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Study of the hysteresis cycle in Cu–Zn–Al shape-memory alloys by high resolution thermal analysis

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Abstract

A high resolution thermal analysis is used to study the martensitic transformation in Cu–Zn–Al shape memory alloys. The characteristics of the single-interface single-variant transformation induced either by temperature or by stress are analyzed and calorimetric measurements on this type of transformation are reported. Thermoelasticity, stabilization of martensite and recovery of the β phase, pinning points and coalescence of plates of the same variant appear as phenomena which prevent the reproducibility of the transformation path. The evolution of the spontaneous global transformation with cycling is measured calorimetrically and the effect of ageing at 373 K is estimated.

INTRODUCTION

Before shape memory alloys can be reliably used for technological applications, an accurate description of the response of the sample to external fields (temperature and stress) is required. Consequently, it is desirable to obtain the hysteresis cycle of the various alloys, their dependence on temperature and external stresses, and their reproducibility after repeated cycling.

Conduction calorimetry is an important tool in the analysis of hysteresis cycles in shape memory alloys because it yields accurate dynamical information on the transformation. In fact, the measured thermal output thermogram gives direct information on the transient state of the alloy. This is useful, of course, in determining any peculiar behavior of the alloy after repeated cycling or as a function of the state of external stress. The thermogram, however, also includes changes due to changes in the heat capacity of the sample, in the sensitivity of the detectors with temperature,

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in thermal couplings between the sample and the detectors, etc. These effects place some limitations on the accuracy of the measured energies.

Systematic studies require some kind of automatic procedure to allow thorough studies of the behavior of the alloy as a function of the number of cycles, of the thermal treatment prior to the cycling, etc. The transformation properties are very sensitive to the previous history of the sample and time is a very important parameter. Thus, the number of relevant variables that must be systematically analyzed is, of necessity, quite large. In addition, fluctuations in behavior can also be observed owing to a large number of variables not directly accessible to experiment. Hence, reliable measurements require averages over measurements performed in identical conditions (as far as the parameters can be controlled).

Our study has mainly concentrated on the reproducibility and evolution of the transformation. On the one hand, single-interface single-variant hysteresis cycles are studied by following the interface position as a function of the temperature. This provides information about the problems involved when one looks for a reproducible behavior. Moreover, calorimetric measurements of this type of transformation are also reported. On the other hand, the evolution of the transformation, which has already been observed in the single interface transformation, is parametrized in a global spontaneous transformation and the effect of the ageing at 373 K is studied.

EXPERIMENTAL APPARATUS

A high resolution thermal analysis apparatus has been used, the characteristics of which have been described in detail elsewhere [1,2]. Two devices were built according to the specific needs of the measurements to be performed (acoustic emission [3], thermomicroscopy and resistance measurements [2]). One device is specially suitable for studying single-interface single-variant transformations (in this type of transformation there is a unique plate of martensite crossing throughout the sample [4]). This system works near room temperature and usually cycling up to 5 K is used in these studies. The transformation can be followed by optical microscopy.

A second device (see ref. 1) was designed to work as a differential scanning calorimeter, programmed for temperature over a temperature range of up to 50 K. By using a thermostatic bath the working domain can be set between 225 and 350 K. This system is suitable for studying the heat released during the spontaneous transformations induced by temperature changes.

In both devices, the programmed temperature $T(t)$ of the working space is controlled by a personal computer. The computer controls a thermobattery that uses the Peltier effect to transfer heat to the sample through a block of copper. Its temperature is measured using a platinum resistance

(Pt-100) thermometer and a feedback loop corrects the applied intensity so the actual temperature should be equal to the programmed one. The resolution is ±0.003 K (±0.001 Ω); the stability of the temperature is ±0.003 K and, when a periodic temperature program is used, the reproducibility is better than 0.01 K.

The calorimetric signal is provided by two semiconductor thermobatteries mounted in opposition. The sensitivity is about 350 mV W^{-1} at room temperature. The fluctuations of the intensity required to maintain the desired temperature $T(t)$ enhance the noise level. Nevertheless, this noise can be subtracted and the resolution of ±1 μV is equivalent to a power of ±3 μW delivered at room temperature.

The samples used are single crystals with $e/a = 1.48$ and compositions: (A) Cu–14.6% Zn–16.7% Al; (B) Cu–15.1% Zn–16.9% Al; (C) Cu–17.9% Zn–7.6% Al; (D) Cu–16.1% Zn–7.5% Al; (E) Cu–16.7% Zn–7.3% Al. Preparation of the samples has already been described elsewhere. For sample A and B see, for example ref. 4. Sample D was educated with stabilized martensite. The education process can be found described in ref. 5.

To study the single-interface single-variant transformation, a planar specimen with a necked shape was used. After the thermal treatment and after polishing the surface, a single plate of martensite was forced to appear by combining temperature and stress. Once the plate had been obtained it was left at constant temperature and stress until it stabilized and the load could be removed. Thereafter, on cooling, the martensite grew by the movement of the interfaces limiting the plate.

Usually, the sample was stressed by means of a weight. This provided a suitable constant load. However, a spring was used ($k = 0.99$ N cm^{-1}) when continuous variation of the stress was required. This happened in a preliminary study of the stress–strain–temperature surface in the single-interface transformation.

EXPERIMENTAL RESULTS

Stability of cycling

We have studied simple transformations in which a unique plate of martensite, separated from the β phase by two parallel single interfaces, is present in the sample. It has been found that even in this case a continuous cooling of the sample is needed to force the growth of the martensite [4]. This has been called intrinsic thermoelasticity and is measured as $\mu_{th} = -\mathrm{d}T_g(x)/\mathrm{d}x$, where x is the position of the interface measured in length units on the surface of the sample and in the direction of its movement, and $T_g(x)$ is the temperature at which that position is reached. Intrinsic

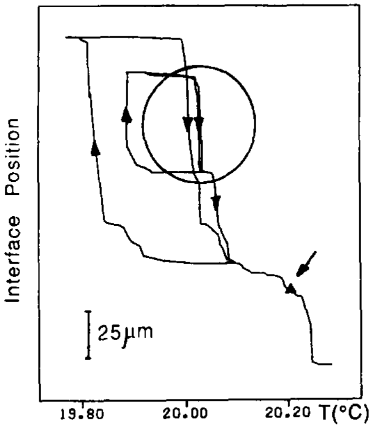

Fig. 1. Single-interface partial cycling. Partial subcycles can appear out of a larger partial cycle by the time-recovery of β-phase and stabilization of martensite (encircled zone). The arrow indicates the m → β transformation for a partially stabilized zone.

thermoelasticity is due to the interaction of martensite with dislocations and therefore depends on the thermal treatment to which the sample has been subjected. The temperature $T_g(x)$ also depends on that treatment and on the elapsed time since it was applied. Moreover, $T_g(x)$ depends on the type of previous cycling that the sample has undergone: the recuperation of the β-phase and the stabilization of the martensite takes place and modifies $T_g(x)$ according to the time that the material between x and $x + \mathrm{d}x$ has been in the β and m states [6]. As a consequence, and given a particular thermal history, an arbitrarily complex hysteresis cycle can be observed (see the encircled zone in Fig. 1). This shows one of the problems involved when partial cycles are dealt with.

Pinning points have a notorious effect on the cycling. When we deal with partial loops and subloops, a pinning point can change the path $x(T)$ of the interface. If, on cooling, the interface overcomes a pinning point, then on heating, the interface stays immobile and the retransformation does not take place until a higher temperature is reached. Then the interface goes back quickly. In the same way, if two single-interface plates of the same variant coexist in a sample, it has been observed that when the nearest interfaces join each other the hysteresis width increases: an overheating is needed in order to separate the interfaces. In all the observed cases, the interfaces split up at the same places as where they joined. In some experiments it happens that the undercooling is such that a self-accommodating plate nucleates and grows so that it touches the single-interface. Again, an overheating is needed so that the interface can come away from the self-accommodating plate and move backwards. This overheating is of the same order of magnitude as before (≈ 0.5 K).

Single-interface single-variant calorimetric measurements

Two kinds of calorimetric measurements were performed in a single-interface single-variant transformation, depending on whether it was induced by temperature or by stress. The progress of the transformation was followed simultaneously by optical microscopy. The thermal treatment applied to the samples was 15 min at 1153 K followed by air quenching (TT1).

Temperature-induced transformation

A single interface was forced to move by varying the temperature of the sample. This evolution of the temperature produced a variation in the base line of the calorimeter which had to be removed before the energy delivered could be calculated. This was done by reproducing the programming just above the A_s temperature, outside the transformation domain, and subtracting this signal from the thermogram, taking into account the temperature-dependence of the sensitivity [8].

For sample A, the amplitude of the temperature programming was about 0.4 K (placed near 293 K). Four cycles were measured and the energies under the calorimetric peaks had mean values: $Q^{\beta\rightarrow m} = -16$ mJ and $Q^{m\rightarrow\beta} = 19$ mJ (for a discussion on the possible metastability effects see ref. 7). It should be noted that we were unable to determine the result in energy per gram because it was very difficult to obtain an accurate measurement of the amount of transformed material. Only as an estimation can we calculate the mass transformed from the approximate volume in martensite. We obtained 7 J g^{-1} ($\rho = \rho_{Cu} = 8.9$ g cm^{-3}).

The results for sample B are shown in Fig. 2. The temperature for these measurements lies near 300 K and a maximum amplitude of 1.4 K was used

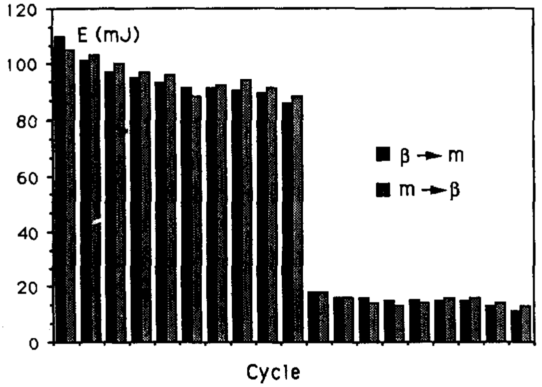

Fig. 2. Energies measured in several forward and reverse temperature-induced single-interface single-variant transformations.

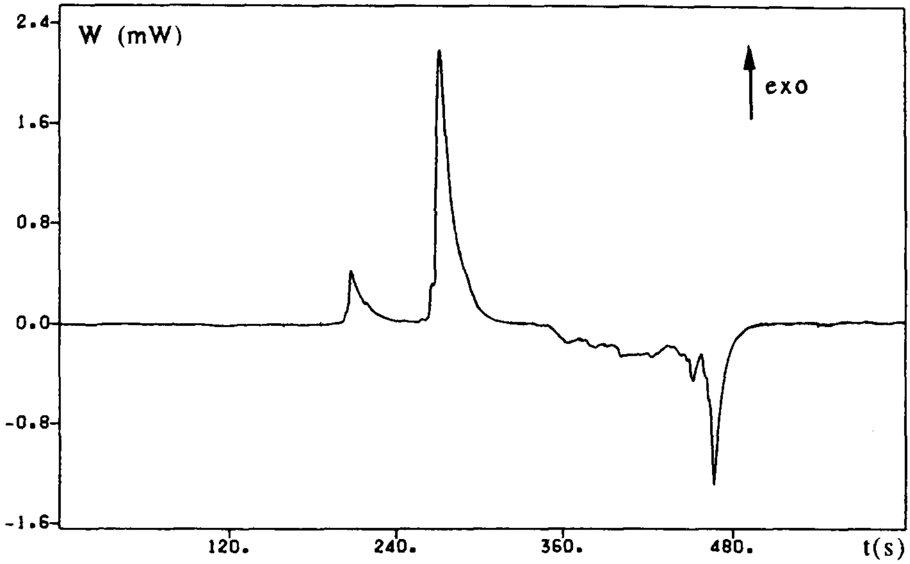

Fig. 3. Thermogram for a single-interface single-variant transformation induced by temperature after the base line has been subtracted. This corresponds to the second cycle in Fig. 2.

in the cycling. The thermogram after the drift of the base line has been removed is shown in Fig. 3. The error on these measurements is determined by the subtraction of the base line. From the difference between several experimental base lines, an error bar of about 4 mJ is expected. Preliminary analysis of the calorimetric results and the base line effects are available from ref. 7.

Stress-induced transformation

The transformation can be induced either by temperature or by tension. In this latter case, the problem of the evolution of the base line is not present. The heat exchanged at constant temperature (≈ 295 K) during the forward and reverse transformations by stressing sample A was measured and the results obtained are shown in Table 1. The stress was increased while the position of the interface was followed by optical microscopy. When the interface reached a given point in the sample the stress was kept constant for ≈ 100 s (the calorimetric response had a time constant of about 10 s) and then reduced again until the interface came back to its initial position next to the stabilized region. In Fig. 4 the calorimetric signal for two complete transformation–retransformation cycles is shown. Our results are consistent with direct measurements of friction work (see next paragraph) [8,9].

Intrinsic thermoelasticity $d\sigma(x)/dx$ and interface friction

There is a need for an undercooling (overheating) in order to maintain the growth (shrinkage) of the martensite in a single-interface single-variant

TABLE 1

Energy evolved during single-interface single-variant transformations induced by tension

$Q^{\beta\to m}$	$Q^{m\to\beta}$	Δx [a] (μm)	$Q^{\beta\to m}$ (mJ μm^{-1})
−3.72	3.72	80	0.0464
−3.56	3.59	77	0.0461
−3.79	3.76	80	0.0472
−7.91	7.90	166	0.0475
−8.14	8.11	169	0.0475
−8.03	7.93	166	0.0477
−8.16	7.93	163	0.0499
−11.13	11.20	234	0.0475
−18.69	18.60	394	0.0471

[a] Δx is the interface displacement which is approximately proportional to the amount of transformed material (sample section ≈ 0.5 mm^2).

transformation. A similar effect appears when the transformation is induced by stressing the sample, and it will be necessary to increase or decrease the force applied in order to continue the forward or reverse transformations. Despite the poor resolution of the system used (arising from difficulties in measuring the elongation of the spring used to stress the sample) it is clear that there is an intrinsic thermoelasticity $d\sigma(x)/dx$, as there was for the temperature. Here σ is the shear stress resolved on the habit plane. The thermoelasticity in stress has been evaluated as 0.005 MPa μm^{-1}.

From these measurements we estimated a preliminary value of the frictional force which resists the interface motion. The width of the hysteresis cycle $x(F)$ is about 2 N. When the hysteresis cycle $x(T)$ is

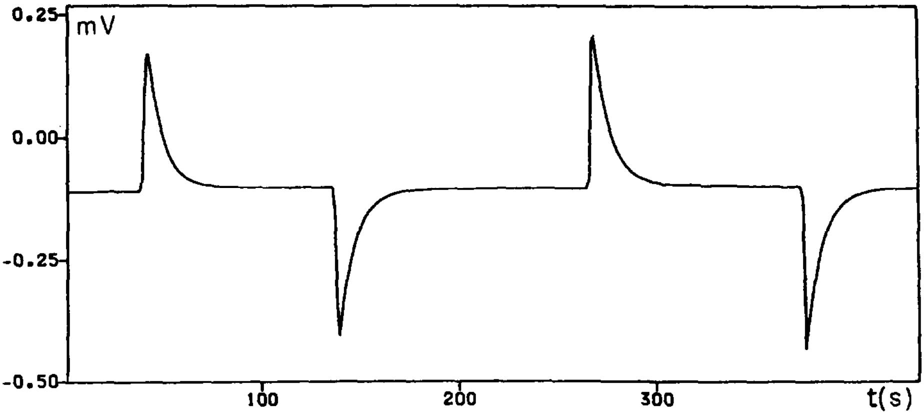

Fig. 4. Thermogram obtained for two consecutives cycles of stress-induced transformation (data shown as acquired).

considered, it is seen that the stressing device itself contributes to the measured width. If the same plate is cycled without applied stress the hysteresis width diminishes tenfold. This was also assumed to be true for the cycle $x(F)$. So, the frictional force is assumed to be 0.1 N. The error bar on this number could be very high, but we are only trying to obtain an initial value for it. The cross section of the interface was measured as approximately 0.55 mm^2 and, for this area the energy expenditure due to the friction is 0.01 mJ when the distance covered is 100 μm. It is worth comparing this energy with the heat evolved during the transformation of the same amount of material ($\approx$ 5 mJ).

The force needed to bring the interface to some fixed points was measured at three different temperatures. In this way we obtained a Clausius–Clapeyron-like equation with $\mathrm{d}\sigma/\mathrm{d}T = 2$ MPa K^{-1}.

Global transformation

In previous work, the evolution of the state of the material has been observed by following the characteristics of the hysteresis cycle of a single-interface transformation [6]. This evolution can also be observed in the global transformation. Taking advantage of the possibilities of the programmable calorimeter, a large number of thermal cycles have been performed and from the thermograms acquired, that evolution was parameterized. Furthermore, the reduction of that evolution by ageing at 373 K was investigated.

Entropy production

The number of heat peaks in the calorimetric signal obtained depends on the cooling rate. At sufficiently low cooling rates, the thermogram can be split up into a continuous or thermoelastic background, plus discontinuous or "burst" events. The background itself can also be divided into actual thermoelastic growth and small "burst" events. If the cooling rate is kept constant, an evolution in the characteristics of the thermogram is observed. The thermogram usually spreads over a large range of temperatures and the discontinuous part of the transformation diminishes with cycling.

Every peak is related to the transformation of a given amount of material. On transforming, this material undergoes an overheating and then heat flows outwards until its temperature equals that of its surroundings, i.e. the rest of the sample and the calorimeter. In this process, the irreversible heat flow from the transformed plate to the surroundings means an entropy production. If it is thought that martensite transforms to produce a hot martensite plate which afterwards cools down, the entropy production related to this latter process will be

$$\Delta S_{\mathrm{u}} = mc\left(\frac{\Delta T}{T} + \ln\left(\frac{T}{T+\Delta T}\right)\right)$$

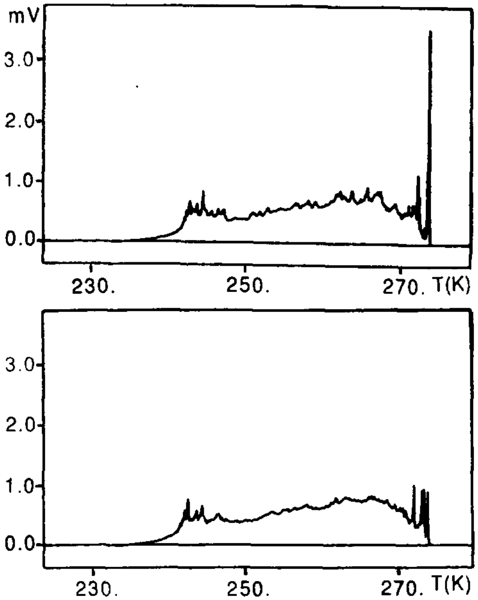

Fig. 5. Fifth and tenth cycles of a continuous cycling for a sample with spontaneous transformation induced by temperature.

This can be used to parametrize the evolution of the transformation. The heat capacity of martensite is denoted by c and the mass of the transformed region by m. The temperature increase ΔT is unknown, so an estimate of it should be made. The maximum ΔT would appear when the plate transforms adiabatically. Assuming that this was the case for every peak, an upper limit for that expression would be obtained. Using the average heat released in the transformation (6 J g^{-1}) and the specific heat of copper, a ΔT of 14 K is obtained. This ΔT is too high because the A_s temperature would be surpassed, which means that the transformation cannot be produced adiabatically. Anyhow, the specific value of ΔT is not required to follow the evolution of the parameter, and some constant value can be taken, for instance 14 K, or the difference between the temperature of the sample and A_s.

In Fig. 5, the fifth and the tenth cycles of a continuous cycling for sample C with TT1 are shown. In Fig. 6, the evolution of the production of entropy is shown as a function of the number of cycles. Table 2 shows the values obtained for sample D which has ($\approx$ 10%) stabilized martensite.

Time scales

Several samples of alloy E were maintained at 1123 K for 15 min and then quenched in water at 373 K. They were kept at this temperature for a time t_{100} and then left at room temperature in the martensitic state also a different time t_m. The ageing at 373 K was used to accelerate the diffusion

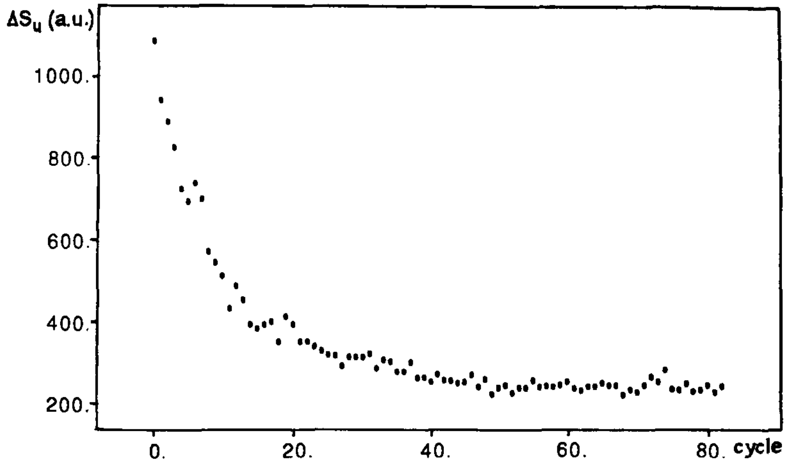

Fig. 6. Evolution of the entropy production with cycling.

TABLE 2

Entropy production (μJ g^{-1} K^{-1}) during the transformation of sample D (with stabilized martensite)

	Cycle							
	1	2	3	4	10	11	12	13
ΔS_u	19	43	21	23	8	14	26	39

TABLE 3

Evolution of the retransformation temperatures as a function of the times t_{100} [a] and t_m [a]

t_{100}	t_m	$A_s(1)$ [b]	$A_s(2)$ [b]
Temperatures from calorimetric data			
120 s	6 h	55.8	56.0
240 s	6 h	57.3	59.7
20 min	6 h	56.9	58.5
120 s	7 d	59.3	58.0 *[c]
240 s	7 d	59.1	58.2 *[c]
20 min	7 d	56.3	57.9
Temperatures from resistance data			
5 min	45 h	70.6	61.5 *[c]
5 min	6.5 d	73.9	66.9 *[c]
12 min	45 h	65.5	65.0 *[c]
12 min	6.0 d	66.7	62.5 *[c]
60 min	45 h	61.3	62.5
60 min	5.5 d	61.3	61.6

[a] See text. [b] $A_s(i)$ = austenite start temperature in °C for cycle i. [c] See text (Discussion).

TABLE 4

Evolution of the transformation temperature (°C) after the thermal treatment [a]

Cycle	M_s	A_s	A_f
1	63.7	59.1	67.6
2	64.8	59.2	68.7
3	64.9	59.4	69.1
4	64.9	59.8	69.4
5	-	60.1	69.4

[a] See text for details.

processes which take place in the material and was selected because, being below the precipitation region, it was easy to obtain.

The interest was put in the retransformation temperatures in the first and second cycle. Table 3 shows the results obtained. The retransformation temperatures was measured either from the calorimetric signal or from resistance measurements. Table 4 shows the evolution of the transformation temperatures during cycling when this was started just after the thermal treatment. Between successive cycles ($T = 9410$ s), the sample was maintained in the β state for 1 h, 2 h, 4 h and 6 h.

DISCUSSION

Single-interface single-variant transformations are very interesting to study because they are the simplest transformations. They involve neither interactions between variants (as in global transformation) nor elastic interactions with the matrix (as in the transformation of microplates). However, their analysis requires a high resolution thermal device and the temperature should be controlled carefully (to at least 0.01 K). This resolution is not used in metallurgical work and, therefore, can provide insight into known phenomena at a new level, or even provide new observations. Intrinsic thermoelasticity in a single-interface is an example of such a new observation.

Stabilization of the martensite and recovery of the β phase occurs when the single interface moves. Although these phenomena cause only a weak displacement of the transformation temperature (≈ 0.1 K) they strongly affect the characteristics of the partial loops and subloops. Hence, reproducible behavior cannot be achieved (at least not while the material is evolving). Moreover, it has been observed that because of the pinning points and the coalescence of the interfaces, the hysteresis cycle is modified. This causes additional difficulties in describing the state of the material at a given temperature and stress.

The study of single-interface transformations requires very careful work. Therefore, the way in which the time constant of the evolution of the material can be reduced by ageing, at a temperature higher than room temperature, was investigated in global transformations. After the thermal treatment and during the first 24 hours, there is a clear evolution towards higher values of the transformation temperature (see Table 4). Afterwards, the effect of the time elapsed in the martensite phase or in the β phase appears more clearly. Looking at the difference between the A_s of the first and second cycles (Table 3), it is obvious that for a fixed t_{100}, a higher t_m means increased stabilization. It is also seen that for a fixed t_m, a higher t_{100} means less evolution. Annealing at 373 K seems to homogenize and to suppress the effects of stabilization. The difference between the retransformation temperature of the first and the second cycle after a fixed time t_m has been compared for different times at 373 K. The three pairs of points labelled with an asterisk in Table 4 were used to evaluate the evolution of the time scale with time, at 100°C (t_m constant). The value ranges from 100 to 800 s, with a mean value near 400 s. Therefore, the difference $A_s(2) - A_s(1)$ decreases with increasing t_{100}, with a time scale of the order of 400 s. In this way, the ageing at 373 K seems to be useful as a quantitative tool for reducing the time of evolution of the material. The time scale of stabilization has been evaluated in the same way (t_{100} fixed, t_m variable) and a time constant of about 4 days that is quenching rate dependent has been found. These time constants can be used to determine the annealing time needed to diminish the evolution of the transformation temperatures.

The existence of an intrinsic thermoelasticity is of paramount importance because it ultimately determines the characteristics of the global free transformations. It limits the maximum growth that can be achieved by a plate because when the temperature is lowered to move its interfaces, the nucleation probability of other plates increases. Limiting its size limits the number of plates which appear and this number determines the amount of dislocations produced in the material during transformation. The intrinsic thermoelasticity increases with the number of dislocations and, consequently, this quantity affects the characteristics of the subsequent transformation cycles.

The relationship between the amount of dislocation and the average number of plates has been observed experimentally [10]. It has also been observed that the number of plates increases with cycling and their size decreases. It has been argued that an increase in dislocation facilitates nucleation (M_s or the martensite start temperature increases), but when the number of plates increases it is harder to complete the transformation [10]. Moreover, it is expected that the magnitude of discontinuous events will decrease. These phenomena have been followed calorimetrically and quantified with a parameter related to the entropy production. This parameter seems to be useful for following the increase in the number of defects with cycling. It is worth noting that the spontaneous transformation path changes significantly, at least during the first 50 cycles in an air-cooled sample. This evolution seems to be absent in samples with stabilized martensite, for which the transformation path does not evolve significantly.

Much work has been concerned with the energy balance of a whole transformation cycle. Some experiments in global spontaneous transformation shows an inconsistency in the heats measured in the forward and reverse transformations. Where this difference comes from is a matter of interest: acoustic emission, dislocation creation or internal friction are some of the suggested causes (see, for example, ref. 11). Nevertheless, the simplest case had not been studied. In this paper, the single-interface transformation, induced either by stress or by temperature, has been measured. We have found that, within experimental error, there is no difference between the amount of heat evolved in the forward and in the reverse transformations ($Q^{\beta \to \mathrm{m}} + Q^{\mathrm{m} \to \beta} \approx 0$) and that mechanical friction causes less than 0.1% of the evolved heat.

CONCLUSIONS

The martensitic transformation in Cu–Zn–Al alloys has been studied, paying special attention to the single-interface case. The reproducibility of this transformation is affected by the evolution of the state of the material and the presence of pinning points. Coalescence of plates also changes the path of the transformation in partial cycles. The intrinsic thermoelastic behavior of a single interface appears both in temperature-induced and in stress-induced transformations. The friction work due to interface movement has been evaluated as less than 1% of the enthalpy change. In both cases, the heat evolved in a complete calorimetric cycle is zero. The global spontaneous transformation cycling in temperature has been parametrized with the entropy production and the transformation of an air-cooled sample evolves during more than 50 cycles. Annealing at 373 K diminishes the effect of stabilization and a time scale of 400 s has been estimated.

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