

Thermodynamic models of pseudoelastic behaviour of shape memory alloys

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WITHIN THE FRAMEWORK of classical thermodynamics two workable models of pseudoelastic behaviour of shape memory alloys are developed. The so-called R -model undergoes only reversible processes and constitutes the generalization of the classical Maxwell model of phase transformation. The other model (R_L -model) includes interaction energy. It predicts formation of external and internal hysteresis loops, and complies with the Clausius-Duhem inequality. The full set of coupled incremental constitutive relations are derived for both models. They enable us to determine phase composition, stress and heat exchange with surroundings under imposed strain and temperature variations, and are presumed to be valid at complex stress state. Specific form of kinetic law for phase transformations is suggested which contains only two constants.

Notation

$\text{tr } \mathbf{A} \rightarrow A_{mm}$; $\mathbf{A} \cdot \mathbf{B} \rightarrow A_i B_i$ or $A_{ij} B_{ij}$, $\mathbf{AB} \rightarrow A_{ij} B_j$ or $A_{ij} B_{kl}$.

1. Introduction

SINCE THE TIME of discovery of shape memory effect (in gold-cadmium alloy at the beginning of fifties), the number of alloy systems showing this effect has gradually increased, together with the systematic growth of the area of their applications. There is no doubt that complicated („anomalous”) behaviour of these alloys under applied thermomechanical loadings is caused by ongoing forward martensitic and reverse martensite-parent phase transformations. The behaviour has been intensively investigated from the metallurgical point of view, and the results gave better understanding of the fundamental mechanisms of shape memory phenomenon, e.g. the mechanism of twin boundary movement in the martensite phase, mechanism of transformation from one type of martensite phase into another type, and the effect of ageing by diffusion [1-5].

At the same time the numerous experiments performed in usual mechanical laboratories displayed the typical uniaxial response of the alloys to the imposed stress cycle (cf. e.g., the review [6]). Presuming that the stress amplitude is smaller than the usual yield stress of weaker phase, one can roughly distinguish three temperature ranges corresponding to different response:

a) At temperature $T > A_f^0$ (A_f^0 being the conventional austenite-finish temperature at stress-free state, frequently employed in engineering) in vicinity of A_f^0 , the typical pseudoelastic behaviour is observed (cf. Fig. 3). It is characterized by formation of closed hysteresis loop caused by ongoing forward martensitic and reverse martensite-parent phase transformations. In tension the extra-strain due to martensitic transformation is positive, whereas in compression it is negative, just opposite to the situation observed when reverse martensite-parent phase transformation takes place in the strain recovery part of the hysteresis loop. In this temperature range at stress-free state the specimen returns to its original shape after every thermomechanical loading-unloading path.

b) In the temperature range $M_s^0 < T \leq A_f^0$, where M_s^0 is the conventional martensite-start temperature at stress-free state, certain amount of permanent strain is observed after unloading, provided that the stress amplitude is sufficiently large. This is due to incomplete reverse transformation. The permanent strain may be relatively large at temperatures $T \leq A_s^0$ ($A_s^0 \geq M_s^0$ is the conventional austenite-start temperature at stress-free state) where the reverse transformation is precluded. It is sometimes said that in this temperature range the pseudoelasticity is coupled with inelasticity ("plasticity") [7].

c) In the temperature range $M_f^0 < T \leq M_s^0$ (M_f^0 being the conventional martensite-finish temperature) the specimen is initially in two-phase state, and every thermomechanical process terminating at stress-free state produces a permanent strain. No reverse transformation proceeds, and the stress-induced martensite formed from the residual parent phase has usually different metallurgical character from the initial temperature-induced martensite.

The experiments have also confirmed one of the most important features of the stress-induced martensitic transformations in shape memory alloys: they produce negligible volumetric and large distortional changes. Contrary to the martensite formed in conventional steel elements, where volumetric changes are dominant and are main sources in generation of the stresses during e.g. the heat treatment operations (cf. [8]), in the case of shape memory alloys the distortional changes in shape associated with martensitic transformations determine the mechanical behaviour of alloys.

In view of existence of strong cross-effect between the thermomechanical interactions and internal phase transformations, the development of physically plausible and possible simple constitutive equations for shape memory alloys is not an easy task. In the simple situation, when current temperature, stress, strain and amount of martensite (weight fraction) is known, they should enable us to determine, e.g., the incremental changes in stress, phase composition and heat exchange with surroundings under prescribed incremental changes in strain and temperature. To this end use of concepts of thermodynamics is instrumental. Some attempts have already been made (cf. e.g., [9–13]). However, in all these studies either the thermodynamical potential has not been specified or/and the implications of the Clausius–Duhem inequality has not been investigated. Just recently MÜLLER [14], and MÜLLER and XU [15] have presented a satisfactory one-dimensional theory for the pseudoelastic temperature range, based on a non-convex free energy function that includes also effects of interactions between the phases. The effects are described by an additive part that depends solely on weight fraction z of martensite and vanishes at the beginning and at the end of forward and reverse transformations. Among others, they have shown that the width of the bounding hysteresis loop is determined by the interaction energy, and presented a number of convincing arguments on the way of possible creation of internal hysteresis loops under more complex deformation paths. The need for introduction of the interaction energy has also been emphasized by DELAEY *et al.* [16], and recently RANIECKI and TANAKA [17] applied a method of continuum thermodynamics to show that incremental interaction energy is directly connected with the surface average of the jump of elastic potential energy at all moving phase interfaces observed at microscale in generic incremental time elapsed.

The growing range of applications of shape memory alloys and the lack of the theoretical basis for the design of structural elements call for the development of appropriate 3-dimensional models that could also be used in non-isothermal situations. In this paper we generalize I. Müller concepts, and attempt to develop two such models, even though

there is still very little evidence on the behaviour of shape memory alloys under complex stress states. We believe that the models will help to systematize the research on the behaviour of these alloys, both experimental and theoretical. The models are presumed to be valid only in the temperature range of pseudoelastic behaviour ($T > A_f^0$) of shape memory alloys. The developed so-called R -model in the sense of thermodynamics is an "ideal device" that undergoes only reversible processes. In fact, it is a generalizations of the classical Maxwell model of phase transformation (cf. [18]). The more realistic R_L -model includes interaction energy and predicts formations of external and internal hysteresis loops in a way that is consistent with the requirements imposed by Clausius–Duhem inequality. In the case of full isotropy it employs only seven additional material constants with respect to conventional linear thermoelasticity. They are not determined here for any specific shape memory alloys. This will be done in a separate note.

2. R -model of ideal pseudoelastic behaviour.

2.1. Free energy at non-equilibrium

Suppose that a non-equilibrium state of a two-phase piece of an alloy is described by the following extended set of independent variables: ϵ_α ($\alpha = 1, 2$) — total intrinsic strains of both phases [strains averaged over instantaneous masses of parent (austenite) phase, $\alpha = 1$, and product (martensite) phase, $\alpha = 2$], h — a set of internal variables representing the current orientations of martensitic active systems in a representative volume V (habit planes plus directions of motions) together with the phase distortions under actual stress, and actual temperature T which is assumed to be close to the equilibrium temperature.

Consider the following form of the specific free energy function Φ_n of a two-phase system

$$(2.1) \quad \Phi_n = (1 - z)\phi^{(1)} + z\phi^{(2)},$$

where z is the mass fraction of martensite ($z = M^{(2)}/M$; M is the total mass of a system equal to the initial mass of the parent phase, $M^{(2)}$ is the instantaneous mass of the product phase), $\phi^{(1)}$ and $\phi^{(2)}$ are specific free energies of parent phase and product phase, respectively. We neglect the possible inelastic flow within both phases and assume that both phases have equal temperature-independent thermoelastic constants (\mathbf{L} — elastic moduli and α_0 — thermal expansion coefficients), and equal temperature-independent specific heats c_v at constant strains in the temperature range $T > A_f^0$. We stipulate the free energies ϕ^α ($\alpha = 1, 2$) in non-equilibrium to be [20]

$$(2.2) \quad \phi^\alpha = \overset{*}{u}_0^\alpha - T \overset{*}{s}_0^\alpha + (\epsilon_\alpha - \epsilon_\alpha^f) \cdot \mathbf{L}(\epsilon_\alpha - \epsilon_\alpha^f)/2 - (T - T_0)\alpha_0 \cdot \mathbf{L}(\epsilon_\alpha - \epsilon_\alpha^f) + c_v(T - T_0) - T \ln(T/T_0),$$

where internal energies $\overset{*}{u}_0^\alpha$ and entropies $\overset{*}{s}_0^\alpha$ ($\alpha = 1, 2$) at stress-free state and at the chosen reference temperature T_0 are constants, $\epsilon_{(1)}^f = \mathbf{0}$ and

$$(2.3) \quad \epsilon_{(2)}^f = \kappa(h)$$

is the traceless ($\text{tr} \epsilon_{(2)}^f = 0$) strain associated with the formation of the martensite phase. Thus, we assume that the intrinsic elastic strain of the parent phase is equal to the total intrinsic strain of this phase, and intrinsic elastic strain of the martensite is equal to

$\epsilon_{(2)} - \epsilon_{(2)}^f = \epsilon_{(2)} - \kappa(h)$, cf. [20]. In the course of diffusionless martensitic transformation the chemical composition of phases does not change. Therefore, no state variables that represent it are present in the adopted forms of ϕ^α . The intrinsic strains ϵ_α and z are not independent since when the total overall strain ϵ is prescribed, they have to satisfy the relation

$$(2.4) \quad \epsilon = (1 - z)\epsilon_{(1)} + z\epsilon_{(2)}.$$

The intrinsic Kirchhoff stresses τ_α corresponding to ϵ_α are defined by

$$(2.5) \quad \begin{aligned} \tau_{(1)} &= (V - V^{(2)})\sigma_{(1)}/(M - M^{(2)}) = \partial\phi^{(1)}/\partial\epsilon_{(1)}, \\ \tau_{(2)} &= V^{(2)}\sigma_{(2)}/M^{(2)} = \partial\phi^{(2)}/\partial\epsilon_{(2)}. \end{aligned}$$

where σ_α ($\alpha = 1, 2$) are the intrinsic Cauchy stresses acting in both phases, and $V^{(2)}$ is the current volume of already formed martensitic plates.

2.2. Properties at thermodynamic equilibrium

The model we are aiming to construct in this section will describe the equilibrium properties of a system having (at non-equilibrium) the free energy function described by (2.1)–(2.2). It will be called the R -model of ideal pseudoelastic behaviour of shape memory alloys (R — from “reference” and “reversibility”).

Applying the technique of Lagrange’s undetermined multipliers (here — τ) we form the function

$$\bar{\phi}_n = (1 - z)\phi^{(1)} + z\phi^{(2)} + \tau \cdot [\epsilon - (1 - z)\epsilon_{(1)} - z\epsilon_{(2)}].$$

At equilibrium, at constant T and ϵ , this function is supposed to reach an extremum. Hence, the equilibrium values $\epsilon_\alpha^{\text{eq}}, z^{\text{eq}}$ and h^{eq} of ϵ_α, z and h are the functions of ϵ and T that should be determined from the following set of equations

$$(2.6) \quad \begin{aligned} \tau_{(1)} &= \tau_{(2)}, \quad \phi^{(2)} - \phi^{(1)} + \tau_{(1)} \cdot (\epsilon_{(1)} - \epsilon_{(2)}) = 0, \\ \tau_{(2)} \cdot (\partial\kappa/\partial h) &= 0, \end{aligned}$$

and (2.4). Under the adopted form of the free energy function (2.1)–(2.2) the intrinsic stresses and Gibbs potentials (defined by $\mu^\alpha = \phi^\alpha - \tau_\alpha \cdot \epsilon_\alpha$) of the two phases must be equal at equilibrium. Equation (2.6)₃ will be satisfied when, at equilibrium, phase strain κ reaches the extremum, i.e., when $\partial\kappa/\partial h = 0$. As here we do not adopt any special micromechanical model specifying the exact physical meaning of h , we shall utilize only the fact that (2.6)₃ shows that at equilibrium infinitesimal changes in κ occur in the direction normal to the stress-deviator axis in the deviatoric stress space.

Since thermoelastic properties of both phases are assumed to be the same, the difference $\phi^{(1)} - \phi^{(2)}$, at equilibrium, is

$$(2.7) \quad \begin{aligned} \phi^{(1)} - \phi^{(2)} &= \pi_0^f(T), \quad \pi_0^f(T) = \Delta u^* - T\Delta s^*, \\ \Delta u^* &= u_0^{*(1)} - u_0^{*(2)}, \quad \Delta s^* = s_0^{*(1)} - s_0^{*(2)}, \end{aligned}$$

on account of (2.6)₁ and (2.5). In engineering the quantity $\pi_0^f(T)$ is frequently termed “phase chemical potential”. It represents the “driving force” for temperature-induced martensitic transformations at the stress-free state.

The solutions of (2.6) and (2.4) for fixed T , ϵ and $\kappa = \kappa^{eq}(\kappa^{eq} = \kappa(h^{eq}))$ is

$$(2.8) \quad \begin{aligned} \epsilon_{(1)}^{eq} &= \epsilon - z^{eq} \kappa^{eq}, \quad \epsilon_{(2)}^{eq} = \epsilon + (1 - z^{eq}) \kappa^{eq}, \\ z^{eq}(\epsilon, T) &= \frac{\kappa^{eq} \cdot \mathbf{L} \epsilon - \kappa^{eq} \cdot \mathbf{L} \alpha_0 (T - T_0) + \pi_0^f}{\kappa^{eq} \cdot \mathbf{L} \kappa^{eq}} \end{aligned}$$

what implies

$$(2.9) \quad \tau_{(2)}^{eq} = \tau_{(1)}^{eq} = \tau_{eq} = \mathbf{L}[\epsilon - z^{eq} \kappa^{eq} - \alpha_0 (T - T_0)].$$

We shall now stipulate that function $\kappa(h)$ are such that $\kappa \cdot \kappa = \eta = \text{const}$ so that h plays the role of curvilinear coordinates on a sphere in the 5-dimensional deviatoric space, and $\kappa \cdot (\partial \kappa / \partial h) = 0$ for every h . This latter condition will also be satisfied if one assumes that κ is derivable from a potential that is a homogeneous function of order one with respect to five-dimensional h_i ($i = 1, \dots, 5$) (e.g. when the potential is proportional to the modulus of h_i). Under this approximation, the possible solution of (2.6)₃ is expected to have the form

$$(2.10) \quad \kappa^{eq} = \eta \frac{\bar{\tau}_{eq}}{(\bar{\tau}_{eq} \cdot \bar{\tau}_{eq})^{1/2}},$$

where $\bar{\tau}_{eq}$ is the deviatoric part of τ_{eq} . This is, of course, a purely heuristic assumption based upon expectation that after a change of the principal direction of stress and subsequent proportional loading the old martensitic plates will rotate, and the new martensitic systems will be formed in such a way that the overall phase distortion will have the same principal directions as the applied stresses.

Combining (2.9) and (2.8) we find the equilibrium condition

$$(2.11) \quad \tau_{eq} \cdot \kappa^{eq} + \pi_0^f = 0,$$

which must be satisfied in a two-phase state. Provided that κ^{eq} is known, this condition can be used as a reference one for determination of critical stress for the stress-induced martensitic transformation. When martensite-start temperature M_s^0 (of temperature-induced martensite) at $\tau = \mathbf{0}$ is known, one gets the relation

$$\Delta \bar{u}^* - M_s^0 \Delta \bar{s}^* = 0,$$

since $\pi_0^f = 0$ for $T = M_s^0$. As the pseudoelastic behaviour in the shape memory alloys is observed at temperature range $T > A_f^0$ and most frequently $A_f^0 \geq M_s^0$, we assume in this paper that

$$(2.12) \quad \pi_0^f < 0.$$

Combination of (2.10)–(2.11) reduces the equilibrium condition (2.11) to the equation of a sphere in a 5-dimensional space of stress deviator

$$(2.13) \quad \eta \tau_{eq} + \pi_0^f = 0, \quad \tau_{eq} = (\bar{\tau}_{eq} \cdot \bar{\tau}_{eq})^{1/2}.$$

Its radius increases linearly with the temperature. Equation (2.13)₁ can also be regarded as an equation of straight line in the effective stress-temperature plane. Its slope is determined by the coefficient $(3/2)^{1/2} \Delta \bar{s}^* / \eta$, i.e., by the difference $\Delta \bar{s}^*$ in the specific entropies of parent and martensite phases, at temperature T_0 and at stress-free state.

From the set of equations (2.8)–(2.9) one can eliminate κ^{eq} with the aid of (2.10). For general anisotropic solids the solution is lengthy. However, for isotropic solids, when α_0

is the spherical tensor $\alpha_0 = \alpha_0 \mathbf{1}$, and

$$L_{ijkl} = \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \delta_{ij}\delta_{kl}(K - 2\mu/3),$$

the solution has a simple form. The deviatoric part of (2.9) implies

$$(2.14) \quad \bar{\tau}_{eq} = 2\mu(\bar{\epsilon} - z^{eq}\kappa^{eq}) \quad \text{and} \quad \tau_{eq} = 2\mu(\epsilon - z^{eq}\eta), \quad \epsilon = (\bar{\epsilon} \cdot \bar{\epsilon})^{1/2},$$

and in the region of the two-phase states the equilibrium values of z^{eq} , κ^{eq} and $\bar{\tau}_{eq}$ can be found from

$$(2.15) \quad 2\mu\eta(\epsilon - \eta z^{eq}) + \pi_0^f = 0, \quad \kappa^{eq}/\eta = \bar{\epsilon}/\epsilon = \bar{\tau}_{eq}/\tau_{eq},$$

on account of (2.9). Here μ and K are energetic shear and bulk moduli, respectively, and $\bar{\epsilon}$ is the deviatoric part of the total overall strain. In the two-phase state region, there exists a family of spheres in the strain-deviator space (with z^{eq} as a parameter) corresponding to the single sphere (2.13) in the stress space. Transformation starts ($z^{eq} = 0$) when strain invariant ϵ reaches the critical value $\epsilon(A) = \epsilon|_{z^{eq}=0} = -\pi_0^f/2\mu\eta$, and it ends when $\epsilon|_{z^{eq}=1} = \epsilon(A_1) = \eta + \epsilon(A)$. Thus, the constant parameter η represents the thickness of the spherical shell containing the two-phase equilibrium states. It is equal to the total amplitude of pseudoelastic behaviour in $\tau_{eq} - \epsilon$ plane (Fig. 1).

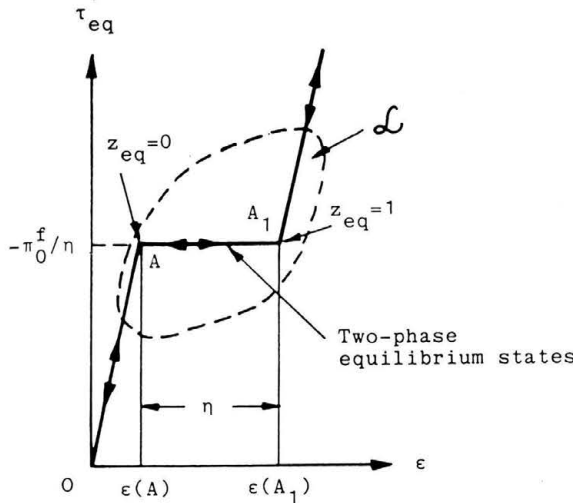


FIG. 1. Schematic representation of the relationship between stress and strain invariants for R -model at fixed temperature.

The transformation-start and transformation-end temperatures under the applied strain can also be illustrated on $\epsilon - T$ plane by two parallel straight lines as shown in Fig. 2.

The ideal R -model that admits only reversible processes does not differentiate between temperatures A_f^0 and M_s^0 , and temperatures M_f^0 and A_s^0 , i.e., $A_f^0 = M_s^0$.

The equations (2.15)_{2,3}, when written in the incremental form at constant T , are

$$(2.16) \quad d\kappa^{eq} = (\eta/\epsilon)\mathbf{P}(\bar{\epsilon})d\bar{\epsilon}, \quad d\tau_{eq} = -[\pi_0^f/(\eta\epsilon)]\mathbf{P}(\bar{\epsilon})d\bar{\epsilon},$$

where

$$(2.17) \quad \mathbf{P} = \mathbf{1}^D - (\bar{\epsilon} \otimes \bar{\epsilon})/\epsilon^2.$$

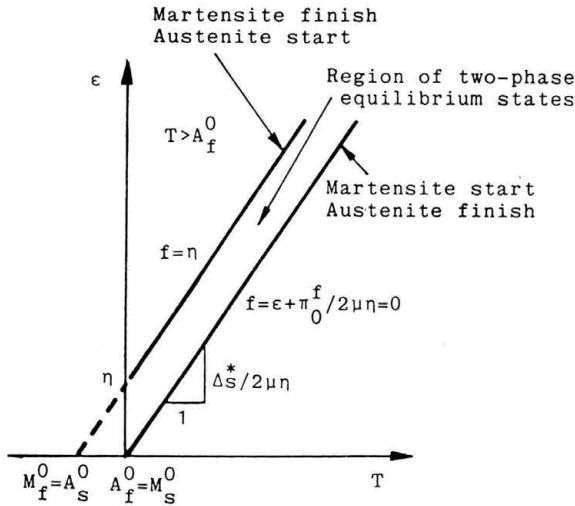


FIG. 2. Illustration of transformation-start and transformation-finish temperature in $\epsilon - T$ plane.

$\mathbf{1}^D$ is fourth-rank unit tensor in the deviatoric space ($1_{ijmn}^D = (\delta_{im}\delta_{jn} + \delta_{in}\delta_{mj})/2 - \delta_{ij}\delta_{mn}/3$). It has the property that $\mathbf{P}\mathbf{P} = \mathbf{P}$, and its determinant vanishes, $\det\mathbf{P} = 0$. Stability of the equilibrium states in the two-phase region is, therefore, indefinite. If $d\bar{\epsilon}$ is perpendicular to the current $\bar{\epsilon}$, i.e., $d\bar{\epsilon} \cdot \bar{\epsilon} = 0$, the phase-transformation process is stopped, and the incremental equilibrium response is linear with the tangent modulus dependent on $\bar{\epsilon}$. The tangent modulus decreases from 2μ (for ϵ corresponding to $z^{eq} = 0$) to the value $2\mu/(1 - 2\mu\eta^2/\pi_0^f)$ (for ϵ corresponding to $z^{eq} = 1$).

2.3. Constitutive equations for R-model

In what follows we shall restrict our attention only to the isotropic solids. By substituting (2.8)₁ and (2.15) into (2.1) one finds the free energy ϕ_n^{eq} in thermodynamical equilibrium. It is a function of $\bar{\epsilon}$ and T that has discontinuous second derivatives at the boundaries of two-phase states,

$$(2.18) \quad \phi_n^{eq}(\epsilon, T) = \phi_n^v(\epsilon_v, T) + \phi_n^s(\epsilon, T) + u_0^{*(1)} - T s_0^{*(1)},$$

$$(2.19) \quad \phi_n^v(\epsilon_v, T) = K \epsilon_v^2/2 - 3K \alpha_0(T - T_0)\epsilon_v + c_v(T - T_0) - c_v T \ln(T/T_0),$$

$$(2.20) \quad \phi_n^s(\epsilon, T) = \begin{cases} \mu\epsilon^2 & \text{if } f(\epsilon, T) = \epsilon + \pi_0^f(T)/(2\mu\eta) \leq 0, \\ -\pi_0^f(T)\epsilon/\eta - (\pi_0^f(T))^2/(4\mu\eta^2) & \text{if } 0 \leq f \leq \eta, \\ \mu(\epsilon - \eta)^2 - \pi_0^f(T) & \text{if } f > \eta. \end{cases}$$

Here, $\epsilon_v = \text{tr}\epsilon$; $\epsilon = (\bar{\epsilon} \cdot \bar{\epsilon})^{1/2}$ and $\pi_0^f < 0$. At fixed $T > A_f^0$, the function (2.20) describes the figure consisting of two parabolas connected by the straight line tangent to both of them. The Kirchhoff stress and the entropy s^{eq} are derivable from (2.18) by the usual relations

$$(2.21) \quad \tau_{eq} = \partial\phi_n^{eq}/\partial\epsilon \quad \text{and} \quad s^{eq} = -\partial\phi_n^{eq}/\partial T,$$

whereas equilibrium amount of martensite is $z^{\text{eq}} = 0$ when $f \leq 0$, $z^{\text{eq}} = 1$ when $f > \eta$, and it can be calculated from (2.15)₁ when $0 \leq f \leq \eta$.

We believe that the idealized R -model in the present form can be applied for rough estimation of transient strains and stresses occurring in structural elements (made of shape memory alloys) in the temperature range of pseudoelastic behaviour $T > A_f^0$. The more practicable form, i.e. the rate-form, of constitutive relations for R -model can be written, in terms of usual Cauchy stress σ , as follows (we neglect the superscript "eq"):

$$(2.22) \quad d\sigma_m = K_0[d\epsilon_v - 3\alpha_0 dT], \quad \sigma_m = \text{tr}\sigma/3, \quad \bar{\sigma} = \sigma - \sigma_m \mathbf{1},$$

$$(2.23) \quad d\bar{\sigma} = \begin{cases} 2\mu_0 d\bar{\epsilon} & \text{if } [f < 0 \text{ or } (f = 0 \text{ and } df \leq 0)], \\ -[d\pi_0^f \rho / (\eta\epsilon)]\bar{\epsilon} - [\rho\pi_0^f / (\eta\epsilon)]\mathbf{P}d\bar{\epsilon} & \text{if } [0 < f < \eta \\ \text{or } (f = 0 \text{ and } df > 0) & \text{or } (f = \eta \text{ and } df < 0)], \\ 2\mu_0 d\bar{\epsilon} - 2\mu_0(\eta/\epsilon)\mathbf{P}d\bar{\epsilon} & \text{if } [f > \eta \\ \text{or } (f = \eta \text{ and } df \geq 0)], \end{cases}$$

where ρ is the mass density of two-phase alloy presumed to be constant, and we have introduced usual elasticity constants μ_0 and K_0 . \mathbf{P} is defined by (2.17), and the phase chemical potential — by (2.7). The function f (cf.(2.20)₁) can also be expressed in terms of μ_0 ,

$$f = \epsilon + \rho\pi_0^f(T)/(2\mu_0\eta).$$

The incremental equation for the amount of martensite reads

$$(2.24) \quad dz = \begin{cases} 0 & \text{if } [f < 0 \text{ or } f > \eta \text{ or } (f = 0 \text{ and } df \leq 0) \\ & \text{or } (f = \eta \text{ and } df \geq 0)], \\ (1/\eta)df & \text{otherwise.} \end{cases}$$

Note that, due to our assumption (2.10) which is presumed to hold also in single-phase martensitic state, the incremental elastic response of pure martensite described by (2.23)₃ is nonlinear. In view of lack of experimental data concerning the behaviour of pure strain-induced martensite at $T > A_f^0$ at complex stress state, we cannot judge whether this prediction is correct or not. For proportional loading both $\bar{\epsilon} \cdot d\bar{\epsilon}$ and the second term occurring on the right hand side of (2.23)_{2,3} vanish. For such paths the predicted response is linear. We shall now derive the rate equation for the temperature. Since all processes described by R -model are reversible, we can combine incremental form of (2.21)₂ with $-\bar{d}q/T$ ($\bar{d}q$ being the heat exchange per unit of mass, positive if it is transferred to surrounding) to get

$$(2.25) \quad \rho c_v dT = -\rho\bar{d}q - 3TK_0\alpha_0 d\epsilon_v + \rho\Delta s^* T dz.$$

Note that, according to this model, the latent heat due to strain-induced (isochoric and isothermal) complete martensitic transformation is equal to $\rho\Delta s^* T$, and in the class of this processes Δs^* could be measured. Another way of determination of Δs^* follows from extrapolation of the line $f = \eta$ (Fig. 2) into the temperature range $T < M_s^0 = A_f^0$. At $T = A_f^0 = M_s^0$ we have $\pi_0^f = 0$, and at $T = M_f^0 = A_s^0$ it is $z^{\text{eq}} = 1$. Hence

$$\Delta u^* = M_s^0 \Delta s^*, \quad \Delta s^* = 2\mu\eta^2/(M_s^0 - M_f^0).$$

The set (2.22)–(2.25) constitutes the full set of coupled equations of R -model for homogeneous processes. An easy combination of (2.25) with the usual Fourier equation of heat conductivity will enable us to apply the equations for continuous structures. The set

contains only 3 constants (Δs^* , Δu^* and η) that do not occur in the set of basic equations of usual linear thermoelasticity.

3. The role of configurational free energy. Unstable equilibria

The highly idealized R -model presented in Sec. 2 can not describe the actual behaviour of crystalline solids under ongoing martensitic transformation above A_f^0 , except (perhaps) of the imaginable situation when in a single crystal all martensitic plates are formed on commonly oriented single habit plane, and when the progress of forward-reverse transformation is completely symmetric in time. Then, e.g., the plates formed at the end of forward transformation disappear at the beginning of the reverse transformation. During the real process of strain-induced martensite in crystalline solids, in a vicinity of equilibrium line (area \mathcal{L} in Fig. 1) the loop is formed as a result of many physical events such as interaction of different martensitic systems and elastic misfit of the differently oriented phase domains within the single crystal, etc. To encompass some effects of the interactions suppose that u_0^* and s_0^* occurring in (2.2) are replaced by

$$\begin{aligned} u^{(1)} &= u_0^{*(1)} + \bar{u}(1-z), & u^{(2)} &= u_0^{*(2)} + \bar{u}(z), \\ s^{(1)} &= s_0^{*(1)} + \bar{s}(1-z), & s^{(2)} &= s_0^{*(2)} + \bar{s}(z), \end{aligned}$$

where functions $\bar{u}(x)$ and $\bar{s}(x)$ can be regarded as the “configurational internal energy and entropy” due to transformations. They are supposed to vanish for $x = 1$. It is expedient to assume that configurational specific free energy of martensite at the beginning of the forward transformation is much higher than at its end — just opposite to the parent phase. Therefore, the term $\bar{u}(z) - T\bar{s}(z)$ is expected to be non-negative. The simplest functions that satisfy the above requirement are the linear functions $\bar{u}(x) = \bar{u}_0(1-x)/2$, $\bar{s}(x) = \bar{s}_0(1-x)/2$, where $\bar{u}_0 - T\bar{s}_0 \geq 0$. It can easily be seen that, instead of altering free energy functions (2.2) of individual phases, one can equivalently add to the function (2.1) a term containing the free energy of internal interaction

$$(3.1) \quad \phi_{it}(T) \cdot z \cdot (1-z); \quad \phi_{it} = \bar{u}_0 - T\bar{s}_0,$$

which is expected to be non-negative ($\phi_{it} \geq 0$). This is the term similar to the one introduced by MÜLLER and XU [15] in their one-dimensional theory of formation of a hysteresis loop due to transformation. Here we use the same classical concepts and consider extended free energy function of two-phase system in non-equilibrium under 3-axial state of stress:

$$(3.2) \quad \phi = (1-z)\phi^{(1)} + z\phi^{(2)} + \phi_{it}z(1-z),$$

where functions ϕ^α are unaltered and are given by (2.2), and intrinsic stresses are defined by (2.5). Repeating the same procedure as that used in Sec. 2.2, it can be found that the equilibrium conditions (2.6)₁ and (2.6)₃ are valid also in this case, whereas (2.6)₂ must be replaced by

$$(3.3) \quad \phi^{(2)} - \phi^{(1)} + \tau_{(1)} \cdot (\epsilon_{(1)} - \epsilon_{(2)}) + \phi_{it} - 2z\phi_{it} = 0.$$

The solution of this new set of conditions under fixed κ^{eq} is again given by (2.8)₁, and

(2.8)₂ now has the form

$$(3.4) \quad z^{\text{eq}} = \frac{\kappa^{\text{eq}} \cdot \mathbf{L}[\boldsymbol{\epsilon} - \boldsymbol{\alpha}_0(T - T_0)] + \pi_0^f - \phi_{\text{it}}}{\kappa^{\text{eq}} \cdot \mathbf{L}\kappa^{\text{eq}} - 2\phi_{\text{it}}}$$

Accepting the assumption (2.10), the counterparts of Eqs. (2.13) and (2.15)₁, for isotropic solids, become

$$(3.5) \quad \begin{aligned} \pi_0^f + \eta\tau_{\text{eq}} - \phi_{\text{it}}(1 - 2z^{\text{eq}}) &= 0, \\ \pi_0^f + 2\mu\eta\epsilon - 2(\mu\eta^2 - \phi_{\text{it}})z^{\text{eq}} - \phi_{\text{it}} &= 0, \end{aligned}$$

whereas the other two equations (2.15)₂, and equations (2.14) remain unchanged.

The locus of two-phase equilibrium states can be illustrated by a segment $A - A_1$ (Fig. 3) of the straight line which now has the negative slope on the invariants plane $\tau_{\text{eq}} - \epsilon$.

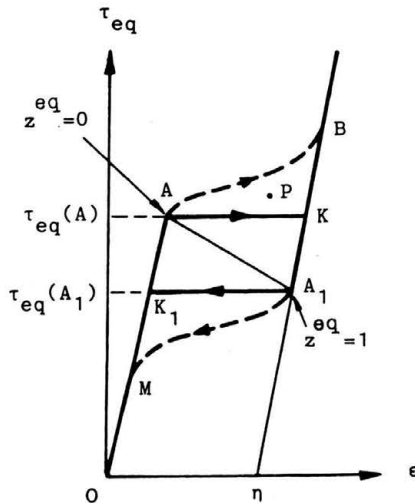


FIG. 3. Schematic representation of hysteresis loop and the seat of equilibrium states (AA_1) in stress invariant-strain invariant plane at constant temperature for R_L -model.

Its equation can easily be derived by eliminating z^{eq} between (3.5)₁ and (2.14)₂

$$(3.6) \quad (\mu\eta^2 - \phi_{\text{it}})\tau_{\text{eq}} + 2\mu\epsilon\phi_{\text{it}} + \mu\eta(\pi_0^f - \phi_{\text{it}}) = 0.$$

The critical stress $\tau_{\text{eq}}(A) = \tau_{\text{eq}}|_{z^{\text{eq}}=0}$ and $\tau_{\text{eq}}(A_1) = \tau_{\text{eq}}|_{z^{\text{eq}}=1}$ at which the forward and reverse transformation could start are

$$(3.7) \quad \tau_{\text{eq}}(A) = (\phi_{\text{it}} - \pi_0^f)/\eta, \quad \tau_{\text{eq}}(A_1) = \tau_{\text{eq}}(A) - 2\phi_{\text{it}}/\eta,$$

and the dependence of z^{eq} on ϵ (or τ_{eq}) in the two-phase region is linear (cf. (3.5)). Since the slope of the segment $A - A_1$ is negative, all equilibrium states are unstable. This can also be proved analytically by repeating the procedure presented in Sec. 2.2. Therefore, no real process of transformation can be observed along a reversible path such as $A - A_1$ shown in Fig. 3. The instability at equilibrium states is the primary source of the formation of hysteresis loop, such as $A - K - A_1 - K_1$, in two-phase crystals.

Its width $\tau_{\text{eq}}(A) - \tau_{\text{eq}}(A_1)$ is equal to $2\phi_{\text{it}}/\eta$ (MÜLLER and XU [15]). The real process of deformation of shape memory polycrystalline alloys, in the range of pseudoelastic behaviour, proceeds along paths such as $A - B$ and $A_1 - M$ shown by dotted lines in Fig. 3. The deviations from the ideal pseudoelastic flow ($A - K$) and from an ideal strain recovery ($A_1 - K_1$) may be thought of to be the effect of interactions between differently oriented crystals. In the next section we shall develop the model that will account for the creation of the hysteresis loop and the observed hardening. It will be called the R_L -model.

4. R_L -model

4.1. Free energy function of constrained equilibria. Thermal equations of state

Most of two-phase states, e.g. the state P shown in Fig. 3, which are reached during actual processes of deformation are not states of absolute equilibrium. This clearly follows from the discussion presented in Sec. 3. On the other hand, when strain (stress) corresponding to the point P shown in Fig. 3, together with the temperature, is kept fixed, the piece of two-phase metallic solid remains at complete rest. We shall say that it is in a "constrained equilibrium" where a thermodynamical rate corresponding to some internal thermodynamic force may vanish, even though the force is non-zero. This concept has been developed by KESTIN and RICE [21], RICE [22] and has been so often used in applied thermomechanics (see, e.g., KLEIBER and RANIECKI [23]) that now it can be regarded as the classical one. To derive the free energy function of constrained equilibria we shall use the adopted function (3.2) (which was assumed to be valid at any non-equilibrium state) and follow other hypothesis (MÜLLER and XU [15]) stating that at a constrained equilibrium the intrinsic stresses are the same (a so-called uniform stress model) and are equal to the overall stress τ , even though neither ϵ_α nor z satisfy the equilibrium conditions discussed in Sec. 3;

$$(4.1) \quad \tau_{(1)} = \tau_{(2)} = \tau.$$

Using (2.5) and (2.2), we can solve the set of equations consisting of (2.4) and (4.1)₁ with respect to ϵ_α , regarding ϵ as a given strain. The solution is

$$(4.2) \quad \epsilon_{(1)} = \epsilon - z\kappa, \quad \epsilon_{(2)} = \epsilon + (1 - z)\kappa,$$

what implies

$$(4.3) \quad \tau = \mathbf{L}[\epsilon - z\kappa - \alpha_0(T - T_0)].$$

By inserting (4.2) into (2.2) and (3.2) one eventually arrives at the following form of the free energy function of constrained equilibria

$$(4.4) \quad \begin{aligned} \Phi_c = & [\epsilon - \epsilon^{\text{pe}}(z, \kappa)] \cdot \mathbf{L}[\epsilon - \epsilon^{\text{pe}}(z, \kappa)] / 2 - (T - T_0) \alpha_0 \cdot \mathbf{L}[\epsilon - \epsilon^{\text{pe}}(z, \kappa)] \\ & + c_v(T - T_0) - c_v T \ln(T/T_0) + \phi^*(z, T), \\ \phi^* = & u_0^{*(1)} - T s_0^{*(1)} - z \pi_0^f(T) + \phi_{\text{it}}(T)(1 - z)z, \end{aligned}$$

where the free energy of internal interaction ϕ_{it} is given by (3.1)₂, ϵ^{pe} is the pseudoelastic strain defined by

$$(4.5) \quad \epsilon^{\text{pe}} = z\kappa, \quad \text{tr}\kappa = \text{tr}\epsilon^{\text{pe}} = 0.$$

and κ represents the intrinsic phase distortion due to parent-martensite transformation, averaged over all the colonies of the martensite present in the representative mass of the polycrystalline alloy element, at a generic instant of homogeneous process of transformation. The general form (4.4) could also be supported on the grounds of micromechanics (cf. [19]). Equation (4.3) constitutes, of course, one of four thermal equations of state that could be derived from (4.4) through $\tau = \partial\phi_c/\partial\epsilon$.

At present very little is known about the evaluation of κ under the action of variable stress (strain) and temperature, and still much experimental and theoretical work has to be done to deduce its satisfactory form. To make some progress we come back to the case of full isotropy and propose to keep the relation (2.10) to be valid also at any constrained equilibrium state. Hence (cf. (2.15))

$$(4.6) \quad \kappa = \eta(\bar{\epsilon}/\epsilon), \quad \epsilon^{\text{pe}} = \eta z(\bar{\epsilon}/\epsilon).$$

The free energy (4.4) for isotropic solids then becomes the function of single internal parameter z ;

$$(4.7) \quad \phi_c(\epsilon, T, z) = \phi_n^v(\epsilon_v, T) + \mu(\epsilon - z\eta)^2 + \phi^*(z, T),$$

where ϕ_n^v is defined by (2.19) and ϕ^* — by (4.4)₂. It employs only 5 additional parameters ($\Delta\bar{u}^*$, $\Delta\bar{s}^*$, \bar{u}_0 , \bar{s}_0 , η) which do not occur in the free energy function for an isotropic linear elastic solids. The stress-strain relations following from (4.7) are (cf. (4.3) and (4.2));

$$(4.8) \quad \begin{aligned} \tau_m &= \text{tr } \tau / 3 = \sigma_m / \rho = K[\epsilon_v - 3\alpha_0(T - T_0)], \\ \bar{\tau} &= \bar{\sigma} / \rho = 2\mu[\bar{\epsilon} - \epsilon^{\text{pe}}]. \end{aligned}$$

Here, μ and K are related to the usual elasticity constant by $\mu = \mu_0/\rho$ and $K = K_0/\rho$, and (4.8)₂ implies relations similar to (2.14)₂ and (2.15);

$$(4.9) \quad \kappa/\eta = \bar{\epsilon}/\epsilon = \bar{\tau}/\tau, \quad \tau = 2\mu(\epsilon - \epsilon^{\text{pe}}) = 2\mu(\epsilon - z\eta),$$

where

$$\epsilon^{\text{pe}} = (\epsilon^{\text{pe}} \cdot \epsilon^{\text{pe}})^{1/2} = z\eta, \quad \epsilon = (\bar{\epsilon} \cdot \bar{\epsilon})^{1/2}, \quad \tau = (\bar{\tau} \cdot \bar{\tau})^{1/2}.$$

We define the entropy of constrained equilibria s and the driving force of the phase transformation π^f by (cf. (2.7)₁)

$$(4.10) \quad \begin{aligned} s(\epsilon, T, z) &= -\partial\phi_c/\partial T = c_v \ln(T/T_0) + 3K\alpha_0\epsilon_v - z\Delta\bar{s}^* + \bar{s}_0^{*(1)} + z(1-z)\bar{s}_0, \\ \pi^f(\epsilon, T, z) &= -\partial\phi_c/\partial z = \pi_0^f(T) + 2\mu\eta\epsilon - 2(\mu\eta^2 - \phi_{\text{it}})z - \phi_{\text{it}}, \end{aligned}$$

what implies

$$(4.11) \quad d\phi_c = -s dT + \tau \cdot d\epsilon - \pi^f dz.$$

Both the entropy and the driving force π^f can easily be expressed in terms of stress τ by use of (4.8),

$$(4.12) \quad \begin{aligned} s(\tau, T, z) &= 3\alpha_0\tau_m + \int_{T_0}^T [c_p(\theta_1)/\theta_1] d\theta_1 - z\Delta\bar{s}^* + \bar{s}_0^{*(1)} + z(1-z)\bar{s}_0, \\ \pi^f(\tau, T, z) &= \pi_0^f(T) + \eta\tau - \phi_{\text{it}}(1-2z), \end{aligned}$$

where

$$(4.13) \quad c_p(T) = c_v + 9T\alpha_0^2 K$$

is the usual specific heat at constant pressure. Equations (4.8) and (4.10) or (4.12) constitute a full set of thermal equations of state for the R_L -model considered. One constitutive equation is missing: the kinetic law for the weight fraction of the martensite. This will be discussed in the next subsection.

4.2. Incremental relations of transformation kinetics

i) Recall the first and the second laws of thermodynamics specified for an infinitesimal homogeneous process;

$$(4.14) \quad \begin{aligned} du &= -\bar{d}q + \tau \cdot d\epsilon, \\ ds + \bar{d}q/T &= \bar{d}\dot{D}/T \geq 0, \end{aligned}$$

where

$$(4.15) \quad u = \phi_c + Ts$$

is the specific internal energy, $\bar{d}q$ represents the heat exchange (cf. Sec. 2.3), and $\bar{d}D$ is the increment of the energy dissipation which cannot be negative. With the aid of (4.11) and (4.15), in a routine way, we eliminate ds and $\bar{d}q$ from (4.14) obtaining the eventual form for the incremental energy dissipation

$$(4.16) \quad \bar{d}D = \pi^f dz \geq 0.$$

Thus, the Clausius–Duhem inequality precludes the parent-martensite transformations at states where $\pi^f < 0$, and prevents the reverse transformations when $\pi^f > 0$. Note that $\pi^f = 0$ implies the equilibrium conditions (3.5) discussed in Sec. 3.

ii) To specify the kinetic equations of phase transformations we presume that there exist two functions $\psi^\alpha(\pi^f, z)$ ($\alpha = 1, 2$), such that an active process of parent phase decomposition ($dz > 0$ — the forward transformation) can proceed only when $\psi^{(1)} = \text{const}$ ($d\psi^{(1)} = 0$), and an active process of martensite decomposition ($dz < 0$ — the reverse transformation) can proceed only if $\psi^{(2)} = \text{const}$ ($d\psi^{(2)} = 0$),

$$(4.17) \quad \psi^{(1)} = \pi^f - k^{(1)}(z), \quad \psi^{(2)} = -\pi^f + k^{(2)}(z).$$

The functions ψ^α are single-valued except possibly the point $z = 1$ for the function $\psi^{(1)}$ and the point $z = 0$ for the function $\psi^{(2)}$.

Since in polycrystalline solids the complete forward and complete reverse transformations are never observed, we assume for simplicity that functions $k^\alpha(z)$ have the following mathematical properties

$$(4.18) \quad \begin{aligned} k^{(1)}(0) &= 0; & \lim_{z \rightarrow 1} k^{(1)} &= +\infty, & \lim_{z \rightarrow 1} (1-z)k^{(1)} &= 0, & k^{(1)} &\geq 0, \\ k^{(2)}(1) &= 0; & \lim_{z \rightarrow 0} k^{(2)} &= -\infty, & \lim_{z \rightarrow 0} zk^{(2)} &= 0, & k^{(2)} &\leq 0, \\ & & dk^\alpha/dz &> 0 & \text{for } 0 < z < 1, & & \end{aligned}$$

and take

$$(4.19) \quad \begin{aligned} k^{(1)} &= -(A_1 + B_1 z) \ln(1-z) + C_1 z, \\ k^{(2)} &= [A_2 - B_2(1-z)] \ln z - C_2(1-z), \end{aligned}$$

where $A_\alpha, B_\alpha, C_\alpha$ are constants ($A_\alpha > 0, C_\alpha \geq 0$). Although the R_L -model developed here is expected to be valid only in the temperature range $T > A_f^0$, it is expedient to extrapolate linearly its properties to the temperature range $T < A_f^0$ for stress-free state ($\tau = \mathbf{0}$), in order to find the relations between constants $\Delta s^*, \Delta \bar{u}, \bar{s}_0, \bar{u}_0, A_\alpha, B_\alpha, C_\alpha$ and the temperatures A_s^0, A_f^0, M_s^0 and M_f^0 which, in engineering, are regarded as characteristics of shape memory alloys. At the initiation of the forward transformation (parent \rightarrow martensite) at $\tau = \mathbf{0}$ and at temperature $T = M_s^0$, the driving force π_f is supposed to vanish. The same should hold at the initiation of the reverse transformation (martensite \rightarrow parent) at temperature $T = A_s^0$, provided that the threshold values for π^f are negligible. Thus for $\tau = \mathbf{0}$

$$\pi^f = 0 \quad \text{for} \quad T = M_s^0, \quad z = 0, \quad \text{and for} \quad T = A_s^0, \quad z = 1.$$

Hence two relations for 4 constants $\Delta s^*, \Delta \bar{u}, \bar{s}_0$ and \bar{u}_0 can be found

$$(4.20) \quad \Delta \bar{u} - \bar{u}_0 = M_s^0(\Delta s^* - \bar{s}_0), \quad \Delta \bar{u} + \bar{u}_0 = A_s^0(\Delta s^* + \bar{s}_0).$$

The stipulated form (4.19) of the function k^α enables us to include the classical relationships for transformation kinetics of temperature-induced martensite discussed in early papers of MAGEE [24] and KOISTINEN and MARBURGER [25]. Magee's development was based upon two postulates: 1. The number of plates of martensite formed in the specimen at time elapsed $(t + \Delta t, t)$ divided by the updated mass of austenite is proportional to the increment of thermodynamic driving force π^f . 2. The volume (mass) of each plate is close to the average volume (mass) of all plates. When these two postulates are adopted and extended to the reverse transformation considered in our case, we must set

$$(4.21) \quad B_\alpha = 0, \quad C_\alpha = 0 \quad (\alpha = 1, 2),$$

which reduces (4.19) to the simple logarithmic relations. However, since now we take into account the interaction free energy ϕ_{it} (that was neglected by Magee) from (4.17) and (4.19) does not follow the empirical exponential relation between z and temperature for temperature-induced martensite found by Koistinen and Marburger for ferrous alloys. Nevertheless, when $|\bar{u}_0/\Delta \bar{u}| \ll 1$ and $|\bar{s}_0/\Delta s^*| \ll 1$, the alteration should not be significant. Moreover, we shall show that for special choice of constants A_α, B_α and C_α the Koistinen and Marburger empirical relation is consistent with (4.19). For shape memory alloys, use of this relation was suggested by TANAKA et al. [11], TANAKA [12] and VACHER and LEXCELLENT [13]. If

$$(4.22) \quad \begin{aligned} C_1 &= 2\phi_{it}(M_s^0), & C_2 &= 2\phi_{it}(A_s^0), \\ a_1 A_1 &= \Delta s^* - \bar{s}_0, & a_2 A_2 &= \Delta s^* + \bar{s}_0, \\ a_2 B_2 &= a_1 B_1 = 2\bar{s}_0, \end{aligned}$$

then the equations $\psi^\alpha = 0$ for $\tau = \mathbf{0}$ can be transformed into the form

$$\begin{aligned} [M_s^0 - T + (1/a_1) \ln(1 - z)][\Delta s^* - \bar{s}_0 + 2\bar{s}_0 z] &= 0, \\ [A_s^0 - T - (1/a_2) \ln z][\Delta s^* - \bar{s}_0 + 2\bar{s}_0 z] &= 0, \end{aligned}$$

on account of (4.12)₂ and (4.20). This implies the required exponential laws

$$(4.23) \quad z = 1 - e^{-a_1(M_s^0 - T)} \quad \text{and} \quad z = e^{-a_2(T - A_s^0)},$$

for forward and reverse transformation, respectively, provided that

$$(4.24) \quad \Delta s^* > |\bar{s}_0|.$$

When (4.22) is adopted, six constants A_α , B_α and C_α are expressed in terms of Δs^* , \bar{s}_0 , \bar{u}_0 and two constants a_1 , a_2 . The latter constants can be estimated when M_f^0 (martensitic transformation stops at $\tau = 0$) and A_f^0 (reverse transformation terminates at $\tau = 0$) temperatures are known. Usually one adopts certain conventional number for the residual z to define M_f^0 and A_f^0 . Most commonly $z_f^M = 0.99$ and $z_f^A = 0.01$ for the forward and reverse transformations, respectively. Using (4.23) we can estimate a_α as follows:

$$(4.25) \quad \begin{aligned} a_1 &= [-\ln(1 - z_f^M)] / (M_s^0 - M_f^0), \\ a_2 &= (-\ln z_f^A) / (A_f^0 - A_s^0). \end{aligned}$$

The use of (4.25) should be made with caution when conventional values z_f^M and z_f^A are not given. It is a frequent practice that M_f^0 and A_f^0 are specified by the linear extrapolation of the data measured for some narrow range of z . Then z_f^M and z_f^A are usually not given and the quoted temperatures M_f^0 and A_f^0 have no clear physical meaning. Under the choice (4.20), (4.22) and (4.25) there will be only three constants unspecified in the set $Y_c = \{\eta, \Delta s^*, \bar{s}_0, \bar{u}_0, A_\alpha, B_\alpha, C_\alpha\}$. One possible way of their identification will be indicated beneath.

iii) Consider two lines $\psi^\alpha = 0$ ($\alpha = 1, 2$). Together with $z = 0$ and $z = 1$ they form the “bounding” loop on the plane $\pi^f - z$ (Fig. 4a) in a sense that no state for which $\psi^\alpha > 0$ is accessible. Some other lines $\psi^\alpha = \text{const}$ are also illustrated in the figure. The lines $\psi^{(1)} = \text{const}$ and $\psi^{(2)} = \text{const}$ are meaningful only when $\pi^f \geq 0$ and $\pi^f \leq 0$, respectively. Processes such that $\pi^f < 0$ and $dz > 0$ or $\pi^f > 0$ and $dz < 0$ are excluded by the Clausius–Duhem inequality (4.16). Therefore, all infinitesimal processes that start from the states $\pi^f \geq 0$ can be either active processes of parent phase decomposition ($dz > 0$) or passive processes ($dz = 0$). Likewise, all infinitesimal processes that begin from the states $\pi^f \leq 0$ can be either active processes of martensite decomposition ($dz < 0$) or passive ($dz = 0$). The typical thermodynamically admissible loops on $\pi^f - z$ plane are illustrated in Fig. 4a, e.g., $A - B - C - D$ or $A - B - C - F - G - E - H$ or $A - B - E - H$.

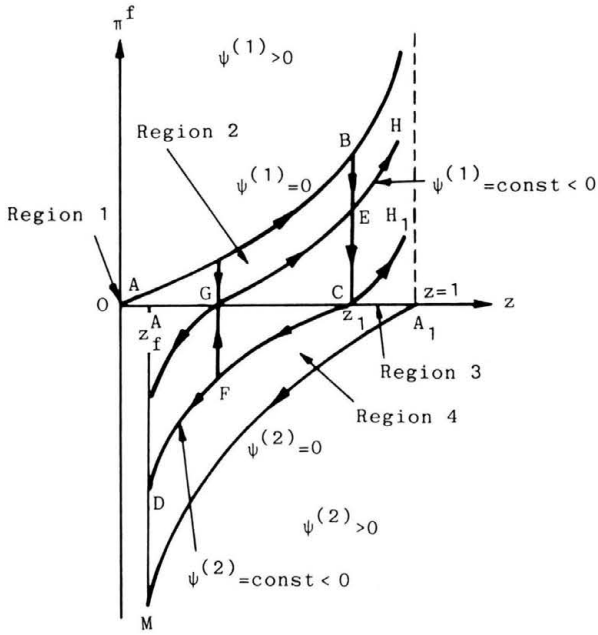
The lines $\psi^\alpha = \text{const} \leq 0$, for fixed temperature T , can be mapped onto $\tau - \epsilon$ plane, shown in Fig. 4b, with the aid of the equations (4.10)₂, (4.12)₂ (or (4.9)₂) and (4.17), where z is regarded as a parameter. The segment $A - A_1$ is the locus of unstable equilibrium states ($\pi^f = 0$). Its equation is the same as the equation of the line $A - A_1$ shown in Fig. 3 and discussed in Sec. 3;

$$(4.26) \quad (\mu\eta^2 - \phi_{it})\tau + 2\mu\epsilon\phi_{it} + \mu\eta(\pi_0^f - \phi_{it}) = 0,$$

and z varies along $A - A_1$ linearly according to (4.10)₂ or (4.12)₂ if $\phi_{it} \neq 0$.

The coordinate lines $z = \text{const}$ (for passive processes) of Fig. 4a are mapped on the plane $\tau - \epsilon$ into the Hooke’s lines $\tau - 2\mu\epsilon = \text{const}$, on account of (4.9)₂. This enables us to use an easy graphical method for determination of the current value of z on any flow curves $\psi^\alpha = \text{const}$, provided that they are known from experiments. It suffices to draw a line $\tau - 2\mu\epsilon = \text{const}$ from a point of the segment $A - A_1$ to a point of intersection of this line with any curve $\psi^\alpha = \text{const}$.

a



b

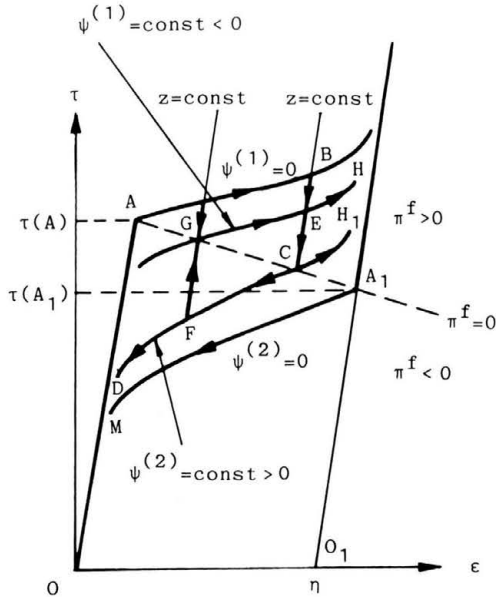
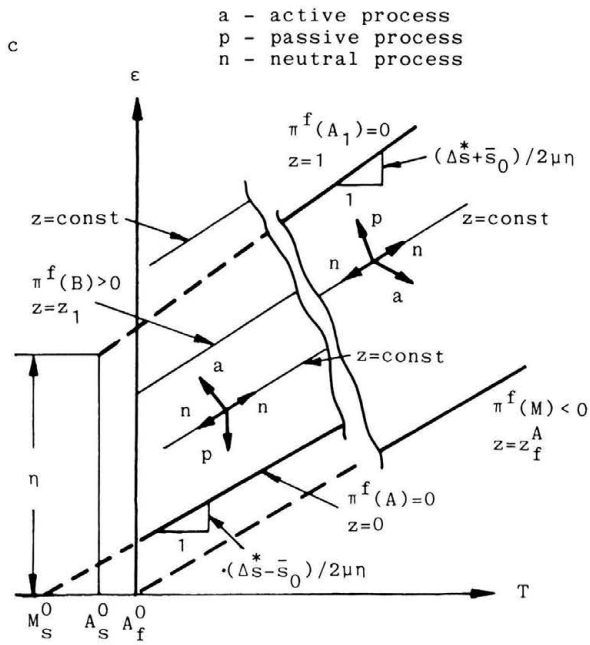


FIG. 4. Illustration of possible thermomechanical processes on:
 a) $\pi^f - z$ plane, b) $\tau - \epsilon$ plane,



d

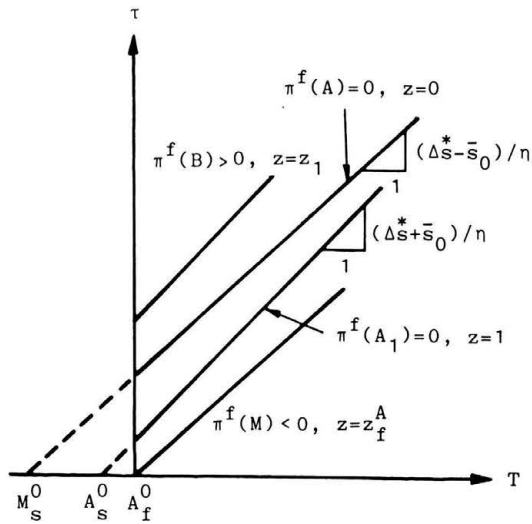


FIG. 4. Illustration of possible thermomechanical processes on:
c) $\epsilon - T$ plane. The transformation-start and -finish temperature in $\tau - T$ plane are illustrated in d).

Since we neglect in this work the possible threshold values for the driving force π^f , no isothermal passive process can be initiated from an unstable two-phase equilibrium state. The two-phase material element being in an unstable state, say C in Fig. 4a, b, tries to find the more stable equilibrium state near the Hooke's straight lines $O - A$ or $O_1 - A_1$. In effect, either the pseudoelastic strain recovery process $C - F - D$ (associated with the negative incremental work) is initiated or pseudoelastic active process $C - H_1$ proceeds. It requires less work to be done (to reach the same strain) than the usual single-phase elastic solid.

We define the isothermal energetic modulus $E_{pe}^{(1)}$ of pseudoelastic active flow, and the isothermal energetic modulus $E_{pe}^{(2)}$ of pseudoelastic strain recovery as follows (cf. Fig. 5a, c):

$$(4.27) \quad E_{pe}^\alpha \equiv (\partial\tau/\partial\epsilon)|_{\psi^\alpha=\text{const}} = 2\mu(1 - \eta z_\epsilon^\alpha),$$

where z_ϵ^α ($\alpha = 1, 2$) are the activity coefficients of isothermal strain-induced transformations;

$$(4.28) \quad \begin{aligned} z_\epsilon^\alpha &\equiv (\partial z/\partial\epsilon)|_{\psi^\alpha=\text{const}} = 2\mu\eta/H_\epsilon^\alpha, \\ H_\epsilon^\alpha &= k_z^\alpha + 2\mu\eta^2 - 2\phi_{it}, \quad k_z^\alpha = dk^\alpha/dz. \end{aligned}$$

The domain of determination for $z_\epsilon^{(1)}$ ($E_{pe}^{(1)}$) is $\psi^{(1)} \leq 0$ and $\pi^f \geq 0$, and for $z_\epsilon^{(2)}$ it is $\psi^{(2)} \leq 0$ and $\pi^f \leq 0$. For easier elaboration of experimental data it is useful to employ the isothermal moduli of pure pseudoelastic flows \overline{E}_{pe}^α and the activity coefficients of isothermal stress-induced transformations z_τ^α defined by (cf. Fig. 5b, d)

$$(4.29) \quad \begin{aligned} \overline{E}_{pe}^\alpha &= E_{pe}^\alpha/(1 - E_{pe}^\alpha/2\mu) = H_\tau^\alpha/\eta^2 = 1/(\eta z_\tau^\alpha), \\ z_\tau^\alpha &\equiv (\partial z/\partial\tau)|_{\psi^\alpha=\text{const}} = \eta/H_\tau^\alpha = [H_\epsilon^\alpha/(2\mu H_\tau^\alpha)]z_\epsilon^\alpha, \end{aligned}$$

where

$$(4.30) \quad H_\tau^\alpha = H_\epsilon^\alpha - 2\mu\eta^2 = k_z^\alpha - 2\phi_{it}.$$

The moduli \overline{E}_{pe}^α determine the slopes of the curves (associated with the active processes) on $\tau - \epsilon^{pe}$ plane. For $H_\tau^\alpha = 0$ the pseudoelastic active flow, and pseudoelastic strain recovery are ideal in the sense that $\tau - \epsilon$ (or ϵ^{pe}) curves are parallel to the ϵ -axis. This special case has been considered by MÜLLER and XU [15] in their $1 - D$ theory. The available experimental data for polycrystalline alloy evidently show that

$$(4.31) \quad H_\tau^\alpha \geq 0,$$

and we assume that this inequality is satisfied for every state within the bounding loop. Note the simple relations which exist between the moduli E_{pe}^α , \overline{E}_{pe}^α representing the mechanical behaviour of an alloy and activity coefficients z_ϵ^α and z_τ^α that characterize the kinetics of phase transformations (cf. Fig. 5). From the discussion presented here it becomes evident that there exist many possibilities of determination of the set of physical constants Y_c . For example, when relations (4.20)–(4.22) and (4.25) are used, the three remaining unspecified constants could be determined from the measured data concerning the initial modulus $E_{pe}^{(1)}$, the slope of the line $A - A_1$ in Fig. 4b (that represent the unstable equilibrium states — cf. (4.26)) and the critical stress $\tau(A)$ at a certain fixed temperature.

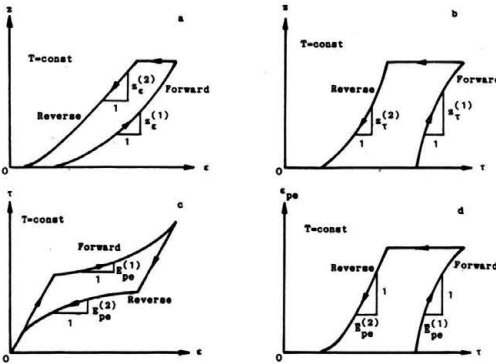


FIG. 5. Activity coefficients of isothermal transformations: a) strain-induced, b) stress-induced. Isothermal moduli of: c) pseudoelastic active flow $E_{pe}^{(1)}$ and pseudoelastic strain recovery $E_{pe}^{(2)}$, d) pure pseudoelastic flows.

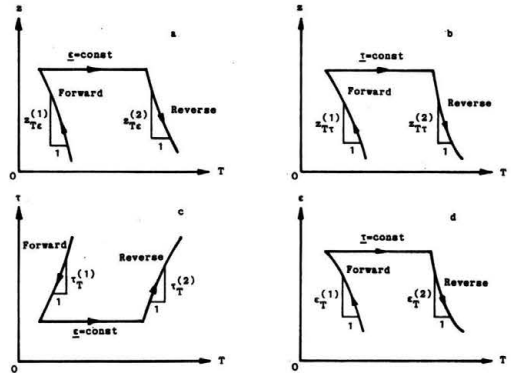


FIG. 6. Activity coefficients of temperature-induced transformations: a) strain-assisted, b) stress-assisted. Coefficients of: c) transformation-induced stressing (isometric), d) transformation-induced straining (isostatic).

Consider now the possible non-isothermal paths. To any state within the bounding loop shown in Fig. 4a there corresponds a straight line in $\epsilon - T$ or $\tau - T$ plane (Fig. 4c, d). The mappings are, respectively, described by (4.10)₂ and (4.12)₂ with fixed values of π^f and z . With the two main points A ($\pi^f = 0, z = 0$) and A_1 ($\pi^f = 0, z = 1$), representing unstable equilibrium states of the bounding loops, are now associated two straight lines that intersect the temperature axis at M_s^0 and A_s^0 , respectively. Those two straight lines constitute the graphical illustration of the effect of stress (strain) upon martensite-start temperature during forward transformation, and austenite (parent phase)-start temperature during reverse transformation. When configurational entropy vanishes ($\bar{s}_0 = 0$), the lines are parallel. The positive \bar{s}_0 , however, increases the tendency for the intersection of the two lines on $\tau - T$ plane at higher temperature. The straight lines corresponding to the points B and M of Fig. 4a are also shown in the Fig. 4c, d. We define the activity coefficients of strain-assisted ($\epsilon = \text{const}$) thermally-induced martensite $z_{T\epsilon}^{(1)}$, and strain assisted thermally-induced austenite $z_{T\epsilon}^{(2)}$ by (cf. Fig. 6a)

$$(4.32) \quad z_{T\epsilon}^\alpha \equiv -(\partial z / \partial T) \Big|_{\substack{\epsilon = \text{const} \\ \psi^\alpha = \text{const}}} = [\Delta s^* - (1 - 2z)\bar{s}_0] / H_\epsilon^\alpha, \quad \alpha = 1, 2.$$

Likewise, the rate of transformations under fixed stress ($\tau = \text{const}$) can be characterized by activity coefficients $z_{T\tau}^\alpha$ of stress-assisted ($\tau = \text{const}$) thermally induced forward ($\alpha = 1$) and reverse ($\alpha = 2$) transformations (cf. Fig. 6b)

$$(4.33) \quad z_{T\tau}^\alpha \equiv -(\partial z / \partial T) \Big|_{\substack{\tau = \text{const} \\ \psi^\alpha = \text{const}}} = [\Delta s^* - (1 - 2z)\bar{s}_0] / H_\tau^\alpha = (H_\epsilon^\alpha / H_\tau^\alpha) z_{T\epsilon}^\alpha.$$

In terms of $z_{T\tau}^\alpha$ and $z_{T\epsilon}^\alpha$ one can express the isostatic ($\tau = \text{const}$) coefficients ϵ_T^α (Fig. 6d) of transformation-induced straining, and isometric ($\epsilon = \text{const}$) coefficients τ_T^α (Fig. 6c) of transformation-induced stressing, respectively,

$$(4.34) \quad \begin{aligned} \epsilon_T^\alpha &= -(\partial\epsilon/\partial T)|_{\substack{\tau=\text{const} \\ \psi^\alpha=\text{const}}} = \eta z_{T\tau}^\alpha, \\ \tau_T^\alpha &\equiv (\partial\tau/\partial T)|_{\substack{\epsilon=\text{const} \\ \psi^\alpha=\text{const}}} = 2\mu\eta z_{T\epsilon}^\alpha = E_{pe}^\alpha \epsilon_T^\alpha. \end{aligned}$$

According to experimental evidence $z_{T\tau}^\alpha$ is not negative, and this condition will be satisfied provided that (4.24) and (4.30) hold. Note the following identity

$$(4.35) \quad 2\mu z_\tau^\alpha z_{T\epsilon}^\alpha = z_\epsilon^\alpha z_{T\tau}^\alpha$$

that enables to determine one of the activity coefficients when the three others are known. It has been used to derive the last equality occurring in (4.34)₂. The relations (4.34) show the interrelations that exists between thermal properties of an alloy and the quantities that characterize the kinetics of thermally-induced transformations. We emphasise again that the domain of determination of the quantities with superscript $\alpha = 1$ (forward transformation) is $\psi^{(1)} \leq 0$, $\pi^f \geq 0$, $0 \leq z \leq 1$, whereas that with superscript $\alpha = 2$ (reverse transformation) it is $\psi^{(2)} \leq 0$, $\pi^f \leq 0$, $0 \leq z \leq 1$.

We shall now consider arbitrary thermo-mechanical process. In the case of non-isothermal infinitesimal processes it is possible to adjust non-zero $d\epsilon$ and dT which will produce no progress of transformation ($dz = 0$). Such infinitesimal passive processes will be termed „neutral processes“. We shall now derive the analytical criteria for infinitesimal neutral, passive and active processes.

Consider a fixed state (ϵ, T, z) corresponding to a point within the bounding loop of Fig. 4a. For prescribed infinitesimal changes in the strain and the temperature ($d\epsilon, dT$), the quantity

$$(4.36) \quad d_\epsilon \pi^f = (\partial\pi^f/\partial\epsilon)d\epsilon + (\partial\pi^f/\partial T)dT = 2\mu\eta d\epsilon - [\Delta\bar{s} + (2z - 1)\bar{s}_0]dT$$

is proportional to the cosine of the angle between the infinitesimal vector $(d\epsilon, dT)$ and the vector normal to the straight line that passes through a point representing the current state in the plane $\epsilon - T$. When $d_\epsilon \pi^f = 0$, the vector $(d\epsilon, dT)$ is parallel to the straight line. We note that, on account of (4.10)₂ and (4.17), $d\psi^\alpha = 0$ implies $d_\epsilon \pi^f = H_\epsilon^\alpha dz$, and since H_ϵ^α is positive (cf. (4.31)), $d_\epsilon \pi^f = 0$ precludes the progress of active phase transformations. Therefore, the appropriate condition for instantaneous neutral process reads

$$(4.37) \quad dz = 0 \quad \text{if } d_\epsilon \pi^f = 0$$

(neutral process of phase transformation).

The response of the proposed R_L -model for $d_\epsilon \pi^f \neq 0$ depends on the state. For example, when $z = 0$ and $\pi^f < 0$ we have $dz = 0$ independently of the sign of $d_\epsilon \pi^f$. Such processes, however, concern the single-phase solid and, therefore, will not be qualified as „passive“. Four different regions of states can be distinguished (cf. Fig. 4a):

- region 1 where $z = 0$ and $\pi^f = 0$ (unstable equilibria, point A — Fig. 4a),
- region 2 where $z > 0$ and $\pi^f > 0$,
- region 3 where $z > 0$ and $\pi^f = 0$ (locus of other unstable equilibrium states),
- region 4 where $z > 0$ and $\pi^f < 0$.

Due to our assumption that passive processes can not be initiated from a two-phase state of unstable equilibrium, the condition for a passive process is

$$(4.38) \quad dz = 0 \quad \text{if} \quad (d_\epsilon \pi^f < 0 \text{ in regions 1 and 2) or } (d_\epsilon \pi^f > 0 \text{ in region 4}).$$

In all other situations the active processes are commenced. The condition for the progress of active austenite (parent phase) decomposition can be written as follows:

$$(4.39) \quad dz > 0 \quad \text{if} \quad d_\epsilon \pi^f > 0 \text{ in regions 1, 2 and 3,}$$

whereas, that for an active decomposition of the martensite reads

$$(4.40) \quad dz < 0 \quad \text{if} \quad d_\epsilon \pi^f < 0 \text{ in regions 3 and 4.}$$

The possible orientations of the infinitesimal vector $(d\epsilon, dT)$ for neutral, passive and active processes are shown in Fig. 4b.

To satisfy (4.37) we take linear relationship between dz and $d_\epsilon \pi^f$

$$(4.41) \quad dz = \lambda^\alpha d_\epsilon \pi^f.$$

In the course of an active process, this relation must comply with the assumed form of the functions ψ^α . Hence the proportionality factors λ^α can be evaluated from the "consistency" relations $d\psi^\alpha = 0$. This gives $\lambda^\alpha = 1/H_\epsilon^\alpha$ (cf. (4.28)). By combining (4.37) and (4.41) one eventually arrives at the following final form of the incremental relations of transformation kinetics:

$$(4.42) \quad dz = \begin{cases} d_\epsilon \pi^f / H_\epsilon^{(1)} & \text{if } d_\epsilon \pi^f \geq 0 \quad \text{and} \\ & [(z > 0 \quad \text{and} \quad \pi^f \geq 0) \quad \text{or} \quad (z = 0 \quad \text{and} \quad \pi^f = 0)], \\ d_\epsilon \pi^f / H_\epsilon^{(2)} & \text{if } d_\epsilon \pi^f \leq 0 \quad \text{and} \quad [(z > 0 \quad \text{and} \quad \pi^f \leq 0)], \\ 0 & \text{if } \{d_\epsilon \pi^f \leq 0 \quad \text{and} \\ & [(z > 0 \quad \text{and} \quad \pi^f > 0) \quad \text{or} \quad (z = 0 \quad \text{and} \quad \pi^f = 0)]\} \\ & \text{or } \{d_\epsilon \pi^f \geq 0 \quad \text{and} \quad (z > 0 \quad \text{and} \quad \pi^f < 0)\} \\ & \text{or } \{z = 0 \quad \text{and} \quad \pi^f < 0\}. \end{cases}$$

where $d_\epsilon \pi^f$ is defined by (4.36). Whenever $H_\tau^\alpha > 0$, the kinetics relations can also be expressed in terms of $d\tau$ and dT . It can be shown that introducing the infinitesimal quantity $d_\tau \pi^f = \eta d\tau - [\Delta \bar{s} + (2z - 1)\bar{s}_0] dT$, it is sufficient for this purpose to replace $d_\epsilon \pi^f$ and H_ϵ^α occurring in (4.42) by $d_\tau \pi^f$ and H_τ^α , respectively.

The other proposal for analytical description of internal hysteresis loops may be found in [26] and [27].

4.3. Incremental form of basic equations for R_L -model

The full set of coupled incremental equations for R_L -model consist of:

- The incremental equations of transformation kinetics (4.42).
- The relation between increments of mean stress, mean strain and temperature — it has the same form as the corresponding relation for R -model, cf. (2.22).
- The relations between deviators of strain and stress that can be obtained from (4.8)₂ and (4.9):

$$(4.43) \quad \begin{aligned} d\bar{\sigma} &= 2\mu_0(d\bar{\epsilon} - d\bar{\epsilon}^{pe}), \\ d\bar{\epsilon}^{pe} &= (\eta/\epsilon)[\bar{\epsilon} dz + z\mathbf{P}(\bar{\epsilon})d\bar{\epsilon}], \end{aligned}$$

where \mathbf{P} is defined by (2.17).

d. The relation for the temperature change which can be derived by eliminating ds between (4.12)₁ and (4.13) (cf. also (4.16));

$$(4.44) \quad c_p dT = -\bar{d}q + \pi^f dz - 3\alpha_0 T d\sigma_m / \rho + T(\Delta \bar{s}^* - \bar{s}_0 + 2z\bar{s}_0) dz.$$

The second, third and the fourth terms occurring on the right-hand side of (4.44) represent: heat due to the energy dissipation, reversible heat of usually small piezocaloric effect and reversible heat due to the phase transformations, respectively. The latter heat, however, is exactly balanced by the part of the heat due to the energy dissipation, what can easily be noted by substituting (4.12)₂ into (4.44). The equivalent form of (4.44) is

$$(4.45) \quad c_p dT = -\bar{d}q + \bar{\sigma} \cdot d\bar{\epsilon}^{pe} / \rho + l(z) dz - 3\alpha_0 T d\sigma_m / \rho,$$

where

$$(4.46) \quad l(z) = \Delta \bar{u}^* - \bar{u}_0(1 - 2z)$$

can be referred to as the „latent heat of phase transformation” at stress-free state. When infinitesimal mass of the parent phase dM is totally transformed into martensite at $\sigma = 0$ then $l(z) dM = M(c_p dT + \bar{d}q)$ is an extra heat transferred to the surroundings. The second term on the right-hand side of (4.45), $\bar{\sigma} \cdot d\bar{\epsilon}^{pe} / \rho = \eta \tau dz$, may be interpreted as the heat due to dissipation of the mechanical work.

Using (4.13), equation (4.45) can be equivalently expressed in terms of c_v and ϵ_v , vis.,

$$(4.47) \quad c_v dT = -\bar{d}q + \bar{\sigma} \cdot d\bar{\epsilon}^{pe} / \rho + l(z) dz - 3\alpha_0 T K_0 d\epsilon_v / \rho.$$

Note that neither $\Delta \bar{s}^*$ nor \bar{s}_0 occur in the equation for the temperature. Therefore, these quantities can not be detected by direct calorimetric measurements, such as discussed e.g. by ORTIN and PLANES [9–10]. The most significant influence on temperature changes in the course of homogeneous adiabatic processes ($\bar{d}q = 0$) have second and third terms occurring on the right-hand sides of (4.45) and (4.47). Both terms oscillate during proportional loading-unloading processes associated with the forward and reverse transformations. While the third term produce zero net change in the temperature after each consecutive cycle, the second term causes its slight gradual increase.

For both models (R -model and R_L -model) the constitutive equations for the pseudoelastic strain $\bar{\epsilon}^{pe}$ are singular at $\epsilon = \mathbf{0}$ (cf. (4.43)). This should not entail, however, any particular trouble when solving the specific engineering problems. At the temperature range $T > A_f^0$, $\epsilon = \mathbf{0}$ implies $z = 0$, so that no two-phase state occurs when $\epsilon = \mathbf{0}$, and at the singular point the incremental relations become the same as that of usual linear thermoelasticity. When applying the numerical methods it is advised to set $z = 0$ and $z = 1$, whenever $z \leq z_A^f$ and $z \geq z_M^f$ (cf. (4.25)), respectively.

5. Concluding remarks

In this paper two workable models of pseudoelastic behaviour of shape memory alloys have been developed. They account for the most significant features of the behaviour of alloys at the temperature range $T > A_f^0$, such as pseudoelastic flow and the formation of the characteristic hysteresis loop (R_L -model) associated with the forward and reverse austenitic-martensitic transformations. They employ the possible least number of physical constants. In fact, in addition to the conventional data normally supplied by the producer, the knowledge of a typical single hysteresis loop at simple tension is sufficient for the specification of all constants. The observed behaviour under uniaxial stress state is

interpreted in terms of relations between second invariants of stress and strain deviators. This hypothesis enables us to derive the incremental constitutive equations for general three-dimensional stress state.

As pseudoelastic flow and pseudoelastic strain recovery are inherently associated with the phase transformations ongoing under applied stress and/or varying temperature, the use of the methods of the thermodynamics seems to be most appropriate. We applied those classical concepts (concerning two-phase systems) that have been advanced and developed for two-phase shape memory alloys by MÜLLER and XU [15], and we combined them with the concepts of thermodynamics of constrained equilibrium developed by KESTIN and RICE [21–22] at the end of sixties and in the seventies. The knowledge of the type of stability and the positions of states of absolute equilibrium in the set of all states accessible during actual thermomechanical processes gave possibility for physically plausible explanation of the abnormal “pseudoelastic” behaviour of shape memory alloys at $T > A_f^0$. It is also instrumental in finding the character of the formation of internal loops which, so far, are not well investigated on experimental ground. Although, the basic equations of the ideal R -model presented here describe only reversible processes, we believe that the model can find some engineering applications, e.g., it may be used for rough estimation of transient stresses that occur in structural elements made of shape memory alloys. The coupled incremental constitutive equations are also derived for more realistic R_L -model. The most important equation of kinetics of phase transformation accomplished formation of bounding and internal loops was deduced here from Clausius–Duhem inequality. The experimental verification of the predictions of R_L -model should not involve special problems. Likewise, both models can easily be implemented into existing numerical codes.

When developing both models we found it extremely difficult to formulate the evolution equation for the parameter κ . We believe that its magnitude undergoes rapid changes at the beginning of the formation of the first martensite plates, and that it remains almost constant at the advanced stage of transformations. The orientation of the principal directions of κ , however, may be much influenced by the changes in the principal directions of the applied stress. What we proposed here is a “proviso” that will be modified in the further studies. At present it makes the generalization of the theory to account for temperature range $T < A_f^0$ very difficult. In view of the lack of appropriate experiments concerning the complex paths, we could not find anything better. The R_L -model, therefore, can be regarded as a reference one that may help to systematize the research in this field.

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