Problems of Solid-Phase Synthesis in Cylindrical Ampoules under Explosive Loading

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Abstract. The peculiarities of solid-phase synthesis are studied experimentally and numerically in the aluminum-fluoroplastic and aluminum-sulfur mixtures in cylindrical ampoules under explosive loading. The experimental results show that the use of a mixture capable of ultrafast exothermic reactions leads to the destruction of a cylindrical ampoule under explosive loading. When the transient shock wave is reflected from the bottom lid of the ampoule as a compression wave, there is a sharp increase in pressure in the lower part of the ampoule, which is accompanied by the increase in rate of the chemical reaction. The high rate of heat release during the chemical reaction in the lower part of the ampoule causes the formation of a gas phase, which leads to a further increase in pressure and destruction of the ampoule.

Introduction

Explosive technologies are commonly used in metal processing, including the technologies of shaping, welding, cutting, hardening, and compaction. At present, the prospective studies are the studies in the area of explosive pressing ceramic powders, which are represented mainly by experimental works [1]. A lot of experiments are conducted to obtain new materials by combining the various physical processes. For example, in [2] the technology is developed for producing composites based on titanium and chromium borides using a one-stage method that combines the self-propagating high-temperature synthesis (SHS) and pressing of hot products. The work [3] demonstrates the fact that there is a possibility to combine welding and explosive compaction with SHS for production of layered ceramic-metal materials. Many of these methods are already used in production, while the possibilities and prospects for the solid-phase synthesis of materials under explosive loading are not sufficiently investigated and have not yet reached the level of technology due to the lack of experimental data and numerical techniques correctly describing the process.

Synthesis of new materials according to equilibrium phase diagrams is exhausted. The perspectives are connected with producing metastable combinations in nonequilibrium conditions. Explosive loading gives big opportunities to create and control such conditions. High pressure and speed of substances create extreme conditions to obtain materials with unique properties. But the substance reaction to such extreme effect can be changed depending on the substance characteristics. It is necessary to take into account short duration of the explosive loading process (~10^-6 s). Since various processes and their stages require different time intervals for the development, not all the processes
have enough time to develop within a short period of time which explosive loading is characterized [4].

The developed numerical models in combination with the available experimental data will provide the possibility to receive reliable information on the behavior of reacting media, including the mechanisms and kinetics of physical and chemical transformations and ways to form new states of substances.

The aim of this work is to study the synthesis of materials in the solid-phase mode and find the reasons for destruction of cylindrical ampoules subjected to explosive loading. A characteristic peculiarity of the studies conducted is an integrated approach combining the experiments and numerical simulation.

1. Formulation of the problem

The system of equations describing the nonstationary adiabatic motion of each component in a solid compressible mixture comprises the equations of continuity, momentum, and energy [5, 6]:

\[
\begin{align*}
\frac{\partial (\rho_i \rho)}{\partial t} + \nabla \cdot (\rho_i \rho \mathbf{v}_i) &= 0, \\
\rho_i \frac{d \mathbf{v}_i}{dt} &= \nabla \sigma_i + \sum_{j=1}^{N} a_{ij} R_{ji}, \\
\rho_i \frac{d E_i}{dt} &= \sigma_i \varepsilon_i + \sum_{j=1}^{N} \Phi_{ji},
\end{align*}
\]

where

\[
\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla.
\]

Here \( t \) is the time, \( \rho_i \) is the density of the \( i \)-th component equal to the mass of \( i \)-th component per unit volume of the \( i \)-th component, \( \mathbf{v}_i \) is the velocity vector, \( E_i \) is the internal specific energy, \( \varepsilon_i \) is the strain rate tensor, \( \sigma_i = -P \delta_i + S_i \) is the stress tensor, \( P \) is pressure, \( S_i \) is the stress deviator, \( R_{ji} \) is the intensity of the momentum exchange between the \( j \)-th and \( i \)-th components, \( \Phi_{ji} \) is the intensity of the energy exchange between the \( j \)-th and \( i \)-th components, \( N \) is the number of components.

Volume fractions of the mixture occupied by each component [5] are given by:

\[
\alpha_1 + \alpha_2 + \ldots + \alpha_N = 1, \quad (\alpha_i \geq 0), \quad \alpha_i = \rho_i^*/\rho_i,
\]

where \( \rho_i^* \) is the reduced density (mass of the \( i \)-th component per unit volume).

To solve the shock wave loading problems of porous reacting mixtures, the finite element method is used [7, 8]. On the basis of this method every component of a mixture simultaneously occupies the same volume as the mixture and consists of a set of the final elements connected with the node points. Inside every element, components interact with each other, exchanging momentum, energy, and mass (in the presence of chemical reactions) within the framework of the multicomponent medium model. After interaction of components and their summary contribution to node forces of an element, the components in a mixture obtain the velocity of the corresponding element.

In modeling chemical reactions under shock wave loading, we use the zeroth-order kinetic relation [9, 10] characterized by a constant rate of chemical transformations:

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

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

here \( T_i \) is the temperature, \( P \) is the matched pressure of components, and \( T_\eta, P_\eta, K_p, K_0 \) are the constants, \( \eta \) is the conversion degree.

Evolution of porosity in the material (compression and growth of pores) is simulated using a kinetic model of the active type, which determines changes in specific volume of pores influencing on the material properties and causing stress relaxation [11]:
where $P_i^* = P_i V_i/(V_i + V_{f_i})$, $P_{si}$ is the pressure in the solid (undamaged) part of the $i$-th component in the mixture, $V_{f_i}$, $V_{si}$, $P_{ki}$, $K_{fi}$ are the experimentally determined constants of the material.

Pressure in the undamaged component of the mixture is a function of specific volume and internal energy, and over the entire range of loading conditions, it is determined by the Mie-Grüneisen equation of state according to the formula [10]:

$$P_i = P_0 u_{ci}^2 \frac{\mu_i}{\rho_{0i}u_{ci}^2} \left[1 - \gamma_0/2 + 2(b_i - 1)\right]u_i^2 +$$

$$\rho_{0i}u_{ci}^2 \left[2(1 - \gamma_0/2)(b_i - 1) + 3(b_i - 1)^2\right]u_0^3 + \gamma_0 \rho_{0i} E_i,$$

where $\mu_i = V_{f_i}/(V_i - V_{f_i}) - 1$, $\gamma_0$ is the Grüneisen coefficient, $V_{f_i}$ and $V_i$ are the initial and current specific volumes, respectively, and $u_{ci}$ and $b_i$ are the constants of the Hugoniot shock adiabat described by the relation:

$$u_{ci} = u_{si} + b_i u_{pi},$$

where $u_{si}$ is the shock wave velocity and $u_{pi}$ is the particle velocity of a component behind the shock wave front.

Studying the deformation of multicomponent media, it is necessary to take into account the state and response of each component, as well as, 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 volume concentrations of the components [9]:

$$P = P_1(V_i, E_i) = P_2(V_j, E_j) = \ldots = P_N(V_N, E_N).$$

The change in porosity is assumed to be influenced only by the spherical stress component or pressure, whereas the components of the stress deviator are bounded by the independent deviatoric yield function [12]:

$$2G_i\left(e_{ij} - \frac{1}{3}e_{ii} \delta_{ij}\right) = \frac{dS_{ii}}{dt} + \lambda_i S_{ii},$$

where $dS_{ii}/dt$ - is the Jaumann derivative given by:

$$\frac{dS_{ii}}{dt} = \frac{dS_{ii}}{dt} - S_{iim}W_{im} - S_{imm}W_{im},$$

and $2W_{ij} = \partial\sigma_{ij}/\partial e_{ii} - \partial\sigma_{ij}/\partial e_{ij}$. The parameter $\lambda$ is zero for elastic deformation, and for plastic deformation is determined from the Mises yield criterion [12]:

$$S_{ii} S_{ii} = \frac{2}{3} \sigma_i^2.$$

Here $G_i$ is the shear modulus and $\sigma_i$ is the dynamic yield point:

$$G_i = G_0 K_i \left[1 + \frac{c_i P_i}{(1 + \mu_i)^{1/3}}\right] \frac{V_i}{(V_i + V_{f_i})},$$

$$\sigma_i = \sigma_0 K_i \left[1 + \frac{c_i P_i}{(1 + \mu_i)^{1/3}}\right] \left[1 - \frac{V_i}{V_{f_i}}\right], \text{ if } V_i \leq V_{f_i},$$

$$0, \text{ if } V_i > V_{f_i}.$$
In the computations, the function $K_T(T_i)$ was chosen to model the nonthermal character of plastic deformation and dynamic strength of solids at high strain rates ($10^4$ s$^{-1}$ or higher).

The temperature was calculated using the following ratio:

$$dT_i = \begin{cases} 
    \frac{d(E_i - E_{0xi})}{c_{pi}}, & \text{if } T_i < T_{mi} \\
    0, & \text{if } T_i = T_{mi} \\
    \frac{d(E_i - E_{0xi} - \Delta H_{mi})}{c_{pi}}, & \text{if } T_i > T_{mi} 
\end{cases}$$

where the specific heat capacity $c_{pi}$ increases linearly with increasing the temperature up to the melting point of a substance, $E_{0xi}$ is the "cold" component of the specific internal energy, $T_{mi}$ is the melting temperature, $\Delta H_{mi}$ is the specific melting heat of the $i$-th component.

2. Experimental results

In the experiments the powder mixture of aluminum and fluoroplastic (Al/TF) was used as a loaded material that was placed in a cylindrical ampoule. The powders were mixed in an AGO-2U planetary mill. The mass fractions of components were 30/70 (Al/TF), which was close to the stoichiometry of the aluminum fluoride (AlF$_3$) formation. The initial porosity of the loaded mixture components was varied in the experiments. In the first case, the initial porosity of the mixture components was 0.5 (ratio between the volume of pores and the total volume) and in the second case, the initial porosity was 0.045. The height of the cylindrical ampoule was 95 mm, the external diameter was 20 mm. The thickness of the lateral wall of the ampoule was 3 mm. The ampoule was closed with lids 10 mm in sickness. The ampoule was loaded by an explosive (ammonite 6GV). The external diameter of the explosive was 45 mm. The density of the explosive was 1.0 g/cm$^3$, and the detonation velocity was 3.85 km/s.

The first ampoule was broken into large fragments (Fig. 1).

![Figure 1. Fragments of the ampoule after explosive loading.](image)

The second ampoule was cracked along the whole length of the material (Fig. 2).

Only the upper layer of the sample 5 mm in thickness was saved after explosive loading (Fig. 2). There are no any traces of the reaction in this part of the sample according to X-ray diffraction analysis.
3. Numerical results

To identify the reasons for destruction of the ampoules, the numerical computations were carried out by using the model of a multicomponent medium [7]. We numerically solved an axisymmetric problem of a cylindrical steel ampoule containing a porous Al–S mixture under explosive loading. The mass fractions of the components were as follows: Al – 0.35; S – 0.65. After initiation of a chemical reaction, aluminum sulfide Al₂S₃ was formed as a reaction product. We chose the reaction initiation criteria in terms of temperature, $T_\eta = 933$ K (aluminum melting point), and pressure, $P_\eta = 0.9$ GPa [7-10]. The reaction rate $K_0$ was taken to be 260.8 GJ/(kg s), and $K_p = 20.0$. Numerical computations have been carried out by using a research software package on the basis of the finite element method modified to simulate the high-speed loading.

Fig. 3 shows the distribution of pressure profiles in the Al–S mixture placed in a cylindrical ampoule at different moments of time, describing the dynamics of the shock wave process during the explosive synthesis of aluminum sulfide.

A shock wave propagates along the sample subjected to the action of explosion products. At the same time, the wave front in the mixture is located behind the wave front in the ampoule walls due to the collapse of pores in the mixture. After the reflection of the shock wave from the bottom of the ampoule as a compression wave, the pressure in the lower part of the sample increases considerably (Fig. 3c) and is higher than 6 GPa.
Analysis of the numerical and experimental results suggests the following dynamics for the development of chemical transformations in exothermic mixtures placed in the cylindrical ampoule under explosive loading. In the upper and central parts of the ampoule, the reaction is initiated in the transient shock wave. After reflection of the transient shock wave from the bottom lid of the ampoule as a compression wave, a sharp increase is observed in the bottom of the ampoule, which leads to the increase in rate of chemical transformations in the lower part of the mixture. The high heat release rate during the chemical reaction in the bottom of the ampoule causes the formation of a gas phase, which, in turn, leads to the increase in pressure in this area and the damage of the ampoule, and the damage process is initiated in the bottom of the ampoule.

Conclusion
The peculiarities of solid-phase synthesis were studied experimentally and numerically in the aluminum-fluoroplastic and aluminum-sulfur mixtures placed in cylindrical ampoules under explosive loading. The experimental results have shown that the use of a mixture capable of ultrafast exothermic reactions leads to destruction of a cylindrical ampoule under explosive loading.

The numerical results have shown that after reflection of the transient shock wave from the bottom lid of the ampoule as a compression wave, there is a sharp increase in pressure, which is accompanied by the increase in rate of chemical reactions. The high rate of heat release during the chemical reaction in the bottom of the ampoule causes the formation of a gas phase, which leads to a further increase in pressure and the destruction of the ampoule.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (project no. 14-03-00666a).

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