On the thermodynamics of thermoelastic martensitic transformations. A critical analysis of calorimetric measurements.

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Introduction

It is well known that in a thermoelastic martensitic transformation the transformational shape and volume changes can be accommodated (in both matrix and product phase) in an elastic way, so that an equilibrium condition between driving and resistive forces is continuously achieved during growth and shrinkage of martensitic plates (1).

Such a thermoelastic equilibrium condition, and the fact that (since the transformation is difusionless) the material can be studied thermodynamically as a single component system, lead to the following fundamental thermodynamic equation (2,3):

$$dH = T\,dS - T\,dS_i - dE_{el} + V_o \sum_{ij} \sigma_{ij}\,d\epsilon_{ij} + V\,dp - dW_i \qquad [1]$$

Here dH and dS are differential changes in chemical enthalpy and entropy (per mol) of the two-phase system, i.e.:

$$\begin{aligned} dH &= d\{x\,H^M + (1-x)\,H^P\} = (H^M - H^P)\,dx\,, \\ dS &= d\{x\,S^M + (1-x)\,S^P\} = (S^M - S^P)\,dx\,, \end{aligned} \qquad [2]$$

where x is the transformed volume fraction. $(-dE_{el})$ is the reversible internal work stored in the system as elastic strain energy and interfacial energy, $(V_o\ \Sigma\,\sigma_{ij}\ d\epsilon_{ij})$ is the non-hydrostatic part of the work performed by external forces to produce the macroscopic deformation and (-p dV) is the hydrostatic part of this same work, where p is the hydrostatic pressure and V the volume of the system. We follow a convention in which heat released by the system is negative and work performed by the system is positive. S_i is the entropy production accounting for the dissipation of internal work as irreversible heat $(dS_i \geq 0)$ and W_i is the internal work irreversibly dissipated in energy forms other than heat $(dW_i \geq 0)$. The dissipative contributions S_i and W_i are included to account for the hysteresis exhibited by the transformation. In our quasistatic formalism these contributions are assumed to include in an effective (averaged) way all the microscopic irreversibilities and to take them as a global steady dissipation. This is a reliable approach provided the characteristic times of the microscopic relaxational processes are much shorter than the times of appreciable variation of the driving force, as the experimental observations suggest.

Eq.[1] shows that T and σ_{ij} play equivalent roles on the transformation, except for the fact that σ_{ij} breaks the degeneracy of the martensitic phase. This type of formalism was applied in our previous works to sort out, from the heat typically measured in a calorimetric experiment, the three different energy contributions to the thermoelastic balance: the latent heat of transformation, the reversible elastic energy and the dissipative energy. The case of a stress-free thermally-induced transformation was studied in (2), while thermally-induced transformations under a constant external stress or strain and stress-induced transformations at constant temperature were studied in (3). In all cases we assumed a negligible entropy production ($dS_i = 0$), so that the whole energy dissipation was assumed to take place in the form of irreversible work.

The purpose of this paper is to consider the influence of S_i and ΔC_p (difference in specific heat between the two phases) on our previous thermodynamic results, for a stress-free thermally-induced transformation. This will enable a more accurate analysis of calorimetric data and, from this, an evaluation of the relative importance of S_i , W_i and ΔC_p on the thermodynamics of the transformation. The paper is divided in two parts: the theoretical thermodynamic framework is developed first, followed by the actual analysis of calorimetric data on the thermally-induced transformation in different alloys of the Cu-Zn, Cu-Zn-Al and Cu-Al-Mn systems.

Thermodynamics

In the absence of applied external stresses σ_{ij} and at constant pressure p eq. [1] takes the form:

$$dH = T\,dS - T\,dS_i - dE_{el} - dW_i \qquad [3]$$

where

$$dQ = T\,dS - T\,dS_i \qquad [4]$$

Q is the total amount of heat exchanged between the transforming specimen and the ambiance in a temperature interval including the transformation considered (forward or reverse), and comes from a double contribution: the heat released or absorbed during the transformation itself and the heat used to change the temperature of the specimen, which depends on its heat capacity. If the heat capacities of both phases are the same, their contribution to the heat exchanged is the same and has a different sign for the forward and reverse transformation, so that it cancels out in a complete cycle. If the transformation would take place without thermal hysteresis, this contribution would also cancel out even if the heat capacities of the two phases were different. In the most general situation, however, this contribution will be different in the forward than in the reverse transformation. From a calorimetric point of view, Q represents the overall heat exchanged with the calorimetric block between the two extreme temperatures of the run, obtained by integration of the recorded thermal power using a base-line given by a null power signal. The contribution to Q arising solely from the transformation process, to be called q, is to be obtained as the integration of the recorded thermal power using now a base-line given by $[C_p^P(1-x)+C_p^M x](dT/dt)$, which at each temperature represents the thermal power used to change the temperature of the two-phase specimen. C_p^P and C_p^M are the specific heats of parent and martensite phases respectively. It should be noted that, since this base-line depends on x, it is not known a priori and is difficult to obtain with high accuracy (4,5). The result of a calorimetric measurement in both transformations is drawn schematically in fig. 1 and the meaning of Q and q indicated.

Integrating eq. [3] through a closed contour including complete forward and reverse transformations leads to:

$$\oint dQ = \oint dW_i = W_i \qquad [5]$$

If we now divide eq. [4] by the absolute temperature T and integrate through the same closed contour we get:

$$\oint \frac{dQ}{T} = - \oint dS_i = - S_i \qquad [6]$$

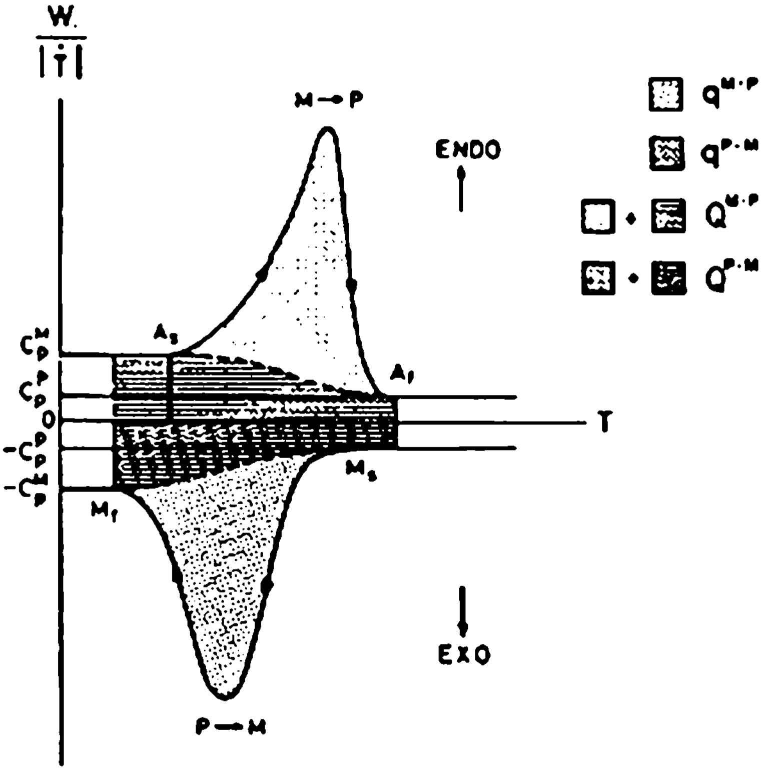

Fig. 1: Schematic plot of the calorimetric curves corresponding to a forward (P-M) and reverse (M-P) thermally-induced martensitic transformation. The thermal power W in the ordinates is rescaled by the absolute value of the cooling or heating rate $|\dot{T}|$; in this way, plotted as functions of temperature, the curves enclose areas Q^{P-M} and Q^{M-P} which give the total heat measured in the forward and reverse transformation, respectively. The broken lines joining the initial and final transformation temperatures represent the base-lines to be considered in order to separate the heats of transformation, q^{P-M} and q^{M-P}, from the heat used to change the temperature of the specimen. These base-lines depend on the values of C_p^P and C_p^M and on the volume fraction of martensite in the specimen at every temperature, x=x(T), and cannot be determined a priori.

Equations [5] and [6] open the possibility of determining the entropy production and the dissipated work directly from calorimetric measurements. These equations are written in terms of the overall heat Q, while only q is usually determined in calorimetric experiments (see fig. 1). It is therefore interesting to rewrite eqs. [5] and [6] in terms of q, so that the influence of $\Delta C_p = C_p^M - C_p^P$ appears explicitely. The result is:

$$q^{P-M} + q^{M-P} = W_i - \Delta C_p \oint x \, dT \qquad [7]$$

$$\int_{M_s}^{M_f} \frac{dq^{P-M}}{T} + \int_{A_s}^{A_f} \frac{dq^{M-P}}{T} = - S_i - \Delta C_p \oint x \frac{dT}{T} \qquad [8]$$

where M_s and M_f are the starting and finishing temperatures of the forward transformation and A_s and A_f the starting and finishing temperatures of the reverse one.

Calorimetric measurements carried out through closed cycles have to satisfy eqs. [7] and [8]. It is worth noting that the closed contour integrals in those equations are either positive or null, and the same applies for the contributions S_i and W_i. Then, depending on the resulting sign in the left member of those equations, restrictive conditions for the values of the dissipative terms W_i and S_i and for the value of ΔC_p, assumed to be unknown, can be obtained. The restrictive conditions are summarized in Table 1, where it is worth noting that three of the possible situations are not thermodynamically allowed.

On the other hand, if ΔC_p is available (e.g. from adiabatic or AC calorimetry) and $x=x(T)$ is known in some way, the dissipative terms W_i and S_i can be obtained from eqs. [7] and [8]. The determination of $x=x(T)$ in an exact way appears to be a difficult task; reliable approximations to $x=x(T)$, however, are easier to obtain since in thermoelastic transformations elastic and dissipative energies are usually much smaller than the transformation latent heat, proportional to x.

In this sense, approximate expressions for eqs. [7] and [8] are obtained considering the following exact results (which can be obtained from eq.[1]):

$$\oint S \, dT = \oint dW_i + \oint T \, dS_i \qquad [9]$$

and (if ΔC_p is not temperature dependent):

$$\oint S \, dT = \oint x \, dT \cdot \Delta S(To) + \Delta C_p \oint x \ln \frac{T}{To} \, dT \qquad [10]$$

where To is the equilibrium transformation temperature. The last integral in eq. [10] is negligible to a first approximation, so that eqs. [7] and [8] can be written approximately in the form:

	$\lvert q^{P-M}\rvert < \lvert q^{M-P}\rvert$	$\lvert q^{P-M}\rvert = \lvert q^{M-P}\rvert$	$\lvert q^{P-M}\rvert > \lvert q^{M-P}\rvert$
$\left\lvert\int_{M_s}^{M_f}\frac{dq^{P-M}}{T}\right\rvert$ $\vee$ $\left\lvert\int_{A_s}^{A_f}\frac{dq^{M-P}}{T}\right\rvert$	$\frac{W_i}{\oint x\,dT} > \Delta C_p > \frac{-S_i}{\oint x\frac{dT}{T}}$	$\frac{W_i}{\oint x\,dT} = \Delta C_p$	$0 \le \frac{W_i}{\oint x\,dT} < \Delta C_p$
$\left\lvert\int_{M_s}^{M_f}\frac{dq^{P-M}}{T}\right\rvert$ $\parallel$ $\left\lvert\int_{A_s}^{A_f}\frac{dq^{M-P}}{T}\right\rvert$	$\Delta C_p = \frac{-S_i}{\oint x\frac{dT}{T}}$	$W_i = S_i = 0$	Impossible
$\left\lvert\int_{M_s}^{M_f}\frac{dq^{P-M}}{T}\right\rvert$ $\wedge$ $\left\lvert\int_{A_s}^{A_f}\frac{dq^{M-P}}{T}\right\rvert$	$\Delta C_p < \frac{-S_i}{\oint x\frac{dT}{T}} \le 0$	Impossible	Impossible

Table 1: Restrictive conditions to be satisfied by W_i, S_i and ΔC_p for all possible calorimetric results of the values q and $\int dq/T$ in forward and reverse transformations.

$$q^{P-M} + q^{M-P} = W_i - \frac{\Delta C_p}{\Delta S(To)}\,[W_i + \langle T\rangle\, S_i] \qquad [11]$$

$$\int_{M_s}^{M_f}\frac{dq^{P-M}}{T} + \int_{A_s}^{A_f}\frac{dq^{M-P}}{T} = -S_i - \frac{\Delta C_p}{\Delta S(To)}\left[\frac{W_i}{\langle T\rangle} + S_i\right] \qquad [12]$$

where $\langle T\rangle$ is a mean temperature in the whole transformation interval (M_f, A_f), which can be evaluated as $\langle T\rangle \approx \frac{1}{2}(M_f + A_f)$, and $\Delta S(To)$ is the entropy difference between the two phases at the equilibrium temperature To and can be evaluated as:

$$\Delta S(To) = - \left[\int_{M_s}^{M_f} \frac{|dq^{P-M}|}{T} + \int_{A_s}^{A_f} \frac{|dq^{M-P}|}{T} \right] \qquad [13]$$

Thus, provided ΔC_p is available, eqs. [11] and [12] form a linear system of algebraic equations which can be solved to obtain the dissipative terms W_i and S_i .

The reader should note however that W_i and S_i could follow directly from calorimetric data using eqs. [5] and [6] if, instead of the heats q, the total heats Q were measured in the calorimetric run. This would lead to great simplification, but it is not the common practice.

Results

We have analysed experimental results on the thermoelastic martensitic transformation (β - β'(9R or 18R)) undergone by several specimens of the Cu-Zn, Cu-Zn-Al and Cu-Al-Mn systems with different compositions. The results are summarized in Table 2, corresponding to averages over two or three equivalent runs.

Alloy system Composition (at%) M_s(K), Reference		q^{P-M} (J/mol) q^{M-P} (J/mol)	$\int_{M_s}^{M_f} \frac{dq^{P-M}}{T}$ (J/K mol) $\int_{A_s}^{A_f} \frac{dq^{M-P}}{T}$ (J/K mol)
Cu-Zn single crystal 60.0-40.0 123 ± 4, (6)	(a)	-130 ± 4 135 ± 4	-1.15 ± 0.05 1.06 ± 0.02
Cu-Zn-Al single crystal 65.16-21.69-13.15 116 ± 2, (6)	(b)	-171 ± 3 170 ± 3	-1.52 ± 0.03 1.42 ± 0.03
Cu-Zn-Al single crystal 68.9-14.1-17.0 248 ± 2, (7)	(c)	-330 ± 2 335 ± 2	-1.41 ± 0.03 1.40 ± 0.02
Cu-Al-Mn polycrystal 70.4-18.0-11.6 130 ± 4, (8)	(d)	-130 ± 6 137 ± 7	-1.07 ± 0.07 0.99 ± 0.06
Cu-Al-Mn polycrystal 70.4-19.8-9.8 235 ± 4, (8)	(e)	-277 ± 9 318 ± 6	-1.24 ± 0.04 1.34 ± 0.03

Table 2: Calorimetric results for thermoelastic martensitic alloys of different compositions.

Practically in all cases one observes that $|q^{P-M}| \leq |q^{M-P}|$ and (except for (e)) that $\int |dq^{P-M}|/T > \int |dq^{M-P}|/T$. Looking at Table 1 we conclude that:

$$\frac{W_i}{\oint x\,dT} \geq \Delta C_p > \frac{-S_i}{\oint x\frac{dT}{T}}$$

Hence ΔC_p can take arbitrarily small values, but if $S_i=0$ then necessarily $\Delta C_p>0$ (i.e. $C_p^M>C_p^P$) while if $W_i=0$ then $\Delta C_p\leq 0$ (i.e. $C_p^M\leq C_p^P$). The exception (e) can be accounted for by a $\Delta C_p<0$.

In order to draw any conclusion about the relative importance of the energy dissipative terms W_i and $\langle T\rangle S_i$ in each case, an accurate experimental determination of ΔC_p around the transformation temperature is required.

Summary

The thermodynamics of thermoelastic martensitic transformations in shape-memory alloys are described in a quasistatic formalism. This includes changes in elastic energy and continuous energy dissipation.

The formalism has been used to investigate the information on the dissipative terms contained in the heat released or absorbed during stress-free thermally-induced transformations, and measured in a typical calorimetric experiment.

Depending on the relative importance of the calorimetric quantities q and $\int dq/T$ between forward and reverse transformations, a complete set of restrictive conditions on the dissipative terms and on ΔC_p , as given in Table 1, can be obtained. Three possibilities result thermodynamically forbidden.

A coupled system of approximate linear equations for W_i and S_i in terms of the calorimetric quantities, of ΔC_p and of a mean transformation temperature $\langle T\rangle$, can also be derived.

Comparison with actual calorimetric data on alloys of the Cu-Zn, Cu-Zn-Al and Cu-Al-Mn systems shows that $\Delta C_p=0$ is compatible with the experimental results but, at the same time, determination of W_i and S_i requires accurate values of ΔC_p around the transformation temperature, currently not available.

References

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