MODEL FREE ENERGY, MECHANICS, AND THERMODYNAMICS OF SHAPE MEMORY ALLOYS

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Abstract—The shape memory effect (SME) in alloys is due to a first order martensitic phase transition. Based on Landau's theory a phenomenological model free energy function is presented which accounts for the SME. The mechanical and thermodynamical consequences of the model (such as stress-strain curves, elastic constants, and the latent heat of the phase transition) are discussed. Comparison with experiments yields the four involved parameters for the alloy Au_{23} Cu_{30} Zn_{47} .

Résumé—L'effet de mémoire de la forme (EMF) dans les alliages résulte d'une transformation martensitique du premier ordre. Nous présentons un modèle phénoménologique de l'énergie libre basé sur la théorie de Landau et rendant compte de l'EMF. Nous discutons les conséquences mécaniques et thermodynamiques du modèle (telles que les courbes contrainte-déformation, les constantes élastiques et la chaleur latente de la transition de phases). La comparaison avec des expériences a permis d'obtenir les valeurs des quatre paramètres du modèle dans le cas de l'alliage Au₂₃Cu₃₀Zn₄₇.

Zusammenfassung—Der Shape-Memory Effekt (SME) in Legierungen hängt mit martensitischen Phasenübergängen 1. Ordnung zusammen. Auf der Basis der Landauschen Theorie wird ein Ansatz für die Freie Energie vorgeschlagen, der den SME liefert. Die mechanischen und thermodynamischen Konsequenzen des Ansatzes (z.B. Spannungs-Dehnungs-Kurven, elastische Moduln, latente Wärme des Phasenübergangs) werden diskutiert. Der Vergleich mit Experimenten an Au₂₃ Cu₃₀ Zn₄₇ liefert die vier vorkommenden Parameter für diese Legierung.

1. INTRODUCTION

In the last few years many alloys turned out to show pseudoelasticity, ferroelasticity, and shape memory effect. (See, for example, the review papers [1, 2]. Applying a large load to such a body at low temperatures we get a residual strain (Fig. 1a). Since ferromagnetic materials show the same behaviour with respect to the field and the magnetization, the alloys are called ferroelastic. However, upon heating the residual strain vanishes and the original shape of the body is restored (shape memory effect). At higher temperatures loading does not lead to a residual strain. Nevertheless the stress-strain curves on loading and unloading differ (Fig. 1b). In particular the body is very soft (rubber elasticity, pseudoelasticity). At very high temperatures the body behaves elastically without anomalies (Fig. 1c). This remarkable behaviour of shape memory alloys is caused by a first order martensitic phase transition [1, 2].

Both the transition as well as the similarity of the stress-strain curves with the field-polarization curves of ferroelectrics suggest a close analogy between these phenomena [3, 4]. Guided by this analogy, the author [3] presented a phenomenological Landau free energy function for shape memory alloys which, in a similar formulation, was introduced for ferroelectrics by Devonshire [5].

The aim of this paper is to investigate the thermodynamics and the mechanics following from the pro-



Fig. 1. Schematic stress-strain curves of shape memory alloys (a) at low temperature: ferroelasticity (b) at intermediate temperature: pseudo-elasticity (c) at high temperature: elasticity.

posed model. The results are compared with experiments.

2. CRYSTALLOGRAPHY OF MARTENSITIC PHASE TRANSITIONS IN SHAPE MEMORY ALLOYS

By cooling shape memory alloys undergo a martensitic phase transition from the high temperature phase (austenite) to the low temperature phase (martensite). This first order phase transition shows hysteresis and can be induced by loading likewise. Typically the crystal structure of martensite is b.c.c. (for example CuZn, CuAlNi, AgCd, AuCd, CuAuZn₂, NiTi, NiAl). The ordered b.c.c. β -phases show different superlattices such as CsCl (B2)-structure, Fe3Al (DO₃)-structure or Cu₂MnAl (L2₁)-structure, which, for our phenomenological theory, are of less importance. On cooling the b.c.c. lattice becomes unstable which has been pointed out by Zener [6]. This decreasing stability gives rise to a premartensitic lattice softening of austenite, i.e. to a decrease of the elastic shear constant $C' = (C_{11} - C_{12})/2$. The low temperature martensitic phase essentially results from austenite by a shear on $\{110\}$ -planes in $\langle 1\overline{10} \rangle$ -directions (Fig. 2), whereas the associated volume change is less than 0.5% [7]. For the various alloys the martensitic phases differ from one another by their stacking sequences of close packed atomic layers and by superlattice structure [2] which are neglected in this paper. From the b.c.c. austenite we obtain 24 crystallographically equivalent martensite twins.

† In the following, the original variables are denoted by capital letters, rescaled variables by small letters.

3. THE MODEL

In the following we examine single crystals under applied shear stress Σ in the $\pm [1\overline{10}]$ -direction. Consequently, we restrict ourselves to shear strain E in the same direction (Fig. 2), which is supposed to be homogeneous throughout the crystal. Vanishing shear strain corresponds to the undeformed austenite. Recently the author [3] has proposed the following Helmholtz free energy F per volume as a function of shear strain E and temperature T

$$F(E, T) = \alpha E^{6} - \beta E^{4} + (\delta T - \gamma)E^{2} + F_{0}(T), \quad (1)$$

where α , β , γ and δ are positive constants depending on the special material. With regard to the Landau theory of phase transitions, *E* is the order parameter. Ansatz [1] is the simplest function which, at various temperatures, yields the observed stress-strain curves (Fig. 1) of shape memory alloys.

For convenience we rescale the free energy F, the strain E, and the temperature T by†

$$f = \frac{\alpha^2}{\beta^3} F \quad e = \left(\frac{\alpha}{\beta}\right)^{1/2} E \quad t = \frac{\alpha\delta}{\beta^2} T - \frac{\gamma\alpha}{\beta^2} - \frac{1}{4} \quad (2)$$

and obtain (Fig. 3)

$$f(e,t) = e^{6} - e^{4} + (t+1/4)e^{2} + f_{0}(t)$$
(3)

In rescaled variables the free energy function is the same for all shape memory alloys. This means we have the theorem of corresponding states as known from van der Waals fluids. The properties of a special material are included in the converting parameters α , β , γ and δ .

According to the symmetry of the crystallographic model (Fig. 2) f is an even function with respect to the shear strain e. At high temperatures (t > 1/12) f has



Fig. 2. Crystal structure of austenite and martensite.



Fig. 3. Helmholtz free energy f over shear strain e with temperature t as parameter [equation (3)]. $f_0(t)$ is omitted. In the dotted regions the crystal is unstable.

only one minimum with respect to e at e = 0. Consequently, if the external load vanishes, austenite is the only stable phase at high temperatures. For -1/4 < t < 1/12 f has three minima. In addition to the stable austenite A at e = 0 we have two stable martensite twins M_+ and M_- at

$$e = \pm e_0 = \pm \left(\frac{1}{3} + \frac{(1-12t)^{1/2}}{6}\right)^{1/2}$$
. (4)

At t = 0 the three phases have the same free energy. For low temperature (t < -1/4) there are only two minima at $e = \pm e_0$ (equation 4), which represent the martensite twins M₊ and M₋.

4. STRESS-STRAIN CURVES, STRESS INDUCED PHASE TRANSITION

The shear stress Σ is defined as derivative of the Helmholtz free energy with respect to the shear strain *E*, i.e.

$$\Sigma(E, T) = \partial F(E, T) / \partial E$$
 (5)

Rescaling by

$$\sigma = \frac{a^{3/2}}{b^{5/2}} \Sigma$$

yields

$$\sigma(e, t) = \partial f(e, t) / \partial t = 6e^5 - 4e^3 + 2(t + 1/4)e \quad (6)$$

In Fig. 4 σ is plotted as a function of e for different temperatures t.

The elastic shear constant is defined by

$$C' = \partial^2 F / \partial E^2 = \partial \Sigma / \partial E \quad c = \partial \sigma / \partial e.$$
(7)

Consequently, we have

$$c(e, t) = 30 e^{4} - 12 e^{2} + 2(t + 1/4).$$
 (8)

In a stable configuration c is positive. For temperatures t > /0.35 this stability condition is satisfied for any strain e. In this temperature domain loading leads to a nearly linear increase of strain (Fig. 4a). At t = 0.35 we have a plateau in the stress for $e = 1/\sqrt{5}$ and $\sigma = 16/(25\sqrt{5})$ (Fig. 4b). In the temperature range -0.25 < t < 0.35 we get stability only for (Fig. 6a)

$$|e| < e_1 = \left(\frac{1}{5} - \frac{(21 - 60t)^{1/2}}{30}\right)^{1/2}$$
 (9)



Fig. 4. Shear stress σ over strain e for different temperatures t [equation (6)]. Unstable regions are dotted.



Fig. 5. Strain e over temperature t for different applied stresses σ . Unstable regions are dotted.

or

$$|e| > e_2 = \left(\frac{1}{5} + \frac{(21 - 60t)^{1/2}}{30}\right)^{1/2}$$
 (10)

For any strain which is not included in these ranges there does not exist a stable homogeneous state of the crystal (dotted region in Fig. 4). Similarly for t < -1/4 we have stability only for $|e| > e_2$ [equation (10)]. When we clamp the crystal in the unstable region of e, we get decomposition into two phases.

For -0.25 < t < 0.35 loading of austenite gives rise to a phase transition from austenite A to martensite M₊ which occurs at the latest when the boundary of the stable region $\sigma = \sigma_1(t) = \sigma(e_1, t)$ is reached (upper horizontal line in Fig. 4c-f, upper solid curve in Fig. 6b). When the whole crystal has transformed from A to M₊ further loading leads to a nearly linear increase of strain in the martensitic phase. On unloading the strain of martensite decreases and the reverse phase transition starts at the latest at the boundary of the stable region $\sigma = \sigma_2(t) = \sigma(e_2, t) < \sigma_1(t)$ (lower horizontal line in Fig. 4c-f, lower solid curve in Fig. 6b). For $1/12 < t < 0.35 \sigma_2(t)$ is positive and the resulting stress strain curves are of the pseudoelastic type (Fig. 4c). For t < 1/12 the stability boundary $\sigma_2(t)$ is negative. Consequently unloading to zero stress leads to a permanent strain e_0 (equation 4), i.e., the crystal is still in the martensitic phase M₊. In Fig. 5 e_0 is plotted as a function of t (curve $\sigma = 0$). For t < 1/12 the reverse transformation from M₊ to A occurs only on reverse loading (Fig. 4d). For 1/60 < t < 1/12 the crystal transforms from the right martensite twin M₊ to austenite and on further loading from austenite to the left martensite twin M_ (Fig. 4d). For t < 1/60 the phase transition on reverse loading immediately runs from the right to the left martensite twin (Fig. 4c,f). If t < 1/12 the stress-strain curves are of the ferroelastic type (Fig. 4d-f).

The discussed stress-induced phase transition exhibits a hysteresis, provided that we have thermodynamic barriers to prevent an equilibrium phase transition. In Fig. 6b the highest possible hysteresis is given by the distance of the solid lines. In practice the phase transition can occur at a lower stress level, earliest at a shear stress $\sigma_3(t)$, where the Gibbs free energies (section 8) of both phases are equal. This condition leads to Maxwell's rule. In a f-e-plot, the stress $\sigma_3(t)$ is determined by the slope of the common tangent at two points of the curve (Fig. 7a). In an σ -e-plot this value is given by a horizontal line which equalizes the dashed areas in Fig. 7b. The stress σ_3 has been calculated numerically as a function of t (dashed curve in Fig. 6b).



Fig. 6(a) Boundaries of stability in strain for martensite (e_1) and austenite (e_2) plotted over temperature t. In the temperature domain -0.25 < t < 0.35 for $|e| > e_1$ martensite is stable, for $|e| < e_2$ austenite is stable, and for $e_1 > |e| > e_2$ we have instability. (b) Boundaries of stability in stress plotted over temperature t. For an applied stress larger than the lower solid curve, martensite is stable. For an applied stress lower than the upper solid curve, austenite is stable. The dashed curve gives the stress where the equilibrium phase transition takes place. For t > 0.35only austenite is stable.



Fig. 7. Maxwell's rule (a) in an *f*-e-plot (b) in an σ -e-plot.

5. ELASTIC SHEAR CONSTANT

The elastic shear constant $c = (a/b^2)C' = (a/2b^2)(C_{11} - C_{12})$ is given by [equation (8)]

$$c(e, t) = 30 e^4 - 12e^2 + 2(t + 1/4).$$
(11)

Of particular interest is c at the stress-free equilibrium positions of austenite A at e = 0 (for t > 1/4 only) and martensite M_+ or M_- at $e = \pm e_0(t)$ (equation 4, for t < 1/12 only). The result

$$c_{\rm A}(t) = 2t + 1/2 \tag{12}$$

$$c_{\rm M}(t) = \frac{2}{3}(1 - 12t) + \frac{4}{3}(1 - 12t)^{1/2} \tag{13}$$

is plotted in Fig. 8. At the stability boundary of austenite $(t = -1/4) c_A$ vanishes, and so does c_M at the

stability boundary of martensite (t = 1/12). Figure 8 shows a linear lattice softening of austenite on cooling for which experimental evidence exists [8–11].

6. ENTROPY, INTERNAL ENERGY, GIBBS FREE ENERGY

The entropy is defined by

$$S = -\partial F/\partial T$$
 $s = -\partial f/\partial t$

where S is rescaled by

$$S = bd/a s$$

From equation 3 we obtain

$$s = -e^2 - df_0(T)/dT.$$
 (14)

Note that s is added up by a strain dependent and a temperature dependent part.

The internal energy is defined by

$$u = f + (t + t_0)s,$$
 (15)

where

$$t_0 = 1/4 + ca/b^2$$
.

Using equation 3 we get

$$u = e^{6} - e^{4} + (1/4 - t_{0})e^{2} + f_{0}(t).$$
(16)

u divides in a strain dependent and a temperature dependent part, too. Consequently, for different temperatures the curves u(e) look alike. The great variety of f(e)-curves result from the term ts(e) in equation 15. For this reason the characteristic stress-strain relation of shape memory alloys is due to entropy and these alloys are called entropy elastic or rubber elastic. (In rubber, elasticity is connected with entropy, too).

Gibbs free energy G (and g) is defined by

$$G = F - \Sigma E, \quad g = f - \sigma e$$
 (17)

However, the corresponding variables for g are t and σ instead of t and e. Consequently, in equation (17) we have to replace e by σ (in f(e, t), too). Since there is no analytical expression for $e(\sigma, t)$, the replacement has to



Fig. 8. Elastic shear constant c of austenite (A) and martensite (M) plotted over temperature t. [equations (12, 13)]. For t > 1/12 martensite is unstable, for t < -0.25 austenite is unstable.



Fig. 9. Gibbs free energy g plotted over stress σ at different temperatures t. The curve marked by A applies to austenite, the curves marked by M_+ and M_- apply to the right and left martensite twins, respectively. The curves end at the dots, where the region of stability ends.

be done numerically. For various temperatures the $g(\sigma)$ -curves are plotted in Fig. 9. Note that there are three functions $g_{M_{\star}}(\sigma, t)$, $g_{M_{\star}}(\sigma, t)$, and $g_{A}(\sigma, t)$ for both martensite twins and austenite, respectively. They cannot be combined to one function $g(\sigma, t)$ which is appropriate for all the phases. In the stress domain where austenite and martensite are stable, to any value σ there are two or three values of Gibbs free energy, one for each phase. Therefore, Helmoltz free energy is more convenient for describing the system.

7. TEMPERATURE INDUCED PHASE TRANSITION

A phase transition can be induced not only by loading at constant temperature but also by heating or cooling at constant load. In Fig. 5 the strain is plotted as a function of t for different loads σ . The dotted parts of the curves indicate regions with negative elastic constant c, i.e. unstable regions. In the stable region the curves have a negative slope. Thus the strain decreases on heating, and mechanical work is done against the load.

For large load ($\sigma > 16/(25\sqrt{5})$) an instability does not occur. For smaller (or vanishing) load on heating the stability boundary of martensite is reached at $t = t_1(\sigma)$ (right solid curve in Fig. 6b). Consequently, at the latest the phase transition from martensite to austenite begins at $t_1(\sigma)$ (right vertical line in Fig. 5). On cooling the stability boundary is reached only at $t = t_2(\sigma) < t_1(\sigma)$ (left solid line in Fig. 6b). The reverse transition from austenite to martensite latest occurs at $t = t_2(\sigma)$ (left vertical line in Fig. 5). For each load $\sigma < 16/(25\sqrt{5})$ the highest possible hysteresis is given by the difference of the stability boundaries t_1 and t_2 (Fig. 6b). The equilibrium phase transition temperature $t_3(\sigma)$ is determined by the condition that in both phases the Gibbs free energies $g(\sigma, t)$ are equal. $t_3(\sigma)$ can be calculated only numerically, using $g(\sigma, t)$ of section 6 (dotted curve in Fig. 6b). On heating as well as on cooling, $t_3(\sigma)$ is the foremost temperature for the phase transition to occur.

In practice it is not obvious to what extent supercooling or superheating takes place. We only can argue that in an elastically homogeneous unstressed single crystal the temperature $M_s(m_s)$ at which, on cooling, the formation of martensite starts, has to be in the domain $-1/4 < m_s < t_3(\sigma = 0) = 0$. Analogously, the temperature $A_s(a_s)$ where, on heating, the formation of austenite starts, has to be in the domain $0 = t_3(\sigma = 0) < a_s < 1/12$. If there are lattice defects, the crystal is self-stressed. Thus we have a distribution of shear stress which, in the neighbourhood of the defect, varies rapidly. Since the temperature of the equilibrium phase transition t_3 as well as the boundaries of the stable temperature domains t_1 and t_2 depend on the shear stress, these temperatures will vary within the crystal, too. Consequently, on cooling the austenite to martensite phase transition earlier begins in regions where, by the self-stress, the temperature t_3 (and t_2) is raised. In regions where t_3 is lowered the phase transition takes place at lower temperatures only. In this way defects serve as nuclei for the phase transition [12].

The driving force for the temperature-induced phase transition is the difference between the Gibbs



Fig. 10. Driving force Δg for the phase transition from austenite to martensite plotted over t, if no external stress σ is applied. The curve ends at the dots, since for t > 1/12, $\sigma = 0$ only austenite is stable and for t < -0.25, $\sigma = 0$ only martensite is stable.

free energies of both phases

$$\Delta g(\sigma, t) = g_{\mathsf{M}}(\sigma, t) - g_{\mathsf{A}}(\sigma, t)$$

which can be taken from Fig. 10. For zero load, Δg is equivalent to Δf which is given by the difference between the austenitic and the martensitic minimum of the *f*-e-curves (Fig. 3). Consequently, we get (Fig. 10)

$$\Delta g(t, \sigma = 0) = f(t, e = e_0) - f(t, e = 0)$$
$$= -\frac{1}{108} - \frac{1}{3}t + \frac{(1 - 12t)^{3/2}}{108} \cdot (18)$$

From Fig. 10 we can see that 1. $\Delta g(t, \sigma = 0)$ vanishes at t = 0 (equilibrium phase transition temperature) 2. $\Delta g(t, \sigma = 0)$ varies nearly linearly with t. The curve $\Delta g(t, \sigma = 0)$ ends at t = -1/4 and t = 1/12 since only in this temperature domain austenite and martensite are stable simultaneously.

8. LATENT HEAT OF THE PHASE TRANSITION

The latent heat of the equilibrium phase transition from austenite to martensite is, at constant load, given by

$$Q(T) = T \Delta S$$

$$q(t) = (t + t_0)\Delta s$$

$$= (t + t_0)[s(t, e_M) - s(t, e_A)],$$
(19)

where $e_{\rm M}$ and $e_{\rm A}$ is the strain of martensite and austenite respectively, which are to be taken at the stress $\sigma_3(t)$ of the equilibrium phase transition (see section 4). Since $e_{\rm M}$ and $e_{\rm A}$ cannot be represented by analytical expressions generally, we confine ourselves to the temperature t = 0, where σ_3 vanishes. Consequently,

from equation 4 we obtain

$$e_{\rm A} = 0$$
 $e_{\rm M} = 1/\sqrt{2}$,

and hence [equations (14,15,19)]

$$q(t = 0) = -t_0/2$$

$$Q(t = 0) = -[1/8 + ca/(2b^2)]b^3/a^2.$$
(20)

9. SHAPE MEMORY EFFECT

The shape memory effect is characterized by the fact that a permanent strain created by loading at low temperature vanishes on heating. In Fig. 11 this effect is accounted for in a *f-e*-plot with temperature t as a parameter. Suppose the undeformed body (e = 0) consists of austenite A at low temperature $t = t_i$. Loading at t_i gives rise to a phase transition to the martensite twin M_+ , which is stable at t_i without applying an external force. Thus we have created a permanent strain. On heating we shift from the *f-e*-curve according to t_i to that one according to t_{il} . As the latter one does not have a second (martensitic) minimum, the martensite becomes unstable and the



Fig. 11. Shape memory effect in an *f-e*-plot. (1) Loading of austenite A at low temperature t_1 leads to a phase transition to martensite M_+ and thus to a permanent strain. Heating to t_{II} (2) causes instability of martensite M_+ and reverse phase transition to austenite A (3). The original shape is restored.

strain changes to the only minimum of f at e = 0, i.e. the crystal retains its original shape. From the curves in Fig. 3 we can see that to get shape memory effect the starting temperature t_i has to be $-1/4 < t_i < 1/12$ and heating must exceed t = 1/12.

10. EXPERIMENTAL DETERMINATION OF PARAMETERS

In the rescaled units the free energy function is independent of a special material (equation 3). Therefore our theory can be fitted to a specific material only by the four rescaling parameters α , β , γ and δ , which are to be determined by comparison with experiments. Since our theory is adapted to single crystals these experiments should have been done on single crystals too. Measurements concerning hysteresis phenomena are not suitable because we can calculate the highest possible hysteresis only which may not be reached in the test. Since the properties of shape memory alloys strongly depend on chemical composition and on processing (quenching, annealing) the comparison of different experiments is difficult.

For the alloy $Au_{23}Cu_{30}Zn_{47}$ Y. Murakami published a set of sufficient data [9], namely lattice parameter (which yields density), latent heat Q, equilibrium phase transition temperature T_0 at zero stress, and the elastic shear constant C' of austenite at different temperatures. The latter shows a linear decrease on cooling which is in excellent agreement with equation (12). The slope of C'(T) gives us the parameter

$$\delta = 24 \,\mathrm{J}\,\mathrm{cm}^{-3}\,\mathrm{K}^{-1}$$

By extrapolating C'(T) to C' = 0 we find the boundary of stability for austenite at zero stress to be $T_2 = 210$ K corresponding to $t_2 = -1/4$. This information yields

$$y = 5,0.10^3 \,\mathrm{J}\,\mathrm{cm}^{-3}$$

From the latent heat Q = 120 cal/mole and $T_0 = 242 \text{ K}(t = 0)$ we get (with the density $\rho = 11.1 \text{ g cm}^{-3}$ from lattice parameter 0.61 nm

$$\beta = 1.5 \cdot 10^5 \text{ J cm}^{-3}$$

 $\alpha = 7.5 \cdot 10^6 \text{ J cm}^{-3}$

From these parameters we get for the unstressed martensite at the equilibrium phase transition temperature (t = 0, $T_0 = 242$ K) a shear strain of 10% with respect to austenite [equations (2,4)], which, unfortunately, is not specified in Murakami's paper. However, this value typically occurs in martensites with the stacking sequence 18 R or 9 R.

11. DISCUSSION

Our model free energy [equation (3)] is the simplest function which qualitatively yields the experimental results on shape memory alloys, for example the stress-strain curves at various temperatures, the lattice softening, the shape memory effect, the stressinduced and the temperature-induced phase transition, and its latent heat. In the language of catastrophe theory the phase transition in shape memory alloys is called the 'butterfly catastrophe'. In the notation of Zeeman [13] the function to be minimized is Gibbs free energy [equations (17,3)] as a function of ewith σ and t as parameters. The one-dimensional state space is built up by the strain e, the normal factor corresponds to the stress σ , and the splitting factor to temperature t. The bias factor vanishes because of symmetry, and the butterfly factor is positive.

In our model we deal with shear strain and shear stress. By rotating the system of coordinates any shear can be expressed as an extension accompanied by transversal contraction such that the volume is preserved. Therefore the tensile test, which is more convenient for experiments, can be treated by the model. However, since there are 12 crystallographically equivalent directions of lowest critical shear stress, we have a lot of competing martensite variants for the phase transition to result in. As selection rule we can apply Schmid's law.

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