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The martensitic transformation entropy values of thermal and mechanical origin in shape memory Cu–Zn–Al single crystals

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Abstract

By using a calorimetric technique, the entropy values of the martensitic transformation of thermal origin have been determined and compared with those obtained by mechanical compression tests for the stress-induced martensitic transformation

INTRODUCTION

The martensitic transformation may be induced by an external stress at temperatures above start transformation temperature (Ms). This stress induced martensitic transformation occurs because the external stress assists the transformation, which is easily understood by considering that the martensitic transformation is caused by a shear-like mechanism [1].

The stress necessary to induce the formation of stress-induced martensite, $\sigma^{\beta \to M}$, is a linear function of temperature. A similar relationship exists for $\sigma^{M \to \beta}$. The stress levels $\sigma^{\beta \to M}$ and $\sigma^{M \to \beta}$ increase with increasing temperature, while the yield stress of the parent phase occurs before stress-induced martensite can be formed [2].

The slope of the linear graphs of stress vs. temperature can be described [3] by the equation

$$\frac{d\sigma}{dT} = \frac{\rho \Delta S}{\Delta \epsilon} \tag{1}$$

where ΔS is the entropy of the transformation under stress, ρ is the density, and $\Delta\epsilon$ is an average of the strains observed in the stress–strain curves.

From eqn. [1], it is possible to determine the transformation entropy ΔS by measuring the transformation strain $\Delta\epsilon$ and obtaining the linear function of stress vs. temperature.

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TABLE 1

Chemical compositions (at %), electron to atom (e/a) ratio, crystal orientations and martensitic transformation strains

Alloy	Cu (%)	Zn (%)	Al (%)	e/a	Crystal orientation	$\Delta\epsilon$
1	67 60	19 30	13 31	1 458	(111)	0 075
2	69 12	13 70	17.16	1.480	(111)	0.060
3	67.70	18.80	13.44	1.457	(111)	0 085
4	69 22	13.96	16.68	1.473	(211)	0 075
5	68 70	16 25	15.15	1.464	(311)	0 065
6	67 91	16.08	16.02	1 480	(321)	0.070
7	68 05	15 49	16 47	1 484	(210)	0.070
8	71.52	14.99	13.49	1.478	(221)	0.070

The change in entropy associated with the transformation $\beta \rightarrow$ martensite can be evaluated from the integration of the heat exchange Q between the temperatures Ms and finish martensitic transformation temperature (Mf) [4].

EXPERIMENTAL PROCEDURE

The calorimetric system used has already been described in previous papers [5,6]. The system allows the measurement of the characteristic temperatures and the entropy variations ΔS calculated by integration of Q over the transformation temperature range.

Compositions of the alloys and electron-to-atom ratios are shown in Table 1, as is the crystalline orientation of each single crystal, which was determined by the Laue method. These single crystals were obtained by the Bridgman method [7].

The cylindrical samples used (5 mm in diameter, 6 mm high, 400 mg in mass) have undergone a heat treatment consisting of 10 min at 850 °C and subsequent quenching in water at room temperature. This flow calorimeter measures differential signals (ΔT) by means of MELCOR thermopiles. The temperature was measured by means of a standard Pt-100 probe [5].

The compression tests were carried out on the same samples, after the calorimetric test, using a Houndsfield W machine at different temperatures. Once the load has been applied to the sample, it is placed in the furnace at 150 °C for 10 min, and the furnace is cooled to room temperature. The speed at which stress was applied to the sample was 10 MN m^{-2} s^{-1} [2].

RESULTS AND DISCUSSION

The values obtained for the martensitic transformation entropy of thermal origin range from 1.25 J mol^{-1} K^{-1} to 2.06 J mol^{-1} K^{-1}, as can be seen in Table 2.

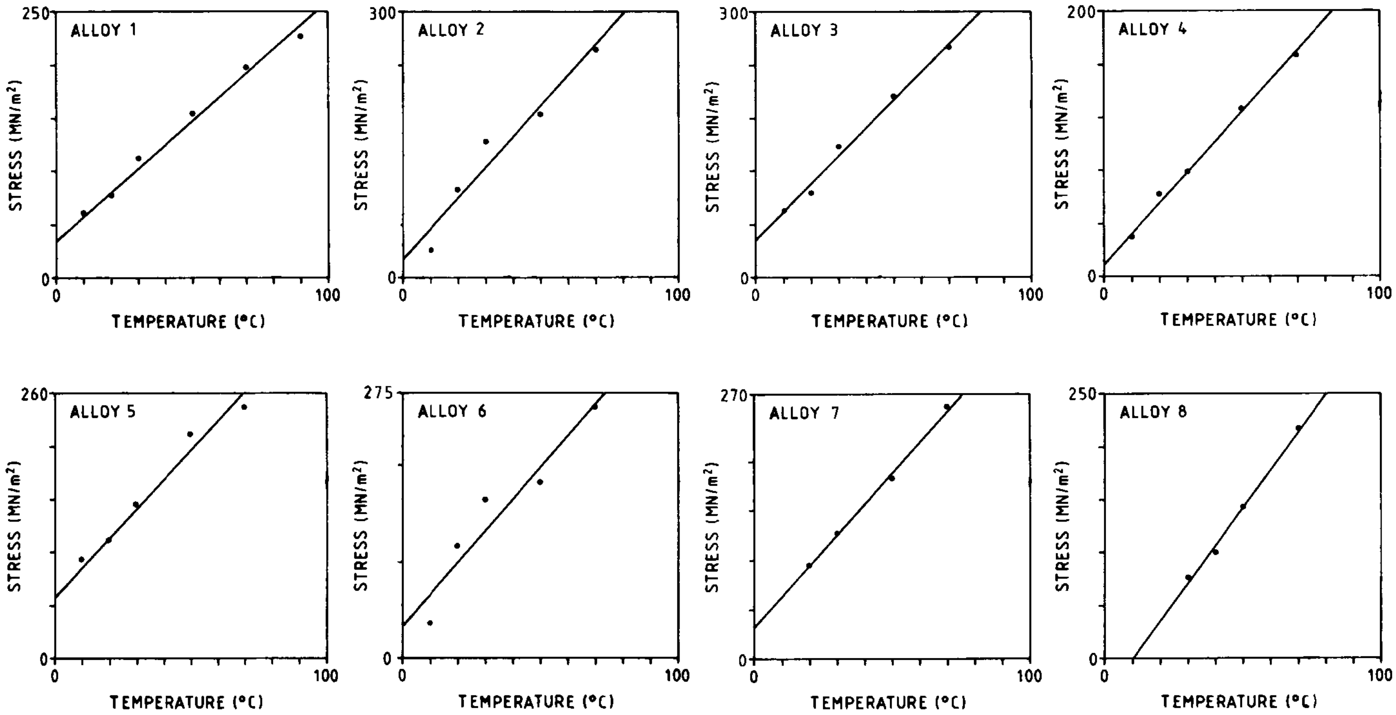

Fig. 1. Representations and equations of transformation stress vs test temperature

TABLE 2

Martensitic transformation entropy values (J mol^{-1} K^{-1})

Alloy	$\Delta S^{\beta\to\mathrm{M}}$	$\Delta S^{\beta\to\mathrm{SIM}}$	$\Delta S^{\beta\to\mathrm{SIM}} - \Delta S^{\beta\to\mathrm{M}}$
1	1.25	1.33	0.08
2	1.55	1.59	0.04
3	2.06	2.10	0.04
4	1.28	1.32	0.04
5	1.30	1.45	0.15
6	1.62	1.80	0.18
7	1.54	1.71	0.17
8	1.45	1.52	0.07

The results of the transformation stress ($\beta \to$ stress-induced martensite (SIM)) for each single crystal and for several test temperatures are shown in Fig. 1. As the temperature increases, an increase in stress can be observed. This increase can be explained by the fact that the stability of the β phase is greater as the temperature increases. The stress has to increase so that the mechanical energy may overcome the increased thermodynamic stability.

The average strain associated with the transformation has been obtained from the stress–strain diagrams; the results can be observed in Table 1. With these results, and considering the average density of the alloys, 7899 kg m^{-3}, the entropy value associated with the stress-induced martensite transformation has been calculated from eqn. (1).

The result for the stress-induced martensitic transformation entropy varies from 1.32 to 2.10 J mol^{-1} K^{-1}, as can be seen in Table 2. It can also be observed that the values of the entropy of mechanical origin are in all cases greater than those of thermal origin. This is because, in a stress-induced martensitic transformation, structural defects are created. These provoke a greater disorder in the system and therefore an increase in the entropy value.

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