeping the temperature rise at permissible level, passivation was proposed to be carried out in two stages with increasing oxidant concentration in the gas phase. Analytical expressions were derived for the minimum switch time between the stages at given temperature rise. Numerical computations confirmed the correctness of the conclusions drawn from the theoretical analysis and also showed a good quantitative agreement between the results of the approximate and numerical calculations.

It was shown that decreasing initial nanopowder temperature leads to a transition from a layer-by-layer passivation mode to a bulk passivation mode, which enables one to perform passivation even at high oxidizer concentrations in the gas. Analytical expressions for determining the boundaries of the layer-by-layer and bulk passivation modes were derived. Numerical calculations confirmed the correctness of the conclusions of the theoretical analysis.

Copper nanopowders were synthesized both by a hydrogen reduction method (a method of chemical metallurgy) and thermal decomposition of copper citrate and copper formate. It is shown that Cu nanopowder synthesized from Cu citrate is not pyrophoric. Its combustion can be initiated by an external source; the velocity of combustion wave makes 1.3 ± 0.3 mm/s. The nanopowder has a specific surface 4 times greater $\sim (45 \pm 5 \text{ m}^2/\text{g})$; it does not practically contain oxides, and it is stable in ambient air. Cu nanopowder obtained by the method of chemical metallurgy is pyrophoric one; however, its passivation leads to formation of noticeable amounts of Cu oxides. Combustion velocities of the passivated and nonpassivated

Cu nanopowder were almost equal (0.3 ± 0.04 mm/s). Dynamics of temperature fields at ignition and combustion of Cu nanopowders obtained by various methods is investigated.

Tungsten nanopowders were synthesized by a hydrogen reduction method (a method of chemical metallurgy) at 440–640 °C from the WO_3 precursors with different specific surface: 2 m²/g (I), 11 m²/g (II), 0.8 m²/g (III). It has been shown that W nanopowder synthesized at 640 °C from the precursors (I)–(III), is α -W; it is not pyrophoric. Its combustion can be initiated by an external source; the combustion develops in the finger-like mode. The nanopowder synthesized at 480 °C from the precursors (I), (II) is the mixture of α -W, β -W and $\text{WO}_{2.9}$; it is pyrophoric at the expense of β -W. Nanopowder synthesized at 480 °C from the precursor (III) is β -W with the traces of WO_3 and $\text{WO}_{2.9}$. The temperature interval of β -W synthesis obtained in the work is very narrow: 470–490 °C. α -W nanopowders have a specific surface 10 ± 2 m²/g; passivated nanopowder of β -W has a specific surface 18 ± 1 m²/g. Dynamics of temperature fields at ignition and combustion of W nanopowders obtained by various methods was investigated.

It was shown that the self-heating of a compacted sample made of nonpassivated iron and nickel nanopowders is not uniform, although it begins simultaneously within the entire surface of the sample. It is found that the maximum temperature of self-heating decreases with an increase in relative density of samples, which indicates that the oxidation process is limited by the diffusion supply of oxidant. It was shown that the process of interaction of samples with air occurs in a superficial mode. A qualitative agreement of the results of the theoretical analysis with experimental data is obtained. The dependence of the mode of interaction of samples with the air on the duration of the exposure of weighing bottles to the air is revealed. The possibility of passivation of compacted samples made of iron and nickel nanopowders is experimentally established.

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