

Thermodynamic parameters of mixtures with allowance for phase transition components under shock-wave loading

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Abstract

The shock-wave synthesis and compaction using powder mixtures are the one of perspective directions of new materials creation. The results of numerical experiments on modeling of shock wave loading of mixtures with allowance for phase transition components in their composition are presented. The significant change in volume in the region of phase transition components included in the mixtures allows us to expand the range of variation of thermodynamic parameters of the mixtures under shock wave loading. The calculation model is based on the assumption that all components of mixture under shock-wave loading are in thermodynamic equilibrium (model TEC). The model TEC allows us to describe the region of the polymorphic phase transition, considering the material in the region of phase transition as a mixture of low-pressure phase and high-pressure phase. The good agreement of these model calculations with the data of different authors defined on the basis of experiments is obtained. Thermodynamic parameters of the nitrides mixture, solid and porous mixtures with quartz as component were reliably described. This model is useful for determining the compositions and volume fractions of the components of the mixture to obtain the specified parameters of solid and porous materials under shock-wave loading.

Keywords: High pressure engineering, Integrated circuits, Mixtures, Phase transitions, Porous materials, Shock waves, Thermodynamic equilibria

1. Introduction

The possibility of changes in the structure and phase composition of mixtures under the action of

shock waves is of interest for the creation of materials with the desired properties. Materials experiencing a phase transition under shock wave loading are of particular interest when solving this task. On one hand, such materials, e.g., quartz, graphite, bismuth and others have a high compression ratio that allows you to expand the field of the feasible thermodynamic parameters [1, 2]. This gives the opportunity to purposefully achieve the conditions necessary for the production of ceramics with the given properties. On the other hand, many materials with unique properties are also experiencing a phase transition, which further stimulates interest in such research. There are different methods for modeling the thermodynamic parameters of shock-wave loading of mixtures [3], which, however, does not describe the data obtained on the basis of the experiment in the whole range of parameters, in contrast to the model TEC [4].

The interest in the research of compressibility of quartz mixtures is related to the properties of quartz and the possibility of creating materials with the required properties (heat-resistant and high-strength ceramics). The wide distribution of quartz in nature has led to much attention to it. The mass fraction of quartz is more than 60% taking into account mix and silicates in the earth's crust; the free quartz content is 12 %. As a consequence, there is the large

base of experimental data on shock-wave loading on quartz and mixture with it that allows you to check the accuracy of the simulation.

Nitrides are often refractory and resistant to stress at high temperatures substances. Nitride coatings are used in energy, space technology, imparts hardness and corrosion resistance of products. The advantage of aluminum nitride AlN over other materials is the unique combination of its physical and electrical characteristics: such as the high thermal conductivity, good insulating properties, the moderate coefficient of thermal expansion at relatively low cost. Recent interest in silicon nitride Si₃N₄ is associated with the discovery of its high-pressure modification with a cubic structure (γ-phase) which has a considerable hardness comparable to that of stishovite—the high-pressure phase of SiO₂. Some researchers believe that stishovite takes the third place in this parameter, after diamond and cubic boron nitride. This feature of the γ-phase allows considering it as a promising technological material, though very high pressures more than 15 GPa and temperatures more than 1000 K required for the formation of γ-Si₃N₄ are a major obstacle not only to industrial use, but also to a detailed study of its properties. Therefore, the selection of optimal conditions under which it would be possible to synthesize relatively large amounts of this substance with a high output at acceptable values of external parameters (pressure and temperature) is a topical task. High temperature is important along with pressure in

the formation of γ -Si₃N₄. The promising method of high-temperature shock compression is used to research phase transition in silicon nitride and achievements of γ phase [5]. This method allows increasing the substance's temperature during compression, thereby promoting the transformation, and significantly reducing the residual temperature after the pressure drop, thereby ensuring quenching of the new phase. The effect is achieved by addition of components with high compressibility and specific heat, such as alkali halide salts, to the samples.

The model TEC that used in this work can reliably describe the thermodynamic parameters of the mixture under shock wave loading, including the region of phase transition of components. It should be noted, that the model TEC uses the parameters of the equation of state of the components and hence allows considering the interaction of mixture components, unlike the mixed method, which is mainly used for high-density mixtures [5].

2. Calculation model

The model TEC is used to describe the thermodynamic parameters of porous solids and mixtures of powders under shock wave loading [1, 4]. The equation of state of the Mie-Grüneisen type is applied when modeling the thermodynamic parameters of condensed phases. The initial internal energy and pressure of the substances are zero under normal conditions, taking into account the fact, that field of use of this model for pressures is over 5 GPa. Hence, the equation of state for condensed component has the form with the current and initial densities ρ and ρ_0 , pressure P , specific heat c_v , and the current and initial temperatures T and T_0 :

$$P(\rho, T) = A \left[\left(\frac{\rho}{\rho_0} \right)^k - 1 \right] + \Gamma(T) c_v (T - T_0) \rho \quad (1)$$

The function $\Gamma(T)$ has the following form:

$$\Gamma(T) = \left\{ \left[\Gamma(T_0) - \Gamma(T_\infty) \right]^{-1} + C(T - T_0) \right\}^{-1} + \Gamma(T_\infty) \quad (2)$$

$$C = \left\{ \left[\Gamma(T_*) - \Gamma(T_\infty) \right]^{-1} - \left[\Gamma(T_0) - \Gamma(T_\infty) \right]^{-1} \right\} (T_* - T_0)^{-1} \quad (3)$$

The parameters C , $\Gamma(T_\infty)$ are chosen from the condition of compliance of the calculated shock adiabats with known experimental results for every component, so that:

$$\Gamma(T) \rightarrow \Gamma(T_0) \text{ when } T \rightarrow T_0,$$

$$\Gamma(T) \rightarrow \Gamma(T_\infty) \text{ when } T \rightarrow T_\infty.$$

Here value of $\Gamma(T_0)$ is taken on the basis of known data at normal conditions. The coefficient C , which allows describing the experimental points upon moderate compression, is determined by the intermediate value $\Gamma(T^*)$ at temperature $T=T^*$. The asymptotic value $\Gamma(T_\infty)$ corresponds to the maximum temperatures. For the gas, we use the equation of state of ideal gas. We write the conditions of dynamic compatibility on the shock wave front, which are laws of conservation of the mass flux for each component of the mixture and laws of conservation of momentum and energy fluxes for the

mixture as a whole [1, 4]. The resultant equations combined with the equation of state for each component are sufficient to find dependences of the type of $P(U)$ or $D(U)$, which can be treated as the shock adiabats of the multicomponent mixture. U and D are the mass and wave velocity, respectively. A , k , and Γ are the coefficients in the equations of state of the condensed component. For the mixture of n condensed components with the initial volume fraction μ_{i0} we can obtain the expression:

$$P = \left\{ \sum_{i=1}^n A_i \frac{\mu_{i0}}{\sigma_i} \left[\left(h_i - \frac{k_i + 1}{k_i - 1} \right) \sigma_i^{n_i} + \frac{2k_i \sigma_i}{k_i - 1} - h_i - 1 \right] \right\} \left[\sum_{i=1}^n \frac{\mu_{i0}}{\sigma_i} h_i + \left(\frac{h_g}{\sigma_g} \right) \left(1 - \sum_{i=1}^n \mu_{i0} \right) - 1 \right]^{-1} \quad (4)$$

Here $h_i = 2/\Gamma_i + 1$, $i = 1 \dots n$, $h_g = 2/(\gamma - 1) + 1$. $\sigma_i = \rho_i/\rho_{i0}$, $\sigma_g = \rho_g/\rho_{g0}$ is the compression ratio of components, ρ_g , ρ_{g0} current and initial gas densities, $\gamma = 1.41$ is the ratio of specific heat. In view of equal temperatures of all components, including gas, we finally have an $n + 1$ equation for $n + 2$ variables P , σ_i ($i=1 \dots n$), σ_g , which allows us to construct a shock adiabat of mixture. A pure substance is considered as a mixture with one condensed component. The volume fraction of gas is assumed zero for calculation of parameters of solid material.

The model TEC may describe the behavior of the materials including the phase transition region. The material is considered as the mixture of low-pressure phase and high-pressure phase in this area. We write the conditions of dynamic compatibility on the shock wave front taking into account the phase transition. It is assumed that the volume fraction α of low-pressure phase passed into high-pressure phase in the region of polymorphic phase transition. The dependence of low-pressure phase, turning into the high-pressure phase, we can specify the following expression $\alpha = k\Delta E$ in the first approximation in the phase transition region. Here $k = (E_f - E_b)^{-1}$, E_b is internal energy at the beginning of the phase transition, E is current internal energy, $\Delta E = E_f - E_b$, E_f is internal energy at the finish of the phase transition, when there are full transition of low-pressure phase to high-pressure phase. The comparison of the calculations with the experimental data has shown that the value of k , defined for one of the porosity, allows one to describe the results for other values of the porosity. As the result, the three regions are set depending on the value of α that determines the volume of low-pressure phase and high-pressure phase of the shock adiabats for the materials with the phase transition [6]:

$$\begin{cases} E \leq E_0 & \alpha = 0 \\ E_0 \leq E \leq E_k & \alpha = k\Delta E \\ E \geq E_k & \alpha = 1 \end{cases}$$

3. Numerical results

The accuracy of the modeling materials used to create materials with desired properties, with the components experiencing a phase transition under shock wave loading, is confirmed, in particular, calculations of the shock adiabats for mixtures of quartz. Calculations of thermodynamic

parameters of the mixtures of quartz with aluminum mass fractions wt. % Al (30) SiO₂ (70), Al (40) SiO₂ (60), Al (50) SiO₂ (50) are shown in Fig. 1. The calculation for pure quartz is given on the same figure for illustration. The possibility of accounting for the phase transition during shock-wave loading for the first time allows us to describe all the data obtained on the basis of experiments for all the considered mixtures.

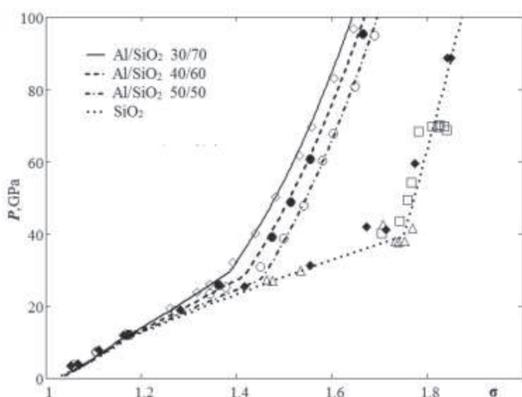


Fig. 1. Shock adiabat in coordinates pressure - compression. The calculation and experimental results for the mixtures of quartz with aluminum of various compositions, and pure quartz. Experimental data from [7].

1. ábra Lökéshullám adiabata vonalak nyomás-kompresszió koordináta rendszerben. Számított és kísérleti eredmények eltérő összetételű kvarc-alumínium keverékekre és tiszta kvarcra vonatkozóan. A kísérleti eredmények forrása [7].

The model TEC allows describing the shock adiabat in the region of the phase transition of quartz mixtures with the significantly different components, in particular by density. Calculations of the mixtures of quartz with tungsten and quartz with teflon, as well as data obtained on the basis of the experiments [7] are shown in Fig. 2. The calculations were performed for the mixtures of following compositions: mixture of quartz with tungsten (density 10.19 g/cm³), weight fraction wt.% W(88) SiO₂ (12) and mixture of quartz with teflon wt.% SiO₂ (55) Teflon (45), (density 2.38 g/cm³). The calculations allow describing the data obtained on the basis of experiments with good accuracy.

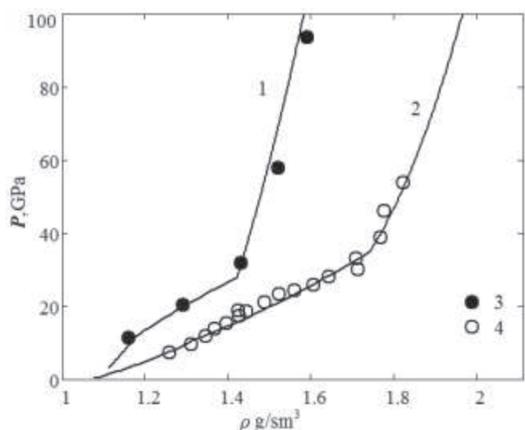


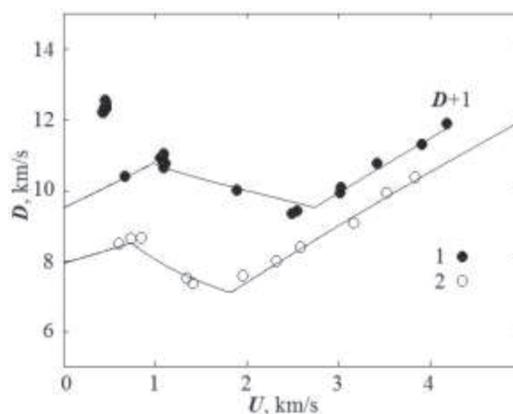
Fig. 2. Shock adiabat of mixture of quartz with tungsten (1), mixture of quartz with teflon (2). Experimental data (3), (4) from [7].

2. ábra Lökéshullám adiabata vonalak kvarc-vólfrám keverékekre (1), kvarc-teflon keverékekre (2). A kísérleti eredmények (3), (4) forrása [7].

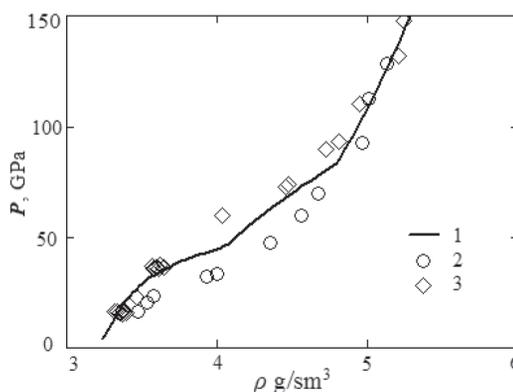
The model parameters allowing reliable description of the thermodynamic parameters of pure nitrides under shock wave loading are used to simulate the parameters of the mixture of nitrides as components [6].

The experimental data [8] for aluminum nitride AlN (initial density 3.23 g/cm³) and the data [9] for silicon nitride Si₃N₄ (initial density 3.44 g/cm³) are used in the calculations of the shock wave loading of these materials with the phase transition.

The shock adiabat is shown in Fig. 3.a with the shift for clarity. The initial pressures of the phase transition for AlN and for Si₃N₄ are prescribed at 20 and 30 GPa respectively. The transition of β -phase into highly-dense c -phase is reproduced in the calculations for Si₃N₄. The first three experimental points respective to the a -phase (corresponding to plastic deformation) did not take into account as it was done in [9]. The calculations show that the model TEC allows one to describe the unusual behavior of the shock adiabat [8] in the phase transition region (reduction of wave velocity with increasing of mass velocity).



(a)



(b)

Fig. 3. Shock adiabat of silicon nitride (1) and nitride of aluminum (2) in the coordinates of wave and mass velocity (a). Shock adiabat of the mixture AlN and Si₃N₄ (1), experimental data of silicon nitride (2) [9] and aluminum nitride (3) [8] in the coordinates pressure and density (b).

3. ábra Lökéshullám adiabata vonalak szilícium-nitridre (1), alumínium-nitridre (2) lökéshullám sebesség és impulzus koordináta rendszerben (a). Lökéshullám adiabata vonalak AlN - Si₃N₄ keverékekre (1), kísérleti eredmények szilícium-nitridre (2) [9] és alumínium-nitridre (3) [8] vonatkozóan, nyomás-sűrűség koordináta rendszerben (b).

The results for the mixture of AlN and Si₃N₄ with equal volume fractions and initial density 3.335 g/cm³ are shown in Fig. 3.b. Here the experimental data for pure AlN and

Si₃N₄ [8, 9] are shown for the comparison. The beginning of the phase transition for AlN and Si₃N₄ in the mixture are determined at the same pressure as that for pure substances.

The calculations for the mixtures of oxides are also performed on account of a large interest in silicon nitride and its compounds. Thermodynamic parameters are simulated for mixtures of Si₃N₄ with oxide, which were obtained on the basis of the experiments data [10]. The calculation for the mixture of Si₃N₄ and periclase MgO is shown in Fig. 4. MgO is used in industry for the production of refractories, including very fine abrasives for cleaning surfaces, in particular in electronics. The simulated mixture is characterized by the weight fraction wt % Si₃N₄ (95) MgO (5) and the density 3.164 g/cm³

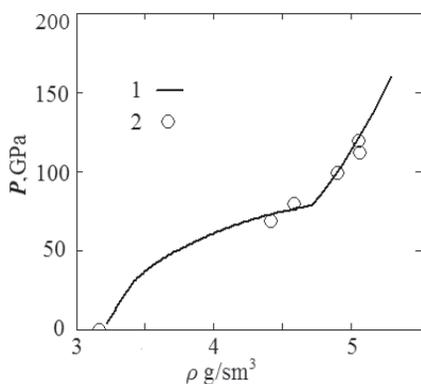


Fig. 4. Calculation for the mixture of Si₃N₄ and MgO with the phase transition (1). Experimental data (2) [10].

4. ábra Számított eredmények Si₃N₄ - MgO keverékre, fázisátalakulással (1). Kísérleti eredmények (2) forrása [10].

The results show the accuracy of the description of thermodynamic parameters of the mixtures of this type under shock wave loading. The prospects of using materials with phase transition are shown taking into account their unique properties and possibility to change the values of pressure and temperature of mixtures in a wider range of values. This approach extends the range of achievable values of thermodynamic parameters.

4. Conclusions

The data of the model TEC calculations correspond well to the experimental data by various authors. The model parameters allow us to reliably describe the behavior of pure materials under shock wave loading were used to simulate thermodynamic parameters of mixtures with components experiencing a phase transition under shock wave loading. It was shown that the TEC model allows us to simulate thermodynamic parameters of mixtures under shock wave loading including mixtures that contain components experiencing phase transitions. The simulation results allow determining the ratio of mixture components with the aim of obtaining specified parameters of solid and porous materials after their exposure to shock waves for the synthesis of ceramics with desired properties.

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Új anyagok kifejlesztésének egyik irányzata a por keverékek nagy nyomás alatti szintézise

A cikk numerikus vizsgálatok eredményeit ismerteti a lökéshullámok által gerjesztett fázisátalakulások területén. A nagymértékű térfogatváltozás a fázisátalakulások során lehetőséget teremt a termodinamikai paraméterek kibővítésére a lökéshullámok által gerjesztett jelenségeknél. Az ismertetett számítási modell alapfeltevése, hogy a keverékek összetevői a lökéshullámok alatt termodinamikai egyensúlyban vannak. A modell lehetőséget nyújt a polimorf fázisátalakulások leírására, feltételezve, hogy az anyag a fázisátalakulás során egy kis nyomású fázis és egy nagy nyomású fázis keveréke. A modell alapján számított eredmények jó egyezést mutatnak a publikált kísérleti eredményekkel. A cikk bemutat nitrid-kvarc keverékekre, tömör és porózus anyagokra vonatkozó eredményeket.

Kulcsszavak: magasnyomású mérnöki módszerek, integrált áramkör, keverék, fázisátalakulás, porózus anyagok, lökéshullám, termodinamikai egyensúly