THERMODYNAMIC DESCRIPTION OF THE BEHAVIOR
OF SHAPE MEMORY ALLOYS BY AN ADDITIVE GIBBS POTENTIAL

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Conditions of satisfying the dissipative inequality are found for the case where the Gibbs potential of a shape memory alloy (SMA) *is assumed to be additive. The effective specific heat of the* SMA *is obtained as a function of temperature, strain, and strain rate in direct and reverse thermoelastic martensite transformations. A coupled one-dimensional problem of direct and reverse transformations in an* SMA *rod is solved.*

Key words: *shape memory alloy, additive Gibbs potential, dissipative inequality.*

Mechanical phenomena typical of shape memory alloys (SMA) are described from the viewpoint of rational thermodynamics in [1–3]. It is normally assumed that the thermodynamic potential of the SMA, which is a two-phase medium, consists of two parts: additive and non-additive. It was assumed in various papers that the non-additive part (the so-called energy of phase interaction, energy of mixing, etc.) possesses various properties usually contradicting each other. In these works, the non-additive part is determined by formulas that have not been adequately justified. In the present paper, we consider the possibility of a thermodynamic description of the SMA behavior without non-additive parts in the Gibbs potential. Most papers dealing with the description of the thermodynamic behavior of the SMA are based on these or those *a priori* hypotheses concerning the values of dissipation or dissipation rates in these materials. The model proposed here does not use such hypotheses.

For an SMA consisting of austenite and martensite phases, the dissipative inequality has the form [2]

$$D = T\left(\rho\dot{S} + \left(\frac{q_i}{T}\right)_{,i}\right) = -\rho\left(\frac{\partial\psi}{\partial T} + S\right)\dot{T} - \left(\rho\frac{\partial\psi}{\partial\sigma_{ij}} + \varepsilon_{ij}^{eT}\right)\dot{\sigma}_{ij} + \sigma_{ij}'\dot{\varepsilon}_{ij}^{ph} - \rho\frac{\partial\psi}{\partial q}\dot{q} - \frac{q_iT_{,i}}{T} \geqslant 0. \tag{1}$$

Here D and ψ are the dissipation rate and Gibbs potential obtained from the expression for the free energy by the Legendre transform with the use of thermoelastic strains ε_{ij}^{eT}, S is the entropy, T and ρ are the absolute temperature and density, respectively, q is the volume fraction of the martensite phase, σ_{ij} and ε_{ij}^{ph} are the macroscopic stresses and phase strains, respectively, and q_i are the components of the heat-flux vector; the primed quantities are deviator components; the subscript after the comma indicates the derivative with respect to the corresponding coordinate.

The Gibbs potential for the austenite–martensite medium is taken in the form $\psi = q\psi_1 + (1 - q)\psi_2$, where

$$\psi_m = -\frac{\sigma_{kk}^2}{6K_m\rho} - \frac{\sigma_{ij}'\sigma_{ij}'}{4G_m\rho} - \frac{\alpha\sigma_{kk}}{\rho}(T - T_0) + C_\sigma\left(T - T_0 - T\ln\left(\frac{T}{T_0}\right)\right) - S_{0m}T + U_{0m} \tag{2}$$

are the Gibbs potentials for martensite ($m = 1$) and austenite ($m = 2$), K_m and G_m are the tripled volume and shear moduli, S_{0m} and U_{0m} are the densities of entropy and internal energy in an unloaded state at a reference temperature T_0, α is the coefficient of temperature expansion, and C_σ is the heat capacity at constant stresses. As a result, we obtain an expression for ψ of the form (2), where the subscript m has to be omitted at all quantities:

$$S_0 = S_{02} - q\Delta S_0, \qquad U_0 = U_{02} - q\Delta U_0,$$

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$$\Delta S_0 = S_{02} - S_{01} > 0, \qquad \Delta U_0 = U_{02} - U_{01} > 0.$$

Assuming that two first terms in the right side of Eq. (1) are equal to zero, we can obtain the constitutive relations for entropy

$$S = \alpha\sigma_{kk}/\rho + C_\sigma \ln(T/T_0) + S_0, \tag{3}$$

and elastic and temperature-induced strains. Using the Fourier law for the heat-flux vector

$$q_i = -k_q T_{,i}, \tag{4}$$

where k_q is the thermal conductivity assumed to be identical for the austenite and martensite phases, we can ensure that the last term in the right side of Eq. (1) is non-negative. Hence, we obtain the following formulation of the "mechanical" part of the dissipative inequality:

$$D_1 = \sigma'_{ij}\dot{\varepsilon}^{ph}_{ij} + (\rho(\Delta U_0 - T\Delta S_0) + Z(\sigma))\dot{q} \geqslant 0, \tag{5}$$

$$Z(\sigma) = \frac{\Delta K \sigma_{kk}^2}{6K_1 K_2} + \frac{\Delta G \sigma_i^2}{6G_1 G_2}, \quad \Delta K = K_2 - K_1, \quad \Delta G = G_2 - G_1, \quad D = D_1 - \frac{T_{,i} q_i}{T}.$$

Let the direct martensite transformation from the austenite state and the reverse transition occur in the absence of macroscopic stresses. In such processes, the macroscopic phase deformations of the shape are zero [4], and inequality (5) can be written as

$$\Delta S_0 (T^* - T)\dot{q} \geqslant 0, \qquad T^* = \Delta U_0 / \Delta S_0, \tag{6}$$

where T^* is the temperature of thermodynamic equilibrium of the phases. According to Eq. (6), the direct transformation ($\dot{q} > 0$ and $\dot{T} < 0$) can occur only at temperatures below the thermodynamic equilibrium point, and the reverse transformation ($\dot{q} < 0$ and $\dot{T} > 0$) can occur only at temperatures above the thermal equilibrium temperature. Therefore, the dissipative inequality is satisfied in thermoelastic martensite transformations in a state free from macroscopic stresses if the following two-sided inequality holds:

$$M_s^0 \leqslant T^* \leqslant A_s^0 \tag{7}$$

(M_s^0 and A_s^0 are the start temperatures of the direct and reverse martensite transformation of the unloaded material, respectively).

In the direct and reverse transformations under the action of macroscopic stresses, the phase strain rate is assumed to satisfy the constitutive relations

$$\dot{\varepsilon}^{ph}_{ij} = c_0 \sigma'_{ij}\dot{q}, \qquad \dot{\varepsilon}^{ph}_{ij} = \varepsilon^{ph0}_{ij}\dot{q}/q_0, \tag{8}$$

which are a particular case of more generic constitutive relations proposed in [5]. Here ε^{ph0}_{ij} and q_0 are the values of ε^{ph}_{ij} and q in the beginning of the reverse-transformation stage considered. Substituting Eq. (8) into Eq. (5), we obtain

$$2c_0\sigma_i^2/3 + \rho(\Delta U_0 - T\Delta S_0) + Z(\sigma) \geqslant 0, \qquad \sigma'_{ij}\varepsilon^{ph0}_{ij}/q_0 + \rho(\Delta U_0 - T\Delta S_0) + Z(\sigma) \leqslant 0. \tag{9}$$

Let the start temperatures M_s^σ and A_s^σ of the direct and reverse transformations in the presence of stresses be determined by the formulas

$$M_s^\sigma = M_s^0 + k\sigma_i + \frac{\Delta K \sigma_{kk}^2}{6K_1 K_2 \rho \Delta S_0}, \qquad A_s^\sigma = A_s^0 + \frac{\sigma'_{ij}\varepsilon^{ph0}_{ij}}{\rho\Delta S_0 q_0} + \frac{Z(\sigma)}{\rho\Delta S_0}. \tag{10}$$

Taking into account Eq. (10) and the fact that $T < M_s^\sigma$ in the direct transformation and $T > A_s^\sigma$ in the reverse transformation, we obtain the following relations from inequality (9):

$$2c_1\sigma_i^2/3 - \rho\Delta S_0 k\sigma_i + \rho(\Delta U_0 - M_s^0 \Delta S_0) \geqslant 0, \qquad c_1 = c_0 + \Delta G/(4G_1 G_2); \tag{11}$$

$$\rho(\Delta U_0 - A_s^0 \Delta S_0) \leqslant 0. \tag{12}$$

Inequality (11) is valid for all non-negative values of σ_i if the first inequality in (7) holds and the transition entropy ΔS_0 is bounded from above:

$$\Delta S_0 \leqslant 4\Delta U_0/(2M_s^0 + \sqrt{4(M_s^0)^2 + 6\rho\Delta U_0 k^2/c_1}). \tag{13}$$

TABLE 1

Alloy	M_s^0, K	A_s^0, K	ΔU_0, J/kg	ΔS_0, J/(kg·K)	T^*, K	k, K/MPa	c_0, MPa^{-1}	$T^* - M_s^0$, K	$\Delta T_{\min}$, K
TiNiCu	324	341	38 245	113.71	336.3	0.11	0.00032	12.3	10.5
Ti–48.7% Ni	338	360	35,931	102.50	350.5	0.10	0.00024	12.5	10.0
Ti–51.5% Ni	160	215	10,179	52.85	192.6	0.19	0.00028	33.0	18.0

Condition (13) can be written as

$$T^* - M_s^0 \geqslant \Delta T_{\min} = (\sqrt{(M_s^0)^2 + 3\rho\Delta U_0 k^2/(2c_1)} - M_s^0)/2. \tag{14}$$

According to Eq. (14), the direct transformation of the unloaded material cannot begin merely when the decreasing temperature reaches the temperature of thermodynamic equilibrium T^*. Some "overcooling" should occur first; the lower boundary of this overcooling is determined by the value of $\Delta T_{\min}$ increasing with increasing amount of latent heat ΔU_0. Inequality (12) holds if the second inequality in (7) is valid. Hence, in contrast to the direct transformation, the condition of a non-negative dissipation rate in the reverse transformation of the loaded material means that no "overheating" is needed for the reverse transformation in the unloaded material to begin. The reverse transformation can start at the moment when the increasing temperature reaches the thermodynamic equilibrium point T^*.

The experimental data of [3] for three SMAs and the values of k, c_0, $T^* - M_s^0$, and $\Delta T_{\min}$ calculated on the basis of these data are listed in Table 1. It follows from Table 1 that the conditions of dissipative inequalities (7) and (14) are satisfied for all materials listed. Restriction (13) on the magnitude of the transition entropy is not violated either.

According to (1) and the last formula in (5), we have

$$D_1 = T\rho\dot{S} + q_{i,i}. \tag{15}$$

Substituting expressions (4) and (5), and formula (3) differentiated in time into (15), we obtain

$$k_q\Delta T = \rho C_\sigma \dot{T} + T\alpha\dot{\sigma}_{kk} - \sigma'_{ij}\dot{\varepsilon}^{ph}_{ij} - (\rho\Delta U_0 + Z(\sigma))\dot{q}. \tag{16}$$

If the phase transitions occur in the absence of macroscopic stresses, it follows from Eq. (16) that

$$A(T) = \frac{\dot{Q}}{\dot{T}} = C_\sigma - \Delta U_0 \frac{dq}{dT}, \tag{17}$$

where $A(T)$ is a function proportional to the function corresponding to the experimental dependence of the differential scanning calorimetry of SMA samples in phase transformations. Thus, within the framework of the model with the additive Gibbs potential, there exists a certain dependence (17) between the shape of the curves of the differential scanning calorimetry and the diagram of the transition in the absence of stresses, which allows obtaining the transition diagram from experimental data.

In the presence of varying stresses, relation (16) with allowance for Eq. (8) can be written as

$$k_q\Delta T = \rho C^* \dot{T} + \varphi(\sigma, \dot{\sigma}, T), \qquad C^* = C_\sigma + \chi(\sigma, T), \tag{18}$$

in the case of the direct transformation, we have

$$\chi(\sigma, T) = \frac{2c_0\sigma_i^2/3 + \rho\Delta U_0 + Z(\sigma)}{\rho(M_s^0 - M_f^0)} f'\left(\frac{M_s^\sigma - T}{M_s^0 - M_f^0}\right),$$

$$\varphi(\sigma, \dot{\sigma}, T) = T\alpha\dot{\sigma}_{kk} - \chi(\sigma, T)\left(\rho k\dot{\sigma}_i + \frac{\Delta K\sigma_{mm}\dot{\sigma}_{kk}}{3\Delta S_0 K_1 K_2}\right),$$
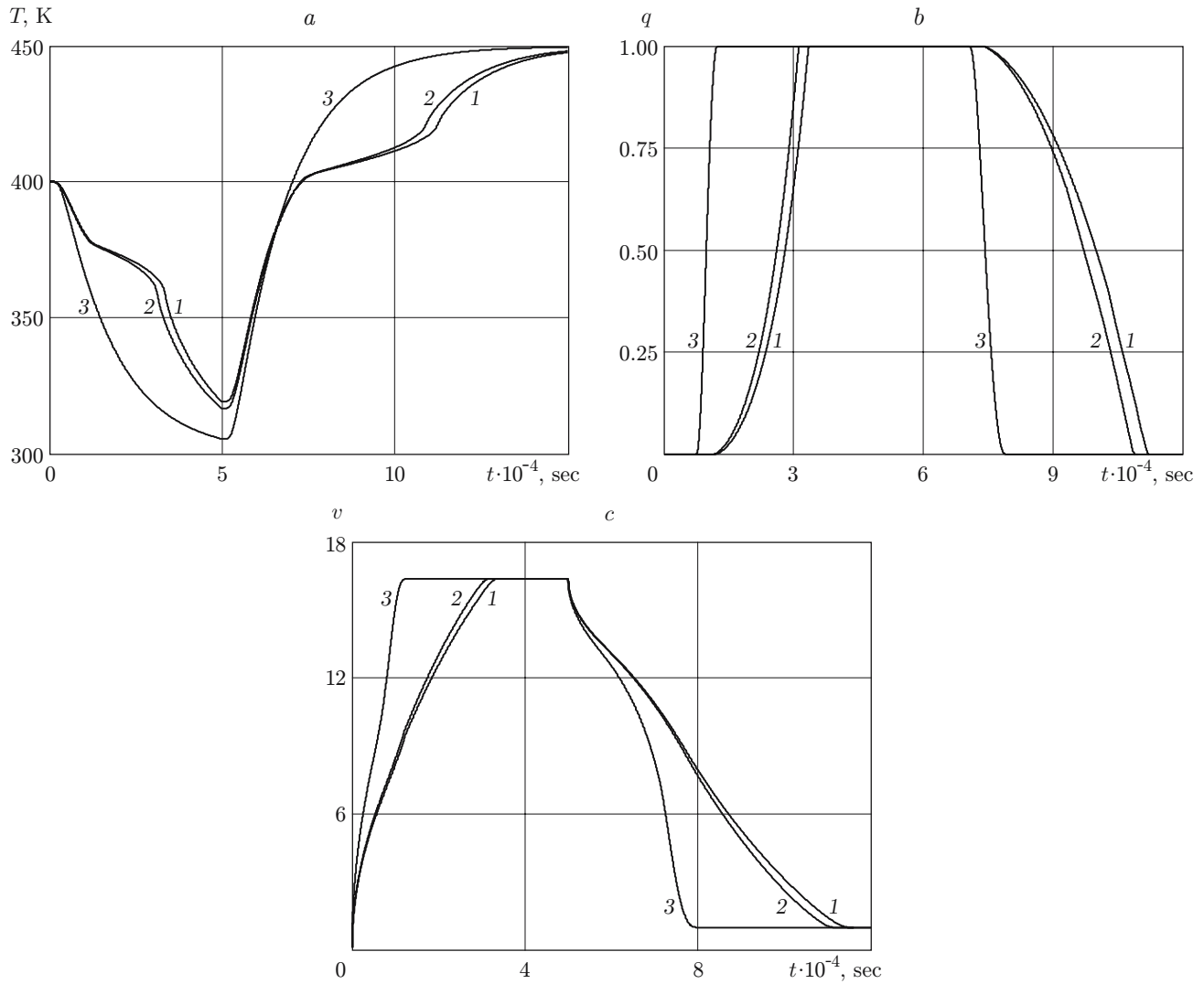
Fig. 1. Temperature (a), phase-composition parameter (b) at the mid-point of the rod, and longitudinal displacement of the non-fixed end of the rod (c) as functions of time in direct and reverse transformations: the problem is solved with allowance for latent heat and dissipation (1), with allowance for latent heat only (2), and with no allowance for latent heat and dissipation (3).

and in the case of the reverse transformation, we obtain

$$\chi(\sigma, T) = \frac{\sigma'_{ij}\varepsilon_{ij}^{ph0}/q_0 + \rho\Delta U_0 + Z(\sigma)}{\rho(A_f^0 - A_s^0)}\, f'\Big(\frac{A_f^\sigma - T}{A_f^0 - A_s^0}\Big),$$

$$\varphi(\sigma, \dot\sigma, T) = T\alpha\dot\sigma_{kk} - \frac{\chi(\sigma, T)}{3\Delta S_0}\Big(\frac{3\varepsilon_{ij}^{ph0}\dot\sigma'_{ij}}{q_0} + \frac{\dot\sigma_{kk}\sigma_{mm}\Delta K}{K_1 K_2} + \frac{\dot\sigma_i\sigma_i\Delta G}{G_1 G_2}\Big).$$

The function $q = f(t)$ is the dependence of the phase-composition parameter on the reduced temperature t [$t = (M_s^0 - T)/(M_s^0 - M_f^0)$ in the direct transformation and $t = (A_f^0 - T)/(A_f^0 - A_s^0)$ in the reverse transformation]; $f' = df/dt$. If the phase transitions occur under the action of constant stresses, we have to use $\varphi = 0$ in Eq. (18).

With the use of Eqs. (18) and (8), Hooke's law for elastic strains, and linear expressions of strains via displacements in direct and reverse transformations that occur under the action of constant stresses $\sigma^+ = \sigma^- = 400$ MPa (uniaxial tension), a coupled one-dimensional problem of the strain, phase, and temperature state of

545

an SMA rod of unit length with a constant section was solved; one end of the rod cannot move in the longitudinal direction, and the other end experiences the action of a constant tensile load. The side surfaces of the rod are free from stresses and are thermally insulated; heat transfer occurs at the end faces only. The initial temperature is identical at all points of the rod $[T(0, x) = 400$ K$]$ and exceeds the start temperature of the direct martensite transformation $M_s^\sigma = 393$ K. The end faces of the rod in the case of cooling and corresponding direct transformation have a temperature constant in time and uniformly distributed over the surface of the end faces $T(t, 0) = T(t, 1)$ = 300 K; this temperature is lower than the finish temperature of the direct transformation $M_f^\sigma = 373$ K. When the rod is heated, the temperature of the end faces increases in a jumplike manner to $T(t, 0) = T(t, 1) = 450$ K, exceeding the finish temperature of the reverse transformation $A_f^\sigma = 423$ K. The direct transformation occurs up to the time $t_1 = 5 \cdot 10^4$ sec. As the initial condition in the problem of the reverse transformation, we used the temperature distribution obtained at $t = t_1$ from the solution of the problem of the direct transformation. The material constants were assumed to have the values $c_0 = 0.000\,283$ MPa^{-1} and $k = 0.2$ K/MPa. The solution was obtained with the use of the piecewise-quadratic approximation of the transition diagram

$$f(t) = \begin{cases} 2t^2, & 0 \leqslant t \leqslant 1/2, \\ 1 - 2(t-1)^2, & 1/2 \leqslant t \leqslant 1, \end{cases}$$

of the corresponding piecewise-linear approximation of the curve of differential scanning calorimetry, as it follows from Eq. (17).

Figure 1 shows the time evolution of temperature, the phase-composition parameter at the mid-point of the rod, and the dimensionless parameter $v = E_2 u/(L\sigma)$ of longitudinal displacement $u = u(t, 1)$ of the non-fixed right end face of the rod. It follows from Fig. 1 that the lack of allowance for latent heat leads to a significant change in the problem solution. The neglect of dissipation can also give significant errors.

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