Method for the Determination of Non-Chemical Free Energy Contributions as a Function of the Transformed Fraction at Different Stress Levels in Shape Memory Alloys

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General equations allowing the determination of the elastic and dissipative energy contributions, as the function of the transformed fraction, \( \xi \), to the martensitic transformation in shape memory alloys are derived. It is shown that the derivatives of these energies by \( \xi \) can be calculated from the measured hysteresis loops. It is illustrated, by the example of our previous experimental results obtained on CuAlNi shape memory alloys at different stress levels, \( \sigma \), that our evaluation method gives consistent results with those obtained from DSC measurements. Furthermore, the \( \xi \)- and \( \sigma \)-dependence of the above derivatives as well as their integral values for \( (0,1) \) and \( (1,0) \) \( \xi \) intervals, i.e. the dissipated energy and the elastic energy stored and released during the forward and reverse transformations, are determined as the function of stress.

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1. Introduction

Determination of the elastic and dissipative energy contributions as the function of the transformed fraction, \( \xi \), during martensitic transformations, is a long-standing demand for better understanding and tailoring of materials for example for shape memory applications (smart materials). Once determined experimentally they can serve as input parameters for modelling of shape memory or superelastic behaviour. In this paper we describe a new method for the determination of the derivatives of the elastic and dissipative energy terms from the measured hysteresis loops. We show that the integrals of these quantities are in a good accordance with the data obtained from DSC measurements, i.e. our evaluation method is consistent. The method is illustrated on the example of our previous experimental results obtained in CuAlNi shape memory alloys at different stress levels.

2. Equations for the Evaluations

2.1 Derivatives of the free energy contributions

Phase transformations in shape memory alloys (SMA) can take place in both directions (i.e. from the austenite, A, to the martensite, M, and reverse)\(^1\) and e.g. for the A \( \rightarrow \) M transformation the change of the Gibbs free energy can be given (if we neglect, as it is usual for SMA, the interface term for nucleation) e.g. as Ref. 2, 3):

\[
\Delta G^\xi = G^M - G^A = \Delta G^\xi M + E^\xi + D^\xi
\]  

(1)

Obviously a similar expression can be written for the M \( \rightarrow \) A transformation as well, using the index \( ^A \). Here \( \Delta G^\xi M \) is the change in the chemical Gibbs-free energy. \( E^\xi \) and \( D^\xi \) are the elastic and dissipative energies, respectively. The elastic energy accumulates as well as releases during the processes down and up just because the formation of different variants of the martensite phase is usually accompanied by a development as well as release of an elastic energy field (due to the transformation strain). It is usually supposed that \( E = E^\xi = -E^A > 0 \). The dissipative energy is always positive in both directions. (In principle, one more additional term, proportional to the entropy production, should be considered, but it can be supposed\(^4-6\) that this can be neglected.)

Let us denote the transformed fraction of the martensite phase by \( \xi (\xi = 1, and \xi = 0 \) correspond to pure martensite and austenite phases, respectively). The transformation temperature (at which the two phases are in equilibrium for a given \( \xi \) can be given as

\[
\frac{\partial (\Delta G)}{\partial \xi} = \Delta G^\xi + e^\xi (\xi) + d^\xi (\xi) = 0
\]  

(2)

where lower cases denote the derivatives of the corresponding energy terms. It is assumed that \( \Delta G^\xi \) is independent of \( \xi \) and

\[
\Delta G^\xi = \Delta h^\xi - T \Delta s^\xi
\]  

(3)

with \( \Delta h^\xi = h^M - h^A \) (\(<0\)) and \( \Delta s^\xi = s^M - s^A \) (\(<0\)) (the M phase is the low temperature phase). Furthermore, at the “equilibrium transformation temperature”, \( T_0 \) (the temperature of zero-change in the chemical free energy):

\[
\Delta G^\xi (T_0) = 0 \quad \text{i.e.} \quad T_0 = \Delta h^\xi / \Delta s^\xi = \Delta h^A / \Delta s^A
\]  

(4)

The temperature at which (2) is equal to zero for \( \xi = 0 \) as well as \( \xi = 1 \) is the martensite start (\( M_s \)) and finish (\( M_f \)) temperature, respectively. In general the \( T^\xi (\xi) \) curve, defined by (2), gives the lower part of the hysteresis curve (i.e. the \( \xi (T^\xi) \)) curve. Similarly, the \( T^\xi (\xi) \) curve, defined similarly as the \( T^\xi (\xi) \) curve, but for the M \( \rightarrow \) A transformation, gives the upper part of the hysteresis curve. Thus

\[
T^\xi (\xi) = T_0 - [d^\xi (\xi) + e^\xi (\xi)] / [-\Delta s^\xi]
\]  

and

\[
T^\xi (\xi) = T_0 - [d^\xi (\xi) + e^\xi (\xi)] / [-\Delta s^\xi]
\]  

(5)

Obviously from the \( T^\xi (\xi) \) and \( T^\xi (\xi) \) curves one can get the start and finish temperatures (e.g. for \( \xi = 0 \) \( M_s = T_0 - [d_0 + e_0]/[-\Delta s^\xi] \) and \( M_f = T_0 + [d_0 + e_0]/[-\Delta s^\xi] \)), which were used in our previous papers\(^7-11\) for the determination of the derivatives of dissipative and elastic free energy contributions from experimental data at the start and finish of the martensitic transformation as a function of

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uniaxial stress and/or hydrostatic pressure.

In this paper we will extend this method for the determination of these energies as a function of $\xi$ at different constant stress levels. Indeed, from (5) one can write
\[
T^i(\xi) + T^r(\xi) = 2T_0 + [(e^i(\xi) - e^r(\xi))
+ (d^i(\xi) - d^r(\xi))] / [-\Delta s_c^i]
\]
and
\[
T^i(\xi) - T^r(\xi) = [(d^i(\xi) + d^r(\xi))
+ (e^i(\xi) + e^r(\xi))] / [-\Delta s_c^i]
\]
Accordingly measuring the $T^i(\xi)$ and $T^r(\xi)$ curves (which are the inverse of the $\xi^i(T)$ and $\xi^r(T)$ giving the corresponding part of the hysteresis curves in the $\xi(T)$ plots: see Fig. 1 and plotting the $T^i(\xi) + T^r(\xi)$ and $T^i(\xi) - T^r(\xi)$ curves one can get the character of the $\xi$-dependences of the derivatives of the elastic and dissipative terms. As an approximation we can assume that $e^i(\xi) = -e^r(\xi) = e(\xi)$ (from which the assumption $E^i = -E^r = E$ mentioned above, follows as well) and $d^i(\xi) = d^r(\xi) = d(\xi)$. Then
\[
-2e(\xi) - 2\Delta s_c^i T_0 = -\Delta s_c^i (T^i(\xi) + T^r(\xi))
\]
and
\[
2d(\xi) = -\Delta s_c^i (T^i(\xi) - T^r(\xi))
\]
It has to be noted that unfortunately we do not know the value of $T_0$ since there is no way for the direct measurement of this quantity. Thus we can determine the elastic energy as the function of the transformed fraction only irrespective of the additive term containing $T_0$.

### 2.2 Integral quantities

Let us consider the heats of transformation measurable e.g. in a calorimeter during the forward and reverse transformations. Since $\Delta h^i_c$ is the latent heat of transformation (per unit fraction), the heat measured for the A $\Rightarrow$ M transformation (cooling down) as well as for the M $\Rightarrow$ A transformation (heating up) are given by
\[
Q^i = \int_0^1 [\Delta h^i_c + e^i(\xi) + d^i(\xi)]d\xi
\]
and
\[
Q^r = \int_1^0 [\Delta h^i_c + e^r(\xi) + d^r(\xi)]d\xi
\]
respectively. Now, introducing the following notations:
\[
\int_0^1 \Delta h_c^i d\xi = -\int_1^0 \Delta h_c^r d\xi = \Delta H_c (<0);
\int_0^1 d^i(\xi)d\xi = D^i (>0);
\int_0^1 e^i(\xi)d\xi = E^i (>0);
\int_0^1 d^r(\xi)d\xi = D^r (>0);
\int_0^1 e^r(\xi)d\xi = E^r (<0);
\]
the relations
\[
Q^i = \Delta H_c + E^i + D^i
\]
and
\[
Q^r = -\Delta H_c + E^r + D^r
\]
are obtained.

Taking also into account that, according to our assumptions above, $E^i = -E^r = E (>0)$ and $D^i = D^r = D (>0)$:
\[
Q^i - Q^r = -2\Delta H_c - 2E
\]
and
\[
Q^i + Q^r = 2D
\]
It is important noting that the last equations are strictly valid only if after a cycle the system has come back to the same thermodynamic state, i.e. it does not evolve from cycle to cycle. Furthermore, it can be shown\(^3\) that (15) is only valid if the heat capacities of the two phases ($c_p^M$ and $c_p^A$) are equal to each other. If it is not the case then
\[
2D = Q^i + Q^r + (c_p^M - c_p^A)(T_A - T_M)
\]
should be used, where $T_A$ and $T_M$ are the corresponding peak temperatures.\(^5\)

It can be seen that from the integral of (8) and (9) relations (14) and (15) can be obtained respectively, which—if $-\Delta s_c^i$, is also known from an independent measurement— offer a way for the comparison of the integral of the differential quantities determined from the hysteresis loop and the integrated quantities obtained e.g. from a DSC measurements. This can serve as a condition for the self-consistency of our analysis for the determination of the $\xi$ dependence of the dissipative and elastic terms. It is important noting that this condition can be applied even in those cases when $e^i(\xi) = -e^r(\xi) = e(\xi)$ ($E^i = -E^r = E$) as well as $d^i(\xi) = d^r(\xi) = d(\xi)$ ($D^i = D^r = D$) are not supposed, because the corresponding integrals of (6) and (7) should yield the difference and the sum of (12) and (13), respectively. Thus the above suppositions are necessary only to construct the $d(\xi)$ and $e(\xi)$ functions but the correspondence between the integrals of the derivative quantities (characterized by the $T^i(\xi)$ and $T^r(\xi)$ curves) and the proper combinations of heats measured in a DSC should be valid in general.

### 2.3 Stress dependence

To determine the stress dependence of the dissipative term $d(\xi)$ one has simply measure the dependence of the hysteresis loop on the uniaxial stress, $\sigma$, and from (9) the $d(\xi, \sigma)$ function can be calculated. On the other hand, for the determination of the $e(\xi, \sigma)$ function one has also to take into account that in (8) $T_0$ can be a function of $\sigma$ as well. Since the stress dependent part of $\Delta g_c$ can be expressed as: $-\sigma e^a(\sigma)$
where $\varepsilon^i(\sigma)$ is the transformation strain and using that $\partial(\Delta g_c)/\partial T = -\Delta x_c$ and $\partial(\Delta g_c)/\partial \sigma = -\varepsilon^u$, from the Clausius–Clapeyron equation:

$$\frac{\partial(\Delta g_c)}{\partial \sigma} + \frac{\partial(\Delta g_c)}{\partial T} \frac{dT}{d\sigma} = 0,$$

we have

$$\frac{dT}{d\sigma} = -\frac{\varepsilon^u}{\Delta x_c},$$

where is was also assumed that $\Delta x_c^{-1}$ and $\Delta h_c^{-1}$ do not depend directly on the temperature and stress. Thus, integrating (18)

$$T_0(\sigma) = T_0(0) - \int_{0}^{\sigma} \varepsilon^u(\sigma') d\sigma'$$

which has to be also used in (8) when the stress dependence of $e(\xi)$ term from the $T^i(\xi, \sigma)$ and $T^i(\xi, \sigma)$ curves is also determined.

3. Data Analysis

The experimental results, obtained by us in Ref. 11) on wires (1 mm in diameter and 50 mm long) of Cu–24 at%Al–2.2 at%Ni samples with 0.5 at%B addition, will be used in the analysis described above. For the details of preparation of samples and measurements see Ref. 11), where the temperature dependence of the resistance and elongation of samples at different stress levels (up to 10 MPa) were measured. Applying equations (5) at $\xi = 0$ as well as $\xi = 1$, the derivatives of the elastic and dissipative energy terms were determined as the function of $\sigma$ from the transformation temperatures ($A_\sigma, A_M, M_0, M_1$–$\sigma$-plots). The transformation entropy was calculated from the straight line with the slope $\varepsilon^u$ obtained. $\Delta x_c^{-1}$ relation$^{9)}$ on the basis of the measured DSC curves and $\Delta x_c^{-1} = -1.38 \times 10^3 J/Km^3 = -1.02 J/molK$ was obtained. $^{10)}$ It is worth noting that this relation again is valid only if the heat capacities of the two phases are equal to each other, $^{5)}$ but this correction term $((\varepsilon^m_p - \varepsilon^m_A) ln(T_M/T_M))$, is much more negligible as compared to the similar correction in (16). For the sake of simplicity in the following figures $\Delta x_c^{-1} = \Delta x_c$ notation will be used.

In Ref. 11) the $\varepsilon^u(\xi)$ was also measured (see Fig. 5 of Ref. 11) and it was obtained that it can be approximated by a straight line with the slope $2.2 \times 10^{-3} MPa^{-1}$.

Now we extend the analysis made in Ref. 11) and determine the complete $d(\xi, \sigma)$ as well as $e(\xi, \sigma)$ functions and the integrals of (8) and (9) will be compared with (14) and (15) calculated from the DSC measurements.

In order to get the necessary $T^i(\xi)$ and $T^i(\xi)$ functions first the measured hysteresis loops had to be normalized. This was done already in Ref. 11) by removing the transformation independent parts from the original elongation-temperature hysteresis loops and renormalizing their vertical axis to 1. Here we show, as an illustration, a corresponding inverse function $T(\xi)$ in Fig. 2.

Thus from the $T(\xi)$ functions the $T^i(\xi)$ and $T^i(\xi)$ were obtained and, according to (8) and (9), the $e(\xi) + T_0(0)\Delta x_c$ as well as the $d(\xi)$ function were constructed at different stress levels. It is worth noting that while the determination of $T^i(\xi)$ and $T^i(\xi)$ between $\xi = 0.1$ and $\xi = 0.9$ is easy, the error in reading for $\xi \to 0$ and $\xi \to 1$ is higher. Nevertheless, it can be seen in Figs. 3 and 4 that at the end points (i.e. at $\xi = 0$ and $\xi = 1$) the values determined in the usual way from $M_0$, $M_1$, $A_\sigma$ and $A_M$ values obtained in Ref. 11) and denoted by full symbols, usually fit (except one point at $\xi = 1$ for 9.15 MPa) within the error or reading to the values calculated from the normalized hysteresis loops. From such a comparison we recognized that in one case we probably made an error of reading for $M_1$ at 2.59 MPa in Ref. 11). Furthermore, in order to get more points on the dissipative energy derivative versus $\sigma$, at small stress level an additional measurement was carried out at $\sigma = 0.86$ MPa as well. Thus, we think it is worth to present here the corrected and extended curves corresponding to Figs. 4 and 6 in Ref. 11); see Figs. 5 and 6. The behaviour is similar for the $d(\sigma)$ curves (only the corrected point for $T(1)$ at 2.59 MPa is different, but this value fits better to the overall tendency): both $d(0)$ and $d(1)$ is approximately constant at low stresses and they show a small increase above 5 MPa. On the other hand the $e + T_0(0)\Delta x_c$ versus $\sigma$ functions are a bit different: for $\xi = 0$ this functions shows a decreasing tendency while for $\xi = 1$ it is practically constant within the experimental errors.

It can be seen in Figs. 3(a) and 4 that both the $e(\xi) + T_0(0)\Delta x_c$ and $d(\xi)$ functions increase with increasing $\xi$, and then they change by about 10–40%, respectively between $\xi = 0$ and $\xi = 1$. It is worth to note that in Fig. 3(a) the $e(\xi) + T_0(0)\Delta x_c$ values have negative sign. From this we can make an estimation for the lower limit of $T_0$. Since for a given $\sigma e(\xi, \sigma) + T_0(0)\Delta x_c$ has always the lowest value at $\xi = 0$ (Fig. 3(a)) and taking also into account Fig. 6 (which shows that the $e(0, \sigma) + T_0(0)\Delta x_c$ function decreases with increasing $\sigma$) we can require that $e(0, 9.15 MPa) > 0$. From this $T_0(0)\Delta x_c > e(0)/(-\Delta x_c)$ and $T_0 \geq (M_1 + A_1)/2$. Figure 3(b) shows the $e(\xi)$ ($\geq e(\xi)$) function obtained by taking $-T_0(0)\Delta x_c = 414 J/mol$. From this $T_0(0) \geq 406 K$ follows. (This condition also corresponds to the well-known relation — see the relations below eq. (5)—$M_1 + A_1)/2 = T_0 - e(0)/(-\Delta x_c)$ since for $e(0) \geq 0,$ $T_0 \geq (M_1 + A_1)/2$.)
symbols denote the \( Q^1 - Q^1 \) as well as \( Q^1 + Q^1 + (c^M_p - c^A_p)(T_A - T_M) \) values calculated from the data \((Q^1, Q^1, T_A, T_M)\) obtained from DSC measurements in Ref. 11), while for \( c^M_p - c^A_p \approx 11 \text{ J/mol K} \) was taken in accordance with Ref. 5). It can be seen that both of them increase monotonically with \( \sigma \), and the increase in the dissipative energy is small (is about 5%) and detectable only above a certain stress (5 MPa). On the other hand (taking \( -\Delta H_c = -T_0(0)\Delta S_c \approx 414 \text{ J/mol} \)) an estimate of the relative change of the elastic energy gives about \(-50\%\) in the stress interval investigated.

Finally Figs. 9 and 10 show the integral of the elastic and dissipative energies versus \( \xi \) respectively. For calculation of the \( E'/(\xi) \) curve again the \( T_0(0) = 406 \text{ K} \) value was used as above (i.e. the numerical value can be considered as upper bounds of \( E \)).

In the interpretation of our results it is worth considering that systematic experimental investigations on the stress dependence of \( D \) or \( E \) are very rare in the literature and they have not been well understood (for a review of this problem see e.g. Ref. 12, 13)). Furthermore there are no experimental data on the \( \xi \)-dependence of the derivatives or integrals of the elastic and dissipative energy terms, and different assumptions have been used in the simulations on the value of \( D \) (in
many cases it was considered to be independent of $\sigma$ or on the $\xi$-dependence of $d(\xi)$ and $e(\xi)$ derivatives (e.g. in Ref. 14) it was assumed that $e(\xi)$ is a linear and thus $E(\xi)$ is a quadratic function of $\xi$. We believe that our proposal for the analysis of experimentally measured hysteresis loops provide a simple, useful routine for the parallel determination of the above functions in the same sample, and can help to analyze e.g. the relation between the changes of dissipative and elastic terms (see e.g. Ref. 13), where only $\sigma$-dependence of $D$ was evaluated and was rationalized by considering the dissipation of elastic strain energy).

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