The Gibbs free energies of thermal and stress-induced martensite formation in Cu–Zn–Al single crystal shape-memory alloys

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Abstract

The free energies of the martensitic transformation of both thermal and mechanical origin have been evaluated in Cu–Zn–Al single crystals. The free energy variation has been studied in relation to the applied stress for stress-induced martensite formation.

INTRODUCTION

Diffusionless transformation can be considered thermodynamically as a one-component system. The relation between the free energies of the martensite (m) and β-phases can be seen in Fig. 1a, which shows the change in chemical free energy of the martensite and β-phase with temperature where T_0 is the thermodynamic equilibrium temperature at which both β-phase and martensite are in equilibrium [1].

When not subjected to applied stress the martensitic transformation starts at M_s and the difference between β and martensite free energies, $\Delta G^{\beta \rightarrow m}$, at the M_s is the critical free chemical energy which brings about the transformation.

In general, the free energy change associated with a martensitic transformation can be written

$$\Delta G = \Delta G_c^{\beta \rightarrow m} + \Delta G_{nc}^{\beta \rightarrow m} \tag{1}$$

$\Delta G_c^{\beta \rightarrow m}$ has a negative value (below T_0) and is proportional to the amount of martensite formed, while $\Delta G_{nc}^{\beta \rightarrow m}$ is the non-chemical energy opposing the transformation, consisting principally of elastic energy and surface energy [2].

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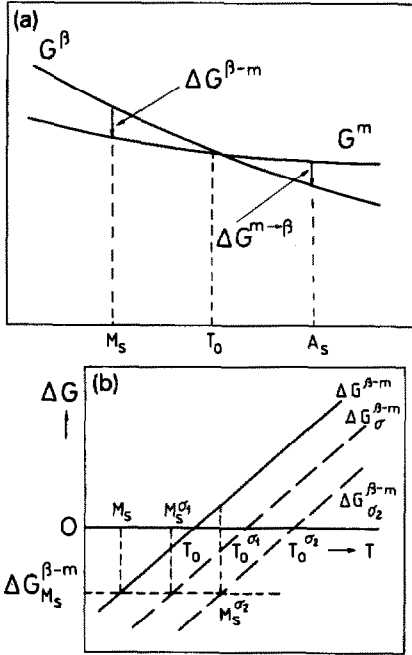
Fig. 1. a, Relation between the free energies of the martensite (m) and β-phase; b, Gibbs free energy versus temperature in relation to applied stress.

The free energy change upon martensitic transformation nucleation at $T = M_s$ is given by

$$\Delta G_{M_s}^{\beta \to m} = (T_0 - M_s)\Delta S^{\beta \to m} \tag{2}$$

Stress is also a variable in the martensitic transformation. The M_s^σ temperature is increased with application of stress (Fig. 1b), with a proportional shift of T_0 of T_0^σ. At a temperature $M_s^\sigma > T_0$, such as M_s, the free energy change consists of the thermal component

$$\Delta G_{t,M_s^{\sigma_1}}^{\beta \to m} = (T_0 - M_s^\sigma)\Delta S^{\beta \to m} \tag{3}$$

and the stress-induced component

$$\Delta G_{\sigma,M_s^{\sigma_1}}^{\beta \to m} = \sigma_a \epsilon_m = (M_s^{\sigma_1} - M_s)\Delta S^{\beta \to m} \tag{4}$$

σ_a being the applied stress and ϵ_m the total strain tensor associated with the transformation. This implies that once the martensite phase has been formed by stress-assisted nucleation, it is thermodynamically stable in the stress-free state. On the other hand, at temperatures $M_s^\sigma > T_0$, such as $M_s^{\sigma_2}$, the nucleation free energy is

$$\Delta G_{M_s^{\sigma_2}}^{\beta \to m} = \Delta G_{\sigma,M_s^{\sigma_2}}^{\beta \to m} - \Delta G_{t,M_s^{\sigma_2}}^{\beta \to m} \tag{5}$$

The stress-dependent term contains the nucleation free energy and a positive contribution by the chemical free energy difference opposing the transformation [3].

EXPERIMENTAL PROCEDURE

The calorimetric system used has already been described in previous papers [4,5]. The system allows the measurement of the characteristic temperatures, and the enthalpy (ΔH) and entropy (ΔS) variations calculated by integration of the calorimetric graph over the temperature–transformation range.

The compositions of the alloys and the electron-to-atom ratios are shown in Table 1; the single crystals were obtained by the Bridgman method [6].

The cylindrical samples (5 mm diameter, 6 mm high, 400 mg mass) underwent a heat treatment consisting of 10 min at 850°C following by quenching in water at room temperature. The flow calorimeter measures differential signals (ΔT) by means of Melcor thermobatteries. Temperature was measured by means of a standard Pt-100 probe [7].

The compression tests were carried out on the same samples, after the calorimetric test, using a Houndsfield W machine at different temperatures. The speed at which stress was applied to the sample was 10 MN m^{-2} s^{-1} [7].

The temperatures obtained for transformations of both thermal and mechanical origin, correspond to the first transformation cycle, because in successive cycles the transformation is produced at slightly higher temperatures. This is due to the fact that the presence of defects created by the different cycles favours martensitic transformation [8].

RESULTS AND DISCUSSION

Table 2 shows the results of the measurements of transformation temperatures, as well as the enthalpy and entropy associated with the $\beta \rightarrow$ martensite transformation. These thermodynamic quantities reach similar magnitudes

TABLE 1

Chemical compositions (wt.%) and electron-to-atom ratios of the alloys

Alloy	Cu	Zn	Al	e/a
A	76.4	8.04	15.56	1.480
B	77.2	8.15	14.65	1.470
C	73.0	6.15	20.85	1.457
D	76.4	7.81	15.79	1.473
E	75.8	7.81	16.36	1.478

TABLE 2

Transformation and equilibrium temperatures, and the enthalpy, entropy and free energy associated with the $\beta \to$ martensite transformation

Alloy	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_0 (K)	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (J mol^{-1})
A	277	252	269	283	280	412	1.48	4.45
B	301	278	291	306	304	419	1.43	4.29
C	267	251	255	273	270	361	1.94	5.82
D	273	253	262	283	278	342	1.26	6.30
E	279	262	269	283	281	391	1.94	3.88

in all the alloys because they are very similar in chemical composition. The equilibrium temperature was taken from the Tong and Wayman approximation [9]

$$T_0 = \tfrac{1}{2}(M_s + A_f) \tag{6}$$

which is more widely used in systems that show the thermoelastic martensitic transformation.

The Gibbs free energy for the thermal transformation is calculated by applying the eqn. (3) which yields values ranging from 3.88 to 6.30 J mol^{-1}, as show in Table 2. These values are lower than those obtained for other systems such as Cu–Al–Ni (29 J mol^{-1}) [10].

The calculation of the Gibbs free energy for stress-induced martensite formation is achieved by compression tests at different temperatures. The sample is kept at a constant temperature, stress is applied and, at a critical stress level, transformation takes place. The experimental temperature is M_s^σ for the critical applied stress. Table 3 gives the different applied stresses and the corresponding temperatures. By applying eqn. (4), the Gibbs free energy can be obtained for stress-induced martensitic transformation.

The results show that $M_s^\sigma > T_0$; this implies that the stress-dependent term contains the nucleation free energy and a positive contribution by the chemical free energy difference opposing the transformation in eqn. (5). Correspondingly, the martensitic plates may be formed by stress-assisted nucleation above T_0 but this is thermodynamically unstable in the stress-free state during temperature formation.

The theoretical model used in this paper is more simple than Patel and Cohen's but the results are just as accurate as theirs [11]. This model considers that the interaction between the applied stress and the transformation reduces the free energy of the system by the transformation strains.

The energy values increase as the temperature rises because raising the temperature stabilises the β-phase and makes greater stress necessary in order to produce transformation. These values are very similar to those of other copper-based alloys such as Cu–Zn and Cu–Al whose enthalpy energy

TABLE 3

Applied stress, transformation temperatures and free energies of the $\beta \rightarrow$ martensite stress-induced transformation

Alloy	σ (MPa)	M_s^σ (K)	ΔG (J mol^{-1})
A	30	283	8.9
	99	293	22.9
	152	303	38.5
	183	323	68.1
	256	343	97.7
B	40	303	2.8
	62	313	17.1
	76	323	31.3
	153	343	59.8
C	75	283	31.0
	94	293	50.4
	146	303	69.8
	202	323	108.7
	258	343	147.4
D	5	273	0.1
	30	283	12.6
	62	293	25.2
	79	303	37.8
	126	323	63.0
	166	343	88.2
E	10	283	7.7
	28	293	27.1
	100	303	46.5
	121	323	85.3
	180	343	124.1

for stress-induced transformation at 20°C was 12.5 J mol^{-1} [12] and 20.9 J mol^{-1} [13], respectively.

The significance of this different behaviour will be discussed with reference to the growth. The essential contribution to the growth process of a martensite plate is the thermal component of the Gibbs energy, $\sigma_a \cdot \epsilon_m$, which is expressed as the applied stress, σ_a, multiplied by the macroscopic shape-strain associated with the martensite plate growth. These driving energies are opposed by resistive energy, composed of several terms: the elastic strain energy stored due to the internal stress built up by the applied stress and the transformation strain; the interfacial energy of the $\beta/$ martensite interface; the defect energy due to the recoverable defects produced inside the martensite by the lattice-invariant shear; and finally, a dissipated energy due to the friction and irreversible defect production in the β-phase and martensite during transformation.

If the Gibbs free energy is plotted against applied stress, a linear relationship results, as can be seen in Fig. 2., which can be expressed by equations
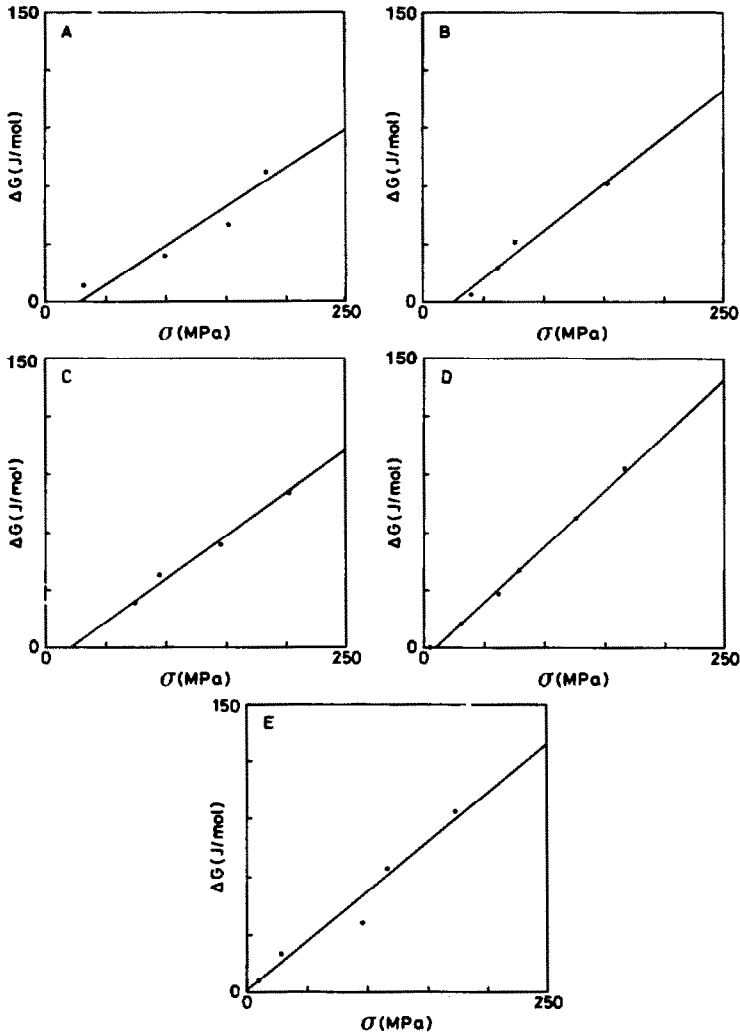
Fig. 2. Gibbs free energies of the stress-induced martensite versus the applied stress for β-Cu–Zn–Al single crystals.

of the type of eqn. (4), the slopes being the strain values associated with the transformation. The intersection along the stress axis corresponds to the dilational strain [14]

$$\epsilon_0^{\beta \rightarrow m}(1 + \cos 2\theta) \tag{7}$$

where ϵ_0 is the dilational transformation strain and θ is the angle between the applied stress and the habit plane normal.

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