THERMODYNAMICALLY COMPLETE EQUATIONS OF STATE FOR α-, ε-, AND γ-IRON

A. V. Zhukov

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The numerical model of $\alpha \leftrightarrow \varepsilon$ phase transition in iron in stress waves described in [1] contains equations of state with a limited range of applicability. They do not consider thermal excitation of conduction electrons and the presence of and $\alpha - \varepsilon$-triple point on the phase equilibrium curve, the effect of which should appear in shock loading of porous or preheated specimens. The present study will offer thermodynamically complete equations of state for the α-, ε-, γ-phases of iron, free of these shortcomings.

A slight modification of the method developed in [2] allows writing the following equation for the thermodynamic entropy potential S as a function of the intrinsic variables density ρ and specific internal energy E:

$$S(\rho, E) = S_0 + h \ln(1 + y + Ly^2), \quad y = \frac{E - E_s(\rho)}{hT_0\Theta(\rho)}, \tag{1}$$

where $E_S(\rho)$ is the energy on the isentrope passing through the initial point (pressure p = 0, temperature T = 293°K); h = 3R/A = 0.4466 kJ/(kg·deg); L = $\nu T_0/R/6$ = 0.029; ν is the electronic specific heat coefficient, identical for all phases; R is the ideal gas constant; A is atomic weight; and Θ is the relative characteristic temperature.

To represent the functions E_S and Θ we use the same expressions as [1]:

$$E_s(\rho) = \frac{B_0}{\rho_0}\frac{9}{2\mu^2}[e^{2\mu(1-x)} - 2e^{\mu(1-x)} + \beta_0], \tag{2}$$

$$\Theta(\rho) = e^{\gamma_0(1-x^3)}, \quad x = (\rho_0/\rho)^{1/3}.$$

Here B_0 is the modulus of volume adiabatic compressibility; γ_0 is the Gruneisen thermodynamic coefficient; and μ is a parameter of the expression.

One can obtain expressions for the temperature $1/T = \partial S/\partial E$, pressure $p = -T\rho^2\partial S/\partial\rho$, and other quantities from Eqs. (1), (2) in the conventional manner.

Table 1 presents the parameters of Eqs. (1), (2) for the α-, ε-, γ-phases of iron. The normalizing constants S_0, β_0 were chosen to provide an identical level for calculation of the energy and entropy of all phases relative to the corresponding values for the α-phase under normal conditions. The parameters are defined so as to optimally describe experimental phase boundaries, discontinuities in the thermodynamic quantities thereon, shock adiabats of the α-, ε-phases, and the isobars of the γ-phase.

Without considering the kinetic aspects of the phase transitions, we will present a number of examples to illustrate the possibilities of the proposed equations. Figure 1 shows a phase diagram defined by equality of the thermodynamic potentials $\Phi = E + p/\rho - TS$. The calculated parameters of the triple point p = 10.4 GPa, T = 750°C are close to the values presented in [4, 5].

Table 2 shows changes in thermodynamic quantities at the triple point. The entropy changes show fair agreement between the present calculations and the values of [4], while for the change in volume the divergence is more marked. This is related to the use in [4] of a low value of Δv for the $\alpha \leftrightarrow \varepsilon$-transition. Comparison of the present calculations

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TABLE 1

Phase	ρ_0, $\frac{kg}{10^3 m^2}$	B_0, GPa	γ_0	μ	β_0	S_0, $\frac{kJ}{kg \cdot deg}$
α	7,85	169	1,69	3,56	1,0	0
γ	8,13	180,7	1,90	3,646	1,015974	0,105
ε	8,36	197,9	1,94	3,755	1,011806	0,02

Note: $\beta_0^{\gamma} = \frac{B_0^{\alpha} \rho_0^{\gamma} \mu_{\gamma}^2}{B_0^{\gamma} \rho_0^{\alpha} \mu_{\alpha}^2}$, $\beta_0^{\varepsilon} = \frac{B_0^{\alpha} \rho_0^{\varepsilon} \mu_{\varepsilon}^2}{B_0^{\varepsilon} \rho_0^{\alpha} \mu_{\alpha}^2}$.

TABLE 2

Transition	Source	Δv, $\frac{cm^3}{kg}$	ΔS, $\frac{kJ}{kg \cdot deg}$
$\alpha \leftrightarrow \varepsilon$	calculat.	—6,48	0,0223
	[4]	—4,92	0,0224
$\varepsilon \leftrightarrow \gamma$	calculat.	2,82	0,0823
	[4]	2,42	0,0863
$\gamma \leftrightarrow \alpha$	calculat.	3,66	—0,105
	[4]	2,50	—0,109

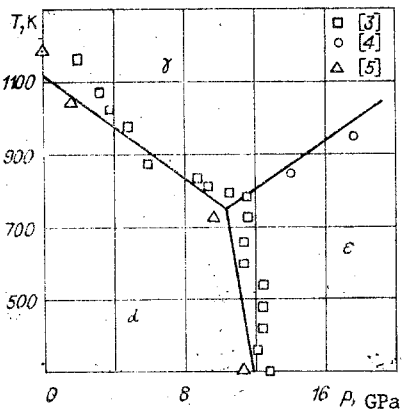

Fig. 1

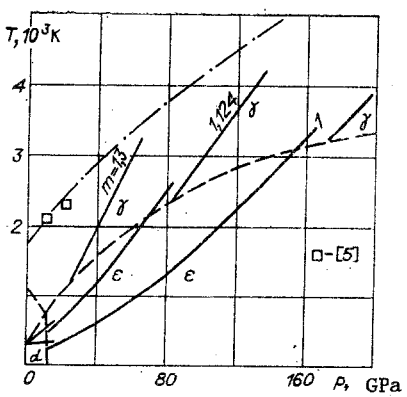

Fig. 2

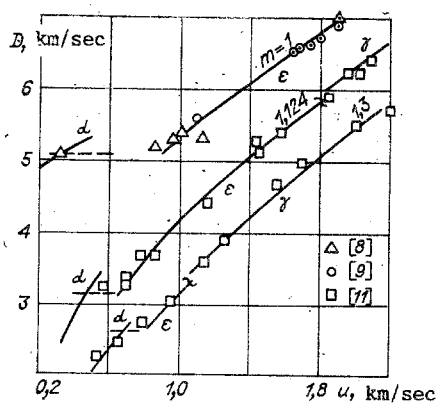

Fig. 3

with the experimental results of [6] and theory of [7] on volume change for the $\alpha \leftrightarrow \varepsilon$- and $\alpha \leftrightarrow \gamma$-transitions indicates the validity of the values presented.

The dashed line of Fig. 2 shows the predicted $\gamma \leftrightarrow \varepsilon$-phase equilibrium at pressures to ~200 GPa. The quantity ΔS changes insignificantly, decreasing slightly, while Δv decreases by more than order of magnitude. Also shown are calculated shock adiabats of stable and metastable phases, defined by the equation $2E = p(mv_0^{\alpha} - v)$, where m is the porosity of the α-phase in the initial state. The dash-dot line indicates fusion by Lindenman's criterion [2].

Using the coordinates mass velocity u, shock wave front velocity D, Fig. 3 shows calculated adiabats, with the dashed lines being boundaries for loss of stability in the α-phase, and the wavy lines, similar boundaries for the ε-phase. The points show experimental results. There is fair agreement between calculation and experiment. However while there is no doubt of the presence of the $\alpha \leftrightarrow \varepsilon$-transition on the experimental adiabats, it is difficult to speak of the $\varepsilon \leftrightarrow \gamma$-transition, since the difference between the calculated adiabats of the ε- and γ-phases is comparable to the experimental uncertainty.

The $\alpha \leftrightarrow \gamma$ transition can be observed in preheated specimens at temperatures up to ~800°K. Change in the initial temperature does not lead to a significant shift in the phase adiabats relative to each other.

The study of the equations of state presented above shows that they may be used for analysis and numerical simulation of phase transitions in compression waves over a wide range of initial conditions.

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