Construction of the equations of state for polycrystalline solids for the purpose of the numerical solution of problems of continuous medium mechanics

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Abstract. The equations of state for polycrystalline solids which are in region of compression are developed on experimentally defined shock Hugoniot adiabat and dependence of specific heat on density and temperature. These equations are convenient for the numerical solution of problems of continuous medium mechanics. The numerical method for definition of specific cold energy and the Gruneizen function at $T = 0$ K depending on compression ratio is proposed. Results of comparison for temperatures behind shock wave in sapphire by means of the developed equations of state and other methods are given.

1. Introduction
The equations of state (EOS) [1, 2] are required for the solution of problems of continuous medium mechanics (CMM) by numerical methods [3]. In general case it is convenient to represent EOS in the form of dependences of specific internal energy and pressure on density and temperature [3, 4]. The construction of EOS in such a form requires to meet a conditions of thermodynamic compatibility.

Development of EOS becomes more simple for polycrystalline bodies due to their isotropy and a possibility of application of the Debye theory of specific heat. Moreover the class of polycrystalline bodies includes constructional materials which are important for practice (in particular, metals and their alloys). The representative data sets required for construction of EOS is accumulated for such materials.

The CMM equations (conservation laws) are complemented with tabular wide-range and semi-empirical EOS [2, 5] that leads to a set of difficulties [4, 6] in the numerical solution of these equations. Large times of calculation and deviation from a condition of thermodynamic compatibility at approximation on a two-dimensional grid of temperatures and density are the main of them. The requirements for tabular EOS and their approximations for the solution of CMM problems are formulated in [3, 4].

Thus the wide-range EOS, where the approximations on two-dimensional grids are not required, are necessary for development of effective numerical CMM codes. A significant amount of works (in relation to area of shock compression see, for example, [7, 8, 9]) is devoted to
development of the simplified variants of analytical EOS for the solution of problems of CMM. Unlike these works the Gruneizen function at absolute zero and cold pressure depending on density is offered to be represented in a tabular form (a grid is one-dimensional in this case). Methods of creation of these functions and EOS which takes into account a contribution of electronic components in specific heat are considered in the present article.

2. Basic relations
Data from shock wave experiments in combination with data on its thermophysical properties are traditionally used for construction of the equations of state for substances. In particular the dependence of specific heat on density and temperature can be the basis for creation of EOS. In this case the equations of state can be constructed in the form of ratios like Mi-Gruneizen

\[ E = E(\rho, T) = E_c(\rho) + E_T(\rho, T) = E_c(\rho) + \int_0^T C_v(\rho, T) dT, \]  

\[ P = P(\rho, T) = P_c(\rho) + \Gamma(\rho, t) \rho E_T = \rho \frac{dE_c}{d\rho} + \Gamma(\rho, t) \int_0^T C_v(\rho, T) dT, \]

where \( \rho \) is substance density; \( E, E_c, E_T \) are full cold and thermal specific energy; \( P, P_c, P_T \) are full cold and thermal pressure; \( \Gamma = \Gamma(\rho, T) \) is Gruneizen function; \( C_v \) is specific heat.

Two unknown functions \( E_c(\rho) \) and \( \Gamma(\rho, T) \) (the dependence of specific heat on density and temperature is considered known) are included into EOS (1), (2). They can be found from data of shock – wave compression experiments using a condition of thermodynamic compatibility

\[ \left( \frac{\partial E}{\partial \left(1/\rho\right)} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_\rho - P. \]  

We receive the equation for definition of the Gruneizen function by substituting (1), (2) in (3)

\[ \left( \frac{\partial T E_T \Gamma}{\partial T} \right)_\rho - 2 T E_T \Gamma = \left( \frac{\partial E}{\partial \left(1/\rho\right)} \right)_T, \]

Then we find

\[ \Gamma(\rho, T) = \frac{T}{E_T(\rho, T)} \int_0^T \left( \frac{\partial E_T(\rho, T)}{\rho \partial \left(1/\rho\right)} \right)_T \frac{dT}{T^2}, \]

integrating (4) with an initial condition (it’s considered that at \( T \to 0 \) and \( C_v \to 0 \))

\[ \left. \frac{T E_T \Gamma}{T^2} \right|_{T=0} = \lim_{T \to 0} \frac{C_v TT}{T} = \lim_{T \to 0} C_v \Gamma = 0. \]

By substituting the expression for thermal energy through thermal capacity in (5) and integrating by parts (\( v = 1/\rho \)) we receive

\[ \Gamma(\rho, T) = \frac{E_{T0}}{E_T} T \frac{T}{T_0} \left( \Gamma_0(\rho) + \left( 1 - \frac{T_0}{T} \right) \frac{dE_{T0}}{E_{T0} \partial v} \right) + \frac{T}{E_T} \int_{T_0}^T \left( \frac{\partial C_v}{\rho \partial v} \right)_T \frac{dT}{T} - \frac{1}{E_T} \int_{T_0}^T \left( \frac{\partial C_v}{\rho \partial v} \right)_T dT, \]

where \( \Gamma_0(\rho) \) is the Gruneizen function at a normal temperature.
Let’s note that the constant value of thermal capacity at compression when temperature exceeds normal temperature of \(T_0\) is accepted in the simple models of EOS \([7, 8, 9]\) (\(E_T(T) = E_{T0}(\rho) + C_v(T - T_0)\)). Then the Gruneizen function (6) takes a form

\[
\Gamma(\rho, T) = \frac{E_{T0}}{E_T} \left( \Gamma_0(\rho) + \left( 1 - \frac{T_0}{T} \right) \frac{dE_{T0}}{E_{T0} \rho d\rho} \right)
\]

(7)

Two opportunities follow from (7). If function \(\Gamma_0(\rho)\) is taken from experimental data then the Gruneizen function depends also on temperature. Besides we can demand independence from \(T\) that gives according to (7)

\[
\Gamma(\rho) = \Gamma_0(\rho) = \frac{1}{C_v T_0 - E_{T0}} \frac{dE_{T0}}{\rho d(1/\rho)}
\]

(8)

Integrating by parts (5) for Debye approach when \(E_T(\rho, T) = T e_T(\theta_D(\rho)/T)\) and \(C_v(\rho, T) = C_v(\theta_D(\rho)/T)\), we receive

\[
\Gamma(\rho) = \Gamma_{00}(\rho) = -\frac{d\ln \theta_D}{d\ln(1/\rho)},
\]

(9)

where \(\Gamma_{00}(\rho)\) is the Gruneizen function at absolute zero. According to (9) the Gruneizen function does not depend on temperature in Debye approach. Let’s note that the dependence (9) provides implementation of a condition of thermodynamic compatibility.

In more common case the specific internal energy is defined considering a contribution of electronic components in thermal capacity

\[
E_T(\rho, T) = T e_T \left( \frac{\theta_D(\rho)}{T} \right) + \frac{C_e T^2}{2} \left( \frac{\rho_0}{\rho} \right)^\gamma_e,
\]

(10)

where \(\rho_0\) is substance density under normal conditions; \(C_e\) is coefficient of electronic heat conductivity; \(\gamma_e\) is an electronic analog of Gruneizen coefficient.

We find from (5), (9) and (10)

\[
\Gamma(\rho, T) = \left[ \frac{T}{E_T(\rho, T)} \right] \left[ \Gamma_{00}(\rho) e_T \left( \frac{\theta_D(\rho)}{T} \right) + \gamma_e C_e T \left( \frac{\rho_0}{\rho} \right)^\gamma_e \right],
\]

(11)

According to (11) Gruneizen function depends also on temperature when the contribution of electronic heat capacity is considered. But this function is still defined by functions of one variable \(\theta_D(\rho), \Gamma_{00}(\rho)\).

Thus in all considered special cases the Gruneizen function can be calculated from the known functions of one variable \(\rho\). These functions can be presented in a tabular form.

3. Definition of cold energy and the Gruneizen function in the compression region

The shock compressibility is used for finding the specific cold energy \(E_c = E_c(\rho)\). Hugoniot relation at the front of a shock wave has the form (the index zero notes the values at normal conditions):

\[
E - E_0 = \frac{1}{2} (P_H(\rho) + P_0) \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right)
\]

Using (1), (2) and Hugoniot relation for Debye approach (\(\Gamma(\rho) = \Gamma_{00}(\rho)\)) we find

\[
E_T(\rho, T_H(\rho)) = \psi(\rho) - E^*_c
\]

(12)

\[
\psi(\rho) = \frac{1}{2} (P_H(\rho) + P_0) \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right) + E_{T0}, \quad E^*_c = E_c(\rho) - E_c(\rho_0).
\]
Here \( T_H(\rho) \) is temperature on a shock Hugoniot curve. Let’s note that if the experimental Hugoniot can be approximated by linear dependence \( D = \alpha + \beta U \) between wave and particle speeds (\( D \) is wave speed; \( U \) is particle speed, \( \alpha, \beta \) are experimentally defined coefficients) then the shock compressibility is determined by the known relation

\[
P_H(\rho) = \rho_0 DU = \rho_0 \frac{\alpha^2(1 - \rho_0/\rho)}{[1 - \beta(1 - \rho_0/\rho)]^2}.
\]

The equations of state are applicable on a shock Hugoniot curve too and we have for \( \Gamma(\rho) = \Gamma_0(\rho) \)

\[
- \frac{dE_c^*}{d(1/\rho)} + \Gamma_0(\rho) \rho E_T(\rho, T_H(\rho)) = P_H(\rho).
\]

Function \( \Gamma_0(\rho) \) is calculated for a polycrystalline solid from the known and common relation \( (\gamma = 2t/3) \)

\[
\Gamma_0(\rho_0) = 2\beta - \frac{2 + t}{3}.
\]

The ordinary differential equation of the third order for definition of specific cold energy depending on density follows from (12)-(14)

\[
\frac{d^3 E_c^*}{d\rho^3} = 2 \left( \frac{2 + t}{3} + \frac{P_H(\rho) - \rho^2 dE_c^*/d\rho}{\rho(\psi(\rho) - E_c^*)} - 3 \right) \left( \frac{d^2 E_c^*}{\rho^2 d\rho^2} + (2 - \gamma) \frac{dE_c^*}{\rho^2 d\rho} \right) + (3 - \gamma)(2 - \gamma) \frac{dE_c^*}{\rho^2 d\rho}. \tag{15}
\]

Initial conditions for the equation (15) are set at the normal density \( \rho = \rho_0 \)

\[
E_c^*|_{\rho=\rho_0} = 0, \quad \frac{dE_c^*}{d\rho}|_{\rho=\rho_0} = \frac{P_0}{\rho_0^2} - \Gamma_0 E_{T_0}/\rho_0, \quad \frac{d^2 E_c^*}{d\rho^2}|_{\rho=\rho_0} = - \frac{dP_H}{\rho^2 d\rho}|_{\rho=\rho_0} - \frac{2P_0}{\rho_0^2} - \frac{\Gamma_0 E_{T_0}}{\rho_0^2}(\Gamma_0 - 2).
\]

The first condition is obvious from determination of \( E_c^* \). The second condition follows from (13). The third condition for the second derivative can be received from a condition that a shock Hugoniot and isentrope line have common tangent \( ((\partial P/\partial \rho)_{H0} = (\partial P/\partial \rho)_{S0}) \).

The differential equation (15) is written in a form of a system of three ordinary differential equations of first order and integrated numerically by Runge – Kutta method of the fourth order of accuracy with a variable step on density.

Debye temperature is defined after calculation of function \( E_c^* = E_c^*(\rho) \) and its derivatives

\[
\theta_D(\rho) = \theta_D(\rho_0) \left( \frac{\rho}{\rho_0} \right) \sqrt{\frac{d(\rho^{-\gamma} P_c)/d\rho|_{\rho=\rho_0}}{d(\rho^{-\gamma} P_c)/d\rho|_{\rho=\rho_0}}}, \quad P_c = - \frac{dE_c^*}{d(1/\rho)}.
\]

Then temperature on a shock Hugoniot curve is calculated as the solution of the nonlinear equation (12)

\[
T_H(\rho) e^{\gamma}(\theta_D(\rho)/T_H(\rho)) = \psi(\rho) - E_c^*(\rho).
\]

The system of five differential equations is integrated in more common case when contribution of electronic components in the specific heat (see (10), (11)) taking into account. The differential equations for temperature and Debye temperature having the corresponding initial conditions are added.
4. Equations of state for Sapphire
Sapphire is widely used for measurements of temperature of shock compression of metals and their alloys [10, 11, 12, 13]. Up to now the shock compressibility of sapphire is experimentally defined in pressure range of 80-340 GPa by means of the two stage gas gun [14]. Action of powerful laser radiation was used for measurement of shock compressibility at pressure of 0.7-2 TPa [15, 16, 17].

**Figure 1.** Hugoniot temperature vs density. Experiment: • this work, □[19, 20]. Calculations: ——this work, ·····semiempirical EOS [19], ······SESAME table EOS [20], · ——QMD simulation [21]

Pressure range of of 340-700 GPa experimentally was not studied. We used plane shock compression generator [18] for creation of pressure of this range. Temperature behind the front of the shock wave propagating in sapphire was measured by optic pyrometry methods.

Data on a shock Hugoniot curve [19] were used for construction of sapphire EOS. Specific heat was calculated from Debye theory. The contribution of electronic components in thermal capacity was not considered as sapphire is dielectric under normal conditions.

Numerical and experimental results for sapphire temperature on a shock Hugoniot are shown on a figure 1. Our calculations were made with use of the developed EOS. It is visible that our data of pyrometric measurements are slightly below than results of these calculations.

5. Conclusions
(i) New method for construction of the wide-range EOS for polycrystalline materials is proposed. In this method the experimental data on dynamic compressibility of materials are reproduced with any required accuracy (5% as a rule).
(ii) The proposed EOS are convenient for the solution of problems of CMM as the interpolation of data is required only on one-dimensional tables.

(iii) Comparison of numerical and experimental data for temperatures behind the front of a shock wave demonstrates satisfactory agreement.

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References
[1] Bushman A V, Lomonosov I V, Fortov V E 1992 The equations of state of metals at the high density of energy (Chernogolovka: IPCP RAS)
[2] Fortov V E 2016 Thermodynamics and equations of state for Matter: from ideal gas to quark-gluon plasma (USA: World Scientific Publishing)
[3] Kuropatenko V F 2007 Models of mechanics of continuous media (Chelyabinsk: Chelyabinsk state University)
[4] Kim V V, Lomonosov I V, Ostrik A V 2015 Constructions from composite materials 2(138) 39–45
[5] Sapozhnikov A T, Gerschuk P D, Malyshkina E L, et al 1991 VANT: Math. mod. of phys. proc. 1 9–16
[6] Prokopov V G 2005 VANT: Math. mod. of phys. proc. 4 98–101
[7] Belkheeva R K 2009 The Bulletin of the Nizhny Novgorod State University: Math., Mech. and Inf. 9:3 23–32
[8] Kinelovsky S A, Mayevsky K K 2014 Thermophysics of High Temp. 52, 6 843–852
[9] Ostrik A V, Utkin A V 2017 J. Mat. Phys. and Mech. 31, 1–2 48–51
[10] Tan H, Ahrens T J 1990 High Pressure Research 2, 3 159–182 10
[11] McQueen R G, Isaak D G 1990 J. of Geophys. Res. 95, 21 753–765 11
[12] Anderson W A, Ahrens T J 1996 J. of Geophys. Res. 101(B3) 5627–5642 12
[13] Hare D E, Webb D J, Lee S H, et al 2002 AIP Conf. Proc. 2 1231–1234 13
[14] Erskine D 1994 High-Press. Sci. Techn.-1993, ed. S. C. Schmidt et al 141–143 14
[15] Hicks D G, Celliers P M, Collins G W, et al 2003 PRL 91, 3 035502
[16] Root S, Magyar R, Lemke R, et al 2013 Top. Conf. on the Sh. Comp. of Mat.
[17] Ozaki N, Nellis W J, Mashimo T, et al 2016 Scientific Reports 6:26000
[18] Nikolaev D, Ternovoi V, Kim V, et al 2014 J. of Phys: Conf. Ser. 14 1–5
[19] Kerley G I 2009 Scientific Reports 1306:6877
[20] Miller J, Boehly T R, Meyerhofe D D, et al 2006 Presentation at http://www.lle.rochester.edu/media/publications/presentations/documents/APS06/Miller_APS06.pdf
[21] Liu H, Tse J S, Nellis W J 2015 Scientific Reports 5:12823