INITIATION AND DEVELOPMENT OF EXOTHERMIC REACTIONS DURING SOLID-PHASE SYNTHESIS UNDER EXPLOSIVE LOADING

by

Vladimir F. TOLKACHEV[a], Oksana V. IVANOVA[b], and Sergey A. ZELEPUGIN[a, b*]

[a]National Research Tomsk State University, Tomsk, Russia
[b]Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia

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The previous numerical and experimental studies of the solid-phase synthesis of porous reactive mixtures (Al-S and Al-Tf) placed into cylindrical ampoules subjected to explosive detonation revealed the sharp increase in temperatures and pressures. The results have shown that high heat release and high increase in pressure due to exothermic reactions in the mixture, on the one hand, promote the faster development of reactions and, on the other hand, contribute to the formation of a gas phase that, in turns, may lead to the damage or even fracture of ampoules. This problem is solved by adding an inert porous aluminum layer to the bottom part of the mixture. Computations are carried out using the model of a multicomponent medium and the finite element method. Numerical simulation has shown that in this case the fracture of cylindrical ampoules is not observed.

Key words*: solid-phase synthesis, exothermic reaction, explosive loading, cylindrical ampoule, fracture*

Introduction

By now, the solid-phase synthesis of materials placed in cylindrical ampoules under explosive loading has been insufficiently studied and, therefore, it is of great interest for further research. This direction has not yet reached the level of technology due to the lack of experimental data and numerical techniques correctly describing the process. During shock-wave compression a significant energy release due to exothermic reactions in reactive mixtures takes place, which, on the one hand, can lead to self-sustaining propagation of chemical reactions in mixtures and, on the other hand, to the damage of ampoules, as well as to the complete fracture [1-4]. It is worth noting that there are the works which propose that solid-phase chemical reactions can develop in the detonation mode [5, 6]. If the reaction rate is high enough, then solid phase (or gasless) detonation may occur.

To analyze these processes, it is necessary to develop mathematical models that includes additional parameters and equations describing the kinetics of chemical reactions, initial parameters and characteristics of reactive components, as well as appropriate computational algorithms. Developed numerical models and available experimental data will provide the reliable information on reactive media, and mechanisms and kinetics of physical and chemical transformations.

* Corresponding author, e-mail: szel@yandex.ru

The goal of this work is to diminish the effect of high pressures and temperatures during explosive synthesis in cylindrical ampoules under explosive loading.

Formulation of the problem

The governing equations of continuity, momentum, and energy for the non--stationary adiabatic motion of each component in some fixed volume, *V*, of a compressible mixture bound by surface, *S*, with allowance for the exchange of momentum, energy and mass between components can be written in the form [7-9]:

$$\frac{\partial}{\partial t}(\alpha_i \rho_i) + \nabla \alpha_i \rho_i \upsilon_i = 0, \quad i = 1, 2, ..., N \tag{1}$$

$$\frac{\partial}{\partial t}(\alpha_i \rho_i) + \nabla \alpha_i \rho_i \upsilon_i = 0, \quad i = 1, 2, ..., N \tag{2}$$

$$\alpha_i \rho_i \frac{d_i E_i}{\mathrm{d}t} = \sigma_i \varepsilon_i + \alpha_i \sum_{j=1}^{N} \alpha_j F_{ji}, \quad i = 1, 2, ...N \tag{3}$$

where $\frac{d_i}{\mathrm{d}t} \equiv \frac{\partial}{\partial t} + \upsilon_i^k \frac{\partial}{\partial x^k}$

Here, t is the time, ρ_i – the density of the i^{th} component equal to the mass of the i^{th} component per unit volume of the i^{th} component, υ_i – the velocity vector, E_i – the internal specific energy, ε_i – the strain rate tensor, $\sigma_i = -P_i\delta_i + S_i$ – the stress tensor, P_i – the pressure, S_i – the stress deviator, R_{ji} – the intensity of the momentum exchange between the j^{th} and i^{th} components, F_{ji} – the intensity of the energy exchange between the j^{th} and i^{th} components, and N – the number of components.

Volume fractions of the mixture occupied by each component are given by:

$$\alpha_1 + \alpha_2 + ... + \alpha_N = 1, \quad (\alpha_i \geq 0), \quad \alpha_i = \frac{\rho_i^*}{\rho_i}$$

where ρ_i^* is the reduced density (mass of the i^{th} component per unit volume).

The mixture components interact with each other by exchanging momentum R_{ji}, energy F_{ji}, and mass J_{ji} in the presence of chemical reactions within the framework of the multi-component medium model.

In modeling chemical reactions under shock wave loading, the zeroth-order kinetic relation characterized by a constant rate of chemical transformations is used [7, 10, 11]:

$$J_{ji} = \frac{\mathrm{d}\eta}{\mathrm{d}t} = \begin{cases} 0, & \text{if } \eta = 1 \text{ or } (T_i < T_\eta \text{ and } P < P_\eta) \\ f(P_\eta), & \text{if } \eta < 1 \text{ and } (T_i \geq T_\eta \text{ or } P \geq P_\eta) \end{cases}$$

$$f(P_\eta) = \begin{cases} K_0, & \text{if } P < P_\eta \\ K_p K_0, & \text{if } P \geq P_\eta, \end{cases}$$

where T_i is the temperature, P – the matched pressure of components, T_η, P_η, K_p, K_0 are the constants, and η – the conversion degree.

Studying the deformation of multicomponent media, it is necessary to consider the state and response of each component, and, in contrast to a homogeneous mixture, not only

the displacement of the external boundaries of the selected volume, but also the displacement of components in the selected volume of the mixture. Here, we consider the equal pressures of the components to be a condition for joint deformation of components during the interaction in the mixture, which determines the volume concentrations of the components [12, 13]:

$$P = P_i\left(V_i, E_i\right) = P_j\left(V_j, E_j\right) = \ldots = P_N\left(V_N, E_N\right)$$

To achieve mechanical equilibrium in the components of the mixture, the proposed approach is used. In this case, it is necessary to find a new pressure that is the same to all components, and mechanical equilibrium is achieved when the condition $\alpha_1 + \alpha_2 + \ldots + \alpha_N = 1$ is satisfied. Such mechanical equilibrium can be achieved by solving the system of equations:

$$P = P_i + \Delta P_i = P_i - \frac{K_i}{\alpha_i}\Delta\alpha_i$$

$$\sum_{i=1}^{N}\Delta\alpha_i = 0$$

where $K_i = \alpha_i\rho_i c_i^2$ is the volume compression modulus, and c_i is the volume velocity of sound. The new value of the volume fraction of the components $\Delta\alpha_i$ is determined from the equations:

$$P = \frac{\sum_{i=1}^{N}\frac{\alpha_i P_i}{K_i}}{\sum_{i=1}^{N}\frac{\alpha_i}{K_i}}$$

$$\Delta\alpha_i = \frac{\alpha_i}{K_i}\left(P_i - P\right)$$

After equalizing the pressures of the components, a new value of the internal energy E_i is determined:

$$\alpha_i\rho_i E_i = \alpha_i\rho_i E_i - P\Delta\alpha_i$$

To provide the mass conservation of the mixture, it is necessary to obtain a new value of density:

$$\rho_i = \frac{\alpha_i\rho_i}{\alpha_i + \Delta\alpha_i}$$

All equations are applied iteratively with an appropriate evaluation of the equation of state for determining the pressure and volume compression modulus of each component.

Numerical results

To study the explosive loading of reactive porous mixtures, numerical computations were carried out using the model of a multicomponent medium and the finite element method [14, 15]. The axisymmetric problem of explosive loading was considered for a porous Al-S mixture placed in a cylindrical steel ampoule. The mass fractions of the components were as follows: Al – 0.35 and S – 0.65, which corresponded to the stoichiometry of aluminum sulfide (Al_2S_3).

The height and diameter of the cylindrical sample were 65 mm and 14 mm, respectively. The thickness of the lateral wall of the ampoule was 3 mm and the thickness of the lids was 20 mm. The external diameter of the ampoule was 20 mm. In the computations the explo-

sive surrounding the ampoule was simulated in terms of pressure acting on the upper part of the ampoule in an axial direction and on the lateral surface of the ampoule in a radial direction during the propagation of the detonation front. The detonation velocity used in the numerical computations was measured experimentally and was equal to 3.3 km/s.

In the work, the reaction initiation criterion (pressure criterion) and the reaction rate are assumed to depend on the initial dispersity of powders. For aluminum and sulfur powders with low dispersity, the reaction initiation criteria on temperature was 933 K (melting temperature of aluminum) and on pressure was 1.6 GPa. Reaction rate, K_0, was equal to 280.8 GJ/(kg s), and K_p = 2.0. For aluminum and sulfur powders with high dispersity, the reaction initiation criteria on temperature was 933 K and on pressure was 1.0 GPa.

Figure 1 demonstrates the pressure profiles for the Al-S low-dispersed porous reactive mixture placed in the cylindrical ampoule during the explosive synthesis of aluminum sulfide for different times.

A shock wave caused by the explosive propagates along the sample. It is worth noting that the wave front propagating in the sample is behind the wave front propagating along the ampoule. This fact is explained by collapsing the pores in the sample, figs. 1(a) and 1(b). When the shock wave reflects from the bottom of the ampoule and encounters the shock wave propagating in the sample, the pressure increases by several times, fig. 1(c), and is greater than 18 GPa. After the encounter, the shock waves propagate in opposite directions, fig. 1(d). The high residual pressures are observed in the sample and reach more than 4 GPa for the high-dispersed mixture and 2 GPa for the low-dispersed one, fig. 1(e).

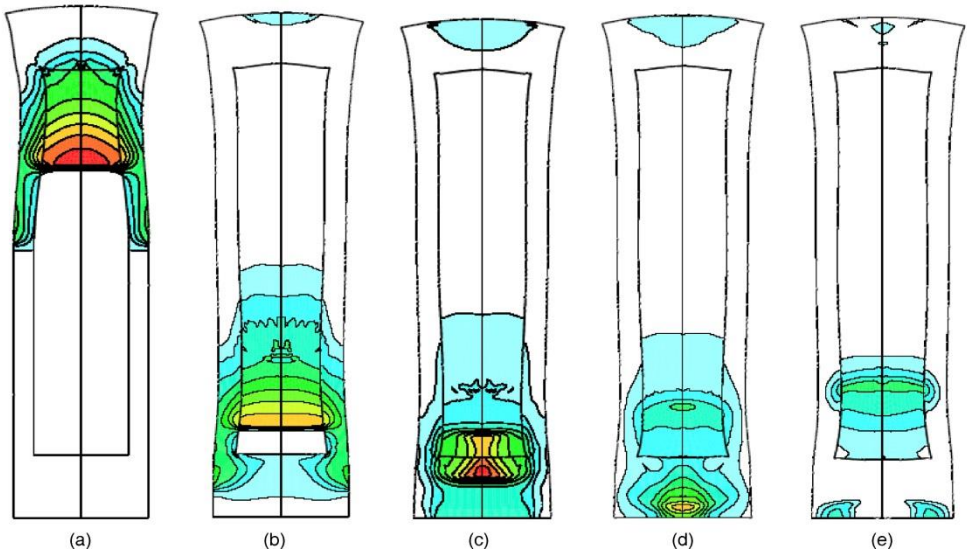

Figure 1. Distribution of pressure profiles (GPa) in the low-dispersed reactive mixture (Al-S) in an axial section of the ampoule for different times; (a) 12 μs, (b) 24 μs, (c) 26 μs, (d) 27 μs, and (e) 28 μs (*for colour image see journal web site*)

Based on the experimental and numerical results, it can be concluded that the high heat release and high increase in pressure due to the chemical reaction contribute to the formation of a gas phase that may become a reason of the damage or even fracture of the ampoule.

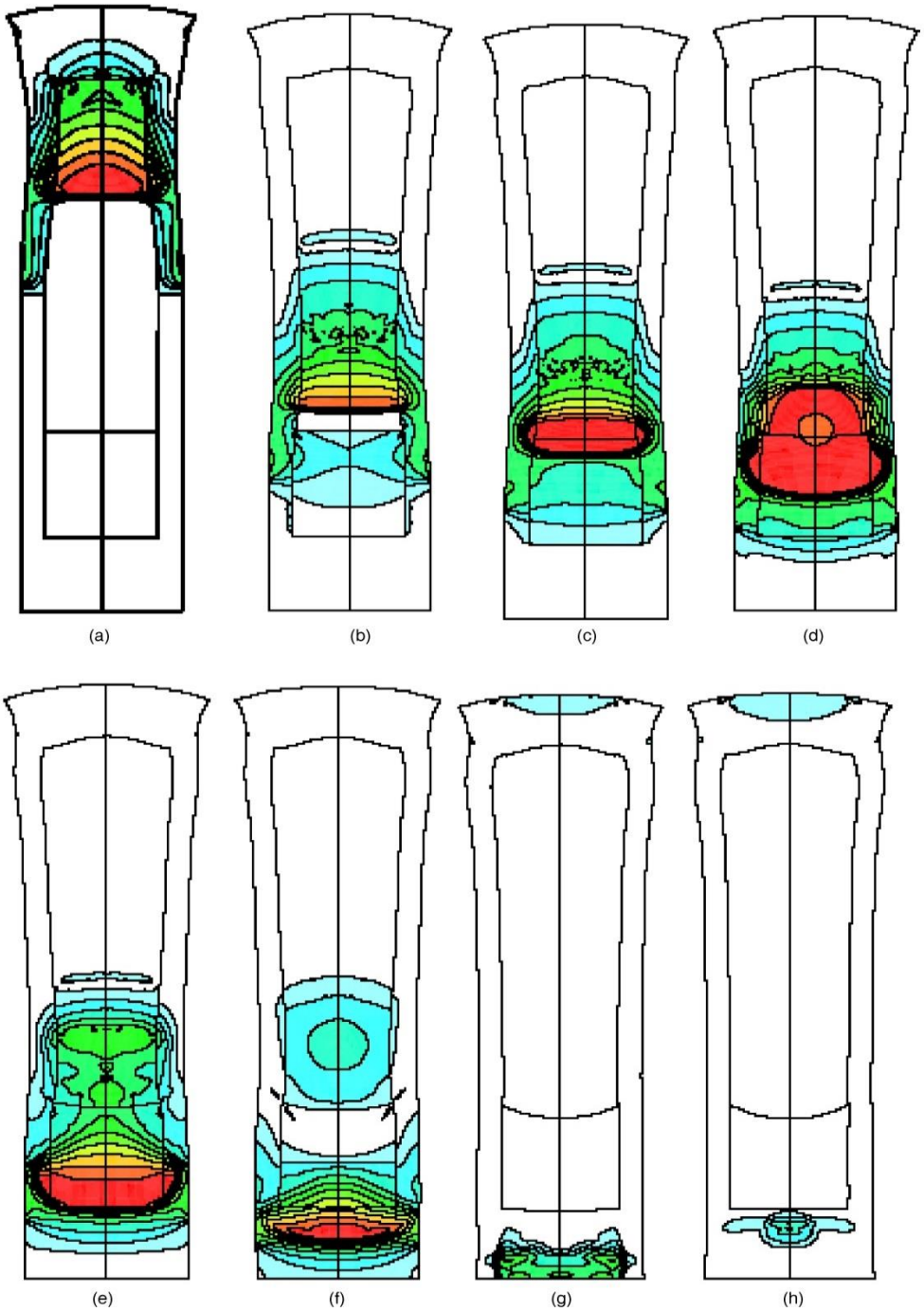

Figure 2. Distribution of pressure profiles (GPa) in the low-dispersed reactive mixture (Al-S) with an inert bottom layer of Al in an axial section of the ampoule for different times; (a) 14 μs, (b) 20 μs, (c) 21 μs, (d) 22 μs, (e) 23 μs, (f) 24 μs, (g) 26 μs, and (h) 27 μs
(*for colour image see journal web site*)

To solve this problem of explosive loading, an inert porous aluminum layer was added to the bottom part of the mixed Al-S sample. In this case, the height and diameter of the porous reactive Al-S sample were 49 mm and 14 mm, and the height and diameter of the inert aluminum layer were 16 mm and 14 mm, respectively.

Figure 2 demonstrates the distribution of pressure profiles in the Al-S low-dispersed porous reactive mixture with an inert bottom layer of Al placed in a cylindrical ampoule subjected to explosive loading for different times.

The shock wave propagation in the low-dispersed porous reactive mixture of Al-S with an inert bottom layer of Al is characterized by the different dynamics of the shock wave process during the explosive synthesis of aluminum sulfide. In this case, the shock wave propagating along the ampoule does not reflect from the bottom lid of the ampoule. The inert aluminum layer does not contribute to pressure and temperature rise due to the absence of chemical reactions, fig. 2(b). Due to the absence of additional contribution from chemical reactions the shock wave propagating along the ampoule encounters the shock compression wave in the inert layer, which leads to the increase in the pressure, fig. 2(c) not as high as the pressure in the previous numerical computations. After the encounter, the shock waves propagate in opposite directions, figs. 2(d) and 2(e). The residual pressures are observed in the sample for short time, figs. 2(f), 2(g), and 2(h).

The numerical computations have shown that in this case the fracture of the cylindrical ampoule is not observed.

Conclusions

The previous numerical and experimental results have shown that high heat release and high increase in pressure due to exothermic reactions can cause problems for solid-phase synthesis in cylindrical ampoules subjected to explosive detonation. Propagation of shock waves in reactive mixtures initiates exothermic reactions, as well as high pressures and temperatures. In this case the high heat release and high pressure due to chemical reactions contribute to the formation of the gas phase that may become a reason of the damage or even fracture of the ampoule.

This problem of explosive loading was solved by adding an inert porous aluminum layer to the bottom part of the reactive mixture. The numerical computations have shown that in this case the fracture of the cylindrical ampoule was not observed. The inert aluminum layer prevents the sharp increase in pressures and temperatures. It can be concluded that an inert porous aluminum layer can be used to solve the problems of explosive loading and eliminate the fracture of cylindrical ampoules.

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