Thermochimica Acta, 106 (1986) 209–217
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYSTEMATIC STUDY OF THE MARTENSITIC TRANSFORMATION IN A Cu–Zn–Al ALLOY. REPRODUCIBILITY OF THE THERMAL ENERGY RESULTS AND CYCLING EFFECTS

C. PICORNELL, C. SEGUI and V. TORRA

Departament de Fisica, Facultat de Ciencies, Universitat de Palma de Mallorca, Crtra. de Valldemossa km 7.5, 07071 Palma de Mallorca (Spain)

C. AUGUET, Ll. MAÑOSA and E. CESARI

Departament de Termologia, Facultat de Fisica, Universitat de Barcelona, Av. Diagonal 645, 08028 Barcelona (Spain)

R. RAPACIOLI

Div. Metales, Centro Atomico Bariloche, 8400-San Carlos de Bariloche (Republica Argentina)

(Received 26 February 1986)

ABSTRACT

A systematic study of the thermal energy released in the martensitic transformation undergone by a monocrystalline alloy of composition 74.41 Cu–18.18 Zn–7.41 Al (wt%) has been made. The values for ΔH in the $\beta \rightarrow$ M and M $\rightarrow \beta$ transformations have been determined, as a function of the heat treatment and the number of cycles. The experimental results establish that the transformation enthalpy is reproducible when the initial conditions are well determined. For different samples, in thermal cycles 1 to 10, ΔH is approximately constant, and by rapid cycling, the enthalpy of the 100th cycle is slightly smaller. Thermal cycling makes the effects of heat treatment less important and smooths the picture of the transformation dynamic. A qualitative study of several features of the acoustic emission produced during the transformation, as its signal/noise ratio and waveform, has also been carried out.

INTRODUCTION

The martensitic transformation undergone by shape-memory alloys is very sensitive to the thermomechanical history of each sample. This means that a large number of parameters must be taken into account to describe the initial state of a sample. Some recorded phenomena may be considered random or non-reproducible since the initial state is not well defined. Furthermore, dynamic study of the transformation gives rise to new limitations. It is possible to obtain good reproducibility of some integral magnitudes, but the transformation kinetics can be altered in its discontinuous

0040-6031/86/$03.50

components. A series of essays clearly showed that there are several dynamic behaviours according to the thermomechanical treatment of the material [4–6]. This promoted a systematic study under well-determined initial conditions.

In the present work the enthalpy change of a Cu–Zn–Al alloy submitted to two different heat treatments, its evolution with successive thermal cycling and the evolution of the transformation kinetics have been analysed. Simultaneously, a preliminary and qualitative study of the acoustic emission generated in the successive cycles has been carried out (signal/noise ratio, waveform of bursts). To eliminate the additional effects associated with annealing (stabilization, diffusion, etc.), an alloy which transforms below 273 K has been used.

EXPERIMENTAL

For the present work a monocrystalline alloy with a nominal composition of 74.41 Cu–18.18 Zn–7.41 Al (wt%) and a reputed M_s (martensitic starting temperature) of about 240 K has been used. From the original monocrystal several disc-shaped samples of 6 mm diameter and thicknesses ranging from 1.5 to 3 mm were cut. Before thermal cycling, the samples were maintained for 10 min at 850°C, and either slowly cooled in air to room temperature (TT1) or quenched in a mixture of ice and water, and annealed at room temperature (TT2). Twenty-four hours after treatment, the study of the transformation enthalpies was initiated; it consisted of a thermal cycling between 200 and 300 K, at a temperature change rate of $dT/dt \approx 0.3$ K min^{-1}. Cycles 1 to 10 were carried out with a separation period between

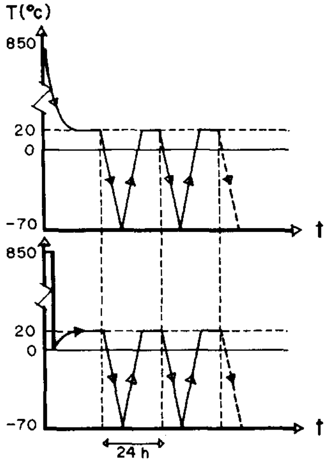

Fig. 1. Thermal treatments and subsequent cycling diagrams: (upper) TT1; (lower) TT2.

them of 24 h (Fig. 1), while cycles between the 11th and 99th were performed without any intermediate pause, at a higher heating rate (~ 180 K min^{-1}).

The series of experiments has been carried out in two similar calorimetric and data-acquisition systems in order to check the coincidence of the results. The microcalorimeters employed are based on the same design: they use semiconducting fluxmeters and have a sensitivity of ~ 400 mV W^{-1} at 300 K and a main time constant of ~ 12 s. The calorimetric system [1–3] allows simultaneous detection, by means of a piezoelectric ceramic (5 mm diameter and 0.5 mm thickness) directly placed on the sample, of the acoustic emission released during the transformation. In our preliminary study, the acoustic signal, after amplification via a Bruel and Kjaer chain, is recorded in a Canberra multichannel or in a Prowler oscilloscope which allows a detailed analysis of its characteristics (amplitude, period, duration, etc.).

Numerical treatment of the experimental thermograms taking into account the evolution of the sensitivity with temperature leads to an accurate determination of ΔH associated with the direct and reverse transformations.

CALORIMETRIC RESULTS

Table 1 shows the average values and standard deviation for the overall enthalpy changes in the direct and reverse transformations. The average has been calculated for different samples with identical preparation, for different cycles and for both thermal treatments TT1 and TT2.

Table 2 shows, likewise, the average values and standard deviation for the enthalpy changes measured in the two first cycles when heat treatment TT1 is repeated several times on the same sample.

The set of results indicates that, though acceptably small standard deviations are obtained in all cases (less than 10%), the enthalpy values are more reproducible when repeating the thermal treatment on the same sample.

TABLE 1

Average values for the enthalpy changes (J g^{-1}), standard deviations, and numbers of samples (N) with identical preparation, for different cycles and for the thermal treatments TT1 and TT2

Cycle	TT1			TT2		
	$\Delta H^{\beta\to M}$	$\Delta H^{M\to\beta}$	N	$\Delta H^{\beta\to M}$	$\Delta H^{M\to\beta}$	N
1	-5.8 ± 0.5	6.0 ± 0.3	5	-5.1 ± 0.3	5.6 ± 0.3	4
2	-5.7 ± 0.4	6.0 ± 0.3	5	-5.0 ± 0.3	5.6 ± 0.3	4
10	-5.8 ± 0.3	6.0 ± 0.1	5	-5.0 ± 0.4	5.5 ± 0.3	4
100	-4.6 ± 0.3	5.3 ± 0.2	4	-4.7 ± 0.1	5.4 ± 0.1	4

TABLE 2

Average values and standard deviations (J g^{-1}) for the first and second cycles, in the case of repeating the thermal treatment TT1 N times

Mass changes of the sample due to the heat treatment have been found to be negligible

	1st cycle		2nd cycle		N
	$\Delta H^{\beta\rightarrow M}$	$\Delta H^{M\rightarrow\beta}$	$\Delta H^{\beta\rightarrow M}$	$\Delta H^{M\rightarrow\beta}$	
TT1	-6.1 ± 0.1	6.1 ± 0.2	-6.1 ± 0.2	6.1 ± 0.1	9

To give support to this statement, a study of heat evolution during the transformation points out that different samples with identical preparation can present substantially different dynamic behaviours, as can be seen in Fig. 2.

Successive cycling of the samples does not significantly influence the transformation enthalpies in the first cycles. However, Table 1 shows that standard deviations decrease when the number of cycles performed increases. After a high number of cycles, the energy values associated with different heat treatments also converge. In our case rapid thermal cycling between the 10th and 99th cycles tends to eliminate the differences due to individual peculiarities of the samples and also the overall heat treatment effects [7]. Anyhow, some distinguishing features between TT1 and TT2 remain. In particular, quenched samples always present a lower M_s and a higher acoustic emission rate [4–6], features which remain even after 100 cycles. As an example, Table 3 gives, for both thermal treatments and different cycles, the values of the martensitic starting temperature, M_s, corresponding to the first signal of thermal activity observed in the thermogram (see, for example,

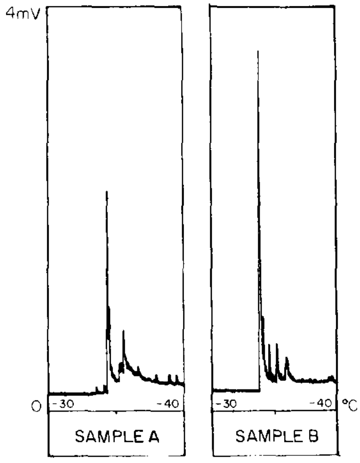

Fig. 2. Interval corresponding to the $\beta\rightarrow M$ transformation in a second cycle for two different samples with thermal treatment TT1, showing different dynamic behaviour.

TABLE 3

Temperatures corresponding to the first signal of detected thermal activity (M_s) and to 10% of the total energy dissipation (M_s^*), for samples with thermal treatments TT1 and TT2 for different cycles

Cycle	TT1		TT2	
	M_s	M_s^*	M_s	M_s^*
1	−34.4	−34.7	−38.0	−40.7
2	−32.8	−34.3	−41.9	−42.2
10	−33.8	−36.1	−41.6	−42.6
100	−34.9	−37.4	−42.7	−45.8

Fig. 2) with a resolution near 40 μV. Observation of the same thermogram with a greater resolution (~ 1 μV) shows preliminary peaks at higher temperatures. The same behaviour is observed when using the acoustic emission technique [14]. Also, the M_s^* temperature corresponding to 10% of the total energy released is given in Table 3. On the other hand, successive cycling generally leads to a more reproducible and thermoelastic transformation.

Figure 3 shows the typical evolution of calorimetric curves recorded during the $\beta \rightarrow M$ and $M \rightarrow \beta$ transformations, as the number of cycles increases, for a sample with TT1 (a) and TT2 (b). In order to study this evolution in detail, one sample was submitted to TT1 and cycled in the usual way, but acquiring calorimetric data at a higher rate (11 Hz). Deconvolution of the thermograms was then carried out in order to obtain the actual thermal power released or absorbed by the sample. This procedure gave a clear separation of the calorimetric peaks. The results (number of peaks vs. temperature) are summarized in Fig. 4.

The first cycle shows a "burst" like the first stage of growth, evidenced by a high calorimetric peak. This rough transformation produces lattice defects and, as a consequence, the transformation in this first cycle is not fully thermoelastic [8–10]. The defects produced, principally dislocations, make nucleation easier on further cycling, leading to an increase in M_s, observed in the samples submitted to TT1. Though calorimetry is not able to describe the initial part of the transformation in more detail, a parallel analysis by acoustic emisson [11] suggests that this initial part is only apparently continuous, and is actually formed by an addition of discontinuous thermal power contributions.

After the first cycle, a progressive disappearance of the burst phenomena can be observed, and hence an increase in the number of calorimetric peaks. Considering that the formation of martensite plates is correlated with the appearance of calorimetric peaks [12], such an observation is a consequence of the increase in the number of nucleation sites. This increase leads to the appearance of a higher number of martensite plates which grow and shrink

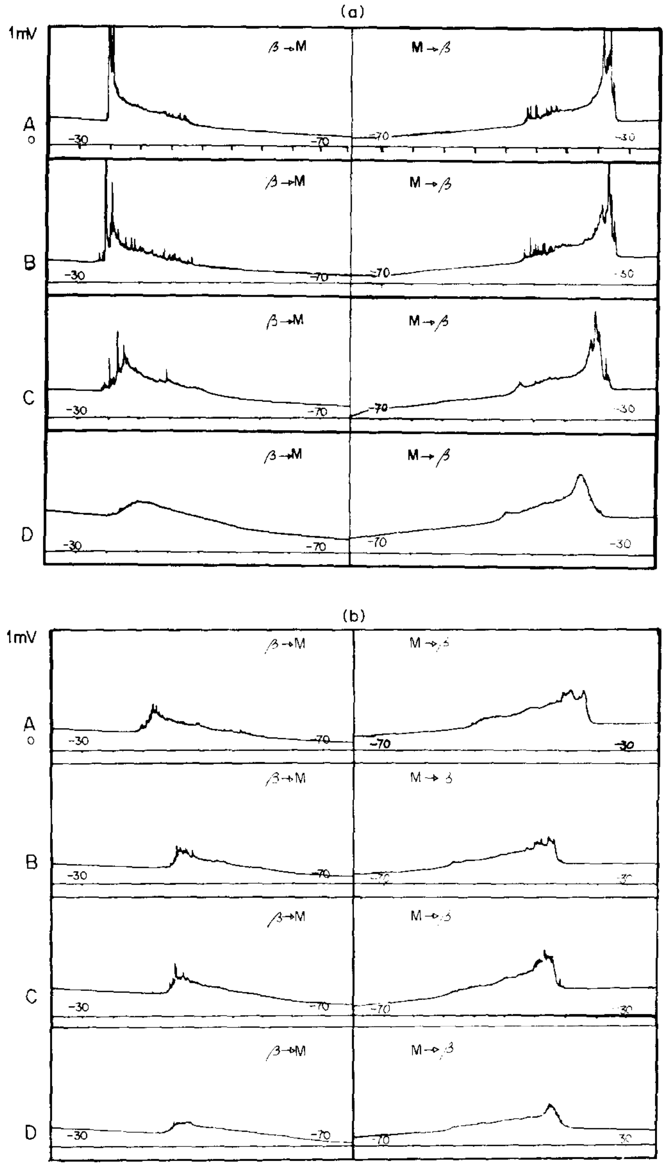

Fig. 3. Characteristic evolution of the thermogram for the direct and reverse transformation during thermal cycling, for a sample submitted to TT1 (a) and TT2 (b) and subsequent cycling: (A) 1st cycle; (B) 2nd cycle; (C) 10th cycle; (D) 100th cycle.

in a thermoelastic way. In following cycles, a progressive decrease in the number of calorimetric peaks is observed. Optical microscopy observations indicate that a small amount of stabilized martensite is present in the surface at temperatures above A_f. This can be one of the causes of the observed decrease in the transformation enthalpy pointed out in Table 1, though, attending to the observed amount of stabilized plates, there must be another

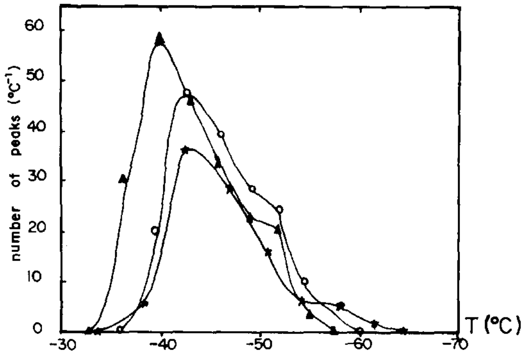

Fig. 4. Variation of the recorded number of calorimetric peaks with temperature for a $\beta \rightarrow$ M transformation during the 1st (○), 2nd (▲) and 100th (★) cycles.

cause responsible for this decrease. Furthermore, the transformation temperature range extends with thermal cycling (($M_f - M_s$) increases from ~ 20 °C in the first cycle to ~ 24°C in the 100th), leading to a higher indetermination in the enthalpy change results for the 100th cycle.

ACOUSTIC OBSERVATIONS

A study of the acoustic signals was carried out with a Prowler oscilloscope during cycles 1 and 106 after a TT1 treatment. The rate of change in temperature was $dT/dt \approx 0.5$ K min^{-1}. The number of oscillations (or arcs) in the acoustic wave recorded per event in our experimental set-up was ~ 80–100 [13]. A small difference (< 20%) in the number of arcs per pulse between the direct and reverse transformation has been noticed, the higher value corresponding to heating.

The acoustic signals displayed do not generally present a damped sinusoidal form and, qualitatively, their characteristics do not change appreciably during thermal cycling.

When using the Prowler oscilloscope, as the number of studied signals is limited (only less than a 15% of the total number of arcs produced during the transformation are recorded), the signal/noise ratio is ~ 80 in the $\beta \rightarrow$ M transformation and ~ 160 in the M $\rightarrow \beta$ one. However, the measurements carried out with the Canberra multichannel analyser in a continuous acquisition mode give a signal/noise ratio of ~ 10^3 on cooling and ~ 2×10^3 on heating. These figures mean that it is difficult to obtain quantitative results of the energy of acoustic emission since an experimental system able to detect acoustic signals differing by three orders of magnitude in amplitude would be required.

CONCLUSIONS

The thermal energy results for the martensitic transformation in a 74.41 Cu–18.18 Zn–7.41 Al (wt%) alloy are reproducible by more than 10%, either using different samples with the same preparation or repeating the thermal treatment on the same sample. There is a decrease in the enthalpy change for both the direct and reverse transformations after a large number of cycles (rapid cycling from cycles 10 to 99), partially due to stabilization of a small amount of martensite. Furthermore, there is an evolution in the dynamics of transformation, which progressively smooths down as the thermal cycling proceeds.

Though a quantitative study has not been done, our results concerning acoustic emission indicate that:

(1) The signal/noise ratio in our experimental set-up and with the material studied is higher than 10^3 in the direct transformation and near 2×10^3 in the reverse transformation.

(2) Bursts, as seen with our experimental set-up, have around 100 arcs per event and only few of them show exponentially damped waveforms. A small increase in the number of arcs is observed for the reverse transformation.

(3) Features of acoustic signals do not change appreciably during cycling.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Dr. J. Ortin for his helpful remarks. The present work has been carried out in the frame of the cooperation between the Universities of Illes Balears and Barcelona, and also with Centro Atomico de Bariloche. Materials Research at the University of Illes Balears is supported by a grant of the CAICYT (No. 3562-83). C.S. also acknowledges a fellowship from the "Ministerio de Educacion y Ciencia" within the "Plan Nacional de Formacion de Personal Investigador".

REFERENCES

1 H. Tachoire, J.L. Macqueron and V. Torra, in M.A.V. Ribeiro da Silva (Ed.), Reidel, Dordrecht, 1984, pp. 77–126.

2 J.P. Dubes, H. Tachoire, J.L. Macqueron, J. Ortin, C. Picornell, C. Segui and V. Torra, Proc. Jornades de Transformacions Termoelastiques, Palma de Mallorca, 1985, pp. h01–h07.

3 C. Picornell, C. Segui, V. Torra, J. Hernaez and C. Lopez del Castillo, Thermochim. Acta, 91 (1983) 311–320.

4 R. Rapacioli and M. Ahlers, Acta Metall., 27 (1978) 777.

5 R. Rapacioli, J.L. Macqueron and G. Guenin, Proc. Jornades de Transformacions Termoelastiques, Palma de Mallorca, 1984, pp. b01–b09.

6 M. Mantel, Thesis, INSA, Lyon, 1985.

7 A. Planes, J.L. Macqueron, M. Morin and G. Guenin, Phys. Status Solidi A, 66 (1981) 717.

8 H. Pops and T.B. Massalski, Trans. TMS-AIME, 230 (1965) 1662.

9 J. Perkins and W.E. Muesing, Metall. Trans. A, 14 (1983) 33–36.

10 A. Planes, J.L. Macqueron, M. Morin, G. Guenin and L. Delaey, J. Phys. (Paris), C-4, 43 (1982) 615–620.

11 J. Ortin, C. Picornell, C. Segui, V. Torra and R. Rapacioli, Proc. Seminari sobre Materials amb Memoria de Forma, Palma de Mallorca, 1985, pp. 55–60.

12 V. Torra, J. Ma. Guilemany and E. Cesari, Thermochim. Acta, 99 (1986) 19.

13 C.H. Caceres, W. Arneodo, R. Pascual and H.R. Bertorello, Scr. Metall., 14 (1980) 293–297.

14 G. Guenin, J.L. Macqueron and R. Rapacioli, private communication.