Thermodynamic parameters of mixtures with epoxy as a component under shock wave loading

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Abstract. The results of numerical experiments on modeling of shock wave loading of mixtures are obtained by using thermodynamic equilibrium model TEC (thermodynamic equilibrium components) are presented. The thermodynamic parameters are modeled for the mixtures that include epoxy resin as a component. The model allows taking into account the phase transition under shock wave loading, when the substance in the region of phase transition is considered as mixture of low-pressure phase and high-pressure phase. Interest in the investigation of compressibility of such mixtures is associated as with the possibility of creating materials that have the required properties and the properties of the materials themselves. The good agreement of these model calculations with the data of different authors that defined on the experiments basis is obtained. The model allows to describe dynamic loading of solid and porous mixtures comprising epoxy resin and various components such as quartz SiO₂, periclase MgO, corundum Al₂O₃, spinel MgAl₂O₄, enstatite Mg₂[Si₂O₆].

1. Introduction

The investigations of thermodynamics parameters of porous materials including, in particular, the solid organic substances under shock-wave loading are of interest in many problems of modern science; in this regard new models appear for the description of the behavior of such materials, for example [1–8]. These investigations are important in solving the applied problems of dynamic compaction, shock-wave synthesis, and other explosive technologies.

Interest in the study of compressibility of mixtures comprising as component epoxy resin due to their properties [9,10]. The composite materials combining the properties of the components are created on base on these mixtures. Epoxy resins are characterized by high resistance to the action of halogens, some acids, alkalis; they also have high adhesion to metals. Additional properties of the composite materials are obtained by using various additives to the mixture. For example, quartz SiO₂ is widely used in optical and electronic devices, in the manufacture of silica refractories and quartz glass. An additional important property of quartz is the existence of polymorphic phase transition under shock wave impact. Substantial change in the volume of such components included in the mixtures allows expanding the range of changes of thermodynamic parameters of the mixtures under shock wave loading. Periclase MgO is important component of magnesite and dolomite refractory. Abrasive materials are produce from corundum Al₂O₃. Spinel MgAl₂O₄ is rare mineral of cubic crystal structure. It is a mixed oxide of magnesium and aluminum (volumetric fraction MgO 28.2%; Al₂O₃ 71.8%). The name of mineral enstatite Mg₂[Si₂O₆] is derived from the Greek words ενστατής (enstates) “the enemy”, “the resistance”,...
which is associated with resistance to the melting of enstatite. In the present work, we show
the capabilities of modeling mixtures of such components. The modeling of thermodynamic
parameters for the mixtures with such components are performed for development of promising
direction obtaining materials with desired properties. The modeling results allow us to determine
the ratio of mixture components with the aim of obtaining the specified parameters of solid and
porous materials after shock waves loading for the synthesis of new materials.

2. Calculation model
In order to calculate thermodynamic parameters of porous mixtures under dynamic loadings,
a model of shock-wave loading with allowance for gas in the pores is used [11–13]. The model
was able to describe the parameters in a wide range of pressures under shock wave loading,
with the possibility of taking into account polymeric phase transition of the components of
the mixtures. The model is based on the assumption of thermodynamic equilibrium of all the
components of a material under shock-wave loading (model TEC—thermodynamic equilibrium
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\[
P(\rho, T) = \rho C(\rho) + P_T(\rho, T), \quad E(\rho, T) = Ec(\rho) + ET(T),
\]

where \( P_T \) and \( Ec \) are the potential and thermal components of pressure and specific
energy, respectively; \( c_T \) is the specific heat capacity; \( T_0 \) is the initial temperature; and
the function \( \Gamma = P_{TC}V/Ec \) that determines the contribution of the thermal component
depends explicitly only on the temperature \( \Gamma(T) \) in the model [11–13]. By taking into account
the pressure region of applicability of this model \( \geq 5 \) GPa that is of interest to us, initial energy
\( E_0 \) of a substance under normal conditions is considered to be equal to zero. Cold pressure
component \( Ec \) is described by a Tait-type equation. Therefore, the thermal and caloric forms
of the equation of state for a condensed component with current density \( \rho \) and initial density \( \rho_0 \)
are as follows:

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

\[
E(\rho, T) = A \frac{\rho}{\rho_0} \left[ \frac{1}{k - 1} \left( \frac{\rho}{\rho_0} \right)^{k-1} + \frac{\rho}{\rho_0} - \frac{k}{k - 1} \right] + ET.
\]

The ideal gas equation of state is taken for a gas. The conditions of dynamic compatibility
at the wave front are written, namely, the conditions of conservation of the mass flux for each
component of the material and the conditions of conservation of momentum and energy fluxes
for the media considered as a whole. The obtained equations, together with the equations of
state of each component, are sufficient to find dependences \( P(U) \) or \( D(U) \) \( P, U, \) and \( D \)
are the pressure, mass velocity, and wave velocity, respectively). These dependences can be treated
as a shock adiabat of a multicomponent material. The following expression can be obtained for
a material with \( n \) condensed components (\( \mu_{i0} \) is the volume fraction of the \( i \)-th phase of the
substance):

\[
P = \frac{\sum_{i=1}^{n} \left( \mu_{i0}/\sigma_i \right) A_i \left( (h_i - (k_i + 1)/(k_i - 1)) \right) \sigma_i^{k_i} + 2k_i \sigma_i/(k_i - 1) - h_i - 1}{\sum_{i=1}^{n} \left( \mu_{i0}/\sigma_i \right) h_i + h_0/\sigma_g (1 - \sum_{i=1}^{n} \mu_{i0}) - 1}.
\]

Here \( h_i = 2/\Gamma_i + 1, i = 1, n, h_0 = 2/(\gamma - 1) + 1; \sigma_i = \rho_i/\rho_0, \sigma_g = \rho_g/\rho_0 \) are the compression
ratio of the corresponding component, \( \mu_{i0} \) are the volume fraction, \( \rho_{i0}, \) \( \rho_0 \) are the density of the \( i \)-th phase of the substance ahead of the shock wave front and behind it, respectively \( (i = 1, \ldots, n, \)
and $g$; $\gamma = 1.41$ (ratio of specific heats); $A_i$, $k_i$ are the coefficients in the equations of state of corresponding condensed component. By adding to equation (5) $n$ relationships that follow from the equations of state of $n+1$ components and expressing the equality in the temperatures of all the components, we finally have $n+1$ equations for $n+2$ unknowns $P$, $\sigma_i$ ($i = 1, \ldots, n$ and $g$), which allow us to construct the shock adiabat of the material. The function $\Gamma = P C_v / E_F$ that determines the contribution of the thermal component depends explicitly only on the temperature $\Gamma(T)$ in the model [11–13].

The model 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 [14]. It is assumed that the volume fraction $\alpha$ of low-pressure phase passed into high-pressure phase in the region of polymorphic phase transition. The beginning of the phase transition is determined from the accordance to experiment.

The dependence of low-pressure phase, turning into the high-pressure phase, we can specify as $\alpha = \tau \Delta E$ in the first approximation in the phase transition region. Here $\tau = (E_f - E_b)^{-1}$, $E_b$ is internal energy at the beginning of the phase transition, $E$ is current internal energy, $\Delta E = E_b - E_f$, $E_f$ 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 $\tau$, defined for one of the porosity, allows us to describe the results for other values of the porosity. As the result, the three regions are set depending on the value of $\alpha$, that determines the volume of low-pressure phase and high-pressure phase of the shock adiabats for the materials with the phase transition [14]:

$$
\alpha = \begin{cases} 
0, & \text{for } E \leq E_b, \\
\alpha, & \text{for } E_b \leq E \leq E_f, \\
1, & \text{for } E \leq E_f.
\end{cases}
$$

3. Modeling results and discussion

The simulation results for the thermodynamic parameters of epoxy resins with average density $\rho_0 = 1.2$ g/cm$^3$ and the data obtained by experiments [15–17] is shown in figure 1 in the variables pressure $P$ versus compression ratio $\sigma$. The truthful description of the available data is obtained. Subsequent calculations showed that the parameters defined for the epoxy resin, allow to describe data both for pure materials and for mixtures of solid and porous with the accuracy of the experiment.

At the moment there is uncertainty about the phase transition in epoxy resin under shock wave loading. The scatter of the experimental data does not allow clear answer now. The authors [18, 19] performed experiments to determine the temperature of shock-wave compression to address this issue. Although the data given in [19], as the authors noted, do not give a definitive answer to the question of the existence of a phase transition, they allow us to estimate the accuracy of the calculations by model TEC. The data obtained on the basis of the experiment for epoxy resin are shown in figure 2 by the solid line the calculations from [19] and the dashed line calculations by model TEC in the variables temperature–pressure. Both the models allow describing the data of most experiments. However, the presence of drop-down points confirms the need for further work in this direction. In this work, the possibility of polymorphic phase transition in the epoxy resin is not taken into account by the model TEC.

The accuracy of the description of thermodynamic parameters of the mixtures, taking into account phase transitions of the components under shock wave loading, was determined by calculations of shock wave loading of mixture with quartz. In figure 3 the results are shown obtained for the mixtures of the epoxy-quartz mixture, volume fraction vol % epoxy (60) SiO$_2$
Figure 1. The shock adiabat of epoxy: solid line is from the calculation with the model TEC; diamonds and squares are from work [15]; dark circles are from work [16]; open circles are from work [17]; dark diamonds are from paper [18].

Figure 2. The shock adiabat for epoxy: solid line is from paper [19]; dotted line is from the calculation with the model TEC; experimental points are from papers [18, 19].

(40) $\rho_0 = 1.66 \text{ g/cm}^3$ consequently. The calculation corresponds well to the data of the experiments until the value of pressure 50 GPa. It is assumed that the phase transition of the components of the mixture starts under the same conditions as for the pure substances. Due to the fact that the calculation was carried out for the mixtures with low porosity, the
Figure 3. Shock adiabat for the epoxy–quartz mixture in coordinates pressure–compression ratio: solid line is the calculation for the mixture taking into account phase transition; dotted line is the calculation for mixture with quartz; dash-dotted is the calculation for mixture with stishovite; open circles are from work [17].

estimated the pressure value to the beginning of the phase transition can be considered justified. This assumption has been confirmed by the calculations of the mixtures with two components undergo phase transition [20].

The parameters that gave the opportunity to reliably describe the thermodynamic parameters of epoxy resins in a wide range of dynamic parameters, has allowed to describe with the precision of the experiment the thermodynamic parameters of the mixtures with other materials, which are characterized by high strength and heat resistance. The calculated and experimental data for these mixtures in the coordinates pressure–compression ratio are shown in figure 4–7. It is necessary to know the composition and density of the mixture for the description of dynamic loading. The component parameters are taken the same as in the description of pure substances. Based on the simulation it can be concluded that the proposed scheme description of the thermodynamic parameters of the mixture under dynamic loads allows to describe the behavior of continuous and porous mixes. The results obtained for the mixture of epoxy resin with periclase, volume fraction, vol % epoxy (60) MgO (40), respectively, \( \rho_0 = 2.219 \text{ g/cm}^3 \), \( m = 0.9 \) are shown in figure 4. The porosity \( m \) is defined as the ratio of the density of the sample to the density of monolithic material.

It should be noted, that the model allows in the absence of complete information about the experimental data to determine with sufficient accuracy the porosity of the mixtures under shock wave loading. Thus the problem of “systematic” deviations was resolved previously for alconite—mixtures of copper and tungsten [11]. The values of porosity were determined for the mixtures according to the model TEC on the basis of data [17] obtained by the experiments. Thermodynamic parameters for the mixture of epoxy resin with corundum, volume fraction, vol % epoxy (60) \( \text{Al}_2\text{O}_3 \) (40), respectively, \( \rho_0 = 2.307 \text{ g/cm}^3 \), \( m = 0.93 \) are described in figure 5.

The modeling results of the thermodynamic parameters for the mixture of epoxy resin with spinel, volume fraction, vol % epoxy (60) \( \text{MgAl}_2\text{O}_4 \) (40), \( \rho_0 = 2.171 \text{ g/cm}^3 \), \( m = 0.97 \) are shown in figure 6.
The experiments data from [17] and modeling results of thermodynamic parameters, which are defined by the model TEC for mixture of epoxy resin with enstatite, volume fraction, vol % epoxy (60) Mg$_2$[Si$_2$O$_6$] (40), respectively, $\rho_0 = 2.017$ g/cm$^3$, $m = 0.93$ are shown in figure 7.

The good correspondence of the calculations to data obtained on the basis of experiments for mixtures with epoxy resin are shown. The deviation of the calculated points for the mixture of quartz at pressure above 60 GPa and for the other mixtures above 80 GPa are probably due, in part, to the possible existence of polymorphic phase transition including for epoxy resin. In the presence of experimental data that allow to accurately, determine the region of phase transition,
Figure 6. Shock adiabats for epoxy–spinel mixture: solid line is from the calculation with the model TEC; open circles are from work [17].

Figure 7. Shock adiabats for the epoxy–enstatite mixture: solid line is from the calculation with the model TEC; open circles are from work [17].

the model TEC can be used in this case. The possibility of calculating the thermodynamic parameters of a mixture with multiple components that are experiencing a phase transition under shock wave loading was shown in [20].

4. Conclusion
The equation of state of the Mie–Grüneisen type together with the thermodynamic-equilibrium condition for the mixture components gives a closed system of equations that defines the parameters of dynamic loading. The assumption on the thermodynamic equilibrium implicitly takes into account the interaction between the components, which becomes especially significant
in the case of porous media. The selected model parameters are allowed to reliably describe the thermodynamic parameters of the pure epoxy resin and mixtures on its basis, including with components experiencing a phase transition under shock wave loading. The parameters of the model for other components of the alloy were determined separately. As a result, in order to describe the behavior of a mixture under dynamic loadings, it is necessary to know only the volume fractions of its components. The present model made it possible to choose the ratios between the mixture components in order to obtain the prescribed characteristics under the shock-wave loading of solid and porous heterogeneous materials.

References
[1] Sundqvist B, Sandberg O and Bäckström G 1977 J. Phys. D: Appl. Phys. 10 1397–403
[2] Bushman A V, Lomonosov I V, Fortov V E and Khishchenko K V 1994 Khim. Fiz. 13(1) 64–81
[3] Lomonosov I V, Fortov V E and Khishchenko K V 1995 Khim. Fiz. 14(1) 47–52
[4] Khishchenko K V, Lomonosov I V, Fortov V E and Shlenskii O F 1996 Dokl. Akad. Nauk 349 322–5
[5] Khishchenko K V, Lomonosov I V and Fortov V E 1996 Equations of state for organic compounds over wide range of densities and pressures Shock Compression of Condensed Matter—1995 ed Schmidt S C and Tao W C (New York: AIP Press) pp 125–8
[6] Khishchenko K V 1997 High Temp. 35 991–4
[7] Khishchenko K V, Zhernekletov M V, Lomonosov I V and Sutulov Yu N 2005 Tech. Phys. 50 197–201
[8] Root S, Mattsson T R, Cochrane K, Lemke R W and Knudson M D 2015 J. Appl. Phys. 118 205901
[9] Lukyanov A A 2010 Eur. Phys. J. B 74 35–45
[10] Dattelbaum D M, Coeb J D, Rigg P A, Scharff R J and Gammel J T 2014 J. Appl. Phys. 116 194308
[11] Kinelovskii S A and Maevskii K K 2013 J. Appl. Mech. Tech. Phys. 54 524–30
[12] Kinelovskii S A and Maevskii K K 2016 High Temp. 54 675–81
[13] Kinelovskii S A and Maevskii K K 2016 Tech. Phys. 61 1244–9
[14] Maevskii K K and Kinelovskii S A 2014 AIP Conf. Proc. 1623 391–4
[15] Trunin R F, Gudarenko L F, Zhernekletov M V and Simakov G V 2006 Experimental Data on Shock Compressibility and Adiabatic Expansion of Condensed Substances 2nd ed (Sarov: RFNC-VNIIEF)
[16] Bushman A V, Efremov V P, Fortov V E, Kanel’ G I, Lomonosov I V, Ternovoi V Ya and Utkin A V 1992 Equation of state of composites under high energy densities Shock Compression of Condensed Matter—1991 (Amsterdam: North-Holland) pp 79–82
[17] Marsh S P 1980 LASL Shock Hugoniot Data (Berkeley: Univ. California Press)
[18] Bordzikovskii S A, Karakhanov S M and Khishchenko K V 2013 Combust., Explos. Shock Waves 49 121–4
[19] Bordzikovskii S A, Voronin M S, Karakhanov S M and Merzhiievskii L A 2014 Phys. Dokl. 59 176–80
[20] Maevskii K K and Kinelovskii S A 2016 AIP Conf. Proc. 1783 020143