

Review

Thermoelasticity, pseudoelasticity and the memory effects associated with martensitic transformations

Part 3 *Thermodynamics and kinetics*

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The pertinent thermodynamic relations, nucleation and growth and the influence of stress are considered and applied to thermoelasticity and the memory effects.

1. Introduction

In Parts 1 and 2 it was shown that the effects of temperature and stress on the thermoelastic, pseudoelastic and shape memory phenomena are functions of the components and composition of the alloy and thus of its thermodynamic properties and of the energy terms of the nucleation and growth processes. In this paper the pertinent thermodynamic relations, nucleation and growth are first discussed in general terms and then applied to the individual phenomena.

2. Thermodynamic relations

2.1. Free energy of transformation

Since alloy phases undergoing diffusionless transformations can be considered as one-component systems thermodynamically [1] the relation between the free enthalpies of the martensite (M) and parent (P) phases can be represented as shown in Fig. 1. The function $G(T)$ of the individual phases is unknown for most of the alloy phases of present interest. But the function $\Delta G^{P-M}(T)$ which is required for quantitative treatments of martensitic transformations can be derived more directly from measured data. From

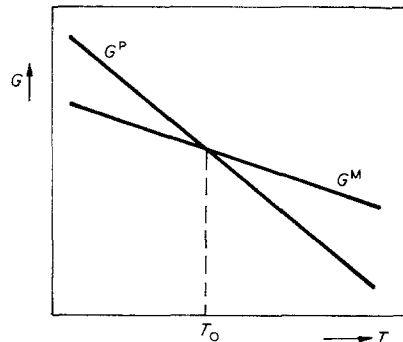


Figure 1 Temperature dependence of the free enthalpies G^P and G^M of a parent (P) and a martensitic product (M) phase.

$$\Delta G^{P-M} = G^M - G^P = \Delta H^{P-M} - T\Delta S^{P-M}, \quad (1)$$

where ΔH^{P-M} is the enthalpy and ΔS^{P-M} the entropy of transformation, we obtain

$$\Delta H^{P-M} = T_0\Delta S^{P-M} \quad (2)$$

where $\Delta G^{P-M} = 0$, for the equilibrium temperature T_0 . Since ΔH^{P-M} can be measured calorimetrically and T_0 can be obtained more or

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TABLE I Typical thermodynamic data of martensitic transformations

Alloy	$\Delta H_{T_0}^{P-M}$ (cal g-atom ⁻¹)	T_0 (K)	ΔS^{P-M} (cal g-atom ⁻¹)	$\Delta G_{M_s}^{P-M}$ (cal g-atom ⁻¹)	$\Delta T_h = A_f - M_f$ References (K)
AuCd	62.7-98.0	330-350	0.2 ± 0.1	2 ± 1	26
	88-106	266-363	0.3 ± 0.1		16
Au-Cu-Zn	120-170	0-275	0.75 ± 0.25	4 ± 1	10-50
Cu-Al	40-65	300-800	0.08 ± 0.02	5 ± 2	40
Cu-Zn	75	0-300	0.25	3	48
			0.31 0.01		20
Ti-alloys				50-60	28
Fe-C			1.4	150-450	
Fe-Ni	600-700				200-400
Fe-Cr				70-350	1, 29

less accurately from the relations* $T_0 \simeq (A_s - M_s)/2 \simeq (A_f - M_f)/2 \simeq (M_d - A_d)/2$, it is possible to compute

$$\Delta S^{P-M} = \Delta H^{P-M}/T_0 = \delta \Delta G^{P-M}/\delta T. \quad (3)$$

Some characteristic data are listed in Table I. Since ΔS^{P-M} gives the rate of change of the free enthalpy difference with deviation from T_0 it is an essential quantity in relation to the transformation behaviour with and without applied stress.

Further thermodynamic data, as well as information regarding the mechanical behaviour, can be obtained from the elastic constants. Zener [2] has pointed out that the stability of bcc β phases decreases with decreasing temperature. This decrease is exhibited, in particular, by the positive temperature coefficient $\delta C'/\delta T$ of the elastic shear constant $C' = (C_{11} - C_{12})/2$ on approaching T_0 ; it pertains to waves on $\{1\bar{1}0\}\langle 110\rangle$. This behaviour has been found for numerous alloys that undergo martensitic transformations, e.g., Cu-Zn [3], AuCd [4], Au-Cu-Zn [5], In-Tl [6], NiAl [7]. Nakanishi *et al.* [5] have made use of this information quantitatively for Au-Cu-Zn alloys. Following their arguments, the free enthalpy change ΔG^{P-M} can be expressed as

$$\Delta G^{P-M} = \Delta H^{P-M} + \Delta G_{\text{vib}}^{P-M} - T\Delta S_{\text{cont}}^{P-M} + \Delta G_{\text{elec}}^{P-M}, \quad (4)$$

where $\Delta G_{\text{vib}}^{P-M}$ = difference in vibrational free enthalpy, $\Delta S_{\text{cont}}^{P-M}$ = difference in con-

figurational entropy and $\Delta G_{\text{elec}}^{P-M}$ = difference in electronic free energy. Nakanishi assumed that $\Delta S_{\text{cont}}^{P-M}$ and $\Delta G_{\text{elec}}^{P-M}$ are negligible because the ordered structure of the parent phase is inherited in the martensite and the electronic free enthalpies of the Heusler phase and orthorhombic martensite phase (in Au-Cu-Zn) can be considered to be of similar magnitude (according to the free electron theory). Thus the free enthalpy change upon transformation can be expressed as

$$\Delta G^{P-M} = \Delta H^{P-M} + 3kT \frac{1 - \exp(-\Theta_D^P/T)}{1 - \exp(-\Theta_D^M/T)} \quad (5)$$

where k is the Boltzmann constant and Θ_D^P and Θ_D^M are the Debye temperatures of the parent and martensitic product phases. If ΔH^{P-M} is known from calorimetric measurements and Θ_D^P has been derived from the elastic constant values extrapolated to 0K, the values of $\Delta G^{P-M}(T)$ and of Θ_D^M can be calculated. Nakanishi *et al.* found from their data that Θ_D^P and Θ_D^M were nearly equal, varied strongly with composition and had a minimum where T_0 was highest. From this they concluded that at T_0 the vibrational entropy is at a maximum in both phases and that the shear vibration along $\{110\}\langle 1\bar{1}0\rangle_P$ of the bcc parent phase and along the corresponding $\{001\}\langle 010\rangle_M$ of the orthorhombic martensite phase becomes maximum at this temperature. Thus, the magnitudes of the pertinent shear constants of both the

*These relations imply that the nucleation and growth processes for direct and reverse transformation involve identical energy terms. This is not the case for most martensitic transformations. In particular, $A_s < M_s$ for most thermoelastic transformations. Bracketing procedures will, therefore, have to take into account the energy contributions to nucleation and growth as treated in this paper. *Note added in proof.* Recently, Dunne and Wayman [31] and Tong and Wayman [32] have investigated the characteristic temperatures of thermoelastic martensites and have developed energy considerations similar to those presented here.

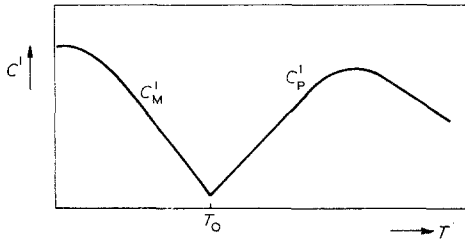


Figure 2 Schematic plot of the temperature dependence of the shear constants C'_P and C'_M near the equilibrium temperature T_0 .

parent and the martensite phase approach very low values or zero at T_0 , (Fig. 2). Although it is generally impossible to measure the single crystal elastic constants of martensitic structures (since most cannot be obtained in a single crystalline state) strong support for the hypothesis of a pronounced lattice softening may be derived from Young's modulus measurements as a function of temperature below T_0 : Young's modulus of martensite in several non-ferrous systems decreases much more strongly with increasing temperature than according to the normal temperature dependence in stable phases. Experimental evidence of this behaviour has been reported, e.g. for Au-Cu-Zn [5] and NiTi [8] and has also been found for NiAl [7].

The consequences of the elastic anomalies for the energy balance during growth and the resulting behaviour will be discussed further below.

2.2. Effects of stress

Scheil [9] pointed out as early as 1932 that the stress required to induce a martensitic transformation decreased with decreasing temperature to become zero at M_s . Burkart and Read [10] and Patel and Cohen [11] investigated this relation quantitatively. The problem was to compute the change in T_0 due to changes in stress as a state variable under the assumption that the driving force required for nucleation remains constant in a first approximation. The work done on the stressed specimen is calculated in the more complete second treatment [11] on the basis of a uniaxial tensile or compressive applied stress which induces shear as well as volume stresses in the specimen. This work can be expressed as:

$$W = \tau\gamma_0 + \sigma\epsilon_0 \quad (6)$$

where τ is the shear stress and γ_0 the shear strain,

σ the longitudinal stress and ϵ_0 the corresponding strain associated with the transformation. There are essentially two possible choices for γ_0 : the strain given by the lattice strain (as employed, e.g. in [5]) and the total transformation strain [11]. Microstructural observations indicate that applied stresses may lead to transformations where only the lattice strain occurs and that in other cases the same total shape strain, as in quench-induced transformations, is operating. Therefore, the term $\tau\gamma_0$ has to be chosen according to the operative strain in each individual case.

The stress dependence of the free energy change is obtained from

$$W = \Delta G_{\sigma}^{P-M} = \frac{1}{2} \sigma_a [\gamma_0 \sin 2\theta \pm \epsilon_0 (1 + \cos 2\theta)] V_m \text{ cal g-atom}^{-1} \quad (7)$$

where ΔG_{σ}^{P-M} is the free enthalpy difference under stress, σ_a the applied stress, θ the angle between the stress axis and the normal to the operative shear plane, and V_m the molar volume. The maximum effect is obtained for the transformation shear system for which

$$\Delta G_{\sigma}^{P-M} = 0. \quad (8)$$

From this, the condition for the direction of the applied stress to the shear system most prone to transformation is

$$\tan 2\theta = \pm \gamma_0/\epsilon_0. \quad (9)$$

If we assume that $G(T)$ is a linear function and $\Delta G_{M_s}^{P-M}$ is constant we equate

$$\frac{\delta \Delta G_{\sigma}^{P-M}}{\delta T} = \frac{\delta \Delta G^{P-M}}{\delta T} = \frac{\Delta H^{P-M}}{T_0} = \Delta S^{P-M}. \quad (10)$$

Also with

$$\frac{\delta \Delta G_{\sigma}^{P-M}}{\delta \sigma_a} = \frac{1}{2} [\gamma_0 \sin 2\theta \pm \epsilon_0 (1 + \cos 2\theta)] V_m = \epsilon_M \quad (11)$$

where ϵ_M is the total strain tensor associated with the transformation, we obtain:

$$\frac{\delta T_0}{\delta \sigma_a} = \frac{\delta T}{\delta \Delta G^{P-M}} \cdot \frac{\delta \Delta G_{\sigma}^{P-M}}{\delta \sigma_a} = \frac{T_0}{\Delta H^{P-M}} \quad (12)$$

$$[\gamma_0 \sin 2\theta \pm \epsilon_0 (1 + \cos 2\theta)] V_m = \frac{\epsilon_M}{\Delta S^{P-M}}.$$

Fig. 3 illustrates the relation graphically. The curve of the free energy change accompanying the transformation ΔG^{P-M} (as derived from the functions for the individual phases, Fig. 1) is

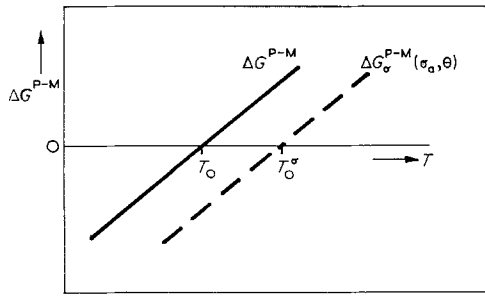


Figure 3 Temperature dependence of the transformation free enthalpy G^{P-M} and the influence of stress.

displaced as a function of external stress. The magnitude of the displacement is inversely proportional to the transformation entropy such that, with reference to Table I, the stress effects on some of the Cu- and Au-based alloys are expected to be considerably larger than on Fe-based alloys, if ϵ_M is assumed to be approximately equal. It should be noted that ΔG_{σ}^{P-M} depends also on the orientation, as indicated by the angle θ .

A rough approximation of Equation 12 may be obtained by using the relation

$$\frac{\delta\sigma_a^{P-M}}{\delta T} = \frac{\rho \cdot \Delta H^{P-M}}{\epsilon^{P-M} \cdot T_0} \quad (13)$$

where σ_a^{P-M} is the applied stress at which pseudoelastic martensite is formed at testing temperature T , ρ the density, and ϵ^{P-M} the strain corresponding to complete transformation; σ_a^{P-M} and ϵ^{P-M} are taken from the stress-strain curve. It can be shown that this estimate and experimental values of $\delta\sigma_a^{P-M}/\delta T$ agree well within experimental accuracy. Thus, for Au-47.5 at. % Cd with $\Delta H^{P-M} = 88$ cal g-atom⁻¹, $\epsilon^{P-M} = 3.8\%$, $\rho = 14.2$ g cm⁻³ and $T_0 = 65^\circ\text{C}$, Equation 13 yields $\delta\sigma_a^{P-M}/\delta T = 0.265$ kg mm⁻² · K⁻¹ whereas $\delta\sigma_a^{P-M}/T = 0.25$ kg mm⁻² · K⁻¹ was found experimentally [12].

Different directions and amounts of applied stress σ_a may lead to a transformation into different crystal structures. Thermodynamically this can be represented as shown in Fig. 4. Two martensite phases M_1 and M_2 are associated with different functions $\Delta G^{P-M_1}(T)$, $\Delta G^{P-M_2}(T)$. Since these, in turn, depend differently on σ_a and θ according to Equation 12, the stress-induced transformations may lead, for instance, to the

transformation to M_1 at lower stresses and to M_2 at higher stresses as indicated for a temperature T_1 in Fig. 4.

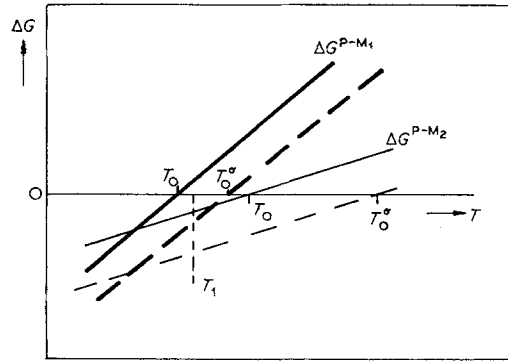


Figure 4 Same as Fig. 3, but for two different martensite phases M_1 and M_2 .

3. Nucleation

The free enthalpy change upon nucleation of a martensitic transformation at $T = M_s$ is given by

$$\Delta G_{M_s}^{P-M} = (T_0 - M_s)\Delta S^{P-M}. \quad (14)$$

A graphic representation of Equation 14 in terms of a $\Delta G(T)$ plot is given in Fig. 5. We shall assume throughout that $\Delta G_{M_s}^{P-M}$ is independent of T and the applied stress σ_a . This simplifying assumption is justifiable for the present qualitative description because the variation is generally small and will, therefore, not affect the semiquantitative estimates and the principal conclusions.

Turning to the nucleation under an applied stress σ_a , it may be seen from Fig. 5 that the corresponding transformation start temperature $M_s^{\sigma_a}$ is raised proportionally to the shift of T_0 to T_0^{σ} . At a temperature $M_s^{\sigma} < T_0$ such as $M_s^{\sigma_1}$ the free enthalpy change consists of the thermal component

$$\Delta G_{t, M_s^{\sigma_1} P-M}(T_0 - M_s^{\sigma_1})\Delta S^{P-M} \quad (15)$$

and the stress-induced component

$$\Delta G_{\sigma, M_s^{\sigma_1} P-M} = \sigma_a \epsilon_M = (M_s^{\sigma_1} - M_s)\Delta S^{P-M}. \quad (16)$$

This implies that the martensite phase, once it is

*In detailed accounts of martensite nucleation, stress- and strain-induced nucleation are distinguished [13]. In the present context the elementary processes of nucleation are not considered. Consequently, the effects of stress on nucleation are not subdivided.

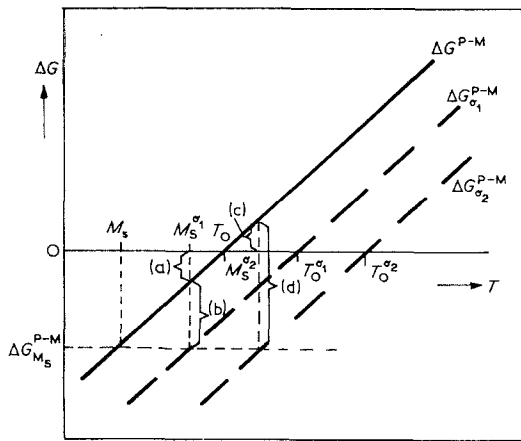


Figure 5 Same as Fig. 3, but indicating the nucleation free enthalpy $\Delta G_{M_s}^{P-M}$ and the shift of M_s as a function of applied stress $\sigma_a = \sigma_1, \sigma_2$, (a) $\Delta G_{t, M_s}^{\sigma_1}$; (b) $\Delta G_{\sigma, M_s}^{P-M \sigma_2}$; (c) $\Delta G_{t, M_s}^{P-M \sigma_2}$; (d) $\Delta G_{\sigma, M_s}^{P-M \sigma_2}$.

formed by stress-assisted nucleation, is thermodynamically stable in the stress-free state. On the other hand, at temperatures $M_s^\sigma > T_0$, such as $M_s^{\sigma_2}$, the nucleation free enthalpy is

$$\Delta G_{M_s^{\sigma_2}}^{P-M} = \Delta G_{\sigma, M_s^{\sigma_2}}^{P-M} - \Delta G_{t, M_s^{\sigma_2}}^{P-M} \quad (17)$$

i.e. the stress-dependent term contains the nucleation free enthalpy and a positive contribution by the chemical free enthalpy difference opposing the transformation. Correspondingly, the martensite phase may be formed by stress-assisted nucleation above T_0 but it is thermodynamically unstable in the stress-free state at its temperature of formation.

A large quantitative difference exists between the Cu-, Ag- and Au-based and the Fe-based alloys in their nucleation behaviour. This is obvious from Table I and from Fig. 6 which shows a $\Delta G(T)$ plot based upon experimental data. Apart from the difference in transformation entropy the most striking disparity is in the nucleation free enthalpy which differs by two orders of magnitude. The significance of this different behaviour will be discussed in combination with the growth and overall transformation further below.

4. Growth

The basic problem in quantitative treatment of the effects of present interest is an assessment of

*It will be noted that we tacitly assume the absence of any plastic deformation at this stage; this would alter the number and properties of nuclei.

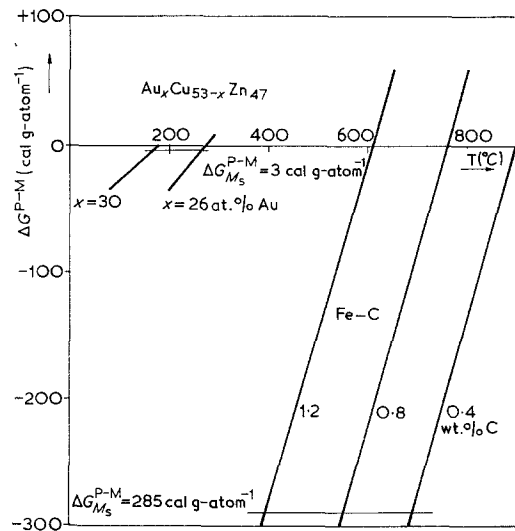


Figure 6 Temperature and composition dependence of the transformation free enthalpy ΔG^{P-M} of $\text{Au}_x\text{Cu}_{53-x}\text{Zn}_{47}$ [5] and of Fe-C [1] and the free enthalpy of nucleation $\Delta G_{M_s}^{P-M}$ of both alloys.

the growth process in relation to the thermodynamic properties and nucleation behaviour. We have indicated above that the driving free energy at the onset of transformation $\Delta G_{M_s}^{P-M}$ may be considered to be independent of applied stress and temperature of formation in a first approximation, i.e. the critical event of nucleation – whatever its mechanism in detail – occurs at the same value of $\Delta G^{P-M}(T, \sigma_a)$ at any temperature T , regardless of the relative fractions of thermal and mechanical energy contributing to ΔG^{P-M} . Therefore, the treatment of all transformation phenomena concerned is reduced to a treatment of the free enthalpy changes and of the growth (and shrinkage) processes of martensite crystallites as a function of temperature and applied stress.

The essential contributions to the growth process of a martensite plate are: the thermal component of the driving energy ΔG_t^{P-M} and the mechanical driving energy $\sigma_a \epsilon_M$ given by the applied stress σ_a multiplied by the macroscopic shape strain associated with the martensite plate growth. These driving energies are opposed by the resistive energy, composed of several terms: the elastic strain energy $\sigma_i \epsilon_M$ stored due to the internal stress built up by the applied stress and by the transformation strain (inside the martensite plate as well as in the surrounding parent

phase); the interfacial energy γ_M of the matrix/martensite interface; the defect energy γ_d due to the recoverable defects produced inside the martensite by the lattice invariant shear (this term will be included in $\sigma_i \epsilon$ for convenience); finally, a dissipated energy ξ has to be included which is due to friction and irreversible defect production in the matrix and martensite during transformation. ξ is a function with the dimension of a stress whose argument is discussed in [14]. These terms yield an equation for the growth process which has essentially been developed for twin growth [14] and has been modified for martensitic growth [13]. Considering the incremental growth or shrinkage of a martensite plate by a volume element dV_M (and a corresponding surface element dA) we can write:

$$\Delta G_t^{P-M} dV_M - \sigma_a \epsilon_M dV = \sigma_i \epsilon_M dV_M + \gamma_M dA + \xi \epsilon_M dV_M. \quad (18)$$

If the driving energy ΔG_d^{P-M} on the left side of Equation 18 and the resistive energy ΔG_r^{P-M} on the right are plotted as a function of the fraction transformed V_M/V , a relation as shown schematically in Fig. 7 is obtained. It is shown, in particular, that the effective free enthalpy difference, ΔG_{eff} , becomes zero at some intermediate stage of growth, indicating that growth will cease without any influence by an obstacle if $\Delta G_d^{P-M} = \Delta G_r^{P-M}$.

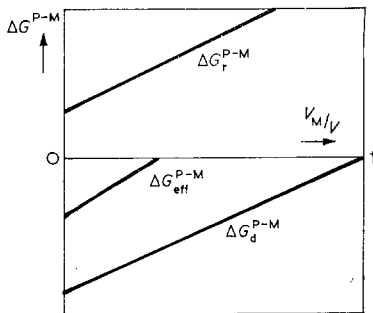


Figure 7 Schematic representation of the driving and resistive energies and the effective free energy difference during growth as a function of the volume fraction V_M/V transformed martensitically.

For the present purpose Equation 18 has been simplified by omitting shape and volume factors which are required for an exact treatment. Reasonably quantitative estimates can still be derived from it. However, it will mainly serve to

discuss the terms and their temperature and stress dependence qualitatively. For convenience in the following discussion we may divide the equation by dV (i.e. all terms refer to transformation of a unit (molar) volume in a particular ideal configuration, e.g., one plate in a total volume sufficiently large for boundary effects to be negligible) and obtain

$$\Delta G_t^{P-M} + \sigma_a \epsilon_M \leq \sigma_i \epsilon_M + \gamma_M A' + \xi \epsilon_M \quad (19)$$

where $A' = dA/dV$ is a shape factor. This relation shows the interchangeability of ΔG_t^{P-M} and $\sigma_a \epsilon$ as driving forces for growth, in correspondence with the same effects on T_0 and nucleation, respectively.

Excluding the trivial case of stoppage of a growing plate by a grain boundary or equivalent obstacle, we may differentiate the cases of equality and inequality in this relation. Equality implies that any change in the thermal or mechanical term of the driving energy will cause growth or shrinkage of the martensite plate considered. This *thermoelastic equilibrium* is the basis of thermoelastic martensite formation. At M_s a supercritical nucleus will be in thermoelastic equilibrium immediately and will grow only with decreasing temperature. Nuclei which become supercritical at $T < M_s$ will either be in thermoelastic equilibrium immediately or will grow fast until they reach a finite plate size at which $\Delta G_{\text{eff}}^{P-M} = 0$.

If the driving energy is larger than the resistive energy and remains so until growth is stopped by an obstacle, spontaneous growth will result from every nucleation event; this is the characteristic behaviour of burst martensite. The third case in which the driving energy is smaller than the resistive energy will arise when the effective friction force reaches some critical value due to the formation of irreversible lattice defects such that upon reduction of the driving force the martensite plate does not shrink accordingly because its interfaces are pinned by lattice defects which have been formed during growth. For this condition a reversibility parameter may be defined as the fraction of recoverable (or reversible) to total resistive energy:

$$R(T, \sigma_a) = \frac{\sigma_i \epsilon_M + \gamma_M}{\sigma_i \epsilon_M + \gamma_M + \xi \epsilon_M}, \quad (20)$$

where $R = 1$ if the growth process is completely reversible because $\xi = 0$, so that all driving energy is stored; $R \rightarrow 0$ if energy dissipation by irreversible processes predominates.

5. Application to the individual phenomena

The perfect generality of the interactions of martensitic transformations with internal and applied stresses shows that the four effects of present interest are not limited in principle to any specific structure or structural group of martensite or parent phases, although the structure-dependent energy terms in specific systems impose effective limits. In this section we shall apply the above considerations to the four effects specifically.

5.1. Thermoelastic martensite growth

The characteristic feature of thermoelastic martensite is its gradual appearance and disappearance as the temperature is decreased and increased below M_s , i.e. the absence of spontaneous, burst-like growth. Two factors contribute to this transformation mode: at M_s the driving energy is sufficiently small such that it is balanced by the resistive energy at the onset of growth; the rate of increase in driving free enthalpy (ΔG_T^{P-M}) upon further cooling is greater than the rate of increase in resistive energy components such that the growth proceeds. In terms of Equation 19,

$$\Delta G_{M_s}^{P-M} = \sigma_1 \epsilon_M + \gamma_M A' + \xi \epsilon_M \quad (21)$$

is the condition for thermoelastic martensite.* In an estimate based on experimental data for Au-Cu-Zn alloys, Nakanishi *et al.* [5] obtained $\Delta G_{M_s}^{P-M} \approx (4 \pm 1)$ cal g-atom⁻¹; they derived $\sigma_1 \epsilon_M$ by using the shear elastic constant C_{β}' and the transformation shear strain $\epsilon_M = (1/6) \langle 1\bar{1}0 \rangle \{110\}_{\beta}$, both pertaining to the parent β phase, to obtain $\sigma_1 \epsilon_M \approx (1/2) C_{\beta}' (\Delta \epsilon)^2 \approx (7.5 \pm 2.5)$ cal g-atom⁻¹. Thus, even when the terms of the interfacial and dissipated energy are omitted, this approximation yields equality of the driving and resistive free energies to a reasonable accuracy in a system known to exhibit thermoelastic behaviour. Since $(\delta \Delta G_T^{P-M} / \delta T) > 0$ the driving energy increases with decreasing temperature. The terms on the right vary with temperature much more slowly than ΔG_T^{P-M} . If the temperature is decreased, the volume of the martensitic phase is increased so that $\Delta G_{eff} = 0$ and thermoelastic equilibrium is maintained accordingly.

In some alloys such as Cu-Zn, thermoelastic

growth occurs at $M_s > T > M_b$ whereas spontaneous burst-like martensite growth prevails at $T < M_b$ [15]. It appears that the transition at M_b arises because a critical value of ΔG_T^{P-M} is exceeded. For the Cu-Zn system, the transformation entropy $\Delta S^{\beta_2-\beta_2''} = 0.25$ cal g-atom⁻¹ K⁻¹. The temperature dependence of the stored elastic energy (*elastic entropy*) may be estimated to be $\delta \sigma_1 \epsilon_M / \delta T = (1/2) (\delta C' / \delta T)_{\beta_2} \cdot \epsilon_M^2 = 0.019$ cal g-atom⁻¹ with $(\delta C' / \delta T)_{\beta_2} = 10^8$ dyn cm⁻² K⁻¹ [3] and $\epsilon_M = (1/6) \langle 1\bar{1}0 \rangle \{110\}_{\beta_2}$, neglecting the comparatively small volume change and γ_M . Fig. 8 shows these relations for a Cu-40 at. % Zn alloy. It is seen that the driving force increases rapidly while the restoring force decreases slowly with decreasing temperature, so that at M_b the critical temperature is reached below which for a given configuration

$$|\Delta G_T^{P-M}| > |\sigma_1 \epsilon_M|. \quad (22)$$

The martensite forming at $T < M_b$ will grow spontaneously. Whereas in several Cu-, Ag- and Au-based β phase alloys this transition at M_b can be observed, this is not the case for ferrous alloys because $\Delta G_{M_s}^{P-M}$ is higher by two orders of magnitude (Table I, Fig. 6) while the term $\sigma_1 \epsilon$ is comparable in magnitude to that of β phases but has a negative temperature coefficient, i.e. the normal temperature coefficient of the elastic constants.

For these reasons martensite growth in ferrous alloys will generally be spontaneous. If

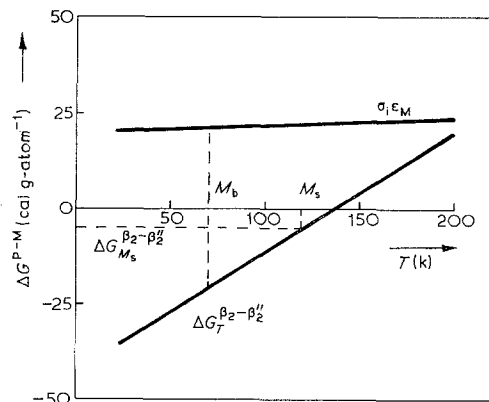


Figure 8 Temperature dependence of the driving energy ΔG_T^{P-M} and the elastic term $\sigma_1 \epsilon_M$ of the resistive energy in a Cu-40 at. % Zn alloy.

*Note added in proof: while this paper was in print Tong and Wayman [32] have discussed the characteristic temperatures of thermoelastic martensites in detail. Their treatment is essentially an explicit analysis of Equation 21 with respect to the transformation temperatures.

ordering occurs in iron alloys, as in Fe₃Be [14], and Fe₃Pt [31] then their behaviour approaches that of noble metal base alloys.

5.2. Pseudoelasticity by transformation

In Fig. 5 of Part 2 the stress-strain curves at $T > -55^\circ\text{C}$ (218 K) and $T < -45^\circ\text{C}$ (228 K) differ characteristically in that the transformation stress oscillates irregularly along both branches of the pseudoelastic transformation cycle in the low temperature range whereas it is a slowly increasing and decreasing function of strain in the high temperature range. This difference arises from the testing temperature (and corresponding martensite start temperature) $T = M_s^\sigma$ in relation to T_0 .

At $T = M_s^\sigma < T_0$ nucleation is stress-induced; but since $\Delta G_{T^P-M} < 0$ in this temperature range, growth will be possible without further mechanical driving energy if $\Delta G_{T^P-M} > \sigma_{1\epsilon_M} + \gamma_{MA'} + \xi_{\epsilon_M}$ for the supercritical nuclei. The discontinuous yielding phenomena observed indicate that this is the case, since each yield drop is associated with the stress relaxation due to the formation of one or several martensite plates whose shape strain reduces the effective stress. Since the onset of growth of each newly formed supercritical nucleus is associated with a yield drop it is most probable that the response to the applied stress is due to the preferred nucleation of plates, whose transformation shear strain reduces the applied stress. But this is no *a priori* consequence. The direction of applied stress of maximum effectiveness for nucleation need not be identical to that which maximizes the shape strain during growth. Furthermore, stress-assisted nucleation may lead to burst transformation, i.e. subsequent plates are formed by catalytic nucleation due to transformation stresses and strains. These do not respond to the applied stress and the shape strains will not, therefore, be related to the direction of the applied stress. Consequently, under the conditions defined above, the applied stress will not necessarily lead to the maximum possible anisotropic macroscopic strain.

The comparatively large hysteresis of the stress-strain curve of pseudoelastic transformation in this temperature range even for single crystals indicates that the growth process is associated with formation of lattice defects and interaction of the advancing phase interfaces with these obstacles during reverse transformation, so that the reversibility parameter takes a

value in the range $1 < R < 0.5$ because of a large value of ξ .

At $T = M_s^\sigma > T_0$ both nucleation and growth are stress-induced since the martensite phase is unstable in this temperature range in the stress free state. The resulting pseudoelastic stress-strain curve is essentially smooth because the driving energy for growth which increases with increasing applied stress will lead to a concomitant steady growth of martensite plates in constant balance with the resistive energy. Only interactions of growing plates which may be associated with sudden events of stress release, e.g. upon penetration of one plate through another, lead to discontinuous strain in this temperature range. The comparatively small hysteresis of the stress-strain curve for pseudoelastic transformation of single crystals in this temperature range results from a crystallographically nearly perfect progress of the transformation in constant elastic equilibrium with the parent phase such that only lattice friction and a weak interaction of moving interphase boundaries with lattice defects contribute to ξ . Consequently, the reversibility factor R will be close to unity.

The break in the $\sigma_a^{P-M}(T)$ curve is probably due to the transition in pseudoelastic behaviour at T_0 since the stress component of the effective driving free energies for nucleation alone and for nucleation plus growth will have a different temperature dependence. But a change in slope may also be caused by one or more additional effects: (i) onset of concomitant plastic deformation of the matrix, (ii) the same for the martensite, (iii) reorientation of the martensite, (iv) transformation into a different martensite structure as discussed in relation to the effects of stress on the thermodynamic functions (Fig. 4). The V shape of the σ_1^{P-M} curve in the immediate vicinity of M_s probably contains two contributions: the apparent V-shaped temperature dependence of the elastic constants C' of the parent and the corresponding shear modulus of the martensite phases (Fig. 2) and the monotonic increase of the stress required with increasing temperature to compensate for the decrease in the thermal driving of the driving free energy:

$$\left(\frac{d\sigma_a}{dT}\right) = \frac{\Delta S^{P-M}}{\epsilon_M}. \quad (23)$$

The ferrous alloys are not expected to show pseudoelastic behaviour for the same reasons as

in the case of thermoelasticity: the free enthalpy difference ΔG_{Ms}^{P-M} at nucleation is too high to be balanced by elastic energy $\sigma_i \epsilon_M$ stored during growth. Ordered Fe base alloys appear to be exceptions as mentioned in the preceding section.

5.3. Shape memory effect by transformation

In Part 2 it was shown that the stress at which the reverse transformation takes place in a pseudoelastic transformation cycle decreases with decreasing temperature until reverse transformation will no longer occur at $\sigma = 0$. The stress-induced transformation which is not reversed upon releasing the applied stress is the first stage of the shape memory effect; the irreversible fraction of the resistive energy exceeds the reversible components, i.e. $R \leq 0.5$. This is due to an increasing amount of lattice defects formed by an increasing fraction of rapid spontaneous growth with decreasing temperature and to a concomitant decrease of the thermal component of the driving free energy for reverse transformation. The martensite is then retained until, in the second stage of the shape memory treatment, the driving free energy for reverse transformation ΔG_d^{M-P} is increased by heating, so that

$$|\Delta G_d^{M-P}| > |\Delta G_r^{M-P}|. \quad (24)$$

The temperature A_s at which the reverse transformation sets in is not necessarily the same as for quench-induced martensite. Rather it will depend on the effects of the deformation process in the first stage. It is evident that since $R \leq 0.5$ no shrinkage of martensite plates will be possible below T_0 . Since, on the other hand, thermally-induced reverse transformation of quench-induced martensite starts at A_s° ($\equiv A_s$ for quench-induced martensite) it is to be expected that $T_0 \leq A_s \leq A_s^\circ$. The reverse transformation and, thus, the shape recovery will be completed at A_r , i.e. the temperature of complete reverse transformation of both quench-induced and stress-induced martensite.

5.4. Pseudoelasticity by reorientation

Pseudoelasticity by reorientation of a fully martensitic structure is a particular case of elastic mechanical twinning occurring in a finely twinned microstructure [16, 17]. The martensite plates of alloys exhibiting pseudoelastic behaviour are frequently arranged in self-accommodating groups such that the resi-

due stresses are comparatively low. Upon stressing, the twin and plate boundaries are displaced in such a way as to accommodate the imposed macroscopic strain by changing the relative volume of the twin variants. Ideally, the deformation energy is stored elastically. Upon release of the applied stress this stored energy acts as a resistive energy in complete analogy to the case of thermoelastic martensite. However, whereas for thermoelastic martensite $\sigma_a = 0$, for pseudoelasticity by reorientation $\Delta G_r^{P-M} = 0$, so that Equation 19 becomes:

$$\sigma_a \epsilon_R \geq \sigma_i \epsilon_R + \gamma_M A' + \xi \epsilon_R, \quad (25)$$

where the subscript R indicates that reorientation rather than transformation strain is involved. This formulation is generally used in treatments of the energy balance of elastic mechanical twinning [14, 18-21]. At variance to ordinary mechanical twinning, the displacement of existing twin (and plate) boundaries rather than the formation of new interfaces dominates the process, so that the term $\gamma_M A'$ will be small.

The elementary process consists most probably of ledge motion along the existing twin boundaries [21] so that the corresponding critical shear stress is comparatively low. Another factor affecting the low resistance to twin boundary displacement is the lattice softening of the martensite structure resolved on the twin plane on approaching T_0 [12].

The internal friction associated with pseudoelasticity by reorientation (Part 2) is implicitly contained in the term $\xi \epsilon_M$. The formation and motion of ledges with the accompanying formation and frictional energies will contribute to the damping behaviour and to the hysteresis loop. The elementary processes and their energetics have not been investigated in detail.

It should be noted that pseudoelasticity of the type discussed here is not restricted to martensitic alloys. Similar finely twinned structures arise from antiferromagnetic polarization, e.g. in Mn—Cu alloys [22], and from electrical polarization in ferroelectrics [23] due to changes in lattice symmetry, usually from cubic to tetragonal or orthorhombic. The twinned structures exhibit completely analogous behaviour, i.e. pseudoelasticity as well as high damping capacity which are combined in these cases with a "switching effect", since the polarization changes with the amount and direction of the applied stress.

Finally, pseudoelasticity by reorientation

occurs in ordered interstitial alloys in which ordering produces a tetragonal or orthorhombic distortion of the basically cubic metal lattice and an internally twinned structure. The direction of elastic polarization may be changed by an applied stress inducing jumps of the interstitial atoms into energetically more favourable sites and, thus, by the growth of lamellae of favoured orientation variants. The accompanying internal friction effects are mainly coupled to the interstitial diffusion coefficient in this case.

5.5. Shape memory by reorientation

If reorientation of a fully martensitic structure by an applied stress is associated with a sufficiently high frictional energy such that $R \leq 0.5$, shape recovery by reorientation will not take place upon releasing the applied stress.

Upon heating, two stages of shape recovery may be differentiated. The first stage is small in magnitude and occurs below A_s . If we consider that the stored elastic energy $\sigma_i \epsilon_R$ is the driving energy and frictional component of $\xi \epsilon_R$ is the main term of the resistive energy the more rapid decrease of the shear elastic constants may lead to

$$\left| \left(\frac{\partial \sigma_i \epsilon_R}{\partial T} \right) \right| < \left| \left(\frac{\partial \xi \epsilon_R}{\partial T} \right) \right|. \quad (26)$$

i.e. the resistive energy decreases more rapidly than the driving energy with increasing temperature. Thus, partial reorientation takes place. It may be supported by the temperature dependence of the tetragonality of the martensite as suggested for In-Tl [24].

The main stage of shape recovery of martensite deformed by reorientation, however, begins at A_s and ends at A_f . This indicates clearly that it is associated with reverse martensitic transformation [25]. The driving energy of this process is the same as for the shape memory by transformation (Section 5.3), whereas the resistive energy contains the dissipated energy terms of both reverse reorientation and reverse transformation such that for this process:

$$(\xi \epsilon)_{\text{eff}} = \xi_R \epsilon_R + \xi_M \epsilon_M \quad (27)$$

corresponding to the two successive stages of which the process is composed. The subscripts R and M of ξ indicate that this term will also differ for the two stages.

6. Conclusion

The thermodynamic and kinetic treatments of

the effects under consideration are mainly qualitative at this stage. However, it is evident that an analysis of the transformation and deformation processes involved can fully account for the observed phenomena.

The differences between the behaviour of ferrous and non-ferrous martensitic alloys can be related to their nucleation free energies which differ by up to two orders of magnitude.

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Received 1 February and accepted 19 February 1974.