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Mathematical modeling of phase separation in three-phase melt formed behind the combustion wave

K G Shkadinsky[1], N I Ozerkovskaya[2] and P M Krishenik[2]

[1]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russia
[2]Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka 142432, Russia

E-mail: shkad@ficp.ac.ru

Abstract. A mathematical model of the exothermic chemical interaction of a high-calorie solid powder mixture in the presence of centrifugal forces is considered. The process of mathematical modeling is studied for the $3NiO + (2 + \alpha)Al \rightarrow Al_2O_3 + (3 - \alpha)Ni + \alpha NiAl$ thermite composition, as an example. Such models are used to describe the process of high-temperature synthesis for the production of target products in the combustion wave propagating through the initial mixture. This technological process represents a combination of high-temperature combustion with the transformation of the solid porous mixture to liquid products, their separation, and subsequent cooling. A distinctive feature of the proposed model is the use of a "through" description, which makes it possible to examine the mutual influence of the individual stages on the dynamics of the process. This feature provides a more realistic description of the actual process.

1. Introduction

The combustion of high-calorie mixtures is used in high-temperature synthesis [1] to produce desired products. It occurs under extreme conditions: high temperatures and pressures, melt dispersion, and onset of an explosive dynamic frontal mode. The front propagation velocity ranges from several millimeters to several centimeters per second. Typically, three main stages of the process are distinguished: combustion; gravity (or centrifugal) separation of the medium (metal phase, ceramics, oxidizing gas); and cooling and crystallization of products. The process is controlled by changing the temperature of the chemical interaction (the initial mixture composition is changed), pressure or centrifugal forces (melt dispersion is suppressed and phase separation is promoted), and dispersity and quality of mixing (initial mixture density affects the burning rate and the properties of the products). Extreme combustion conditions limit the possibility of performing direct experiments and motivate the use of modeling methods based on the fundamental laws of physics and chemistry. The SHS metallurgy is characterized by the use of models for individual stages of the process with the rest of the factors being treated as perturbations. In what follows, we develop a "through model" that takes into account the mutual influence of the stages on the overall dynamics of high-temperature synthesis. High temperature in the combustion front melts the medium, a process under the action of centrifugal forces, changes the conditions for transport of reagents into the reaction zone. Mass-transfer alters the effect of the force field on the reaction medium and the process of phase separation. In constructing the "through model," we use simplifications that make the problem tractable while preserving the interaction of the stages inherent in the real process.

2. Mathematical model

The process of exothermic chemical interaction of a mixture of condensed reagents is investigated within the framework of the mechanics of multicomponent chemically active continuous media [2].

2.1 Properties of the Medium

The condensed components of the ith medium are assumed to be incompressible. Their volume fraction is designated as v_i, hence, the density of the ith component in the composition $\rho_i = \rho^0{}_i v_i$. For the gas component, $v_g = 1 - \Sigma_i \rho_i$. The gas medium is assumed to be an ideal gas obeying the equation $\rho_g = p\mu_g/RT_g$, where T_g is the gas temperature, R is the universal gas constant, p is the pressure, and μ_g is the molecular mass of the gas. A concrete analysis is performed by the example of the interaction $3NiO + (2 + \alpha)Al \rightarrow Al2O3 + (3 - \alpha)Ni + \alpha NiAl$. The macrokinetics of the interaction is rather complicated and is the subject of a separate study. We limited ourselves to an intermediate "truncated" description of the kinetics of the interaction, which can be extended to take into account the details of interest. According to the reference data, above 1503 K, solid β-phase NiO decomposes into metallic nickel and oxygen:

$$2NiO \xrightarrow{\;W_0(T)\;} 2Ni + O_2. \tag{1}$$

By this time, the preheating zone of the synthesis front in the porous composition contains molten Al (melting point 933 K, whereas the melting point of the Al_2O_3 film around is ~ 2300 K). In the reactor conditions, this refractory film partially dissolves and collapses under the action of centrifugal forces, being partially restored by the interaction of oxygen with aluminum with heat release Q:

$$4Al + 3O_2 \xrightarrow{\;W_1(T)\;} 2Al_2O_3 + Q. \tag{2}$$
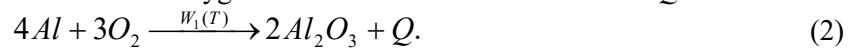
A less rapid and less exothermic stage

$$Ni + Al \xrightarrow{\;W_2(T)\;} NiAl + Q_1, \tag{3}$$

produces an intermetallic compound. With increasing temperature, the initially strong skeleton of the porous material is converted into a mobile liquid melt, which when being centrifuged is pressed to the initial porous medium. The permeability of the initial medium in the preheating zone changes, and the filtration of oxygen formed into the low-temperature initial medium and into the liquid products is impeded. The concentration of oxidizer in the narrow reaction zone motivates using a simplified kinetic scheme of "gas-free" interaction instead of (1) and (2):

$$3NiO + 2Al \xrightarrow{\;W(T)\;} 3Ni + Al_2O_3 \tag{4}$$
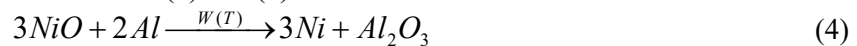
2.2 Mass Transfer

Thus, behind the combustion front, a suspension of liquid metal, liquid ceramics, and oxidizer are formed with some characteristic dimensions of the components (for simplicity, we set them identical to the initial ones) and individual velocities of movement. The reactants involved in chemical interaction change their mass, and, consequently, the field of centrifugal forces. Taking into account that, in the condensed state, the diffusion transfer is concentrated in the reaction zone, being partially allowed for in the macrokinetic description of the chemical interaction rate, we confine ourselves to considering convective masstransfer and the mass transfer caused by chemical interaction:

$$\frac{\partial \rho(NiO)}{\partial t} = -2W_0(T)\mu(NiO) - \frac{\partial}{\partial x}(\rho(NiO)\upsilon(NiO)), \tag{5}$$

$$\frac{\partial \rho(Al)}{\partial t} = -\left[4W_1(T) + W_2(T)\right]\mu(Al) - \frac{\partial}{\partial x}(\rho(Al)\upsilon(Al)), \tag{6}$$

$$\frac{\partial \rho(NiAl)}{\partial t} = W_2(T)\mu(NiAl) - \frac{\partial}{\partial x}(\rho(NiAl)\upsilon(NiAl)), \tag{7}$$

$$\frac{\partial \rho(Ni)}{\partial t} = \left[2W_0(T) - W_2(T)\right]\mu(Ni) - \frac{\partial}{\partial x}(\rho(Ni)\upsilon(Ni)), \tag{8}$$

$$\frac{\partial \rho(AL_2O_3)}{\partial t} = 2W_1(T)\mu(Al_2O_3) - \frac{\partial}{\partial x}(\rho(Al_2O_3)\upsilon(Al_2O_3)), \tag{9}$$

$$\frac{\partial \rho(O_2)}{\partial t} = [W_0(T) - 3W_1(T)]\mu(O_2) - \frac{\partial}{\partial x}(\rho(O_2)\upsilon(O_2)). \tag{10}$$

Here, the density of each reacting element is the product of the true density and its volume fraction. For the incompressible media (all except for the gas), these equations describe the dynamics of the change in the volume fraction of the reagents. The velocity of movement and the temperature of a particular reagent depend on its spatial location and chemical content. Such a multi-velocity and multi-temperature description of mixed continuous media hugely complicates the mathematical model. For simplicity, the property characteristic of solutions is used: typically, the solubility is high when "like dissolves in like" (oxide in oxide, metal in metal). All the components, we categorized into three groups: metal, ceramics, and oxidizing gas. Accordingly, we consider a three-velocity, three-temperature combustion model for a mixture of continuous media, assuming that, in each group, the characteristics of the medium depend on its location. The laws of momentum conservation for the metal, ceramics, and oxidizing gas components moving at velocities much lower than the speed of sound in the test mixture are reduced to the balance of the principal forces acting on the medium. For the metal group,

$$\rho_m\left(\frac{\partial \upsilon_m}{\partial t} + \upsilon_m\frac{\partial \upsilon_m}{\partial x}\right) = 0 = -v_m\frac{\partial p}{\partial x} + v_m\frac{\partial}{\partial x}\left(\eta_m\frac{\partial \upsilon_m}{\partial x}\right) - f(L+x)\omega^2\rho_m - \alpha_{11}v_m\upsilon_m$$
$$+ \alpha_{12}(\upsilon_k - \upsilon_m) + \alpha_{13}(\upsilon_g - \upsilon_m) + W_0(T)\mu(Ni)(\upsilon_k - \upsilon_m). \tag{11}$$

For the metal component, the pressure gradient multiplied by the cross-sectional area (proportional to v_m) is balanced, first, by the centrifugal forces acting on the metal components in the emulsion and, secondly, by the forces of viscous interaction with other components of the emulsion in their relative motion, as well as by momentum exchange during chemical mass transfer. Similar equations are valid for the ceramics and gas:

$$\rho_k\left(\frac{\partial \upsilon_k}{\partial t} + \upsilon_k\frac{\partial \upsilon_k}{\partial x}\right) = 0 = -v_k\frac{\partial p}{\partial x} + v_k\frac{\partial}{\partial x}\left(\eta_k\frac{\partial \upsilon_k}{\partial x}\right) - f(L+x)\omega^2\rho_k - \alpha_{22}v_k\upsilon_k$$
$$+ \alpha_{21}(\upsilon_m - \upsilon_k) + \alpha_{23}(\upsilon_g - \upsilon_k) + W_1(T)(4\mu(Al)(\upsilon_m - \upsilon_k) + 3\mu(O_2)(\upsilon_g - \upsilon_k)), \tag{12}$$

$$\rho_g\left(\frac{\partial \upsilon_g}{\partial t} + \upsilon_g\frac{\partial \upsilon_g}{\partial x}\right) = 0 = -v_g\frac{\partial p}{\partial x} + v_g\frac{\partial}{\partial x}\left(\eta_g\frac{\partial \upsilon_g}{\partial x}\right) - f(L+x)\omega^2\rho_g - \alpha_{33}v_g\upsilon_g$$
$$+ \alpha_{13}(\upsilon_m - \upsilon_g) + \alpha_{23}(\upsilon_k - \upsilon_g) + W_0(T)\mu(O_2)(\upsilon_k - \upsilon_g) \tag{13}$$

Here, L is the distance from the axis of the centrifuge to the open surface of the reactor; f is the multiplier; η is the viscosity; ω is the angular velocity of centrifugal action on the emulsion components; α_{ii}, α_{ij}, and α_{ji} are the coefficients of viscous interaction forces (I and j are in the range of 1−3).

The laws of mass conservation are represented by the heat conduction equations for the three groups (metal, ceramics, and gas), with consideration given to the mobility of the emulsion components and the heat exchange between the groups and the external environment (its temperature is set constant, equal to the initial T_0). The main sources of heat generation are the exothermicity of the chemical interaction in the group and the energy exchange that accompanies the mass transfer between the groups during the chemical reaction. We disregarded less significant sources and confined ourselves to a one-dimensional description in order to simplify and analyze the results obtained. For brevity, only the equation for the group of metals is given here; for the other groups, the equations have a similar structure:

$$c_m\rho_m\left(\frac{\partial T_m}{\partial t} + \upsilon_m\frac{\partial T_m}{\partial x}\right) = \frac{\partial}{\partial x}\left(\lambda_m\frac{\partial T_m}{\partial x}\right) + (\overline{QW})_m + 2(c\mu)_{Ni}W_0(T)(T_k - T_m) - a_{mk}(T_m - T_k) \tag{14}$$
$$- a_{mg}(T_m - T_{g)} - a_{mw}(T_m - T_0).$$

Here, $\overline{(QW)}_m = Q(\text{Al})W_1(T)\mu(\text{Al}) + Q(\text{NiAl})W_2(T)\mu(\text{NiAl})_l$. The coefficients a_{mk}, a_{mg}, and a_{mw} characterize the heat exchange between the components of the emulsion and wall. The initial conditions read as $T_m = T_k = T_g = T_0$. The boundary conditions at the end faces are written as follows: $T_m(0, t) = T_k(0, t) = T_g(0, t) = TW$ is the condition for initiating the combustion process (they can be pulse type); $\left(\dfrac{\partial T_m}{\partial x}\right)_{(l,t)} = \left(\dfrac{\partial T_k}{\partial x}\right)_{(l,t)} = \left(\dfrac{\partial T_g}{\partial x}\right)_{(l,t)} = 0$ is the condition of adiabaticity at the closed (bottom) end face.

2.3 Quasi-Hydrostatic Approximation

Given that the process of combustion is characterized the velocities of motion of the mixture components much smaller than the speed of sound, a situation arises similar to that described in [3], more specifically, a small parameter appears in the model that leads to its singularity. The liquid combustion products transit into a stressed state, which varies with the composition (density) and the distance from the axis of the centrifuge. Describing the quasi-stationary stress state of the mixture by the equation

$$\frac{\partial p}{\partial x} = f(L+x)\omega^2\left(v_g p\mu_g / RT_g + \sum_i v_i \rho_i^0\right) \tag{15}$$

with boundary conditions at the end faces of the reactor, we do not consider the rapid process of onset of hydrostatic equilibrium. The heat conduction equations for the gas, metal, and ceramics determine the temperature fields for the mixture components. Equations (5−9) determine the composition of the incompressible components in the mixed reaction medium. Hydrostatic equilibrium condition (15) determines the evolution of the pressure in the moving combustion products. Equations (11), (12), and (13) with the appropriate boundary conditions determine the velocities of the gas, metal, and ceramics. In the absence of centrifugal forces, equation (15) corresponds to the quasi-isobaric situation considered in [3]. Note also that singularities and degeneracy can arise in analyzing the system of heat conduction equations under the conditions of phase separation caused by centrifugation. An effective algorithm for approximately solving these equations is assumed known.

3. Results

The results of numerical simulations of the dynamics of the combustion process are presented on the space−time plots of temperature, fractions of reagents, and rates of their convective transfer. The process is initiated by a high-temperature source (spiral) at the open end of the reactor ($x = 0$). As a result, the frontal process of exothermic chemical reaction in the mixed composition sets in. Figure 1 displays successive distributions (from left to right) of the temperature fields in the gas, ceramic, and metal at constant time intervals. These distributions show that a high-temperature region propagating to the right is formed. The structure of the right edge of this region (front zone) stabilizes its characteristics. In fact, they change slowly, so the front is called quasi-stationary; the reasons for this change are explained below. The initial stage of the formation (stage of ignition) being a typical mode of induction ignition of the medium with a relatively low-temperature source contrasts against the background of steady combustion. During this period, an excess of enthalpy arises in the front, which moving together with the front, plays an important role in the analysis of its stability and affects the temperature distribution of the medium when the front reaches the reactor (at $x = 20$). The determining role in the combustion process of the mixed medium is played by the exothermic transformation in the metal phase. Through heat exchange, it influences the processes in the ceramic and gas phases, thereby creating a unified structure of the combustion front of the mixed medium. Note that the specific features of the temperature distribution in ceramics and gas phase are determined not only by classic conduction heat transfer, but also by the energy exchange caused by interphase mass transfer. In the conditions of adiabatic steady combustion (in figure 1, the mixed medium burns in the absence of heat exchange with the external medium), the adiabatic combustion temperature is established in the products behind the combustion front. As can be seen, in this case, superadiabatic temperatures arise in the metal phase in the reaction zone. This contributes to an increase in the propagation rate of the front. We can demonstrate the steady

propagation of the combustion front due to the influence of the varying field of centrifugal forces. The field is determined by the redistribution of the mass of the reagents in the exothermic chemical interaction, the dynamics of which is shown in figures 2 and 3. Here, like in figure 1, the space–time distributions (at the same instants of time as those for the temperature fields) of the specific volumes of the chemical reagents of the mixed medium during its burning are shown.
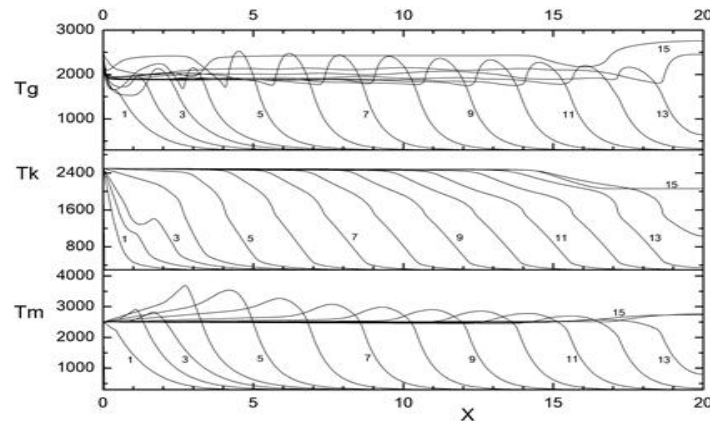

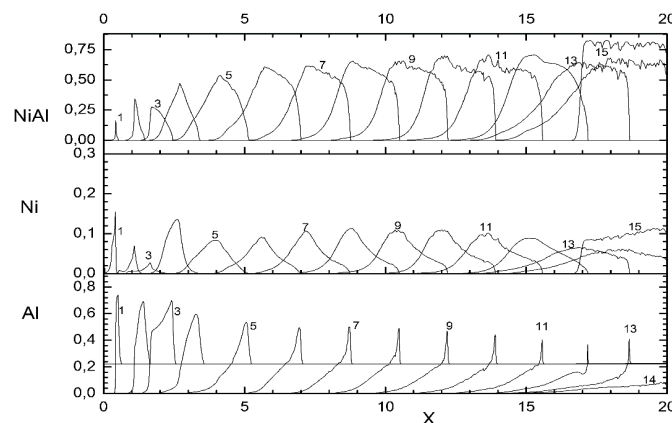**Figure 1.** Space–time distribution of the fields of temperature of gas, ceramics and metal.

Figure 2. Space–time distribution of specific volumes of metal phase reagents in a mixed medium.
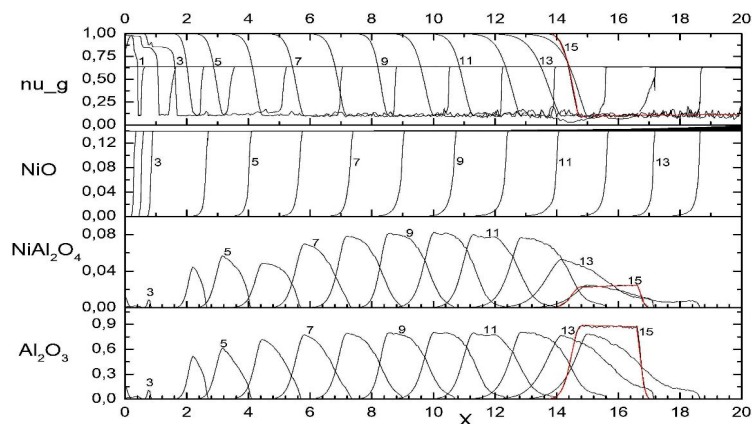

Figure 3. Space–time distribution of specific volumes of ceramics and gas reagents in a mixed medium.

One can see how the composition of the mixture changes during the propagation of the front due to the chemical interaction and convective transfer of the melt under the action of centrifugal forces. We consider convective transport is represented by the space–time distribution of the velocity fields. At the stage of ignition (small x), negative values of the velocity of the medium are seen, which corresponds to the experimentally observed dispersion of the medium. Later, the melt moves due to the densification of the gas-saturated medium under the action of centrifugal forces. Note the localization of the oxidant in the reaction zone of the combustion front.

4. Conclusions

Thus, we obtained a significant volume of information on the process of high-temperature synthesis. First, its frontal character should be emphasized. Selecting a moment of time and collecting the corresponding spatial distributions of temperatures, chemical composition, and convective motion velocities of the reagents, we obtain information about the front of the exothermic chemical interaction. As the synthesis front moves, the chemical composition of the medium and its density change, which, in turn, causes changes in the distribution of the forces acting on the multicomponent medium. The conditions of chemical interaction change, and the synthesis front becomes quasi-stationary. The separation of the products occurs according to the evolution of their temperature. Under adiabatic conditions, stratification occurs. The heavy metal phase is concentrated in the bottom part of the reactor. Above is a ceramic that protects the metal phase from contact with the gaseous medium. Being the lightest gas phase is displaced from the melt. These processes are described by the presented model and are realized during their characteristic times.

References

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