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Computation of Parameters of the Self-Propagating High-Temperature Synthesis

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Computation of parameters of the self-propagating high-temperature synthesis (SHS), which is characterized by the combustion propagation through a matrix of compacted reactive particles and is recognized to hold the practical significance in producing novel solid materials, is presented. The SHS process falls into a category of the flame propagation, because a reaction initiated at one end of a compacted medium by use of the external heating source self-propagates through an unburned medium, in the form of a combustion wave. The high temperature needed for synthesis can be supplied by the self-sustained exothermic chemical reactions. The potential advantages of this process are as follows: rapid synthesis; self-heating; energy savings; self-purification due to enhanced impurity outgassing; near-net-shape fabrication, etc. Compounds synthesized are being considered for use as electronic materials, materials resistant to wear, corrosion, and heat. Furthermore, it can even be applied to the synthesis of shape-memory alloys, hydrogen-storage alloys, and high-temperature superconductors. Thus, it is now well recognized that the SHS process can be of practical significance in producing novel solid materials. Although it has proven effective, it was also recognized that in order to control the manufacturing process, dependence of flame propagation speed on various dominant parameters is indispensable. In addition, range of flammability with respect to various parameters is urgently required because the ignition cannot be maintained outside the range of flammability. Of course, dependence on various parameters is also required in preventing flame extinction.

Keywords: Self-propagating high-temperature synthesis, flame propagation, range of flammability, ignition, ignition delay time, extinction.

1. INTRODUCTION

Self-propagating high-temperature synthesis (SHS) is considered as the exothermic chemical reaction proceeding under the conditions for gasless combustion. As a result of this, computation of new material with the unique physical and chemical properties is synthesized. SHS of property is manifested by the appearance of a three-dimensional structure, which changes both in the transitional and in the end products of reactions. In the broad sense this concept consists of the concepts of the study of the morphology of microstructure, dimensions of crystals and mutual arrangement of phase components, and also macrostructure, which characterizes the non uniformity of the material of times and disseminated closed and open voids, their quantity and quality.

In the known thermal analog simulators [1] of the combustion of the heterogeneous systems [2, 3], comprised according to the diagram of homogeneous processes, the dominant role plays the excitation of synthesis, the thermal effect of chemical reaction and the rate of heat liberation. This course of the process makes it possible to determine rate of combustion and frontal temperature without the detailed information about the mechanisms of the processes, which it occurs in the wave of combustion.

Such a conducting of studies composes only the part of structural macrokinetics, which establishes the evolution of structural medium in the course of chemical transformations, including questions of the formation of the structures of the end products of reaction. The destruction of the structure of prime medium and the formation of new at the stage of excitation and in the process of combustion can occur not simultaneously and preserve the transient amorphous state of material. With the passage of the weak-current processes of combustion in material systems of the zone of chemical transformations and the processes of the formation of structures can poured. Therefore a complete experimental study of structural transformations with the gassless combustion composes urgent contemporary scientific direction. A question of the excitation of synthesis here especially is revealed.

After the discovery of the new form of the heterogeneous processes of combustion, proceeding without oxygen and other gas oxidizers, the newest branch of technologies is developed. In these processes the role of fuel plays metals: Ti, Zr, Hf, Nb, Ta, Al, Mg, Mo, W, etc. Oxidizer in the majority of the cases are here not metals: B, C, Si, O_2, P, S, N_2, etc. After using by local ignition they realize being been self-propagating the regimes, where chemical transformations are directed toward the zone. This zone is extended through the mixture of powder. It is necessary to consider the fact that with the course of reaction gas practically is not separated, the distinctive property of this process, but the entirely condensed products are obtained. In this condensed phase the temperature can grow to 4273 K. This gassless combustion exists due to the liberation of a large quantity of heat with the chemical interaction of materials and the creation of temperature stable products [4 – 8].

Self-propagating high-temperature synthesis means the synthesis of compounds (or materials) in a wave of chemical reaction that propagates over starting reactive mixture owing to layer-by-layer heat transfer. Reaction is normally initiated from the sample surface with a heat flux. After

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initiation, reaction proceeds in the mode of self-propagation. For SHS processes, the type of starting reagents is insignificant. Much more important is relation between the heat release in reaction, on one side, and such parameters as the mode of heat release/transfer, state of aggregation for reactants/products, kinetics of phase/structure transformations. In case of strong heat losses, wave propagation is not sustained altogether. For SHS reactions, thermochemical calculations can be performed either in a concise form for determining only the adiabatic combustion temperature or in the full form for determining both the combustion temperature and product composition [9 – 11].

Comparing the self-propagating high-temperature synthesis with the previously technologies of material production as sintering in the furnaces or using a plasma process, SHS technology has many advantages:

1) The high quality of the synthesized materials;

2) Large productivity and very simple the implement of labor;

3) There is no need for the steady source of energy. It is possible to use thermal energy, which releases in the SHS process;

4) It is possible to produce materials, which cannot be prepared by other methods or their production is unprofitable.

The advantages indicated show that the SHS technology corresponds to contemporary requirements and is promising with the economy to the electric power also of natural resources.

2. CALCULATION OF THE TEMPERATURE CONDITIONS OF SHS

By the authors the conducted experimental investigations showed the possibility of using the SHS process in the production of new materials [12, 13]. The device of conducting experiment and the optimum form of the synthesized model is created. Experimental material ZrO_2 was manufactured in the mixer, adding into the dioxide of zirconium reaction that causing addition, prepared from the connections of magnesium, and intermixing for one hour. The extrusion in the special mold at the 120 MPa pressure was produced after this. In the prepared models the specific process was begun, which was developed stably. The wave of combustion in the model was developed from top to bottom. Further, for the wider use of materials on the basis of the dioxide of zirconium, it is necessary to design the time of ignition T_q, the dependence of pressure p_q on the heat flux density q, dependence of the parameters of ignition on the wall thickness l_2. These calculations are represented below.

In the studies SHS of process is important both quantitative and qualitative information about the course of the process, about the linear rate of combustion, about maximum temperatures and temperature profiles, about the loss of the stability of the front of combustion, about the thermal effects, about the degree of combustion of components and the composition of products. All this predetermines the quality of article and is determined the possibilities of using the outlined product. These results characterize synthesis conditions, evaluate SHS mechanism and experimentally base theoretical conclusions.

In the processes SHS two forms of temperature profiles are determined. In the profiles the temperature smoothly varies from initial to final. In the complex profiles the fractures of profiles are observed, bends with derived that being approaching zero, and isothermal sections also are encountered. Such heterogenities frequently correspond to physical transformations in the material.

Combustion in the isolated adiabatic system is characterized by the fact that the enthalpy of initial mixture at a temperature T_0 is equal to the enthalpy of end products at a combustion temperature T_{ad} [14]. This reason makes it possible to thermodynamically calculate the composition of products and combustion temperature.

If one product is synthesized during the process, only temperature is calculated. This expression is used for the calculation T_{ad} [1]:

$$\int_{T_0}^{T_{ad}} c(T)dt = \Theta - \sum_{i=1}^{n} \mu_f H_f \ ; \qquad (1)$$

where $\mu_i = 0$, when $T_{ad} < T_f$, and $\mu_f = 1$, when $T_{ad} > T_f$; where: c is the thermal capacity, J/(kg·K), θ is the heat of the creation of product (when T_0), J/mol; μ_i is the molecular weight, kg; μ_f is the part in the product of molecular weight with the highest temperature phase, when $T_{ad} = T_f$, kg; T_f and H_f are the accordingly, temperature and the heat of phase transition in the product, K, J/mol; T_{ad} is the temperature of adiabatic combustion, K; values $c(T)$ and θ we can find in the reference books, for example [15, 16], and average values – thermal capacity and the effect of thermal process – we can calculate in this way:

$$\overline{C} = \frac{1}{T_{ad} - T_0} \int_{T_0}^{T_{ad}} c(T)dt \ ; \qquad (2)$$

$$\Theta_{pr} = \Theta - \sum_{i=1}^{n} \mu_f H_f \ . \qquad (3)$$

We obtain, that $T = T_0 + \Theta_{pr} \big/ \overline{C}$, with $T_{ad} = T_f$, $\mu_f = \left[\Theta - \overline{C}\left(T_f - T_0\right)\right] \big/ H_f$ it is equal.

These expressions show, as the estimation of temperatures SHS of processes is produced.

For the binary systems X+Y, in which both reagents are solid materials and the particles of metal have the small sizes (to 50 μm) thermodynamic equilibrium it is always established in the wave of combustion. In the front of the combustion of such systems maximum temperatures are very high. For example, the combustion temperature of system hafnium – coal, with the use of an equivalent composition, reaches 3850K.

In the systems analogous in composition, and also in other similar systems SHS, if the overall sizes of the particles of more than 150 μm, thermodynamic equilibrium it is not established because of the kinetic and diffusion difficulties. With the combustion of such systems maximum temperatures do not exceed 2000 K. The described by SHS mechanisms give information about basic SHS physical processes. It is sufficiently clear that the kinetic parameters and the mechanism of the chemical of reaction, the proceeding in SHS processes, substantially influence parameters and laws governing the propagation of the wave of combustion [17]. At present kinetics and mechanism of the chemical of reaction in the general complex of fundamental a study to the end are not opened. Basic reasons are the unsolved fundamental difficulties during the organization of the mutual interaction between components in SHS systems in the kinetic, but not in the diffusion regime. Here are understood very complex systematic questions with the fulfillment of straight kinetic experiments in the environment of high temperatures. At present basic information about the mechanisms of the kinetics SHS of processes is obtained by the indirect methods: with the measurement of the temperature profiles in the reaction front, including the special additions, with the analysis of influence of which are revealed some dependences of rate of combustion on the variable parameters. Most promising is the kinetic method of obtaining the information, when reaction occurs in the condensed phase at a temperature this (2273 – 4273) K. The method of the gassless combustion, with the aid of which is investigated the connection between speed and combustion temperature.

If the emission of heat into the environment is large, then the wave of synthesis is not created [18]. In practice in the majority of the cases is organized adiabatic combustion behavior, during which the heat losses are small. From the thermal of position SHS the processes can be described in a following manner. The identity, which determines regularity with the propagation of the wave of synthesis and development of its structure with the internal source of heat it is possible to express as follows:

$$c\rho\frac{\partial T}{\partial t}=\lambda\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial t}{\partial r}+\frac{\partial^2 T}{\partial \varphi^2}\right)+\Theta\rho\Phi(T,\eta); \quad (4)$$

We can write down the equation of kinetics thus:

$$\frac{\partial \eta}{\partial t}=\Phi(T,\eta). \quad (5)$$

Then boundary conditions will appear thus:
surface of ignition: $x = 0$;
ignition conditions: $f\left(\frac{\partial T}{\partial x},T\right)=0$;
it means: $x=\infty$; $\frac{\partial T}{\partial x}=\frac{\partial T}{\partial r}=\frac{\partial T}{\partial \varphi}=0$, where $r = R$; (6)

where c is the thermal capacity of product, J/(kg·K), ρ is the density, kg/m^3; λ is the coefficient of the conductivity of heat, W/(m·K); x, r, φ are accordingly, the axial, radial and tangential coordinates, m; θ is the thermal effect of reaction, W/m^3; $\Phi(T,\eta)$ is the kinetic function; T is the temperature, K; R is a radius of model, m.

The side of model is accepted into account thus: $\lambda\left(\frac{\partial T}{\partial r}\right)=\alpha_{ef}(T-T_0)$ – heat losses.

In SHS processes for the propagation of the wave of combustion they frequently have an influence on their accompanying physical chemistry effects, whose influence can be essential. To them it relates the stage of the processes of chemical and phase transformation.

Phase transformations in the wave of combustion SHS it occurs entirely differently from in the chemical reactions. They do not form wave structure, but frequently it substantially changes. Investigating this question it was noted, that the mechanism of phase transformation in the wave of combustion could be different depending on that in what part of the wave it occurs. This depends on the relation of the temperature of phase transition $T_{f.p.}$, temperature in the wave of ignition $T_{b.}$ and $T_0 = 293$ K.

3. CALCULATION OF THE IGNITION WITH THE EXTERNAL SOURCE

The source of ignition is a metallic body heating which it is produced by the concentrated energy from the external source. Phase transformations occur both during the adoption and with the heat liberation. With an increase in the temperature the chemical reactions, which lead to the formation of end product, are developed. We consider that all reactions occur according to the law of Arrhenius and simultaneously, and in the zone of reaction it occurs interdiffusion between all components.

System of equations, that describe this task, taking into account all reasons, in general form we can write down as follows:

$$c\rho\frac{\partial T}{\partial t}=\frac{\partial}{\partial x}\lambda\frac{\partial T}{\partial x}+\sum_{i=1}^{3}k_iQ_in_i^{\gamma_i}\rho_i^{\gamma_i}\exp\left(-\frac{E_i}{RT}\right)+Q_f \quad (7)$$

$$\rho\frac{\partial n_i}{\partial t}=\frac{\partial}{\partial x}\rho D\frac{\partial n_i}{\partial x}-k_i\rho^{\gamma_i}\exp\left(-\frac{E}{RT}\right)+$$
$$+k_{i-1}\rho^{\gamma_{i-1}}n_{i-1}^{\gamma_{i-1}}\exp\left(-\frac{E_{I-1}}{RT}\right) \quad (8)$$

$$i=1\cdots 4; k_0=k_4=0;$$

$$\left(p+\frac{m^2}{\mu^2}\frac{a}{v^2}\right)\left(v-\frac{m}{\mu}b\right)=\frac{m}{\mu}RT, \quad (9)$$

where Q_i, Q_f are the relative heat liberation during the reaction and in the phase transformation, J/kg; n_i is a number of phase transitions; E_i is the activation energy, J; c, λ, D are the thermal capacity, heat conductivity, the effective value of diffusion at a constant volume, J/(kg·K), W/(m·K), m^2/s; m is the mass of material, kg; 1 is the condensed phase; 2 ÷ 4 is the gas phase.

As boundary conditions for the systems (1) – (3) serves the absence of the losses of heat and mutual transformations, and also the equality of heat fluxes and temperatures in the point of contact of the tangency of heater with the condensed material. Absorption and radiation of the incident energy occurs according to the law of Stefan-Boltzman.

Those calculated of material by their characteristics are selected as follows:

1. Model of insulation;
2. Model of the material of the adjustable structure.

We see after the analysis of the results of calculation that in the beginning the heat-conducting shell serves as heat source for the pressed material, while after ignition into it is removed heat- and maximum temperatures they realize at a certain depth of material. All reacting components are used during the continuation of combustion.

Given obtained in the condensed material in first second ignitions for the time of ignition t_q and pressure p_q depending on the density of heat flux are shown in Fig. 1.

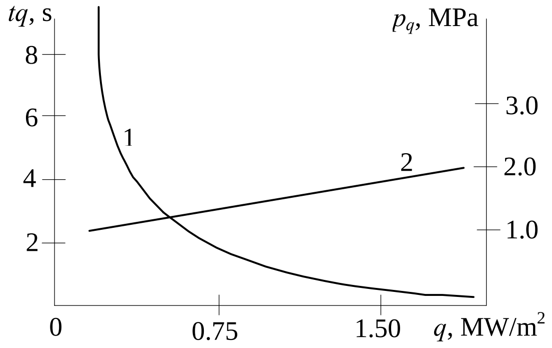

Fig. 1. The dependence of the time of ignition t_q (curve 1) and pressure p_q on the heat-flux density q (curve 2)

Dependence of the parameters of ignition T_q and time t_q depending on the wall thickness with the given one to the intensity of heat flux are shown in Fig. 2.

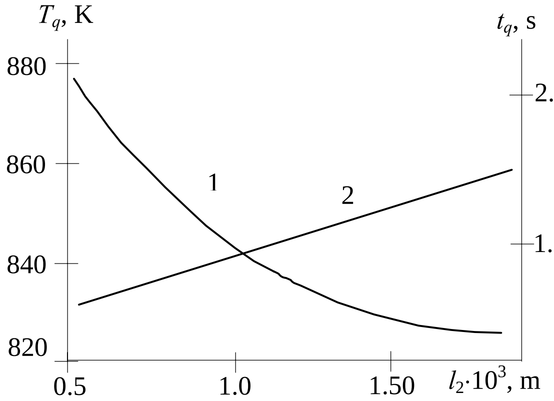

Fig. 2. The dependence of the parameters of ignition T_q (curve 1) and time t_q (curve 2) on the thickness of wall with the heat-flux density q = 2.6·106 MW/m^2

Thus it is possible to solve problem connected with the ignition of the condensed materials in the closed metal shells taking into account the multistage process of combustion. It is possible to calculate the parameters of ignition and combustion depending on the intensity of heat flux and wall thickness.

4. CONCLUSIONS

The study of the mechanism of initialization of the process of the synthesis of the material of the dioxide of zirconium with the igniting addition on the basis of the compounds of magnesium is carried out. The analysis of the mathematical models of synthesis is presented. In this case, the dependence of the time of ignition, pressure on the intensity of the heat flux and parameters of ignition as the functions of the thickness of the wall of shell are defined. It is determined, that the introduced heat-conducting shell serves as heat source for the test specimen.

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