

# MODELING OF MIXTURES THERMODYNAMIC PARAMETERS WITH COMPONENTS THAT UNDERGO PHASE TRANSITION UNDER SHOCK WAVE LOADING

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Shock-wave synthesis and compaction using powder mixtures are the promising direction of creation of new materials. The intensive researches of compressibility of mixtures to create materials with the desired properties, in particular heat-resistant and high-strength ceramics, are held in this direction. A significant change of volume in the region of the phase transition (PT) components included in the mixtures allows us to expand the range of changes of thermodynamic parameters of the mixtures under shock wave loading. This result allow us to create purposefully the necessary conditions for the synthesis of new materials. Active researches of properties and methods of obtaining such materials, particularly nitrides [1 – 6], are conducted. Different compositions of the mixture comprising  $\text{Si}_3\text{N}_4$  as component are considered in [7 – 9].

## Calculation method

Thermodynamic equilibrium model TEC (thermodynamic equilibrium components), taking into account the presence of gas in the pores is used to describe the thermodynamic parameters of the mixtures under shock wave loading [8 – 10]. This model allows us to describe thermodynamic parameters in a wide range of pressures under shock wave loading, including those mixtures, the components of which are experiencing a polymorphic PT. Thermodynamic equilibrium means the equality between the velocities, pressures, and temperatures. In order to describe the behavior of condensed phases, the equations of state of the Mie-Grüneisen type are used in the following form:

$$P(\rho, T) = P_C(\rho) + P_T(T), \quad P_T(\rho, T) = \Gamma \rho E_T(T), \quad E_T(T) = c_V(T - T_0) \quad (1)$$

Here  $P_C$ ,  $P_T$ , and  $E_T$  are the potential and thermal components of pressure and specific energy, respectively;  $c_V$  is the specific heat capacity;  $T_0$  is the initial temperature. By taking into account the pressure region of applicability of this model >5GPa that is of interest to us, initial energy of a substance under normal conditions is considered to be equal to zero. Cold pressure component  $P_C$  is described by a Tait-type equation. The ideal gas equation of state is taken for a gas. The following expression can be obtained for a material with  $n$  condensed components ( $\mu_{i0}$  is the initial volume fraction of the  $i$ -th phase of the substance):

$$P = \frac{\sum_{i=1}^n A_i \frac{\mu_{i0}}{\sigma_i} \left[ \left( h_i - \frac{k_i+1}{k_i-1} \right) \sigma_i^{k_i} + \frac{2k_i \sigma_i}{k_i-1} - h_i - 1 \right]}{\sum_{i=1}^n \frac{\mu_{i0}}{\sigma_i} h_i + \left( \frac{h_g}{\sigma_g} \right) \left( 1 - \sum_{i=1}^n \mu_{i0} \right) - 1} \quad \text{and} \quad h_i = \frac{2}{\Gamma_i} + 1, \quad h_g = \frac{2}{\gamma-1} + 1 \quad \text{and} \quad \Gamma = \frac{P_T V}{E_T} \quad (2)$$

Here  $h_i = 2/\Gamma_i + 1$ ,  $i = 1, n$ ,  $h_g = 2/(\gamma-1) + 1$ .  $\sigma_i = \rho_i/\rho_{i0}$ ,  $\sigma_g = \rho_g/\rho_{g0}$  are the degrees of compression of the corresponding component,  $\rho_{i0}$ ,  $\rho_{i1}$  are the density of the  $i$ -th phase of the substance ahead of the shock wave front and behind it, respectively ( $i = 1, \dots, n$ , and  $g$ );  $\gamma = 1.41$  (ratio of specific heats). The function  $\Gamma(T)$ , which determines the contribution of the thermal components, depends explicitly only on the temperature  $\Gamma = P_T V / E_T$  [10 – 12]. The obtained equations, together with the equations of state of each component, are sufficient to find dependences  $P(U)$  or  $D(U)$  dependences ( $U$  and  $D$  are the mass and wave velocities, respectively;  $A$ ,  $k$ , the coefficients in the equations of state of condensed component). These dependences can be treated as a shock adiabat of a multicomponent material.

The possibility of calculating the behavior of a mixture by the model allows us to describe the thermodynamic parameters of the PT. The material considered in this area as a mixture of the low-pressure phase and high-pressure phase. The possibility of modeling the properties of graphite samples in this region as a mixture of phases was shown earlier in [13]. The dynamic compatibility equations are written on the front of a shock wave with PT [14, 15]. In the region of the PT it is assumed that the volume

fraction  $\alpha$  of phase low pressure moved into the high-pressure phase. The beginning of the PT is determined from the compliance data obtained on the basis of experiments. The dependence  $\alpha$  is close to linear in the region of PT Fig. 1 and can be determined from the following expression:  $\alpha = k\Delta E$ , here  $k = (E_f - E_b)^{-1}$ , a  $\Delta E = E - E_b$ , while  $E$  – current energy. Here  $E_b$  is the internal energy at the beginning of the PT,  $E_f$  – the internal energy at the end of the PT, when there was a complete transition of the phase of low pressure in the high-pressure phase.

The comparison of the calculations with the experimental data shows that the  $k$  value defined for a certain porosity value allows one to describe the results for other porosity values [14]. As a result, three regions are set depending on the value  $\alpha$  that determines the volume of low-pressure and high-pressure phases of shock adiabats for materials with phase transition.

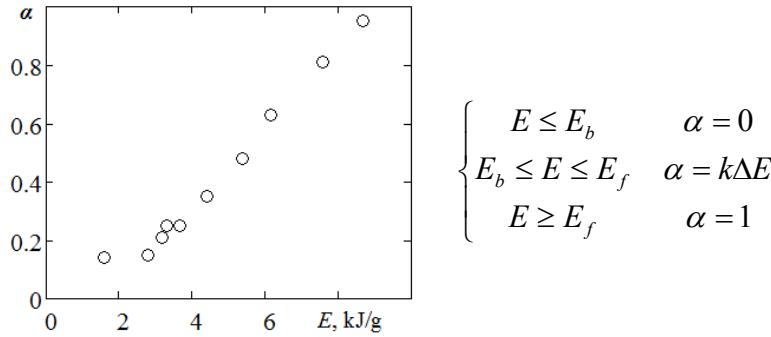


Figure 1. Dependence  $\alpha$  and internal energy for graphite of density  $\rho_0 = 1.52 \text{ g/sm}^3$  [14]

### Modeling of shock wave loading

The calculation of shock adiabats for quartz with consideration for phase transition is shown in Fig. 2(a) in pressure – mass velocity coordinates. Before the phase transition at pressure 11 GPa the calculation coincides with the shock adiabat of quartz without consideration for PT (low-pressure phase). We believe that the PT is completed at pressure above 40 GPa.

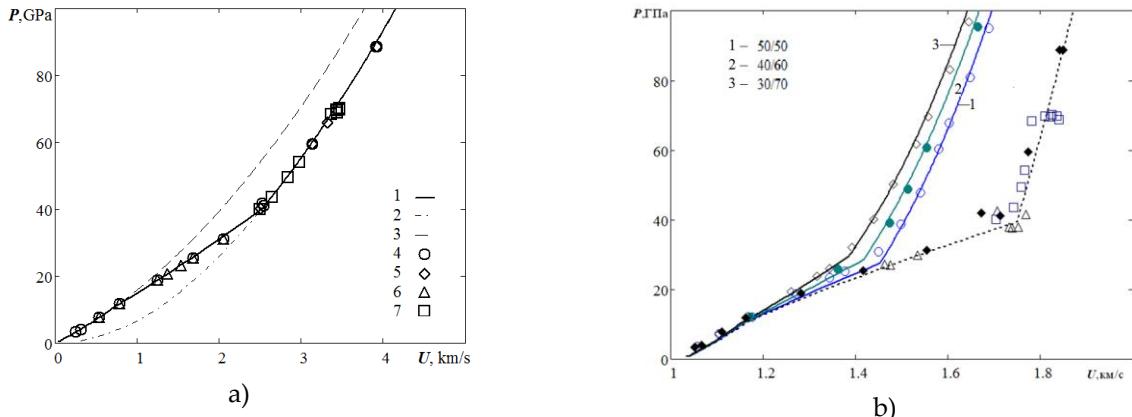
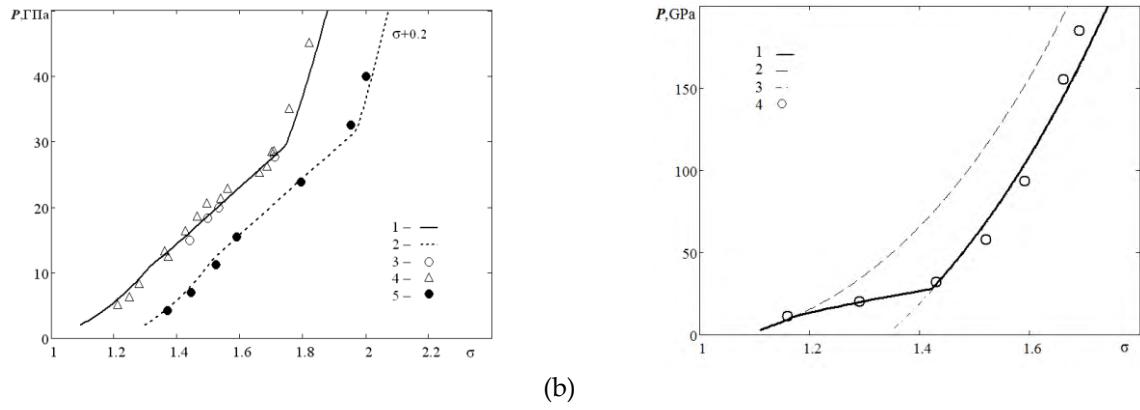


Figure 2. (a) The shock adiabat: quartz  $\rho_0 = 2.65 \text{ g/sm}^3$ . Calculations with consideration for phase transition (solid line 1), without consideration for phase transition (the dotted line 2), and for stishovite  $\rho_0 = 2.65 \text{ g/sm}^3$  (dash-dotted line 3); (b) aluminum-quartz mixture 1–3, and pure quartz 2. Date [16]

The calculation for stishovite with the same initial density as quartz corresponds to the experimental data. Consequently, the stishovite porosity  $m$  (ratio of the density of monolithic sample to the density of porous sample) is 1.63. In the first approximation, we believe that the quartz is transformed into stishovite, bypassing coesite as the intermediate phase. The calculation of thermodynamic parameters for quartz taking into account the PT above 40 GPa is almost identical to the calculation for stishovite.

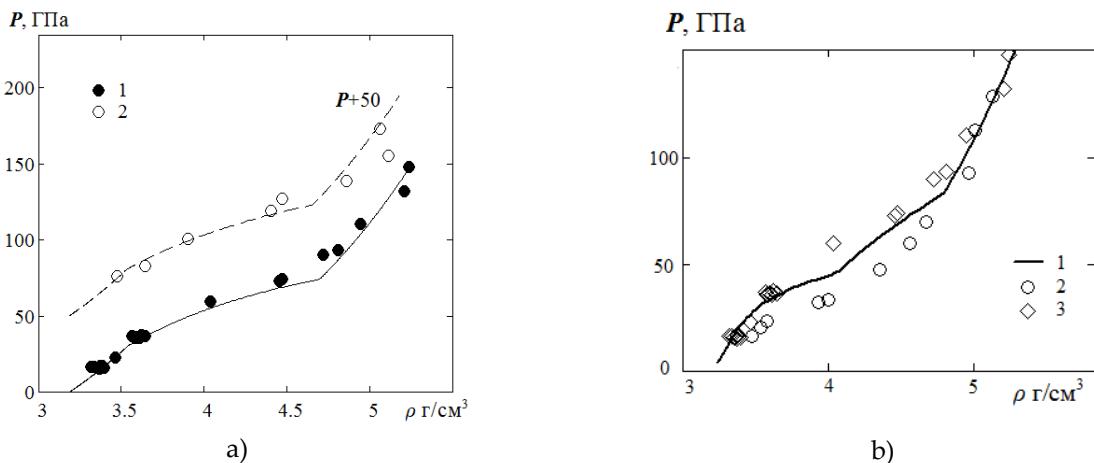
The ability of the model TEC to describe the behavior of materials in a phase transition under high dynamic loads allows us to simulate the thermodynamic parameters of the mixtures with such materials. Figure 2(b) demonstrates the calculation for the quartz-aluminum mixtures with the weight fractions 1-(50:50), 2-(40:60), 3-(30:70). Shock adiabats for pure quartz are shown for the comparison with the experimental data for the aluminum-quartz mixture [16].

The model allows us to calculate the thermodynamic parameters of mixtures of quartz with substantially different components, in particular density. The calculations of the mixtures of quartz with paraffin Fig. 3(a) and quartz with tungsten Fig. 3(b) and the experimental data from [16] are shown. The calculations were performed for the mixtures of the following compositions in Fig. 3(a) the mixture of paraffin with quartz  $\rho_0 = 1.78 \text{ g/cm}^3$ , weight fractions Paraffin (25.5) SiO<sub>2</sub> (74.5) (solid line 1) and mixture  $\rho_0 = 1.92 \text{ g/cm}^3$ , weight fractions Paraffin (18.7) SiO<sub>2</sub> (81.3) (dashed line 2). For clarity, the shock adiabatic is displayed with the shift. The mixture of quartz with tungsten is shown in Fig. 2 (b)  $\rho_0 = 10.19 \text{ g/cm}^3$ , weight fractions W (88) SiO<sub>2</sub> (12).



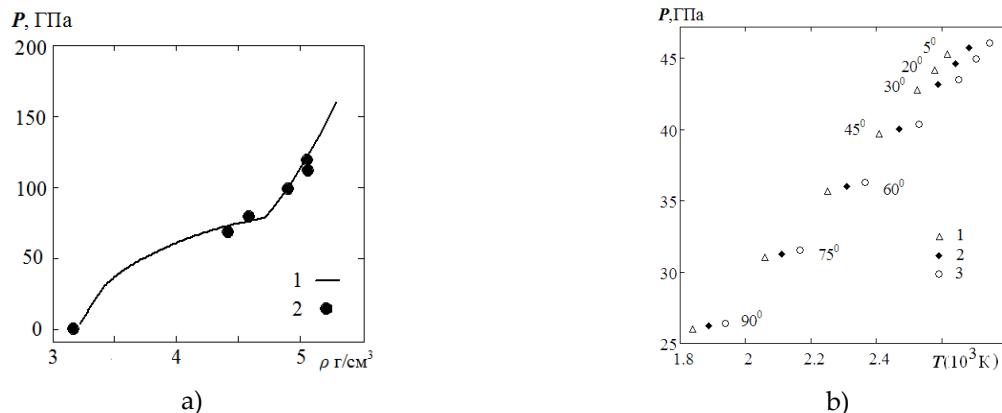
**Figure 3.** Shock adiabats. (a) The mixture of quartz with paraffin. (b) The mixture of quartz and tungsten. Data [16]

We assume that the phase transition of the components in the mixture begins under the same conditions as for pure substances. This assumption was received confirmation in the calculations in mixtures with two components experiencing a PT [15]. The experimental results were presented in [2, 4] for silicon nitride with  $m=1$  and  $m=1.046$ . The state diagram of Si<sub>3</sub>N<sub>4</sub>, which is applied to the calculated shock adiabats for given values of porosity, is shown in Fig. 4(a). The estimated line and data obtained from the experiment shown in Fig. 4(a) with a shift in  $P$  for  $m=1.046$ .



**Figure 4.** Shock adiabats in the coordinates pressure – density. Si<sub>3</sub>N<sub>4</sub> solid line  $m=1$ , dotted line –  $m=1.046$  (a), the mixture AlN and Si<sub>3</sub>N<sub>4</sub> (b). Date [2, 4]

The similar calculations of thermodynamic parameters were performed for aluminum nitride AlN, which is also experiencing a phase transition under shock wave loading. The results obtained allowed us to simulate the thermodynamic parameters of the mixture of the nitrides as components, using the model parameters for pure nitrides [15]. The results obtained for the mixture of AlN and  $\text{Si}_3\text{N}_4$  taken in equal volumetric proportions (initial density  $\rho_0 = 3.335 \text{ g/cm}^3$ ) are shown in Fig. 4(b). Here the data obtained on the basis of experiments for pure AlN and  $\text{Si}_3\text{N}_4$  are shown for the comparison. We assume that the phase transition of the components in the mixture begins under the same conditions as for pure substances. The initial pressures of the phase transition for AlN and for  $\text{Si}_3\text{N}_4$  are prescribed at 20 and 30 GPa respectively. The calculations are performed for non-porous mixture with the density corresponding to solid substance. Hence, the pressures prescribed for the beginning of the phase transition are shown to be reasonable.



**Figure 5.** Shock adiabats for mixtures  $\text{Si}_3\text{N}_4$  and  $\text{MgO}$ . Date: 2 [17]. (b) The pressure and temperature calculated for the case when the conical cumulative powder facings collapse (the wall opening angles are shown on the plot) The calculations: 1 – W:B<sub>4</sub>C:TiB<sub>2</sub>, 2 – W:B<sub>4</sub>C:TiB<sub>2</sub>:Bi (10%), 3 – W:B<sub>4</sub>C:TiB<sub>2</sub>:Bi (20%). [11]

Modeling for mixtures with multiple components experiencing PT was also done due to great interest in  $\text{Si}_3\text{N}_4$  and mixtures. 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  $\text{Si}_3\text{N}_4$  with oxide, which were obtained on the basis of the experiments data [17]. The calculation for the mixture of  $\text{Si}_3\text{N}_4$  and periclase  $\text{MgO}$  is shown in Fig. 5(a). The simulated mixture is characterized by the weight fraction wt %  $\text{Si}_3\text{N}_4(95)$   $\text{MgO}(5)$  and the density  $\rho_0 = 3.164 \text{ g/cm}^3$   $m = 1$ .

To increase the temperature under the same conditions, we propose to add bismuth to the powder and use the density and porosity values as in the initial mixture. The relationship between the initial components varies insignificantly. The calculated temperatures along the shock adiabat, presented in Fig. 5(b) for the considered mixture W : B<sub>4</sub>C : TiB<sub>2</sub> and for the same mixture with the addition of 10 and 20% of bismuth, indicate that the temperature rises at a change in the mixture composition. Additional prospects for the use of materials with phase transition, taking into account their unique properties were shown in [11]. We indicated that it is possible to control the thermodynamic parameters of the process by changing the facing shape, when the pressures and temperatures increase with decreasing wall opening angle, and the envelope powder composition, which makes it possible to increase pronouncedly the temperature value at an insignificant change in pressure.

## Conclusion

The equation of state of Mi-Grüneisen type and the condition of thermodynamic equilibrium of the components of the mixture under shock wave loading gives the closed system of equations that determines the mixture thermodynamic parameters. The selected model parameters allows us describe the parameters of mixtures with components that are experiencing a phase transition under shock wave loading. It is possible to change the values of pressure and temperature of the materials used in a wider range, expanding the scope of possible thermodynamic parameters.

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