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The thermodynamics of Cu–Zn–Al–Mn shape-memory alloys

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Abstract

The particular temperatures of the martensitic transformation, the heat exchanged during transformation, the entropy variation, the chemical origin enthalpy, the contribution of the elastic energy and the friction work for Cu–Zn–Al–Mn shape-memory alloys have all been determined using flow calorimetry.

INTRODUCTION

The interest raised by the new quaternary shape-memory alloys stems from the fact that the addition of manganese brings about an increase in both the mechanical properties and in the range of the transformation temperatures [1].

The relation between the Ms and As transformation temperatures and the chemical composition of this alloy has been recently determined to be in the form of multi-linear equations. A decrease in the temperatures with an increase in the aluminium, zinc or manganese contents when the other elements remain constant has been observed [2]. These equations allow alloys with the desired transformation temperatures to be formulated by varying the chemical composition.

These alloys indicate the coexistence of two types of martensite, starting from an electron-to-atom ratio of 1.430: orthorhombic martensite, 18R, and the hexagonal form, 2H. This fact is clearly seen by transmission electron microscopy and X-ray diffraction, as well as by calorimetry [3–5].

Thermodynamic study of this quaternary alloy has been performed according to the recent thermodynamic model proposed by Ortín and Planes [6] for the thermoelastic martensitic transformation with the possibility of its evaluation by means of calorimetric data.

In the direct exothermic ($\beta \rightarrow$ martensite) transformation, part of the

TABLE 1

Chemical compositions in weight percentage and electron-to-atom ratios (e/a)

Alloy	Cu (%)	Al (%)	Zn (%)	Mn (%)	e/a
1	71.8	18.4	6.1	3.8	1.430
2	71.6	18.4	6.3	3.7	1.431
3	71.4	18.7	6.0	3.8	1.433
4	71.4	18.8	5.9	3.8	1.434
5	71.4	18.8	6.3	3.4	1.438
6	71.3	18.7	6.7	3.3	1.441
7	71.2	19.3	6.3	3.1	1.448
8	70.8	19.5	6.2	3.4	1.452
9	70.6	19.9	6.0	3.5	1.458
10	70.0	19.9	6.2	3.8	1.459

latent heat generated ($-\Delta H_{\text{chem}}$) is stored as elastic energy (ΔH_{el}) and part is absorbed as friction energy (E_{fr}); therefore, the average heat is

$$-Q = -\Delta H_{\text{chem}} + \Delta H_{\text{el}} + E_{\text{fr}} \tag{1}$$

In the reverse (martensite → β) transformation, whilst the latent heat (ΔH_{chem}) is absorbed by the sample, the elastic enthalpy ($-\Delta H_{\text{el}}$) is reversibly recovered. However, work (E_{fr}) is necessary in order to overcome friction impediments which are opposed to the regression of the interphases. The average heat measured is

$$Q = \Delta H_{\text{chem}} - \Delta H_{\text{el}} + E_{\text{fr}} \tag{2}$$

The hypotheses for this model are that friction energy does not diminish as heat, but that it only represents work, and also that the specific heat variation at constant pressure between the matrix and martensitic phase is not taken into account.

EXPERIMENTAL PROCEDURE

Ten polycrystalline alloys (see Table 1 for their chemical compositions) were investigated. Cylindrical test samples 5 mm in diameter, 2 mm high and weighing approximately 400 mg, were submitted to heat treatment (850 °C for 10 minutes and water-quenched at room temperature). The calorimetric measurements were performed twenty-four hours after the heat treatment.

The flow calorimeter used is a highly sensitive model with differential signal detectors made up of 32 thermocouples, the working range of which is from −150 to 100 °C. The temperature was measured by standard Pt–100 sond. All signals were digitised by a multichannel analyser and treated by a computer. The heating–cooling rate was 1 °C min^{-1}. The uncertainty of the enthalpy and entropy variations is 5% and ±0.5 K in temperature values.

The transformation temperatures are taken to be the moment at which a sudden rise in the calorimetric curve takes place and when the signal returns to the base line. The heat absorbed or expelled in the transformation is determined by calculating the area within the curve and the entropy is obtained by integration of the mean heat differential with respect to the temperature. The average chemical energy between the direct and the reverse transformation is calculated by the equation

$$\Delta H_{\text{chem}} = T_0\overline{\Delta S} \tag{3}$$

where $\overline{\Delta S}$ is the average entropy variation between transformation and re-transformation and T_0 is the equilibrium temperature, which cannot be determined by calorimetric techniques as, due to the transformation kinetics, there must be a further cooling to overcome the opposing non-chemical energies so that re-transformation can take place. This temperature can be estimated by the Tong and Wayman approximation [7,8] which is the most widely accepted for the thermoelastic martensitic transformation

$$T_0 = 0.5(\text{Ms} + \text{Af}) \tag{4}$$

By subtracting eqns. (1) and (2) and bearing in mind that $E_{\text{fr}}^{\beta \to \text{M}} = E_{\text{fr}}^{\text{M} \to \beta}$, the elastic energy is obtained as

$$\Delta H_{\text{el}} = \Delta H_{\text{chem}} - \overline{Q} \tag{5}$$

where $\overline{Q}$ is the average for the heat measured experimentally in both processes. The friction energy can be obtained by adding eqns. (1) and (2); however the most accurate method is that which gives the above energy as the area within the hysteresis cycle (normalised entropy versus temperature).

EXPERIMENTAL RESULTS AND DISCUSSION

The transformation temperatures (Ms, Mf, As, Af) were determined from the thermograms obtained; an example is shown in Fig. 1 for alloy 8 in the heating and cooling cycles. These temperatures, as well as the difference between the Af and Mf temperatures, the corresponding hysteresis ($T_{\text{h}} = |\text{Ms} - \text{Af}\,|$) and the equilibrium temperatures, are given in Table 2.

Each of the ten alloys studied underwent various cooling–heating cycles and no significant variations were observed in the results. This means that heating and cooling do not affect the structural order in the appearance or disappearance of defects that could alter the transformation temperatures.

The transformation temperature values fluctuate between the following minimum and maximum values: Ms from 226 to 289 K; Mf from 194 to 272 K; As from 284 to 204 K; and Af from 254 to 310 K.

From the thermograms obtained, two transformations can be seen in both the cooling and heating cycles, showing the coexistence of both types of martensite, the orthorhombic 18R and the hexagonal 2H. On many occa-

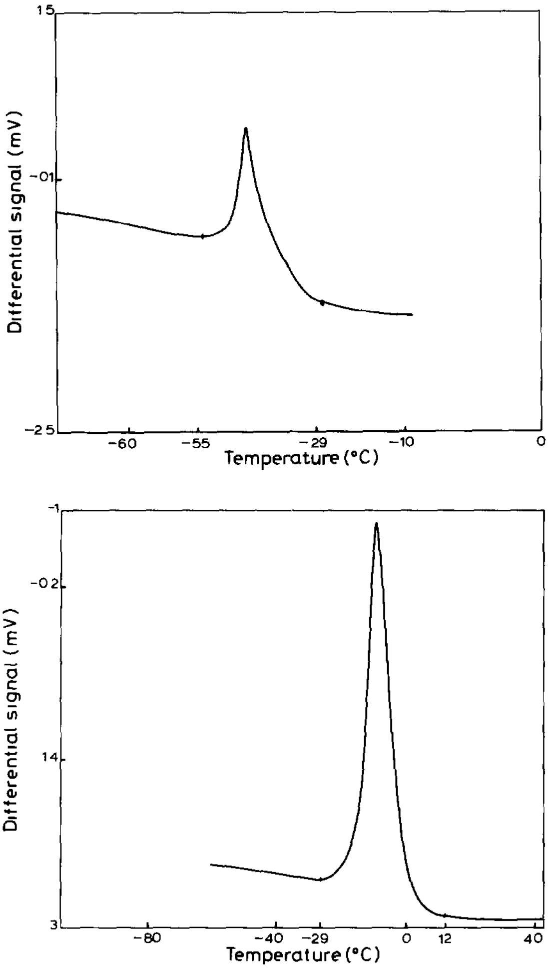

Fig. 1. Thermograms obtained for alloy 8. Top, cooling cycle; bottom, heating cycle.

TABLE 2

Transformation temperatures, hysteresis and equilibrium temperatures (°C)

Alloy	Ms	Mf	As	Af	(Mf−Af)	T_h	T_0
1	276	247	263	285	38	9	281
2	289	263	274	299	36	10	294
3	275	239	253	279	20	4	277
4	277	242	262	310	68	33	294
5	285	255	270	293	38	8	289
6	281	254	268	288	34	7	285
7	289	272	284	303	31	14	296
8	244	218	244	285	67	41	265
9	226	194	204	254	60	28	240
10	269	231	238	281	50	12	275

TABLE 3

Transformation and re-transformation heats (J g^{-1})

Alloy	$Q^{\beta \to M}$	$Q^{M \to \beta}$	$\bar{Q}$
1	6.83	−4.69	5.76
2	7.78	−6.37	7.07
3	6.50	−6.00	6.25
4	6.15	−5.82	5.98
5	6.09	−6.36	6.22
6	4.93	−4.56	4.75
7	5.92	−5.03	5.47
8	5.85	−5.01	5.43
9	5.90	−5.02	5.46
10	6.20	−5.20	5.70

sions, no clear differences were shown during direct transformation in either stage. This was due to the different hysteresis associated with each of the $\beta \rightleftharpoons \beta'$ 18R and $\beta \rightleftharpoons \beta'$2H transformations.

The existing differences between the Af and Mf temperatures are between 20 and 68 °C; these are much higher than those observed in other copper-based alloys, such as those of Cu–Zn–Al which do not exceed 10 °C [9,10]. This is because the heat treatment and subsequent quenching of this quaternary alloy leads to a great number of vacancies and stacking defects which provoke internal stress within the matrix which stabilises the martensite and hampers re-transformation. The high energy levels produced in the martensitic plate interphases of both types of variant also play an important role. These re-transformation difficulties cause the temperatures at the end of the re-transformation to rise and, therefore, the differences between Mf and Af are great.

The total heat values (Q) were obtained by integrating the curves of the calorimetric registers and are shown in Table 3. The average heat levels are between 4.75 and 7.07 J g^{-1}. These heat levels are very close to one another; however, in all cases the direct transformation heat is greater than the reverse transformation heat. This means that some martensitic plates do not return to the original β-phase because they are anchored by defects or by other martensitic plates. This explains why the shape-memory recovery seen in these alloys is not 100% and why it is necessary to raise the heat-treatment temperatures considerably above Af so that there is no permanent strain with respect to the original form.

The entropies obtained by differential heat variations with respect to temperature are shown in Table 4 and have mean values of between 1.74×10^{-2} and 2.48×10^{-2} J g^{-1} K^{-1}. The same trend can be observed in transformation heat as, in all cases, entropy is higher in direct transformation than in the reverse. However, the values of this thermodynamic quantity

TABLE 4

Transformation and re-transformation entropies (J g^{-1} K^{-1})

Alloy	$\Delta S^{\beta\to M}$	$\Delta S^{M\to\beta}$	$\overline{\Delta S}\times 10^{-2}$
1	2.62	−1.70	2.16
2	2.79	−2.18	2.48
3	2.38	−2.20	2.29
4	2.40	−2.00	2.20
5	2.26	−2.47	2.36
6	1.84	−1.63	1.74
7	2.17	−1.58	1.88
8	2.38	−1.90	2.14
9	2.67	−1.98	2.34
10	2.30	−1.90	2.10

are very similar in all the alloys studied because their chemical compositions are very similar.

The chemical energy associated with the transformation is obtained from the product of the average entropy and the equilibrium temperature. The values obtained from this energy are shown in Table 5 and vary from 4.96 to 7.29 J g^{-1}. The difference between chemical type energy and average measured heat gives the elastic contribution of the transformation. These results are shown in Table 5 and vary from 0.08 to 0.6 J g^{-1}. The frictional work values are obtained by calculating the area within the hysteresis cycle, as shown for alloy 8 in Fig. 2. The results, shown in Table 5, are between 0.25 and 0.39 J g^{-1}. This friction energy is mainly associated with everything that hinders β-martensite interphase movement and, in particular, the widening of the plates. The values for this energy in these alloys are higher in copper-based shape-memory alloys due to the interaction of vacancies and lineal defects on the movement of the martensitic plates. Thus the

TABLE 5

Chemical enthalpy, elastic contribution and friction energy

Alloy	ΔH_{chem} (J g^{-1})	ΔH_{el} (J g^{-1})	E_{fr} (J g^{-1})
1	6.07	0.31	0.25
2	7.29	0.22	0.26
3	6.34	0.10	0.28
4	6.47	0.49	0.31
5	6.82	0.60	0.33
6	4.96	0.21	0.33
7	5.56	0.09	0.34
8	5.67	0.24	0.36
9	5.62	0.16	0.37
10	5.78	0.08	0.39

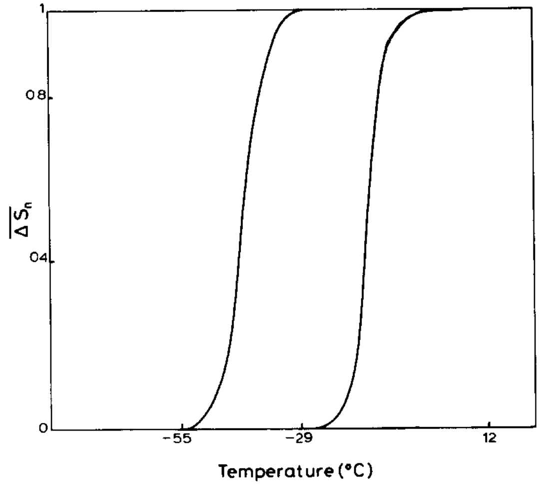

Fig. 2. Hysteresis cycle for alloy 8.

interconnection of the plates of different martensitic structures brings about an irreversible energy dissipation which is demonstrated in the frictional energy values obtained.

The friction energy increases on raising the electron-to-atom ratio in the alloys, as can be seen in the results of the ten alloys studied. This increase can be explained in the following way: on raising the electron-to-atom ratio from 1.43 to 1.46, the percentage of 2H martensite goes from 0% to 46% and, therefore, with an electron-to-atom ratio near 1.46 there will be a greater interconnection between 18R and 2H martensitic plates and, thus, greater friction energy [11,12].

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REFERENCES

1 E. Aernoudt, J. van Humbeeck, L. Delaey and W. van Moorleghem, Proc. Int. Conf. on Copper, Barga, Italy, 1986, pp. 7–8.
2 J.M. Guilemany and F.J. Gil, J. Mater. Lett., 10(3) (1990) 145–148.
3 J.H. Yang, C.S. Zhang, L.C. Zhao and T.C. Lei, Scr. Metall., 21 (1987) 259.
4 C. Seguí, J. van Humbeeck and E. Cesari, Actas del Congreso de la Real Sociedad Española de Física (Proceedings of the Congress of Spanish Royal Society of Physics), Palma de Mallorca, ISBN 84-7632-062-0, University Illes Balears, Spain, 1989, pp. 231–232.
5 J.M. Guilemany and F.J. Gil, An. Quím, 87 (1991) 36–41.
6 J. Ortín and A. Planes, Acta Metall., 36 (1988) 1873–1888.

7 C.M. Wayman and H.C. Tong, Scr. Metall., 11 (1977) 341–344.
8 H.C. Tong and C.M. Wayman, Acta Metall., 22 (1974) 887–890.
9 J.M. Guilemany and F.J. Gil, Rev. Metall., 25(6) (1989) 398–404.
10 J.M. Guilemany and F.J. Gil, Mater. Res. Bull., 25 (1990) 1325–1332.
11 L.C. Zhao, J.H. Yang, C.S. Zhang, T.C. Lei, H. Gu and Y.S. He, Scr. Metall., 20 (1986) 29–32.
12 F.J. Gil, Doctoral Thesis, University of Barcelona, Spain, 1989.