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Ignition and Wave Processes in Combustion of Solids

 Springer

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ISSN 1860-4846

Heat and Mass Transfer

ISBN 978-3-319-56507-1

DOI 10.1007/978-3-319-56508-8

ISSN 1860-4854 (electronic)

ISBN 978-3-319-56508-8 (eBook)

Library of Congress Control Number: 2017937272

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Printed on acid-free paper

This Springer imprint is published by Springer Nature

The registered company is Springer International Publishing AG

The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

In this book, the issues on the combustion of solids raised, which have not been considered in the earlier books “The Modes of Gaseous Combustion” (Springer, Heat and Mass Transfer 2016) and “Key Factors of Combustion, From Kinetics to Gas Dynamics” (Springer, Springer Aerospace Technology, 2017) where only gaseous combustion was the subject to review. It is clear that the problem of combustion of solid fuels makes the understanding of the process more complex as compared to gas combustion. Really, the equation of state in an analytical form is usually missing, therefore, in calculations, the question of finding of the closing equation for the corresponding system of the equations often arises. In addition, the gas–solid, liquid–solid and solid–solid systems possess their unique properties and laws; among them there are, e.g., phase transitions, the problems of stability of nanoparticles as well as flammability of coal–gas suspensions in coal mines, or the nature of solid–solid reactions etc. For instance, in the latter case the problem on the mechanism of the reactions between two different solid powders occurs due to very small diffusivities in solids. Really, in Ta + C system, the reaction rate is quite small, however, the reaction Ti + C proceeds at substantially higher velocities. Thus, the features of kinetic mechanisms in solid–solid reactions have been under discussion in the literature.

The book attempts to analyze the basic approaches to understanding of solid–solid and solid–gas combustion presented in contemporary literature. It focuses also on the application of classical combustion theory to ignition and flame propagation in solids and experimental investigation in the certain areas of filtration combustion, self-propagating high-temperature synthesis and nanopowders protection based generally on the works of the author and original works of his co-authors. The book may be useful for undergraduate and postgraduate students and researchers in the area of experimental studies of combustion.

In this book, contemporary results and achievements of Russian science in the area of combustion of solids are consistently set out for the first time. This applies in particular to theoretical works of one of the co-authors Boris S. Seplyarskii, whose investigations in the area of classical combustion theory form the ideological basis of the book. In addition, analytical formulas are presented in different areas of

combustion in solids (local ignition, filtration combustion, self-propagating high-temperature synthesis, combustion of gas suspensions), which have been already successfully used by Russian scientists for practical application.

The authors note that in the theoretical analysis, they tried to pay the main attention wherever possible to analytical consideration rather than to numerical calculations. It is evident that the development of an analytical approach is always followed by the creation of some ideology of understanding of the essence of a process using certain reasonable assumptions, which allow getting the solution of a complex problem in a rather simple and clear analytical form. Thus, the reader has an opportunity to understand the nature of the phenomenon, without penetrating into a particular architecture of algorithms of a calculation method.

The authors would also like to make the reader more familiar with virtually inaccessible works of Russian authors published up to 2017 in Russian.

It was shown that the problem on a local ignition of condensed substance comes down to the investigation of the dynamics of a reaction zone under condition of cooling of the ignition center with the inert environment; at the same time the power of a chemical heat source during the induction period can be considered approximately constant. The approximate analytical method was applied for analysis of the problem on a local chain-thermal explosion in the reaction of hydrogen oxidation in the presence of chemically active additive. The concept of an intermediate combustion wave with the maximum temperature equal to the initial temperature of the hot spot was introduced. It was shown that key parameters determining the critical size of a local source of ignition, are the temperature in the center of a local ignition zone; the quantity of the active centers of combustion created with the local source; and presence of active chemical additives in combustible gaseous mixture. Comparison to experimental data showed applicability of the developed approach for the analysis of critical conditions of a local ignition in combustible gas mixtures.

The concept of the wave mechanism of formation of a quasi-stationary zone of a chemical reaction was examined for determination of critical conditions and a delay time of ignition with heat losses. It was shown that the connection of the depth of burn-up and the velocity of an intermediate wave with the value of a heat loss coefficient determines the specifics of the ignition under nonadiabatic conditions. The wave theory of the ignition, which showed high efficiency when determining temporary characteristics of ignition in systems with the complex mechanism of chemical interaction (consecutive, parallel, independent reactions) was presented. On the basis of the wave mechanism of formation of a chemical reaction zone main characteristics of the ignition process were determined, namely the time of inert warming up, establishment and failure of a thermal balance; the physical meaning of these characteristics is also clarified. It was shown that the development of a heating process depends on a ratio of characteristic times of formation of a chemical reaction zone capable of independent propagation, and complete burn-out on a sample surface. Critical values of a heat loss coefficient were calculated. It was shown that critical ignition conditions coincide with limiting conditions of occurrence of an intermediate combustion wave ICW. The main characteristics of ignition process for a first-order reaction were determined. The results of numerical

calculations validated the main assumptions as well as the main conclusions of the approximate analysis. It was suggested to find the scale temperature (ignition temperature) from the equality of an external thermal flux to a heat flux from a reaction zone in an intermediate combustion wave, which maximum temperature is equal to ignition temperature. It was shown that at surface temperatures smaller than ignition temperatures, it is possible to consider warming up as inert one; the time of this stage makes the main part of a delay time of ignition τ_{ig} . It allows expressing τ_{ig} through the characteristics of an intermediate combustion wave. The analytical method of calculation of temporary characteristics of ignition of a porous body under conditions of a counter nonstationary gas filtration was created. It was found that the rate of heating of substance during ignition is close to the rate of heating of this substance with an intermediate wave of filtration combustion (IWFC) with the maximum temperature equal to ignition temperature. The analytical method of calculation of temporary characteristics of ignition of a porous sample with a stream of hot gas flowing into the substance (a cocurrent nonstationary filtration) was also suggested.

The convective mechanism of combustion was suggested for the explanation of an abnormally high combustion velocity found in combustion of “gasless” systems, titanium + soot, and also titanium + soot + polystyrene under conditions of one-dimensional filtration of impurity gases. The analysis of the available experimental and theoretical data showed that under conditions of impurity gas emission, the convective combustion mechanism can be provided by the movement of a melted layer of one of reagents under the influence of pressure difference of impurity gases. Physical and mathematical models of convective combustion of “gasless” systems were formulated. It was established that the realization of the accelerating combustion mode requires presence of the free volume, which is not occupied with a sample. It was shown that at an initial stage of combustion as well as at the value of free volume exceeding the sample volume, the velocity of the front and the pressure of gas increase are under the exponential law. Analytical expressions for calculation of the average velocity of convective combustion were obtained. An investigation of the model allowed explaining the distinctions in regularities of combustion of “gasless” systems under conditions of the counter, cocurrent and bilateral filtration of impurity gases. It was shown that depending on the organization of combustion process, the pressure difference of impurity gases can both accelerate, and slow down the penetration of the melt into an initial sample, changing thereby a combustion velocity. The estimates of the width of a warming up zone showed that impurity gas emission in the warming up zone occurs, first of all, at the expense of desorption of the gases and vapors, which are adsorbed on a surface of the particles of a fine component. By means of the new combustion model, the explanation of an increase in combustion velocity of “gasless” systems observed at thermal vacuum processing and reduction of diameter of initial samples was given. Based on the grounds of the convective-conductive theory of combustion (CCTC) of heterogeneous condensed systems it was offered to apply a method of pumping out a sample to control the synthesis. The regularities of combustion by the example of Ti – C powders under

conditions of artificially created pressure difference along the sample were investigated. It was shown that the removal of impurity gases in a warming up zone of the reaction front provides significant increase in the combustion velocity. It was established that preliminary thermovacuum processing TVP of initial mixes leads to an increase in combustion velocity for samples of bulk density. It was revealed that the presence of moisture does not practically influence on combustion regularities and phase structure of products of granulated Ti + 0.5C samples. It was found out that under conditions of Ar coflow the influence of humidity on the phase structure of reaction products decreases and combustion velocity of the powder sample increases. It was shown that the presence of moisture in the Ti + 0.5C powder sample has an impact on the phase structure of combustion products and practically has no influence on the combustion velocity of the sample without gas flow.

Thus, the available literature and experimental data confirm the applicability of the convective–conductive mechanism of combustion wave propagation in the fast-burning “gasless” systems containing a fusible reagent.

The analytical method of calculation of the critical size of the hot spot was created for greater values of a coefficient of heat exchange of particles and gas. By means of numerical calculations the functional dependence of the critical size of the hot spot on parameters following from the theory was validated; the range of applicability of approximate formulas was determined. Two mechanisms of the ignition of gas suspension by the hot spot were revealed for the first time:

- (a) ignition of gas suspension as ignition in quasi-homogeneous single-temperature medium;
- (b) ignition of particles in the center of the hot spot due to violation of thermal balance between the rate of heat allocation on a particle and heat dissipation into the gas.

It was shown that the value of the minimum energy of ignition does not practically depend on the mass concentration of particles in gas suspension at a constant value of initial temperature θ_{in} . The method of calculation of the critical size of the hot spot R_{cr} can be used for determination of R_{cr} for the complex mechanism of interaction of particles with an oxidizer (parallel, consecutive, independent reactions).

Various mechanisms of critical phenomena for the kinetic and diffusion modes of ignition at pulse energy supply were established. At greater values of a heat exchange coefficient Z (a kinetic ignition mode) the critical duration of an impulse is equal to the time of establishment of a zero gradient on a border: a heater–gas suspension. At small values of a heat exchange coefficient Z (a diffusion mode of an ignition) the critical duration of an impulse is less than τ_0 and it is found from the equality $\tau_1 = \tau_2$. Here τ_1 —the time of complete burning out of particles at $\xi = 0$, and τ_2 —the ignition time (a transition to the diffusion mode of a reaction) of particles at $\xi \rightarrow \xi_g + 0$. The expressions, allowing to determine necessary and sufficient conditions of the ignition of gas suspension by a heated body at pulse energy supply were obtained. Numerical calculations showed a possibility of

application of approximate formulas for determining of minimum duration of an impulse necessary for the ignition of gas suspension. By means of numerical calculations, it was established that the minimum time required to attain a high-temperature combustion mode is reached at $\tau_{\text{pul}} = \tau_0$. The investigations described allow calculating the minimum energy of ignition of hybrid gas suspension with a hot spot using the data on the kinetics and thermal effects of gas phase and heterogeneous reactions as well as on the amount of condensed phase in a unit of volume. The results of such calculation are necessary for the creation of safe conditions for carrying out technological processes, in which suspensions of combustible particles in gas containing oxidizer and small additives of combustible gas are formed. It was experimentally shown that at 650–750 °C coal gas suspension containing stoichiometric mixture of natural gas and air does not burn over surface coated with coal powder due to inhibiting effect of gases evolving during thermal treatment of coal powder. The ignition of the gas suspension can be promoted with small amounts of chemically active additive (e.g., dichlorosilane). Thus, we can conclude that the improved model of ignition of gas suspension of solid particles in a mix oxidizer—combustible gas must take into account inhibiting effect of gases evolving during thermal treatment of coal powder. The hydrocarbons (probably PAHs) arising in the ignition of HGS, on the one hand are flammable, and on the other hand have the inhibiting action on methane combustion, as it takes place in the process of inhibition of ignition of H₂–air mixes with small hydrocarbon additives. However, in the presence of small quantities of methane (lean mixtures) the ignition of volatiles evolved from coal, can provide the subsequent methane ignition, because the volatiles are hydrocarbons, probably, polycyclic aromatic hydrocarbons (PAH).

A model of the porous sample ignition was proposed, based on an assumption of a limiting role of the oxidizer diffusion in the ignition mechanism. It was shown that the ignition process can have a two-stage character. The duration of the stages was 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. The nonuniform surface mode of combustion of iron nanopowders and fingering patterns in combustion of nickel nanopowders in the absence of external flows was revealed for the first time. The method of estimation of the extent of passivation of Fe nanopowders with the use of a method of color high-speed filming was offered. It was experimentally established that both the dependencies of the period of a delay of ignition and quantity of the primary centers of combustion on the time of passivation can be used for estimation of the extent of passivation. On the basis of the experimental data, the approximate equation for estimation of the minimum time of complete passivation for the sample of arbitrary thickness was offered. By the method of X-ray phase analysis, it was established that 1 mm thick samples of iron nanopowder treated in a stream of 3% of air + Ar for the time interval more than 6 min contain only metallic iron. Therefore, the method of passivation suggested is rather effective. The effective means of stabilization of iron nanoparticles synthesized by the method of chemical

metallurgy by means of passivation in argon stream + 0.6% O₂ within 6–60 min was offered. It was established that at storage of iron nanopowder in a vessel equipped with the ground-in cover within 5 months in the ambient air any noticeable change of chemical composition of the powder was not observed. It was shown that nanoparticles form crystallites with a size $\sim 20\text{--}100$ nm. The results of Auger's method of spectroscopy are consistent with the fact that nanoparticles of iron contain an iron kernel and an oxide layer of 2–4 nm thick.

The average specific surface area of the passivated nanoparticles of iron determined by the BET method makes up to ~ 9.2 m²/g and does not practically depend on the time of passivation.

The effective method of stabilization of iron nanoparticles synthesized by the method of chemical metallurgy by means of passivation in the dry air at subzero temperatures was offered for the first time. It is experimentally shown that at a certain subzero temperature Fe nanoparticles do not ignite in dry air; however, passivation occurs and makes the particles stable at room temperature. It was shown that combustion modes at room temperature and subzero temperatures differ qualitatively. It was detected that both the content of oxides in the iron nanopowder sample after combustion and the maximum warming up decrease with a decrease in initial temperature. It was shown for the first time that the concepts of the classical macroscopic theory of a thermal explosion are quite applicable to nanoobjects.

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Acknowledgements

Authors are grateful to Prof. Forman A. Williams (Mechanical and Aerospace Engineering Department, University of California) for useful remarks. The authors express particular thanks to Dr. Victor I. Chernysh, Dr. Victor A. Zelensky, leading engineer George I. Tsvetkov (Institute of Structural Macrokinetics and Materials Science of Russian Academy of Sciences), and Alexey B. Ankudinov (Institute of Metallurgy and Material Science RAS) for their permanent support and important comments.

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