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THERMALLY INDUCED MARTENSITIC TRANSFORMATIONS: THEORETICAL ANALYSIS OF A COMPLETE CALORIMETRIC RUN *

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ABSTRACT

A complete calorimetric run of a thermally induced martensitic transformation is described and analyzed in detail by means of a simple model of heat transfer in the calorimeter. The analysis is purely theoretical and no experimental data are presented. Procedures to obtain the difference in specific heat between the parent phase and the martensite, and to perform an adequate baseline correction accounting for such a difference are outlined. All the information obtainable from a calorimetric experiment of this kind is critically reviewed: first, the classical thermodynamic parameters, i.e. the transformation temperatures and the energy and entropy changes; second, the parameters describing the discontinuity of the transformation, its extension in temperature and the thermal hysteresis between the forward and reverse transformations; and third, the difference in specific heat between the parent phase and the martensite.

INTRODUCTION

The martensitic transformation is a diffusionless structural transformation in the solid state between two metastable phases; the parent phase is the high-temperature phase, while the low-temperature phase is called the martensite. The martensitic transformation is the physical mechanism by which several alloys exhibit the shape-memory effect, i.e. a spontaneous recovery of shape when they are cooled or heated after having been deformed (see refs. 1–4 for a review on the shape-memory effect and the physical properties of the martensitic transformation).

In this work we deal with a certain kind of calorimeter which has been particularly designed to measure the thermal properties of shape-memory

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* Dedicated to Prof. W.W. Wendlandt, on the occasion of his 60th birthday, for his undeterred and continuous dedication to bringing Thermochimica Acta to its present level of scientific interest and large circulation.

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alloys during a martensitic transformation induced by a change in temperature [5–7]. We call this calorimeter a differential-heat-conduction-scanning calorimeter because: (i) it works usually by programming the temperature of the block, (ii) the temperature differences inside the calorimeter are very small and therefore the heat transport is mainly due to conduction, and (iii) the thermobatteries, which actually measure the heat flow between the sample (or the reference sample) and the calorimetric block, are assembled in differential to minimize the influence of external perturbations.

The high sensitivity of the device (400 mV W^{-1} at room temperature) is achieved by the use of semiconductor thermobatteries; this, in turn, limits the range of temperature in which the calorimeter can work (−180, +110 °C). The sensitivity is actually dependent on temperature and this effect has to be taken explicitly into account when measuring a complete martensitic transformation which easily extends to a range of 20 or 30 K [8]. The thermal inertia is minimized because the samples are metallic and have small dimensions (rods of 6 mm diameter and 1 mm thickness, for example) and because the calorimetric block is built of copper. The main time constant, highly dependent on the mass of the sample and the specific design of the calorimeter, has a value of 10 s for the calorimeters being used in Palma with samples of 0.5 g [8,9]. The temperature can be programmed from high rates (18 K min^{-1}) to very low ones (~ 0.3 K min^{-1}); it has been recently estimated that, for CuZnAl, the simultaneous transformation of portions of 4 μg are already detectable on the thermogram when working at minimum scanning rates [8].

The physical features of the martensitic transformation for shape-memory alloys are very sensitive to the mechanical and thermal history of the material. Differential-heat-conduction-scanning calorimetry has already played a role in both a qualitative and quantitative characterization of this influence. Planes et al. [10,11] have studied the influence of the degree of long-range atomic order in the parent phase on the temperatures and enthalpy changes of the transformation. Their results suggest that the equilibrium temperature between the two phases is affected by the degree of order in the parent phase, while the thermal hysteresis and the entropy change of the transformation are not modified. Planes et al. [12] and Picornell et al. [13] have shown that, on repetitive cycling between the parent and the martensite phases, the amount of heat evolved in the transformation tends to reach a stable value and most of the sharp peaks in the thermogram, normally not reproducible from cycle to cycle, smooth down during the first ten cycles. Planes et al. [12] and Rapacioli et al. [14] have studied the correlation between the thermal power released or absorbed by the sample and the ultrasonic waves produced during the transformation. These are simultaneously detected as acoustic emission (AE) by placing a piezoelectric transducer on top of the sample inside the calorimeter. Their results show that, although an almost perfect correlation is often observed: (i) the presence of precipitates of other equilibrium phases in the matrix of the parent phase inhibits the acoustic emission, but does not practically affect the calorimetric signal, and (ii) samples transforming above room temperature which have been thermally treated to stabilize the martensite phase, although they only retransform partially or do not retransform at all to the parent phase, still give a large acoustic emission. Mantel [15] has studied in detail the problem of stabilization of the martensite phase, measuring the dependency of transformation temperatures and heat evolved during the transformation upon the degree of stabilization. Picornell et al. [13] have performed systematic studies of the transformation temperatures and of the energy and entropy changes on different samples of the same alloy having the same nominal composition, and on the same sample repeating the thermal treatment each time, to quantify the reproducibility of the calorimetric results under well-defined conditions for the samples. These calorimetric studies have largely contributed to a better understanding of the physical processes involved in a martensitic transformation.

Nevertheless, from the point of view of calorimetry, several assumptions currently in use should be analyzed in detail, namely (i) the change in the specific heat of the sample during the transformation is always neglected, (ii) the influence of this change on the calorimetric baseline is not considered, (iii) the heat measured during a forward or a reverse martensitic transformation is often identified with the enthalpy change or latent heat of the transformation, and therefore the dissipative irreversible processes taking place during the transformation are ignored, and (iv) the entropy change is calculated from the measured heat by an integration through the thermal path that the transformation actually follows, which is not a reversible one.

In this work we assume that a differential-heat-conduction-scanning calorimeter can be reasonably described by a very simple model with localized constants [16–18], and analyze in this framework the assumptions (i) and (ii) listed above. We also discuss, in aqualitative way, the relative importance of assumptions (iii) and (iv) on the accuracy of the calorimetric results. Finally, we consider three parameters [7] related to the thermal hysteresis, the jerky or discontinuous character and the extension in temperature of the transformation, and speculate on their physical meaning.

CHANGE IN SPECIFIC HEAT DUE TO THE TRANSFORMATION

The calorimetric model [8], represented in Fig. 1, has two elements (1 and 2) with heat capacities C_1 and C_2, representing the sample under test and the reference sample, respectively. They are coupled to the calorimetric block, whose temperature is T_0, by the thermal couplings P_1 and P_2. Thermal power dissipation takes place only in element 1, and the differential detectors measure the difference $(T_1 - T_2)$ between the temperatures of the two elements.

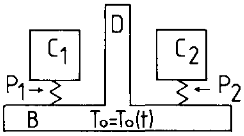

Fig. 1. Model of a differential-heat-conduction-scanning calorimeter. B and D represent the calorimetric block, C_1 and C_2 the heat capacities of the sample under study and of the reference sample, respectively, and P_1 and P_2 the thermal couplings between the samples and the calorimetric block.

The energy balance in every element of the model gives the following equations:

$$W(t) = C_1\frac{\mathrm{d}(T_1 - T_0)}{\mathrm{d}t} + C_1\frac{\mathrm{d}T_0}{\mathrm{d}t} + P_1(T_1 - T_0) \tag{1}$$

$$0 = C_2\frac{\mathrm{d}(T_2 - T_0)}{\mathrm{d}t} + C_2\frac{\mathrm{d}T_0}{\mathrm{d}t} + P_2(T_2 - T_0) \tag{2}$$

If there is perfect identity between both calorimetric elements, $C_1 = C_2 = C$ and $P_1 = P_2 = P$. When performing the calibration of the calorimeter, from an experimental point of view it is not difficult to fulfil this condition. Then, subtracting (2) from (1) we get:

$$W(t) = C\frac{\mathrm{d}(T_1 - T_2)}{\mathrm{d}t} + P(T_1 - T_2) \tag{3}$$

and the sensitivity of the calorimeter is obtained from the relation between the constant output signal obtained for a constant dissipation and the corresponding value of the thermal power:

$$S = \frac{1}{P} \tag{4}$$

As mentioned in the introduction, the sensitivity of the actual calorimeter is highly dependent on the temperature of the calorimetric block. The influence of temperature is due to a double effect [8]: (1) the thermal coupling P is dependent on temperature; (2) the magnitude of the Seebeck effect developed in the thermobatteries is also dependent on temperature. This second effect does not appear in our formulation because we are just considering that the output of the model is the temperature difference $(T_1 - T_2)$, not the electric signal developed in the thermobatteries as a consequence of this difference. We do so because the formulation is easier and is sufficient for future analyses.

Determination of the difference in specific heat between the two phases

In an actual calorimetric run of a martensitic transformation, the variable x will give, at every temperature, the relative fraction of parent phase already transformed into martensite. Therefore, before the forward transformation starts on cooling we have $x = 0$, while at the end of the forward transformation $x = 1$. Considering that the specific heat of the martensite is different from the specific heat of the parent phase, the heat capacity of element 1, representing the transforming sample, will change during the transformation:

$$C_1 = C_1(x) \tag{5}$$

Then, we define $\Delta C(x)$:

$$C_1(x) = C_2 - \Delta C(x) \tag{6}$$

Additionally, we restrict ourselves to a linear program of the block's temperature:

$$T_0(t) = T_{0i} + \dot{T}_0 t \tag{7}$$

and consider two different situations.

(i) The forward transformation has not yet started, and consequently x = *0 and* W = *0, i.e. there is no thermal dissipation*

Then, assuming a linear dependency of T_1 and T_2 on t, solution of eqns. (1) and (2) gives:

$$T_1 = T_{0i} - \frac{C_1(0)}{P_1}\dot{T}_0 + \dot{T}_0 t \tag{8}$$

$$T_2 = T_{0i} - \frac{C_2}{P_2}\dot{T}_0 + \dot{T}_0 t \tag{9}$$

Assuming the thermal couplings to be identical, $P_1 = P_2 = P$, the temperature difference detected by the thermobatteries will be:

$$(T_1 - T_2) = \frac{\Delta C(0)}{P}\dot{T}_0 \tag{10}$$

which is a constant value. This constant temperature difference, arising from the different heat capacities of elements 1 and 2, can be described, conversely, as an extra-dissipation in a perfectly differential model. The extra-dissipation will be

$$W^*(x = 0) = \frac{(T_1 - T_2)}{S} = \Delta C(0)\dot{T}_0 \tag{11}$$

This is in agreement with the result obtained by subtracting eqn. (2) from eqn. (1), considering that $\mathrm{d}T_1/\mathrm{d}t = \mathrm{d}T_0/\mathrm{d}t = \dot{T}_0$ as deduced from eqn. (8), and $C_2 = C$:

$$\Delta C(0)\dot{T}_0 = C\frac{\mathrm{d}(T_1 - T_2)}{\mathrm{d}t} + P(T_1 - T_2) \tag{12}$$

(ii) The forward transformation has already finished and consequently x = *1 and* W = *0, i.e. there is no thermal dissipation*

Following the same procedure, the temperature difference detected by the thermobatteries is given by:

$$(T_1 - T_2) = \frac{\Delta C(1)}{P} \dot{T}_0 \tag{13}$$

and can be regarded again as an extra-dissipation in a perfectly differential model:

$$W^*(x=1) = \Delta C(1) \dot{T}_0 \tag{14}$$

Equations (11) and (14) show that the difference in specific heat between the parent and the martensite phases can be obtained, in every calorimetric run, from the experimental thermogram corrected for sensitivity, as schematically shown in Fig. 2. The difference

$$W^*(x=1) - W^*(x=0) = [\Delta C(1) - \Delta C(0)] \dot{T}_0 \tag{15}$$

between the power dissipated before and after the forward transformation is dependent on the difference in specific heat between the two phases and on the rate of temperature change. The higher the rate of temperature change, the more accurate the difference in heat capacities determined. However, high scanning rates will at the same time enhance any disymmetry in the calorimeter and therefore distort the flatness of the baseline [8]. An approximate value for the specific heat of the parent phase is $C_p^{\mathrm{A}} = 0.420$ J g^{-1} K^{-1} [19]. To our knowledge, there are no measured values for the specific heat of the martensite, but it is always assumed to be very similar to the specific heat of the parent phase. Assuming a 5% difference between them, and a sample of mass 0.310 g, runs at $\dot{T}_0 = 0.3$ K min^{-1} will produce

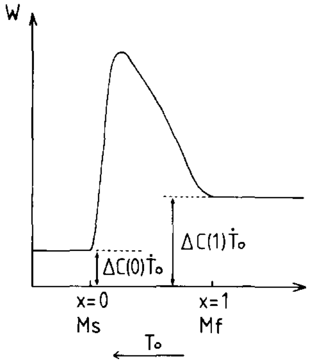

Fig. 2. Schematic plot of the thermogram corresponding to a forward transformation after correction of the calorimetric sensitivity. The difference between the values of the baseline before and after the transformation is proportional to the difference in specific heat between the parent phase and the martensite, the rate of cooling $\dot{T}_0$ being the proportionality factor.

differences in the corrected thermogram of the order of 0.032 mW, which can already be detected by the calorimeter as it has a power resolution around room temperature of 0.0025 mW.

Correction of the baseline

During a thermally induced martensitic transformation the fraction x of parent phase transformed into martensite continuously increases. Correspondingly, the sample is at any moment formed by the addition of a fraction $(1-x)$ of the parent phase and a fraction x of martensite, and therefore its specific heat will be given by:

$$C_p = C_p^{\mathrm{A}}(1-x) + C_p^{\mathrm{M}}x \tag{16}$$

where C_p^{A} and C_p^{M} denote the specific heats of the parent phase (called austenite) and of the martensite, respectively. The change in specific heat of the sample will then produce an evolution in the extra-dissipation, W^*, from the value given by eqn. (11) to that given by eqn. (14):

$$W^*(x) = [\Delta C(0)(1-x) + \Delta C(1)x]\dot{T}_0 \tag{17}$$

This extra-dissipation represents the baseline to be corrected for a proper integration of the thermogram. To monitor the evolution of the baseline with the temperature of the calorimetric block, we need a relationship between this temperature and the transformed fraction x. This is a very difficult question, as it involves, in fact, the whole problem of growth of the martensite in the parent phase. Nevertheless, such a relationship can be easily derived using two reasonable assumptions [20]:

(i) The entropy change is proportional to the transformed fraction, as both come from the same structural change:

$$\frac{\partial \Delta S}{\partial x} \equiv A = \text{constant} \tag{18}$$

(ii) The enthalpy change is proportional to the absolute temperature, i.e. the difference in specific heats between the two phases does not change with temperature:

$$\frac{\partial \Delta H}{\partial T_0} \equiv B = \text{constant} \tag{19}$$

Then, using that

$$\mathrm{d}\Delta S = \frac{1}{T_0}\mathrm{d}\Delta H \tag{20}$$

we have

$$\frac{\partial \Delta S}{\partial x} = \frac{1}{T_0}\frac{\partial \Delta H}{\partial x} = A \tag{21}$$

$$\frac{\partial \Delta H}{\partial T_0} = \frac{\partial \Delta H}{\partial x}\frac{\partial x}{\partial T_0} = B \tag{22}$$

to get

$$\frac{1}{T_0}\frac{\partial T_0}{\partial x} = \frac{A}{B} \tag{23}$$

Integrating between $x = 0$ ($T_0 = M_s$) and $x = 1$ ($T_0 = M_f$) we obtain finally,

$$x = \frac{\ln(T_0/M_s)}{\ln(M_f/M_s)} \tag{24}$$

where M_s and M_f are the temperatures at which the forward transformation starts and finishes, respectively.

Combining eqns. (17) and (24) we have:

$$W^*(T_0) = \left[\Delta C(0)\left(1 - \frac{\ln(T_0/M_s)}{\ln(M_f/M_s)}\right) + \Delta C(1)\frac{\ln(T_0/M_s)}{\ln(M_f/M_s)}\right]\dot{T}_0 \tag{25}$$

A baseline correction based on a straight line joining the values of the thermal power at M_s and M_f would read:

$$W^L(T_0) = \left[\Delta C(0)\left(1 - \frac{T_0 - M_s}{M_f - M_s}\right) + \Delta C(1)\frac{T_0 - M_s}{M_f - M_s}\right]\dot{T}_0 \tag{26}$$

Taking the difference between the two baselines and integrating for the temperature T_0 between M_s and M_f we get:

$$\begin{aligned}
&\int_{M_f}^{M_s}[W^*(T_0) - W^L(T_0)]\,\mathrm{d}T_0 \\
&\quad = \Delta C(0)\left[\frac{M_f - M_s}{\ln(M_f/M_s)} - M_s\right] - \Delta C(1)\left[\frac{M_f - M_s}{\ln(M_f/M_s)} - M_f\right] \\
&\qquad - \tfrac{1}{2}[\Delta C(0) + \Delta C(1)](M_f - M_s)
\end{aligned} \tag{27}$$

which represents the difference in energy below the corrected thermogram resulting from the use of one or other baseline. It is worth noting from eqn. (27) that the difference in energy is independent of the cooling rate at which the run is carried out. Figure 3 is a plot of this difference, using the values of M_s and M_f obtained in an actual run of a $\beta \to \gamma'$ transformation, and the same values of the specific heat and mass of the sample as for eqn. (15) above. The resulting energy difference is 0.0025 J, around 0.15% of the total energy measured in the transformation, and therefore it is negligible in practise. Nevertheless it could become relevant if the difference in specific heat between the austenite and the martensite was much larger than the 5% assumed.

In the preceding analysis we have considered only the forward transformation, i.e. the transformation induced on cooling that brings the parent phase or austenite into the martensite phase. It is not difficult to see, however, that the same features would also appear during a reverse transfor-

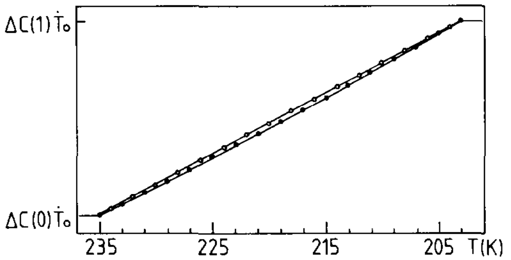

Fig. 3. Comparison between (●) the baseline resulting from the consideration of the change in specific heat of the sample during the transformation and (○) a baseline based on a straight-line interpolation between the beginning and the end of the transformation. The numerical values used in the comparison correspond to an actual $\beta \rightarrow \gamma'$ transformation of a Cu:8.50 Zn:11.30 Al (wt%) alloy performed at a cooling rate $dT_0/dt = -0.31$ K min^{-1}. The specific heat used for the austenite is $C_p^A = 0.420$ J g^{-1} K^{-1} and for the martensite is $C_p^M = 0.441$ J g^{-1} K^{-1}, resulting in a 5% difference. The mass of the sample is $m = 0.310$ g and the transformation temperatures are $M_s = 235$ K and $M_f = 203$ K. The energy enclosed between the two baselines amounts to 0.0025 J, which represents 0.15% of the total energy measured in this transformation.

mation, induced by heating, from the martensite to the austenite, and that the corresponding analysis would follow exactly the same lines as the forward transformation.

RELEVANT PARAMETERS TO BE OBTAINED FROM A CALORIMETRIC RUN

In this section we review the relevant parameters to be obtained, either directly or after certain calculations, from a calorimetric run. We also speculate on their physical significance and in several cases give the procedure to calculate them.

Transformation temperatures

M_s and M_f refer to the temperatures at which the forward transformation (P → M, induced on cooling) starts and finishes, respectively, while A_s and A_f denote the temperatures at which the reverse transformation (M → P, induced on heating) starts and finishes, respectively.

On cooling (heating), the first calorimetric point to become separated from the noise in the baseline determines M_s (A_s), while the last one determines M_f (A_f).

For very low temperature scanning rates, or for highly discontinuous transformations (i.e. transformations with long intervals of no thermal dissipation), these first and last points departing from the baseline can be difficult to determine, and some authors [9] have suggested the use of the quantities M_s^*, M_f^*, A_s^* and A_f^*, defined as the temperatures at 10 and 90% of the total energy dissipation for the forward and reverse transformations, respectively.

Thermal energy of the transformation

The martensite phase nucleates and grows inside the parent phase. Since the shape of the basic unit cell changes, during a martensitic transformation martensite plates with a different shape than the original parent phase are accommodated by strains set up both in the original matrix and in the new phase. During the transformation the strain energy dominates the kinetics and morphology [21,22]. In a completely thermoelastic transformation the strain energy is elastically stored in the material during the forward transformation and elastically recovered in the reverse transformation.

Dissipative energies also appear in the course of a martensitic transformation, mainly due to the frictional resistance at the interfaces between parent and martensite and between martensite with different orientations, and in the grain boundaries of a polycrystalline parent phase.

Finally, since the transformation is first order, there is a latent heat of transformation associated with the structural change, which is probably different for the forward and reverse transformations as they proceed at different temperatures.

The thermal energy measured in a calorimetric run is given by:

$$Q_{\mathrm{M}} = \int_{M_s}^{M_f} [W(T_0) - W^*(T_0)]\, \mathrm{d}t \tag{28}$$

for the forward transformation, and by:

$$Q_{\mathrm{A}} = \int_{A_s}^{A_f} [W(T_0) - W^*(T_0)]\, \mathrm{d}t \tag{29}$$

for the reverse one. It will be the sum of three contributions: the latent heat of transformation, which is exothermal in the forward transformation and endothermal in the reverse one; the strain energy, which is elastically stored during the forward transformation and reversibly recovered during the reverse one; and the frictional energy which, as any dissipative energy, will oppose both the forward and reverse transformations.

The energy E lost in a complete cycle, including a forward and a reverse transformation, can be calculated (neglecting the change in specific heat between the two phases) as $E = -Q_{\mathrm{M}} + Q_{\mathrm{A}}$, corresponding to the area enclosed by the curves:

$$\int_{M_s}^{T} \mathrm{d}Q_{\mathrm{M}}/T \text{ and } \int_{A_s}^{A_f} \mathrm{d}Q_{\mathrm{A}}/T - \int_{A_s}^{T} \mathrm{d}Q_{\mathrm{A}}/T \text{ vs. temperature}$$

where $\mathrm{d}Q_{\mathrm{M}}$ and $\mathrm{d}Q_{\mathrm{A}}$ represent the absolute value of the heat measured at temperature T during the forward and reverse transformations, respectively. The corresponding expression reads:

$$E = \int_{A_s}^{A_f} \mathrm{d}T \left[\int_{A_s}^{A_f} \mathrm{d}Q_A/T - \int_{A_s}^{T} \mathrm{d}Q_A/T \right] + (A_s - M_f) \int_{A_s}^{A_f} \mathrm{d}Q_A/T$$
$$+ \int_{M_s}^{M_f} \mathrm{d}T \left[\int_{M_s}^{T} \mathrm{d}Q_M/T \right] \tag{30}$$

where

$$-Q_M = -\Delta H_M + E/2 \tag{31}$$

and ΔH_M stands for the reversible contributions to the heat measured, namely the elastic energy and the latent heat of transformation.

First estimations of the dissipative energy in a CuZnAl polycrystalline material, based in eqn. (30), give a value around 6% of the total heat. In eqn. (31) we assume that the same amount of frictional energy is present in the forward and reverse transformations and, therefore, its contribution can be separated from the heat measured by calorimetry. To our knowledge, however, there is no way to separate the elastic contribution and the latent heat of transformation.

Entropy change of the transformation

The entropy change is usually calculated from the calorimetric output through the following expressions:

$$\Delta S_M = \int_{M_s}^{M_f} [W(T_0) - W^*(T_0)] \frac{1}{T_0} \mathrm{d}t \tag{32}$$

for the forward transformation, and:

$$\Delta S_A = \int_{A_s}^{A_f} [W(T_0) - W^*(T_0)] \frac{1}{T_0} \mathrm{d}t \tag{33}$$

for the reverse one. The integrals are calculated following the actual thermal path of the transformation, i.e. associating to each temperature T_0 a thermal dissipation $[W(T_0) - W^*(T_0)]$.

For eqns. (32) and (33) to be correct from a thermodynamic point of view, two conditions should be fulfilled: (1) the thermal dissipation measured by the calorimeter should correspond to a reversible process; (2) the thermodynamic path followed in the integration should be a reversible one. The first condition does not hold due to the dissipative energies involved in the transformation, as discussed above. The second one corresponds to the assumption that, if no dissipative energies were released, the transformation would follow exactly the same path on going from the same initial (represented by M_s or A_s) to the same final (represented by M_f or A_f) thermodynamic state. Considering that the dissipative energies are small compared

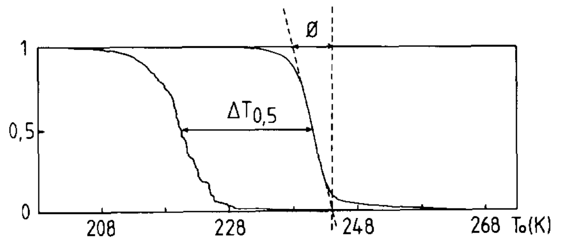

Fig. 4. The accumulated heat released and absorbed during the forward and reverse $\beta \rightleftharpoons \gamma'$ transformations, respectively, of a Cu: 8.50 Zn: 11.30 Al (wt%) alloy, is plotted (in units normalized to unity) versus the absolute temperature T_0 of the sample (in K). The figure shows the geometrical interpretation of the parameters $\Delta T_{0.5}$ and ϕ.

with the total heat measured in the transformation, eqns. (32) and (33) have to be considered as the only possible appoximations to be used for estimating the entropy changes. It should be remembered, however, that these entropy changes will carry not only the contribution of the structural change during the transformation, but also the contribution of the elastic strain and dissipative energies.

Thermal hysteresis

The hysteresis in temperature between the forward and reverse transformations is characterized by a parameter (see Fig. 4):

$$\Delta T_{0.5} = T_{0.5}(M \rightarrow P) - T_{0.5}(P \rightarrow M) \tag{34}$$

where $T_{0.5}$ represents the temperatures at which half of the total energy of the transformation has already been measured. Similar information could be obtained from $(A_f - M_s)$ or $(A_s - M_f)$, and in many cases these quantities will coincide with $\Delta T_{0.5}$.

The thermal hysteresis is originated by the presence of dissipative effects in the transformation, mainly associated with interfacial resistive energies [23]. Under certain assumptions the energy dissipated in a complete cycle, as given by eqn. (30), is directly proportional to the thermal hysteresis $\Delta T_{0.5}$ [20].

Extension of temperature

It has already been mentioned that a thermoelastic martensitic transformation often presents a large extension of temperature, e.g. 20 or 30 K. To characterize this extension, a parameter ϕ is defined as:

$$\phi = \left(\frac{\mathrm{d}T_0}{\mathrm{d}q} \right)_{q=0.5} \tag{35}$$

where q represents the fraction of the heat measured at a certain moment, relative to the total heat of the transformation. ϕ will be measured in units of temperature, and Fig. 4 gives a geometrical interpretation for it. From the figure it is clear that this parameter does not coincide with quantities like $(M_s - M_f)$ or $(A_f - A_s)$; while these quantities are greatly affected by the earlier and later stages of the transformation, ϕ gives the extension of temperature of the bulk of the transformation.

The temperature extension of a thermoelastic martensitic transformation is a consequence of the strain energy set up in the matrix due to the shape change accompanying the transformation. A single-crystal, single-interface transformation, for which no strains need to be accommodated, proceeds isothermally [23] and has $\phi = 0$, although it presents a thermal hysteresis due to the frictional force at the interface.

Discontinuity of the thermal dissipation

Due to the high sensitivity of a differential-heat-conduction-scanning calorimeter the thermogram of a martensitic transformation reveals fine details and a substructure that cannot be observed using standard DSC or DTA equipment. It is interesting to quantify this information by means of a parameter χ which gives a measure of the discontinuity of the thermal dissipation:

$$\chi = 1 - \frac{Q_b}{Q} \tag{36}$$

where Q_b is the energy given by the area delimited by the smooth background of the thermal peaks in the calorimetric curve, and Q is the total energy. The parameter $\chi \to 0$ for a very smooth thermogram in which no peaks can be distinguished from the continuous background, while $\chi \to 1$ if the thermal dissipation is highly discontinuous and a smooth background cannot be defined. Figure 5 shows an example in which the continuous background is drawn below the thermal peaks and the corresponding value of χ is calculated.

The physical origin of the discontinuous character of the thermal emission is not yet clear. Recently [24] it has been related to the sudden growth or shrinkage of the martensite plates at the moment that enough driving force has been created to overcome the energy barriers opposing the continuous growth or shrinkage of the plates. In this sense the parameter χ would be statistically related to the origin of these barriers, namely point defects and dislocations in the parent phase, grain boundaries and interfaces. χ, for instance, decreases practically to zero when a sample is thermally cycled for more than ten cycles [7].

χ is strongly dependent on the performance of the calorimeter (mainly its thermal inertia and its thermal signal resolution), the dimensions of the sample, the cooling or heating rate of the measurement and the calculation

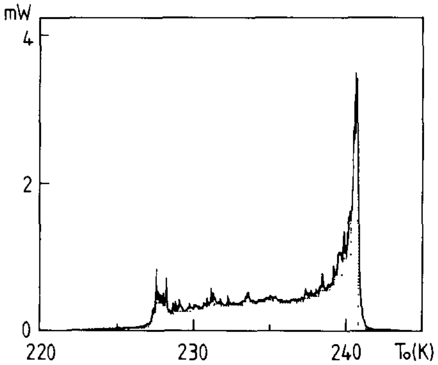

Fig. 5. Thermogram (corrected for calorimetric sensitivity) corresponding to a reverse $\beta' \to \beta$ transformation of a Cu:18.18 Zn:7.41 Al (wt%) alloy. The discontinuous line defines the smooth background of the thermal peaks. In this case $\chi = 0.20$.

procedure used to define the background of the thermal peaks. For this reason χ is only meaningful when comparing different runs of similar samples performed in the same calorimeter at the same scanning rates.

Difference in specific heats

The difference in specific heat between the austenite and the martensite can also be determined in the calorimetric run, as detailed in the preceding section. At the present moment there are no experimental values for this difference, and only few measurements of the specific heat of the parent phase [19].

Nevertheless, apart from their intrinsic interest, the difference in specific heat is important for a proper correction of the baseline and to determine, with other calorimetric data, the dissipative energy in the transformation, as discussed in the preceding sections.

CONCLUSIONS

A complete run of a thermally induced thermoelastic martensitic transformation in a differential-heat-conduction-scanning calorimeter gives the following:

(i) The difference in specific heat between the austenite and the martensite. This difference is obtained from the difference in the constant thermal power (baseline) before and after the transformation. The effect is proportional to the cooling or heating rate. The difference in specific heat has to be taken into account to perform a proper baseline correction, although the correction in energies achieved, independent of the thermal rate, is practically negligible compared to straight-line interpolation (0.15%) for small differences in specific heat (5%).

(ii) The transformation temperatures M_s, M_f, A_s and A_f.

(iii) The total heat released or absorbed during the transformation. Three different kinds of energies contribute to the total heat: the reversible latent heat of the transformation, the reversible elastic energy stored in the matrix and the irreversible dissipative energies mainly due to frictional processes. The latter, however, can be determined independently using the calorimetric data.

(iv) An estimate of the entropy change of the transformation, from the three contributions mentioned before.

(v) The thermal hysteresis between the forward and reverse transformations; an expression of the relative importance of the dissipative contributions in the total energy of the transformation.

(vi) The extension in temperature of the transformation; an expression of the elastic contributions to the total energy of the transformation.

(vii) The discontinuity of the thermal dissipation; probably related to the obstacles and barriers encountered during the growth or shrinkage of the martensite.

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