Equation of state for rhodium at high pressures

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Abstract. An equation of state has been developed for rhodium in a wide range of changes in the specific volume and internal energy. The results of calculations of the thermodynamic characteristics of this metal are presented in comparison with the available experimental data at high pressures. This equation of state can be used in the numerical simulation of hydrodynamic processes under intense impulse influences on matter.

1. Introduction

To solve problems of numerical simulation of hydrodynamic processes in a substance at a high energy concentration, it is necessary to know the thermodynamic properties of the medium in the form of an equation of state (EOS) [1–5]. In particular, this concerns processes in high-speed collisions of solids [6–9], in the interaction of intense laser radiation [10–14] or particle beams [15, 16] with materials, and in the electric explosion of conductors under the action of a powerful current pulse [17–19]. The EOS that closes the system of equations of motion of matter determines the adequacy of the results of the numerical solution of the problem [20–25].

Rhodium is a refractory metal with high hardness, corrosion resistance and high reflectivity in the visible part of the electromagnetic spectrum. This material is used for the manufacture of elements of nuclear reactors and high-power laser systems that carry intense thermal loads.

In this work, an equation of state for rhodium is proposed for a wide its range of changes in the specific volume ($V$), internal energy ($E$), and pressure ($P$). The chosen form of the equation of state is applicable for modeling adiabatic processes. The thermodynamic characteristics of this metal under conditions of cold compression at zero temperature (zero entropy) and loading in shock waves are calculated. The calculation results are presented in comparison with the available experimental data at high pressures.

2. EOS model

To determine the functional relationship between the specific volume, internal energy and pressure, the EOS model [26] is used. It is defined in the following general form:

$$P(V, E) = P_c(V) + \frac{\Gamma(V, E)}{V} [E - E_c(V)],$$

(1)
where $P_c$ and $E_c$ are the cold pressure and internal energy at zero absolute temperature ($T = 0$); and $\Gamma$ is the ratio of the thermal pressure to the thermal energy density.

Cold compression energy is taken as a function of specific volume:

$$E_c(V) = V_{0c} \left[ a_0 \ln \sigma_c - \frac{3}{2} \sum_{i=3}^{8} \frac{a_i}{i} \sigma_c^{-3/i} + \frac{3}{2} \sum_{i=3}^{8} b_i \sigma_1^{3/i} + \frac{3}{2} \sum_{i=3}^{8} \frac{a_i}{i} - \frac{3}{2} \sum_{i=3}^{8} b_i \right]$$

(2)

for $\sigma_c \geq 1$. Here $\sigma_c = V_0/V$; $V_{0c}$ is the specific volume of the substance under consideration at $T = 0$ and $P = 0$. Expression (2) provides the condition at $\sigma_c = 1$:

$$E_c(V_{0c}) = 0,$$

(3)

The value of the coefficient $b_2$ is found from the condition that the energy at high compression ratios coincides with the energy of a degenerate ideal gas of electrons:

$$b_2 = 3^{2/3} 5^{-1} \pi^{4/3} Z^{5/3} a_0^3 \gamma_{\text{H}} [A \sigma_{0c} V_{0c}]^{-5/3},$$

(4)

where $E_{\text{H}}$ is the Hartree energy; $a_0$ is the Bohr radius; $m_0$ is the unified atomic mass unit; $A$ is the relative atomic mass; $Z$ is the atomic number. The rest of the coefficients $b_i$ and $a_i$ are found from the requirement for the minimum root-mean-square deviation of pressure from the results of the calculation by the Thomas–Fermi model with corrections in a certain range of compression ratios, taking into account the conditions for cold pressure $P_c = -dE_c/dV$, the cold bulk modulus $B_c = -VdP_c/dV$ and its derivative with respect to pressure $B'_c = dB_c/dP_c$ at $\sigma_c = 1$:

$$P_c(V_{0c}) = 0,$$

(5)

$$B_c(V_{0c}) = B_{0c},$$

(6)

$$B'_c(V_{0c}) = B'_{0c}.$$  

(7)

The values of the parameters $V_{0c}$, $B_{0c}$ and $B'_{0c}$ are found from the requirement to satisfy the values of the specific volume $V_0$, isentropic bulk modulus $B_S = -V(\partial P/\partial V)_S$ and its isentropic derivative with respect to pressure $B'_S = (\partial B_P/\partial P)_S$ under normal conditions ($P = P_0$, $E = E_0$).

The energy of the cold substance in the expansion region is determined by another function of the specific volume:

$$E_c(V) = V_{0c} \left[ \frac{a_m}{m} \sigma_c^m + \frac{a_n}{n} \sigma_c^n - \frac{a_m + a_n}{l} \sigma_c^l \right] + E_{\text{sub}}$$

(8)

for $\sigma_c < 1$. This relation satisfies condition (5) and the equality of the sublimation energy in the limit of an infinitely large volume: $E_c = E_{\text{sub}}$ at $\sigma_c \to 0$. The requirement to satisfy conditions (3), (6) and (7) leaves only two free parameters ($l$ and $n$) in relation (8).

The coefficient $\Gamma$ is given in the form of a dependence on the specific volume and internal energy:

$$\Gamma(V, E) = \gamma_1 + \frac{\gamma_c(V) - \gamma_1}{1 + \sigma^{-2/3} [E - E_c(V)]/E_a},$$

(9)

where $\sigma = V_0/V$; the quantity $E_a$ determines the characteristic thermal energy of the transition from the case $\Gamma = \gamma_c(V)$ at $T = 0$ to the case $\Gamma \approx \gamma_1$ for a strongly heated substance. The function $\gamma_c(V)$ is given by the following expression:

$$\gamma_c(V) = 2/3 + \left( \gamma_{0c} - 2/3 \right) \frac{\sigma_n^2 + \ln^2 \sigma_m}{\sigma_n^2 + \ln^2 (\sigma/\sigma_m)}.$$ 

(10)

Here the constant $\gamma_c$ corresponds to the value of the Grüneisen coefficient at zero temperature and normal density; and $\sigma_m$ and $\sigma_n$ are the free parameters.
3. Calculation results

The shock compressibility of rhodium is investigated in experiments with traditional explosive systems [27, 28]. Comparison of the calculated shock adiabat of this metal with experimental data [27, 28] is illustrated in figures 1–3. The calculation is carried out by solving the system of equations (1)–(10) and the law of conservation of energy in the shock front [1]:

\[ E = E_0 + \frac{1}{2} (P + P_0)(V_0 - V). \] (11)

The velocities of the shock front and the matter behind the front are calculated using the laws of conservation of mass and momentum [1]:

\[ U_s = V_0 \frac{P - P_0}{V_0 - V}, \] (12)

\[ U_p = \sqrt{(P - P_0)(V_0 - V)}. \] (13)

Good agreement between the calculated shock adiabat and experimental data [27, 28] over the entire range of velocities of the shock wave \( U_s \) and matter behind the shock front \( U_p \), pressures \( P \) and compression ratios \( \sigma \) testifies to the quality of the resulting equation of state for rhodium.

![Figure 1. Shock adiabat of rhodium: line—the result of the calculation of the present work; markers—experimental data (I1 – [27]; I2 – [28]).](image)
Figure 2. Shock adiabat of rhodium: line – the result of the calculation of the present work; markers – experimental data (I1 – [27]; I2 – [28]).

Figure 3. Shock adiabat (H) and cold curve ($P_c$) of rhodium: lines – the result of the calculation of the present work; markers – experimental data (I1 – [27]; I2 – [28]).
Conclusions
Thus, the proposed equation of state for rhodium is in good agreement with the available shock-wave data and can be effectively used in the numerical simulation of hydrodynamic processes at high pressures.

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