Thermochimica Acta, 145 (1989) 237–243
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

γ PRECIPITATES IN β-Cu–Zn–Al: INFLUENCE ON MARTENSITIC TRANSFORMATIONS

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(Received 5 October 1988)

ABSTRACT

The effect of γ precipitates on the martensitic transformation in Cu–Zn–Al shape memory alloys has been studied. Characteristic transformation temperatures, the thermal energy released and the entropy changes have been determined by means of calorimetry with simultaneous acoustic emission detection. The non-chemical energy contributions, elastic and frictional, present in this kind of transformation have also been estimated for several γ precipitate distributions. These distributions produce important changes in the thermal hysteresis of the transformation, showing several mechanisms of interaction between precipitates and martensite.

INTRODUCTION

It is known that martensitic transformations undergone by shape memory alloys are strongly affected by the previous thermal treatment carried out to retain the parent phase at room temperatures (β phase in Cu–Zn–Al alloys) [1–3]. Some of these treatments allow us to introduce different phase precipitates into the matrix, making it possible to study their effect on the martensitic transformation. In particular, several heat treatments generate diverse distributions of γ precipitates in the β phase of Cu–Zn–Al [4–6]. For example, quenching from temperatures near the B2 ordering temperature produces a distribution of γ-type precipitates. By subsequent flash heating, of varying lengths, one obtains different amounts of γ phase in the β matrix. Thus, the parent phase can be modified in a controllable way.

In this work, we present results concerning three thermal treatments which produce different γ precipitate distributions. The effect of these precipitates on the thermally induced martensitic transformation has been studied by means of calorimetry and simultaneous detection of the acoustic emission released during the $\beta \rightleftarrows$ m (martensite) processes.

The evolution of characteristic temperatures for the direct $\beta \rightarrow$ m (M_s, M_f) and the reverse m $\rightarrow \beta$ (A_s, A_f) transformations, as well as the values

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of the heat exchanged and the entropy changes, have been obtained. In addition, the elastic and frictional energy contributions have been calculated from the calorimetric measurements.

Different shifts in the transformation temperature range corresponding to different distributions of γ clearly show that several mechanisms of interaction exist between the precipitates and the martensite, which are also reflected in the elastic energy and frictional work values.

EXPERIMENTAL

Single crystal alloys, with composition Cu 68.4, Al 16.3 and Zn 15.3 at.% (alloy Cl) and Cu 68.4, Al 15.5 and Zn 16.1 at.% (alloy D) were used. For both alloys the electron to atom ratio is 1.48, their nominal M_s is close to 270 K and the B2 ordering temperature is ≈ 820 K. From the original monocrystals, disc-shaped samples of ≈ 5 mm diameter and thickness ranging from 1.5 to 2.5 mm were cut.

In order to obtain γ precipitates, three thermal treatments were performed:

TTB: from the β stability region (1120 K), air cooling to 770 K and, after 180 s at this temperature, quenching in ice–water.

TTC: from the β stability region (920 K), cooling at a rate of ≈ 50 K s^{-1} to room temperature (290 K).

TTD: from the β stability region (1120 K), quenching to room temperature.

For the three thermal treatments, subsequent flash heating at 670 K was performed for variable times $t^{\star}$. The distributions of precipitates were observed by scanning and transmission electron microscopy. Current work, out of the scope of this paper, is being done in order to analyse growth rates and sizes in different distributions.

For each set of samples of alloys Cl and D, the results obtained were compared with those corresponding to a reference thermal treatment (named TT1): air cooling from 1120 K to room temperature, and 24 hours aging before the first transformation cycle.

The calorimetric system, which has already been described [7–8], allows simultaneous detection, by means of a piezoelectric transducer placed directly on the sample, of the acoustic emission (ring-down counting).

RESULTS AND DISCUSSION

Table 1 shows the values of the transformation temperatures M_s, M_f, A_s, A_f, the thermal energy released $Q = (|Q^{\beta \to m}| + |Q^{m \to \beta}|)/2$ and the entropy changes $\Delta S = (|\Delta S^{\beta \to m}| + |\Delta S^{m \to \beta}|)/2$ (calculated as $\int \delta Q/T$ between M_s and M_f, or A_s and A_f [9]) obtained for each sample. The values

TABLE 1

Transformation temperatures, thermal energies (Q) and entropy changes (ΔS) measured for the different thermal treatments and times $t^\star$ of flash heating. Uncertainties: ± 1 K in temperatures, ± 10 J mol^{-1} in Q, and ± 0.04 J mol^{-1} K^{-1} in ΔS

Sample	TT-$t^\star$	M_s (K)	M_f (K)	A_s (K)	A_f (K)	Q (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
C1-3	TT1	265	243	256	274	400	1.57
C1-7	TTC-20 s	274	252	263	277	411	1.54
C1-8	TTC-40 s	276	253	266	281	361	1.35
C1-9	TTC-60 s	282	251	265	286	367	1.37
C1-10	TTC-100 s	283	251	265	287	344	1.28
D1B	TT1	284	256	267	287	449	1.63
D1	TTB-0 s	283	256	270	289	440	1.59
D2	TTB-20 s	280	255	264	284	314	1.16
D3	TTB-40 s	274	238	256	278	241	0.93
D8	TTD-20 s	272	248	261	275	412	1.55
D7	TTD-60 s	254	237	258	276	279	1.09

of Q and ΔS are presented per mass unit of the sample. As the absolute values of $Q^{\beta \to \mathrm{m}}$ and $Q^{\mathrm{m} \to \beta}$ are coincident within the experimental error, as well as the $\Delta S^{\beta \to \mathrm{m}}$ and $\Delta S^{\mathrm{m} \to \beta}$ values, we therefore give the mean values of Q and ΔS.

Assuming that the values of ΔS are proportional to the amount of transformed mass [9], we can estimate the fraction of transformed material, $X = \Delta S(t^\star)/\Delta S(\mathrm{TT1})$, for each sample with precipitates corresponding to a time $t^\star$ of flash heating. The values of X, as well as those of $Q^\star = Q/X$ (thermal energy released per unit of transformed mass) are presented in Table 2. In this table, the elastic, $\Delta H_{\mathrm{el}} = |\Delta H_{\mathrm{el}}^{\beta \to \mathrm{m}}| = |\Delta H_{\mathrm{el}}^{\mathrm{m} \to \beta}|$, and

TABLE 2

Fractions of transformed material (X), thermal energy ($Q^\star$) and non-chemical contributions, elastic (ΔH_{el}) and frictional (E_{fr}) energies, per unit of transformed mass for the different samples

Sample	TT-$t^\star$	X	$Q^\star$ (J mol^{-1})	ΔH_{el} (J mol^{-1})	E_{fr} (J mol^{-1})
C1-3	TT1	1.00	400	24	7
C1-7	TTC-20 s	0.98	419	5	12
C1-8	TTC-40 s	0.86	420	4	13
C1-9	TTC-60 s	0.87	422	2	14
C1-10	TTC-100 s	0.82	420	4	15
D1B	TT1	1.00	449	15	9
D1	TTB-0 s	0.97	454	10	12
D2	TTB-20 s	0.71	442	22	12
D3	TTB-40 s	0.57	423	41	20
D8	TTD-20 s	0.95	434	30	10
D7	TTD-60 s	0.67	416	48	36

frictional, $E_{fr} = E_{fr}^{\beta\rightarrow m} + E_{fr}^{m\rightarrow\beta}$, energies (again referred to unit of transformed mass) are also presented. These non-chemical energies are calculated following the model proposed in ref. 9.

Although the numerical values of ΔH_{el} and E_{fr} are small and, therefore, affected by an important error, they are indicative of the evolution of the non-chemical terms for the different thermal treatments.

The evolution of the transformation temperature domains and the values of E_{fr} (which correspond to the area enclosed by the hysteresis loop in ΔS versus T coordinates) due to the presence of precipitates are very important. Some examples are presented in Fig. 1. It can be observed that for the TTB treatment (Fig. 1(A)) at the considered $t^{\star}$ times, the whole hysteresis cycle is shifted towards lower temperatures compared with the TT1 cycle (see also Table 1, TTB). It is known [10] that for lengthy flash heating ($40 < t^{\star} \leqslant 100$ s), the reverse transformation moves to higher temperatures, even exceeding those of TT1, while the forward one shifts down. For $t^{\star} \geqslant 180$ s, the whole hysteresis cycle moves towards higher temperatures than those of TT1 [4]. For samples submitted to TTC treatment, the transformation is already shifted towards high temperatures at shorter times of flash heating (Fig. 1(B)). This contrary behaviour can be explained in terms of the different values of elastic energy for both TTB and TTC. TTB treatment, followed by flash heating, produces an important increase of ΔH_{el} with respect to TT1, which makes the forward transformation more difficult and favours the reverse one, while, in TTC, the ΔH_{el} values are always lower (see Table 2). The high values of ΔH_{el} obtained for samples D3, D7 and D8 (the last two submitted to TTD, which will be discussed below) are also in accordance with the observed drop of M_f and A_f with respect to TT1.

After TTC treatment, therefore, it seems that the effect of change in the composition caused by the presence of precipitates (which are richer in Al than the matrix) acts in the same direction as the decrease of elastic energy with respect to TT1, yielding an increase in M_s and A_s and shifting the transformation range to higher temperatures. On the other hand, after TTB treatment, the more important elastic energy effect prevails over the composition change effect, at least for $t^{\star} \leqslant 40$ s. After times of flash heating $t^{\star} \geqslant 40$ s, the observed displacement of the reverse transformation towards higher temperatures than those of TT1 [10] has to be attributed to the difficulties in the movement of the β martensite interfaces, which obviously increase E_{fr}. In fact, important distortions of martensite plates that are hindered by the precipitates have been observed by TEM in samples with $t^{\star} \geqslant 40$ s [11]. It has to be said that samples with times of flash heating $t^{\star} \geqslant 100$ s after TTB treatment may not be studied by means of calorimetry, because the high level of γ phase produces very gentle thermograms, which make the accurate measurement of transformation temperatures and thermal energy exchanged very difficult. At $t^{\star} \geqslant 180$ s, the whole transformation cycle is shifted to higher temperatures than those of TT1 and, although the

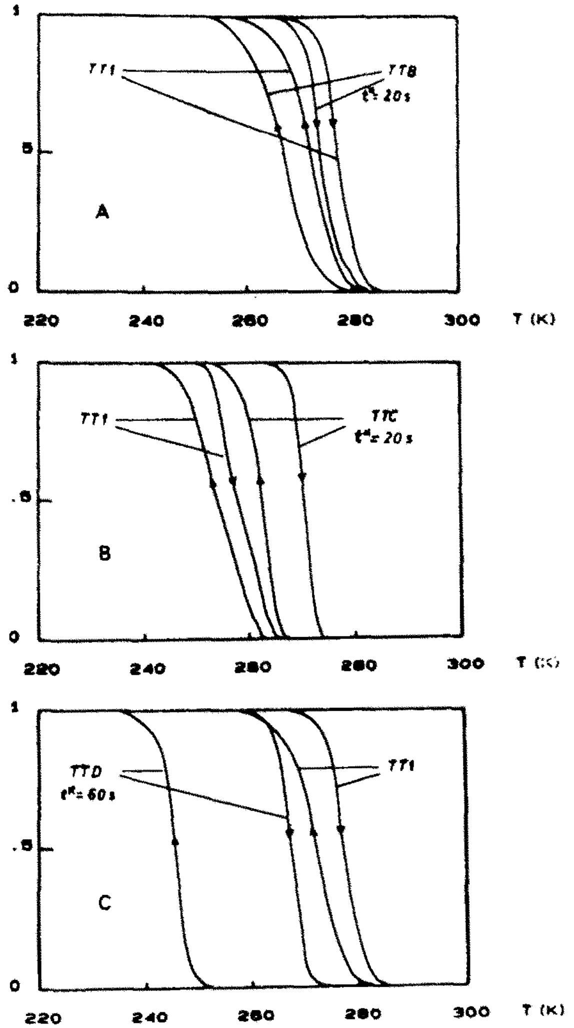

Fig. 1. Thermal hysteresis cycles (ΔS (reduced) versus temperature) for samples: (A) sample D2, TTB, $t^{\star} = 20$ s; (B) sample C1-7, TTC, $t^{\star} = 20$ s; and (C) sample D7, TTD, $t^{\star} = 60$ s, compared with the reference thermal treatment TT1.

elastic energy values are not known (the study was done using electrical resistivity measurements [4]), we can deduce that the composition change is important enough to explain the observed shift.

The differences between the various thermal treatments are in good agreement with the diversity of γ distributions observed by SEM. The quench from 770 K (TTB) generates a very dense distribution of precipitates, reaching sizes of 0.1–0.2 μm for $t^{\star} = 60$ s. A much smaller number of precipitates are observed in TTC, although they have greater sizes (0.8–1 μm with $t^{\star} = 60$ s).

Besides clarifying the role played by quenched-in vacancies on the generation of precipitates, these differences explain the fact that elastic interaction of precipitates with martensite is much stronger following the TTB treatment than with TTC treatment.

The behaviour of samples submitted to TTD is also in agreement with SEM observations. In this case, a distribution of precipitates with an intermediate density between those of TTB and TTC but closer to that of TTB was observed. With $t^\star = 60$ s, the size of precipitates is 0.2–0.3 μm, slightly greater than TTB, but with a lower density, in accordance with the fractions of transformed mass obtained (see Table 2). This fact confirms that the quench from temperatures near the B2 ordering temperature (TTB) is more efficient than TTD treatment in obtaining important precipitate quantities for the same times of flash heating. A competition exists between vacancies and disorder in the generation of precipitates, a competition also observed in the changes of the M_s values for samples quenched from different temperatures [12].

An interesting fact related to the TTD treatment is the possibility of producing variations in the hysteresis cycle and elastic energy similar to those induced by TTB treatment, but produced by introducing a smaller total proportion of γ phase, due to the combination of lower density and slightly greater size of the precipitates.

Acoustic emission (A.E.) results of samples submitted to TTB and TTD show a strong decrease in the total number of counts, with reference to TT1. For flash heating times $t^\star = 40$–60 s, the number of counts recorded for the reverse transformation were ≈ 30 times smaller, while, on cooling, the decrease was still more important, because the signals detected have amplitudes near the noise level of the amplification chain. In the case of samples with TTC treatment, no important decrease is noticed for $t^\star < 100$ s. At $t^\star = 100$ s, the A.E. becomes ≈ 5 times lower than in the TT1 treatment for both $\beta \rightleftarrows$ m processes. Only a small part of these decreases can be explained by the decrease in transformed mass. The fact that smaller martensite plates appear in samples with TTB and TTD treatments than with TT1, as has been observed by means of optical microscopy, can largely account for the observed A.E. behaviour, because, on average, the abrupt movement of large interfaces is diminished, these movements being directly related to a source of A.E. [13]. The different changes in A.E. found for TTB, TTD and TTC treatments agree with the different precipitate distributions observed, showing again a stronger effect in the case of TTB and TTD. The most important decrease of A.E. in the forward transformation is also in good agreement with the important shifts to high temperatures observed in the reverse ones, in spite of the fact that ΔH_{el} increases, which is related to higher friction in the re-transformation.

From the different treatments considered, one can conclude that precipitates give rise to strong effects in the β–m transformation. Interesting possibilities, from the point of view of industrial applications of these alloys, arise from the modification of the hysteresis cycle in a controlled way by means of the introduction of precipitates.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. F.C. Lovey for many helpful discussions and his work on TEM observations. Dr. F. Hierro (servei de microscòpia, UIB) is also acknowledged for SEM observations.

This work was partially supported by the CAICyT (project n. PA86-0079).

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