

# State equation for shape-memory alloys: Application to Cu-Zn-Al

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We deal with the hysteretic behavior of partial cycles in the two-phase region associated with the martensitic transformation of shape-memory alloys. We consider the problem from a thermodynamic point of view and adopt a local equilibrium formalism, based on the idea of thermoelastic balance, from which a formal writing follows a state equation for the material in terms of its temperature  $T$ , external applied stress  $\sigma$ , and transformed volume fraction  $x$ . To describe the striking memory properties exhibited by partial transformation cycles, state variables  $(x, \sigma, T)$  corresponding to the current state of the system have to be supplemented with variables  $(x, \sigma, T)$  corresponding to points where the transformation control parameter ( $-\sigma$  and/or  $T$ ) had reached a maximum or a minimum in the previous thermodynamic history of the system. We restrict our study to simple partial cycles resulting from a single maximum or minimum of the control parameter. Several common features displayed by such partial cycles and repeatedly observed in experiments lead to a set of analytic restrictions, listed explicitly in the paper, to be verified by the dissipative term of the state equation, responsible for hysteresis. Finally, using calorimetric data of thermally induced partial cycles through the martensitic transformation in a Cu-Zn-Al alloy, we have fitted a given functional form of the dissipative term consistent with the analytic restrictions mentioned above.

## I. INTRODUCTION

Shape-memory alloys are able to recover important deformations up to 10%. If the deformation process takes place at high temperatures, the alloys recover their original shape by simply eliminating the applied external stress (pseudoelastic behavior). Deformations produced at lower temperatures are recovered on heating the alloys (shape-memory effect).<sup>1</sup> Among the materials exhibiting this unusual thermomechanical behavior, the more studied are Ni-Ti and some copper-based  $\beta$ -brass alloys such as Cu-Zn, Cu-Zn-Al, and Cu-Al-Ni.

The pseudoelastic and shape-memory effects are intimately related to the thermoelastic martensitic transformation taking place in all the alloy systems mentioned. The martensitic transformation is a solid-state transition with the following essential characteristics<sup>2,3</sup>: (i) it is a first-order transition, (ii) it is displacive, i.e., it takes place without atomic diffusion, (iii) it is accompanied by a distortion of the crystalline lattice with a dominant deviatoric component resulting in macroscopic shape change, and (iv) the transformation kinetics and the morphology of the resulting product, called martensite, are dominated by elastic strain energy.

Martensitic transformations can be induced either by changing the specimen temperature  $T$  or by applying an external stress  $\sigma$ . A martensitic transformation is acknowledged to be thermoelastic when at each temperature and/or applied stress inside the transformation range a thermoelastic equilibrium is achieved. The equilibrium condition is de-

finied by a local balance at the transforming interfaces between chemical forces associated with the structural change, and nonchemical forces such as elastic strain and dissipative energies.<sup>1</sup>

Depending on the crystal symmetry of the high-temperature phase, different crystallographically equivalent martensitic variants may appear. In the absence of an external applied stress they form self-accommodating groups that minimize the total shape change. To the contrary, application of an external uniaxial stress results in the formation of the martensitic variant (or variants) best suited to accommodate the imposed strain.<sup>4</sup>

The transformation exhibits hysteresis: On reverting the sense of variation of the external control parameter (temperature or stress), the system follows a reverse path different than the forward one. In other words, the conjugate variable of the control parameter is multivalued.<sup>4-6</sup> If the transformation is thermally induced, the conjugate variable of temperature is the entropy difference between the two phases, while if the control parameter is an externally applied stress, the conjugate variable is the transformation strain. It can be shown that in both cases the conjugate variable is proportional to  $x$ , the volume fraction of martensite in the specimen.<sup>7</sup> For this reason, in what follows, the transformation path will be described by means of the variable  $x$ .

In a partially or fully transformed multivariant martensitic specimen, application of an external uniaxial stress (tension or compression) produces reorientation of martensitic variants and causes hysteretic behavior in the stress-strain space. In this study we are not dealing with hysteresis

associated with martensitic reorientation, but with hysteresis produced by the transformation itself. For example, we explicitly exclude situations such as (i) application of an external stress once part of the material has been thermally transformed into martensite, and (ii) changes from an extensive to a compressive applied stress at constant temperature.

The transformation path depends not only on the instantaneous value of the control parameter but also on previous extreme values, corresponding to points where the sense of variation of the control parameter has been reverted. Associated with its hysteretic behavior, therefore, the system shows memory features.

Notwithstanding the fact of showing hysteretic and memory properties, it is a good approximation, at the usual experimental time scales, to assume that no relaxational processes occur during the transformation. Thus, the whole set of variables describing the transformation path may be considered time independent. In particular, the transformation path is independent of the rate of change of the control parameter, at least within certain limits. Possible diffusional processes, foreign to the martensitic transformation, might take place simultaneously. They can actually be avoided by previous well-defined heat treatments.<sup>8</sup> To conclude, if no diffusional processes take place, the system shows a stationary behavior in any state within the two-phase region—sometimes called a static hysteretic behavior. Some of the above features of the transformation hysteresis in both temperature- and stress-induced transformations, including partial cycling, have been studied experimentally by several authors.<sup>4,5,9-11</sup> It is worth noting that similar features are observed in the hysteretic behavior of ferroelectric and ferromagnetic<sup>12</sup> materials.

The phenomenological characteristics<sup>13,14</sup> of the hysteretic behavior displayed by shape-memory materials in the martensitic transformation region can be summarized by the following items, schematically drawn in Fig. 1.

(i) All transformation paths are restricted to a region in  $(x, \sigma, T)$  space—the two-phase region. Paths corresponding

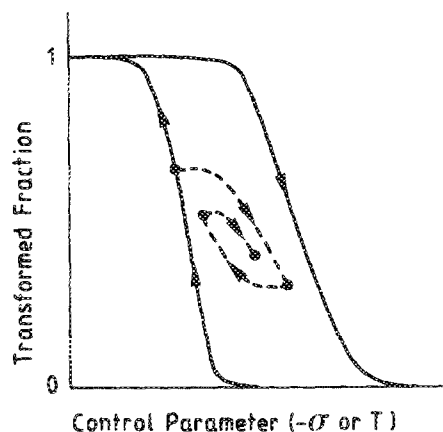


FIG. 1. Schematic behavior of the transformation paths projected on a constant  $T$  or  $\sigma$  plane. The continuous line represents a complete cycle which follows the boundary of the two-phase region. The broken lines represent internal paths within the two-phase region. The broken lines represent internal paths within the two-phase region. The black points correspond to extreme values of the control parameter.

to complete transformation cycles, with  $x$  varying from 0 (parent phase  $P$ ) to 1 (martensite  $M$ ) or from 1 to 0, are located on the boundary of the region.

(ii) Two branches can be defined for each cycle, the first one (+) corresponding to paths of increasing  $x$  and the second one (−) corresponding to paths of decreasing  $x$ .

(iii) All paths tend tangentially to the boundaries of the two-phase region at  $x = 0$  or at  $x = 1$ . Moreover, all internal loops performed between two fixed extreme values of the control parameter are congruent.

(iv) Given an original path in the two-phase region, it can be reproduced if none of the states corresponding to extreme values of the control parameter is modified. The system, therefore, keeps memory of the extreme values reached by the control parameter. Each time that the transformation path passes through a previous local maximum (minimum) of the control parameter, the memory of all the lower (higher) extreme points is erased. Hence, all the memory is erased on reaching the extreme values  $x = 0$  or  $x = 1$ .

(v) Irreversible effects giving rise to hysteresis occur when a change in the control parameter results in a change of  $x$ . If a variation of the control parameter does not result in a modification of the transformed volume fraction, on reverting the control parameter the system follows a path without hysteresis until the starting initial state.

In this work, a general expression of the state equation for shape-memory materials is obtained starting from a thermodynamic fundamental equation describing thermoelastic equilibrium.<sup>7</sup> The hysteretic features appear through a dissipative term, which depends on the value of the state variables at the extreme points of the control parameter in the transformation path. The dependence determines the memory properties of the system. The formalism is applied to the Cu-Zn-Al alloy system, using experimental data partially obtained from the literature.

## II. THERMOELASTIC BALANCE AND STATE EQUATION

The fundamental equation describing the thermodynamics of a thermoelastic transformation reads<sup>7</sup>:

$$dH = T dS - T dS_i - dE_{el} + V_0 \sum_{ij} \sigma_{ij} d\epsilon_{ij} + V dp - dW_i, \quad (1)$$

where  $dH$  and  $dS$  are differential changes in chemical enthalpy and entropy of the system,  $-dE_{el}$  is the reversible internal work stored in the system as elastic strain energy and interfacial energy,  $(\sum_{ij} V_0 \sigma_{ij} d\epsilon_{ij})$  is the nonhydrostatic part of the work performed by external forces to produce the macroscopic deformation,  $(-p dV)$  is the hydrostatic part of this same work,  $dS_i$  is the entropy production associated with dissipation of irreversible heat, and  $dW_i$  is an internal work irreversibly dissipated in forms other than heat and not giving rise to entropy production.<sup>10,15</sup> A detailed description of the contributions included in the term  $-dE_{el}$  is given in Ref. 7. In particular, the elastic strain energy originates from a total deformation consisting of local stress-free strain (including transformation strain and thermal expansion) and local elastic strain. Thermal expansion could be relevant since the transformation extends in a temperature range.

The free energy  $G^*$  is introduced through the following Legendre transformation:

$$G^* = H - TS - V_0 \sum_{ij} \sigma_{ij} \epsilon_{ij}. \quad (2)$$

Equation (1) can be rewritten in terms of this potential and reads:

$$dG^* = -S dT - dE_{el} - V_0 \sum_{ij} \epsilon_{ij} d\sigma_{ij} + V dp - T dS_i - dW_i. \quad (3)$$

For a given temperature  $T$ , pressure  $p$ , and external stress  $\sigma$ ,

$$dG^* = dH - T dS - V_0 \sum_{ij} \sigma_{ij} d\epsilon_{ij}, \quad (4)$$

and taking into account Eq. (3) we obtain:

$$dG^* = -dE_{el} - T dS_i - dW_i. \quad (5)$$

Hence, at each  $T$ ,  $p$ , and  $\sigma$  the change in  $G^*$  compensates for the changes in reversible elastic and dissipative energies. When the transformed fraction  $x$  changes to a value  $x + dx$  we have

$$dG^* = \left( \frac{\partial G^*}{\partial x} \right)_{T,p,\sigma} dx. \quad (6)$$

Taking into account that:

$$G^* = (1-x)G_P^* + xG_M^*, \quad (7)$$

where  $G_P^*$  and  $G_M^*$  stand for the free energies of mutually noninteracting parent and martensitic phases, it follows that:

$$dG^* = (G_M^* - G_P^*) dx. \quad (8)$$

Hence, from Eq. (5) we finally obtain:

$$(G_M^* - G_P^*) dx = - \left( \frac{\partial E_{el}}{\partial x} + \frac{dE_{diss}}{dx} \right) dx. \quad (9)$$

$(G_M^* - G_P^*)$  is the driving force for the transformation and

$$dE_{diss} = T dS_i + dW_i > 0$$

no matter the sign of  $dx$ . It should be noted that  $dx > 0$  in the forward ( $P - M$ ) transformation, and  $dx < 0$  in the reverse ( $M - P$ ) transformation.

Equation (9) expresses the condition of thermoelastic balance in a continuous quasistatic formalism: Any differential variation of the control parameters  $T$  or  $\sigma$  will result in a differential variation  $dx$  of the transformed volume fraction. However, highly sensitive experimental techniques, including calorimetry<sup>16</sup> and resistivity,<sup>17</sup> make evident that  $x$  does not always evolve continuously. Actually, the system goes from  $x$  to  $x + \delta x$  through a relaxational process in which energy is dissipated. Part is released in the form of elastic waves, detected as acoustic emission, and part gives rise to entropy production. In some instances the relaxational effects become important, and experimentally one observes marked discontinuities in the paths giving  $x$  as a function of the control parameter.<sup>18</sup> This is the case of the  $\beta$ (bcc) -  $2H$  transformation in Cu-Zn-Al<sup>19</sup> and Cu-Al-Ni.<sup>20</sup> Nevertheless, the characteristic times associated with the relaxational effects are always much shorter than the characteristic times associated with the variation of the external control parameters  $\dot{T}^{-1}$  or  $\dot{\sigma}^{-1}$ .

Let us now obtain explicit expressions for the driving force in the usual experimental situations.

First, we consider temperature-induced transformations at zero external stress. It is assumed that  $\Delta H$  and  $\Delta S$  are not temperature dependent; this is equivalent to assuming a negligible difference between the heat capacities of the two phases, as is the case in most of the alloy systems considered.<sup>21</sup> From Eq. (2), at a given temperature  $T$  we have

$$(G_M^* - G_P^*) = (G_M - G_P) = \Delta H - T\Delta S = \Delta H \left( 1 - \frac{T}{T_0(0)} \right), \quad (10)$$

where  $G$  is the Gibbs free energy. To obtain this equation we recall that  $\Delta H = T_0(0)\Delta S$ , where  $T_0(0)$  is the temperature of thermodynamic equilibrium between the two ideal phases at  $\sigma = 0$ . Dividing Eq. (9) by  $\Delta H$ , it takes the form:

$$\left( 1 - \frac{T}{T_0(0)} \right) + \frac{\partial \epsilon_{el}}{\partial x} + \frac{d\epsilon_{diss}}{dx} = 0, \quad (11)$$

where  $\epsilon_{el} \equiv E_{el}/\Delta H$  and  $\epsilon_{diss} \equiv E_{diss}/\Delta H$ .

A second case to consider is the stress-induced transformation at constant temperature. We restrict ourselves to a uniaxial stress, denoted by  $\sigma$ , and assume again that  $\Delta C_p = 0$ . The driving force at  $T$  and  $\sigma$  is now given by

$$(G_M^* - G_P^*) = \Delta H - T\Delta S - V_0 \sigma \Delta \epsilon. \quad (12)$$

If we consider the thermodynamic equilibrium between the two phases in the absence of mutual interactions, both subjected to the applied external stress, Eq. (1) leads to

$$\Delta H = T\Delta S + V_0 \sigma_0 \Delta \epsilon, \quad (13)$$

equivalent to the result by Wollants, de Bonte, and Roos.<sup>22</sup>  $\sigma_0$  is the stress required for the transformation to take place in thermodynamic equilibrium at a temperature  $T$ . Inserting (13) in (12), considering Eq. (9), and dividing the final result by  $\Delta H$  we are led to

$$\left( 1 - \frac{\sigma}{\sigma_0} \right) \Delta \epsilon_0 + \frac{\partial \epsilon_{el}}{\partial x} + \frac{d\epsilon_{diss}}{dx} = 0, \quad (14)$$

where  $\Delta \epsilon_0 \equiv (V_0 \sigma_0 \Delta \epsilon) / \Delta H$ .

In the equations above it is important to note that  $\Delta H$ ,  $\Delta S$ , and  $\Delta \epsilon$  have been defined as  $\Delta H = H_M - H_P < 0$ ,  $\Delta S = S_M - S_P < 0$ , and  $\Delta \epsilon = \epsilon_M - \epsilon_P > 0$ . Therefore, a comparison of Eqs. (11) and (14) shows that  $T$  and  $\sigma$  play equivalent roles with opposite sign in the thermoelastic balance.

Finally, let us consider a general situation in which temperature and uniaxial stress are changed simultaneously. Equation (13) is a general expression of the enthalpy difference  $\Delta H$  at any temperature  $T$ , taking into account that  $\sigma_0 = \sigma_0(T)$ . Using Eqs. (12) and (13) it is easy to see that:

$$(G_M^* - G_P^*) = V_0 \sigma_0(T) \Delta \epsilon - V_0 \sigma \Delta \epsilon = [\sigma_0(T) - \sigma] V_0 \Delta \epsilon. \quad (15)$$

On the other hand, combining Eq. (13) and  $\Delta H = T_0(0)\Delta S$  one finds:

$$\sigma_0(T) = -(\Delta S/V_0 \Delta \epsilon) [T - T_0(0)]. \quad (16)$$

This expression is a first integral of the Clausius-Clapeyron equation. A general expression of the thermoelastic balance is finally obtained by inserting (16) into (15), putting the result into (9) and dividing by  $\Delta H$ . The result reads:

$$\left(1 - \frac{T}{T_0(0)}\right) - \frac{V_0 \Delta \epsilon}{\Delta H} \sigma + \frac{\partial \epsilon_{el}}{\partial x} + \frac{d\epsilon_{diss}}{dx} = 0. \quad (17)$$

Straightforward calculations show that the above equation reduces to Eq. (11) when  $\sigma = 0$  and to Eq. (14) when  $T$  is constant.

Equation (17) is a formal expression of the thermodynamic state equation of the system in the  $(x, \sigma, T)$  space. It is important to note that  $d\epsilon_{diss} \geq 0$ , and as a consequence, the equation displays two kinds of branches: branch (+), associated with  $dx > 0$  (forward transformation), and branch (-), associated with  $dx < 0$  (reverse transformation). An explicit expression of the state equation for a given system will be available only when explicit expressions for  $\epsilon_{el}$  and  $\epsilon_{diss}$  are obtained. They might follow from experimental transformation paths or from transformation paths resulting from microstructural models of the transformation.

The transformation paths exhibit memory of the extreme points of the (+) and (-) branches. This property must obviously be a direct consequence of the irreversible effects taking place in the transformation, and therefore should be contained explicitly in the irreversible term  $d\epsilon_{diss}/dx$  of the state equation, since this term determines the hysteresis and hence the memory properties. In a general case  $d\epsilon_{diss}/dx$  will depend not only on the usual state variables  $(x, \sigma, T)$  but also on the extreme values of these variables defining each one of the branches (+) and (-) shown in Fig. 1. In other words:

$$\left(\frac{d\epsilon_{diss}}{dx}\right) = w(\sigma, x, T; \sigma_1, x_1, T_1; \sigma_2, x_2, T_2; \dots). \quad (18)$$

Then, once explicit expressions for  $\epsilon_{el}$  and  $\epsilon_{diss}$  are available, the state equation is to be written as

$$\begin{aligned} x_+ &= x_+(\sigma, T; \sigma_1, x_1, T_1; \sigma_2, x_2, T_2; \dots), \\ x_- &= x_-(\sigma, T; \sigma_1, x_1, T_1; \sigma_2, x_2, T_2; \dots). \end{aligned} \quad (19)$$

### III. CHARACTERISTIC FEATURES OF THE DISSIPATIVE FUNCTION

From now on we restrict our selves to hysteresis loops having  $x = 0$  or  $x = 1$  as one of their two extreme points. The associated reversal curves will be called first-order reversal curves. In such a situation the dissipative function associated with any branch will depend only on the parameters of a single extreme point. Hence, the situation stands for a first-order approach to the general problem; the latter might be treated along the same lines but would give rise to a considerably more involved formalism.

Let us suppose that  $(\partial \epsilon_{el}/\partial x)$  and  $(d\epsilon_{diss}/dx)$  depend only on  $x$ . This is reasonable provided that the system transforms in a narrow range of temperature and stress.

Let  $w_+$  be the function  $(d\epsilon_{diss}/dx)$  in the (+) branch, and  $w_-$  the same function in the (-) branch. It is not difficult to see that for  $\sigma = 0$ :

$$w_+ + w_- = (T_- - T_+)/T_0 = \Delta T/T_0, \quad (20)$$

where  $T_+$  and  $T_-$  are temperatures corresponding to the same transformed fraction  $x$  in the branches (+) and (-), respectively. On the other hand, if the transformation is stress induced, we obtain:

$$w_+ + w_- = (\sigma_+ - \sigma_-)/\sigma_0 = -\Delta\sigma/\sigma_0. \quad (21)$$

In what follows, only temperature-induced transformations will be studied. From the thermodynamic equivalence between  $\sigma$  and  $T$  it is clear that the corresponding equations for stress-induced transformations can be obtained from the equations below by simply replacing  $T$  by  $-\sigma$ .

From the general properties of the hysteresis loops described in the previous section, the characteristic features to be displayed by the functions  $w_+$  and  $w_-$  can be deduced. Comparison between a complete and partial cycle leads to

$$\begin{aligned} w_+(x; \bar{x} = 0, A_f) &\geq w_+(x; \bar{x}, \bar{T}) \quad x > \bar{x}; \quad \forall \bar{x}, \\ w_-(x; \bar{x} = 1, M_f) &\geq w_-(x; \bar{x}, \bar{T}) \quad x < \bar{x}; \quad \forall \bar{x}. \end{aligned} \quad (22)$$

Here  $\bar{x}$  is the extreme point of the partial cycle considered, and  $M_f$  and  $A_f$  are the final temperatures of forward and reverse transformation, respectively. The equality applies for  $x = 1$  in the first equation and for  $x = 0$  in the second one. The equations follow considering that, for a given  $x$ , the external loop is wider than or equal to the partial loop. For this reason,  $w_+$  must be a monotonical decreasing function of  $\bar{x}$ , and  $w_-$  must be a monotonical increasing function of  $\bar{x}$ .

On the other hand, the state equation must satisfy:

$$\begin{aligned} \left(\frac{\partial x_+(T; \bar{x}, \bar{T})}{\partial T}\right)_{x=1, M_f} &= \left(\frac{\partial x_+(T; \bar{x} = 0, A_f)}{\partial T}\right)_{x=1, M_f}, \\ \left(\frac{\partial x_-(T; \bar{x}, \bar{T})}{\partial T}\right)_{x=0, A_f} &= \left(\frac{\partial x_-(T; \bar{x} = 1, M_f)}{\partial T}\right)_{x=0, A_f}. \end{aligned} \quad (23)$$

Computing  $(\partial x/\partial T)$  from (11) the relations above read:

$$\begin{aligned} \left(\frac{\partial w_+(x; \bar{x}, \bar{T})}{\partial x}\right)_{x=1, M_f} &= \left(\frac{\partial w_+(x; \bar{x} = 0, A_f)}{\partial x}\right)_{x=1, M_f}, \\ \left(\frac{\partial w_-(x; \bar{x}, \bar{T})}{\partial x}\right)_{x=0, A_f} &= \left(\frac{\partial w_-(x; \bar{x} = 1, M_f)}{\partial x}\right)_{x=0, A_f}. \end{aligned} \quad (24)$$

Taking for the dissipative functions the ansatz:

$$\begin{aligned} w_+(x; \bar{x}, \bar{T}) &= \alpha(x) [1 - f_+(x, \bar{x})], \\ w_-(x; \bar{x}, \bar{T}) &= \alpha(x) [1 - f_-(x, \bar{x})], \end{aligned} \quad (25)$$

the condition (22) forces  $f_+$  and  $f_-$  to be positively defined, and to satisfy:

$$\begin{aligned} f_+(1, \bar{x} = 0) &= f_+(1, \bar{x}), \\ f_-(0, \bar{x} = 1) &= f_-(0, \bar{x}), \end{aligned} \quad (26)$$

In addition, Eqs. (24) have to be satisfied as well, leading to

$$\begin{aligned} \left(\frac{\partial f_+(x, \bar{x})}{\partial x}\right)_{x=1} &= \left(\frac{\partial f_+(x, 0)}{\partial x}\right)_{x=1}, \\ \left(\frac{\partial f_-(x, \bar{x})}{\partial x}\right)_{x=0} &= \left(\frac{\partial f_-(x, 1)}{\partial x}\right)_{x=0}. \end{aligned} \quad (27)$$

### IV. FITTING TO EXPERIMENTAL OBSERVATIONS

To fit the dissipative functions to experimental observations, in addition to the conditions deduced in Sec. III, we

consider that  $f_+$  and  $f_-$  can be written in the form:

$$\begin{aligned} f_+(x, \bar{x}) &= g_+(x)h_+(\bar{x}), \\ f_-(x, \bar{x}) &= g_-(x)h_-(\bar{x}). \end{aligned} \quad (28)$$

Then, for conditions (26) and (27) to apply,  $g_+$  and  $g_-$  must satisfy:

$$\begin{aligned} g_+(1) &= g_-(0) = 0, \\ \left(\frac{\partial g_+(x)}{\partial x}\right)_{x=1} &= \left(\frac{\partial g_-(x)}{\partial x}\right)_{x=0} = 0. \end{aligned} \quad (29)$$

These conditions are already satisfied by choosing for  $g_+$  and  $g_-$  a polynomial function of second or higher degree without an independent term, of the arguments  $(1-x)$  and  $x$ , respectively.

Considering also that  $w_+$  must be a monotonical decreasing function of  $\bar{x}$  and  $w_-$  a monotonical increasing function of  $\bar{x}$ , it follows that  $h_+$  must increase monotonically and  $h_-$  must decrease monotonically with  $\bar{x}$ . The simplest choice is

$$\begin{aligned} h_+(\bar{x}) &= \bar{x}^n, \\ h_-(\bar{x}) &= (1-\bar{x})^n, \end{aligned} \quad (30)$$

where  $n$  is an exponent to be determined.

First,  $\alpha(x)$  is obtained directly from a fit to the width of the hysteresis loop in a complete transformation cycle ( $x=0 \rightarrow \bar{x}=1 \rightarrow x=0$ ). The equation to be used reads:

$$\alpha(x) = \frac{1}{2} \Delta T(x) / T_0. \quad (31)$$

Second, once  $\alpha(x)$  is known,  $g_+(x)$  and  $g_-(x)$  are obtained from a fit to the width of partial hysteresis loops. For a cycle  $x=0 \rightarrow \bar{x} \neq 1 \rightarrow x=0$  we have

$$g_-(x) = \frac{2}{(1-\bar{x})^n} \left(1 - \frac{\Delta T(x, \bar{x})}{\Delta T(x)}\right) \quad (32)$$

and for a cycle  $x=1 \rightarrow \bar{x} \neq 0 \rightarrow x=1$  we have

$$g_+(x) = \frac{2}{\bar{x}^n} \left(1 - \frac{\Delta T(x, \bar{x})}{\Delta T(x)}\right). \quad (33)$$

It is worth noting that all partial cycles, corresponding to different values of  $\bar{x}$ , are simultaneously fitted by single functions  $g_+(x)$  and  $g_-(x)$  for the  $(-)$  and  $(+)$  branches, respectively.

As an application, the functions  $\alpha(x)$ ,  $g_+(x)$ , and  $g_-(x)$ , given by Eqs. (31), (32), and (33), have been fitted to experimental results of the thermally induced transformation of a Cu;14.1 Zn;17.0 Al (at. %) alloy. The values for the  $(-)$  branch have been taken from Ref. 10, while the values for the  $(+)$  branch, obtained in the same experimental conditions, had not been published previously.<sup>23</sup>

$\alpha(x)$ ,  $g_+(x)$ , and  $g_-(x)$  have been chosen to be polynomial functions, the latter of  $x$  and  $(1-x)$ , respectively, and without independent term. The value of  $n$  together with the order of the polynomials have been optimized to give the best fit using the lowest possible values. The results are summarized in Table I and shown in Fig. 2.

## V. COMMENTS AND CONCLUSIONS

We have formulated, in very general terms, the state equation of a shape-memory material, adopting a continuous quasistatic approach based on the thermoelastic behav-

TABLE I. Parameters obtained in the fit of  $\bar{\alpha}(x)$ ,  $g_+(x)$ , and  $g_-(x)$  to the experimental data with  $\bar{\alpha}(x) \equiv 2T_0\alpha(x) \equiv Ax^3 + Bx^2 + Cx + D$ ,  $g_+(x) \equiv A(1-x)^3 + B(1-x)^2 + C(1-x)$ ,  $g_-(x) \equiv Ax^3 + Bx^2 + Cx$ , and  $n=2$ .

	A	B	C	D
$\bar{\alpha}(x)$	$15.7 \pm 0.1$	$-22.3 \pm 0.1$	$10.2 \pm 0.3$	$2.9 \pm 0.4$
$g_+(x)$	$266 \pm 10$	$-137 \pm 5$	$24 \pm 2$	...
$g_-(x)$	$23 \pm 4$	$-28 \pm 2$	$13 \pm 1$	...

ior of the material. The state equation is composed of three terms: (i) a term explicitly dependent on temperature and/or external stress, representing the driving force for the transformation, (ii) a term giving the reversible variation in stored elastic energy as a function of the transformed fraction, and (iii) a dissipative term including all the irreversible effects manifested at a macroscopic level by the hysteretic behavior. In a quasistatic formalism this last term is assumed to include in an effective (averaged) way all the microscopic irreversibilities, such as the irreversibilities associated with nucleation and elastic energy relaxation, and takes them as a global steady dissipation. This is a reliable approach provided the characteristic times of the relaxational processes involved at a microscopic level are much shorter than the times of appreciable variation of the control parameter, as the experimental observations suggest, so that the quasistatic picture is preserved. Plastic flow processes that would give rise to long-time relaxational processes are explicitly excluded from our treatment since they are acknowledged to be absent in this kind of transformation.

The experimental behavior displayed by partial hysteretic loops inside the two-phase region enables phenomenological modeling of the dissipative term as a function of the transformed volume fraction. This is interesting for two reasons: On the one hand, there are no microscopic theories presently able to give such a dependency. On the other hand, it provides a way to predict the macroscopic behavior of shape-memory materials in the two-phase region, which is of considerable technological interest.

The memory effects displayed by partial hysteretic loops have to be described by thermodynamic variables different than the usual ones: the state of the system is described not only by the instantaneous value of the control parameter ( $T$  or  $-\sigma$ ) and the transformed volume fraction, but depends also on the previous history of the system through the values of both the control parameter and the transformed volume fraction at the previous extreme values of the control parameter.

As a first approximation to the general problem we have been only considering first-order transformation paths, which depend exclusively on the transformed fraction at a single extreme value of the control parameter. This leads to considerable simplification in the formalism and enables writing a set of analytic conditions to be satisfied by the energy dissipation term in the state equation.

We have suggested a very simple expression of the dissipative term consistent with the analytic conditions mentioned above, and this has been fitted to experimental results

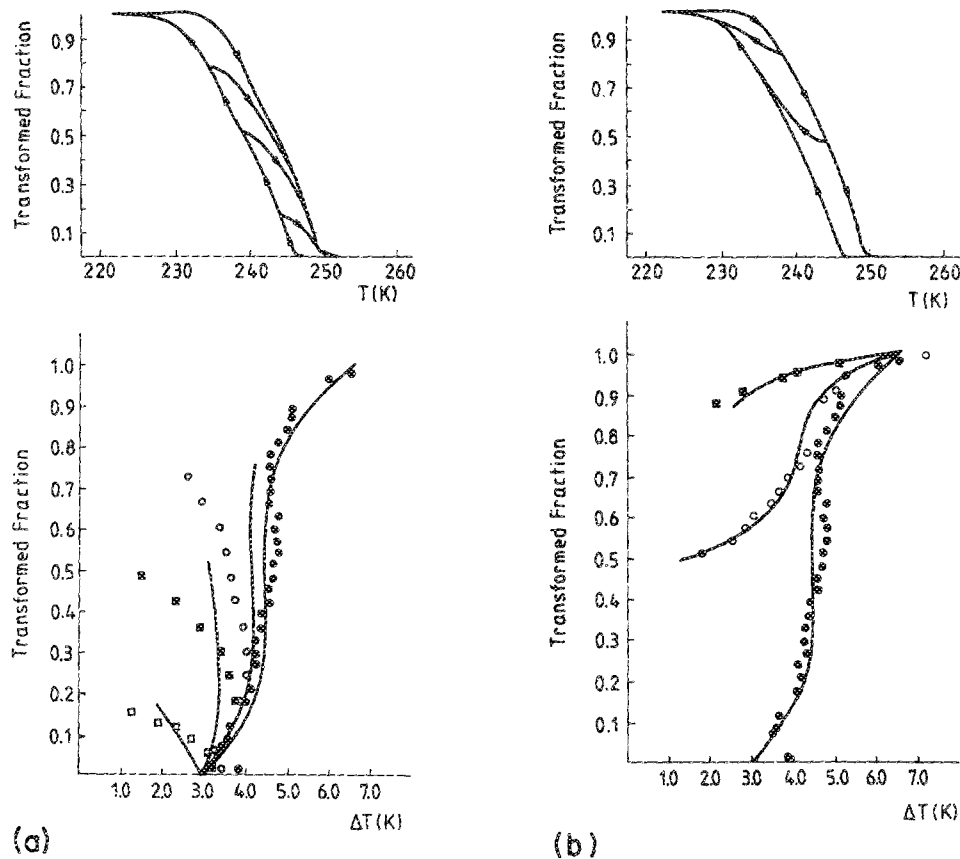


FIG. 2. (a) The upper plot shows the experimental complete cycle together with partial (—) cycles in coordinates of transformed fraction vs temperature, for a Cu;14.1 Zn;17.0 Al at. % alloy. The lower plot shows the transformed fraction  $x$  as a function of the thermal hysteresis  $\Delta T$  for the partial and complete cycles in the upper plot. The different symbols stand for the experimental points corresponding to the following values of the maximum transformed fraction  $\bar{x} < 1$ : (●)  $(1 - \bar{x}) = 0$ , (○)  $(1 - \bar{x}) = 0.22$ , (■)  $(1 - \bar{x}) = 0.48$  and (□)  $(1 - \bar{x}) = 0.82$ . The continuous line shows the fit achieved using a dissipative function of the form  $\Delta T(x, \bar{x}) = \bar{\alpha}(x)[1 - \frac{1}{2}g_-(x)(1 - \bar{x})^2]$  where  $\bar{\alpha}(x) \equiv 2T_0\alpha(x) = 15.7x^3 - 22.3x^2 + 10.2x + 2.9$ ,  $g_-(x) = 23x^3 - 28x^2 + 13x$ , and  $T_0$  is the equilibrium transformation temperature. (b) The upper plot shows the experimental complete cycle together with partial (+) cycles in coordinates of transformed fraction vs temperature, for a Cu;14.1 Zn;17.0 Al at. % alloy. The lower plot shows the transformed fraction  $x$  as a function of the thermal hysteresis  $\Delta T$  for the partial and complete cycles in the upper plot. The different symbols stand for the experimental points corresponding to the following values of the minimum transformed fraction  $\bar{x} > 0$ : (●)  $\bar{x} = 0$ , (○)  $\bar{x} = 0.48$ , and (■)  $\bar{x} = 0.83$ . The continuous line shows the fit achieved using a dissipative function of the form  $\Delta T(x, \bar{x}) = \bar{\alpha}(x)[1 - \frac{1}{2}g_+(x)\bar{x}^2]$ , where  $\bar{\alpha}(x)$  is the same as before and  $g_+(x) = 266(1 - x)^3 - 137(1 - x)^2 + 24(1 - x)$ . In both cases (a) and (b), estimates of the experimental uncertainty give  $\Delta(\Delta T) \approx 0.2$  K and  $\Delta(x) \approx 0.03$ .

obtained by calorimetry of a Cu-Zn-Al alloy. A single polynomial function has been fitted to all partial cycles simultaneously; the order of the polynomial has been selected to be the minimum resulting in a reasonable fit. The result is remarkably good for the forward transformation cycles [partial cycles (+)] and not so accurate for the reverse transformation cycles [partial cycles (-)], the misfit being more important at low transformed-volume fractions. Besides the experimental uncertainty, the reason for the different behavior between the two kinds of partial cycles is not completely clear. Speculating, one could associate the different behavior to dissipative effects not included in the model and associated with the sudden disappearance of the martensitic plates at low transformed fractions, as observed in the optical microscope.

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- <sup>1</sup>L. Delaey, R. V. Krishnan, H. Tas, and H. Warlimont, *J. Mater. Sci.* **9**, 1521, 1536, 1545 (1974).
- <sup>2</sup>M. Cohen, G. B. Olson, and P. C. Clapp, in *Proceedings of the ICOMAT '79*, edited by G. B. Olson and M. Cohen (MIT, Cambridge, MA, 1979), pp. 1-11.
- <sup>3</sup>A. L. Roitburd, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), pp. 317-390.
- <sup>4</sup>I. Cornelis and C. M. Wayman, *Scr. Metall.* **10**, 359 (1976).
- <sup>5</sup>Y. Paskal and L. A. Monasevich, *Phys. Met. Metall.* **52**, 95 (1981).
- <sup>6</sup>L. Delaey, J. Ortín, and J. Van Humbeeck, in *Proceedings of Phase Transformations '87*, edited by G. W. Lorimer (The Institute of Metals, Cambridge, England, 1988), pp. 60-66.
- <sup>7</sup>J. Ortín and A. Planes, *Acta Metall.* **37**, 1433 (1989).
- <sup>8</sup>M. Ahlers, *Prog. Mater. Sci.* **30**, 135 (1986).
- <sup>9</sup>L. Delaey, J. Van Humbeeck, M. Chandrasekaran, J. Janssen, M. Andrade, and N. Mwamba, *Metals Forum* **4**, 164 (1981).

- <sup>10</sup>A. Planes, J. L. Macqueron, and J. Ortín, *Philos. Mag. Lett.* **57**, 291 (1988).
- <sup>11</sup>W. Zhongguo and Y. Dazhi, *Scr. Metall.* **22**, 1245 (1988).
- <sup>12</sup>D. L. Jiles and D. L. Atherton, *J. Appl. Phys.* **55**, 2115 (1984).
- <sup>13</sup>J. S. Cory and J. S. McNichols, *J. Appl. Phys.* **58**, 3282 (1985).
- <sup>14</sup>J. S. Cory and J. S. McNichols, *J. Appl. Phys.* **61**, 972 (1987).
- <sup>15</sup>J. Ortín and A. Planes, *Acta. Metall.* **36**, 1873 (1988).
- <sup>16</sup>G. Guénin, J. L. Macqueron, M. Mantel, C. Auguet, E. Cesari, L. Mañosa, A. Planes, J. Ortín, C. Picornell, C. Seguí, and V. Torra, in *Proceedings of the ICOMAT '86* (The Japan Institute of Metals, Nara, Japan, 1987), pp. 794–799.
- <sup>17</sup>J. L. Macqueron and M. Robin, in *Proceedings of the Jornades de Transformacions Termoelàstiques* (Servei de Publicacions de la Universitat de les Illes Balears, Palma de Mallorca, Spain, 1984), pp. E.01–E.13.
- <sup>18</sup>L. Delaey and G. Hummel, *Film: Institut für den Wissenschaftlichen Film Göttingen, Encyclopedia Cinematographica* (1974).
- <sup>19</sup>A. Planes, J. L. Macqueron, M. Morin, G. Guénin, and L. Delaey, *J. Phys. (Paris)* **43**, C4-615 (1982).
- <sup>20</sup>J. Van Humbeeck, D. Van Huille, L. Delaey, J. Ortín, C. Seguí, and V. Torra, *Trans. Jpn. Inst. Metals*, **28**, 383 (1987).
- <sup>21</sup>R. Tsumura, D. Ríos-Jara, M. Chávez, L. Rodríguez, T. Akachi, and R. Escudero, *Phys. Status Solidi A* **105**, 411 (1988).
- <sup>22</sup>P. Wollants, M. De Bonte, and J. R. Roos, *Z. Metallkde.* **70**, 113 (1979).
- <sup>23</sup>J. L. Macqueron and A. Planes (unpublished).