Journal of Alloys and Compounds, *194* (1993) L9–L10
JALCOM 604

Letter

The influence of the electron-to-atom ratio on the martensitic transformation enthalpy and entropy values in Cu–Zn–Al shape memory alloys

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(Received June 26, 1992; in final form December 8, 1992)

Copper-based shape memory alloys with b.c.c. structures (β phases) undergo a number of different thermoelastic martensitic transformations. The relative stabilities of these different martensitic phases depend on the temperature, electron-to-atom ratio and on the level of externally applied stress [1, 2].

Three types of martensite can occur depending on electron-to-atom ratio: the α′-type, the β′-type and the γ′-type. The α′-type has an ABC stacking sequence and is internally twinned [3]. The β′-type martensite is characterized by a close packing of close-packed planes with the stacking sequence ABCBCACAB [4]. If the β phase shows a B2 order the martensite is called β′ and has the same stacking sequence (orthorhombic structure 9R). If the β phase is in an $L2_1$ order the martensite is called β'_1. The stacking order is ABCBCACABABCBCACAB (orthorhombic 18R) and these three structures can be ascertained from single orthorhombic cells.

The structure of the γ′ hexagonal-type martensite is characterized by an AB stacking of the close-packed planes [5]. Delaey and Cornelis [6] determined that with an electron-to-atom ratio near 1.49 a change in martensitic structure β′ to γ′ is produced.

In this study the electron-to-atom ratio at which a change in martensitic structure β′ to γ′ takes place is determined by means of the entropy changes of the martensitic transformation. Studies of the enthalpy and entropy have been performed according to the recent thermodynamic model proposed by Ortín and Planes [7] for the thermoelastic martensitic transformation with the possibility of the evaluation by means of calorimetric data.

Twenty-five polycrystalline alloys with different electron-to-atom ratios (from 1.45 to 1.50) and a grain size in perimeter of 54 μm were studied. Cylindrical test samples 5 mm in diameter, 2 mm high and weighing approximately 400 mg were submitted to heat treatment (850 °C for 10 min and water quenched at room temperature). The calorimetric measurements were performed 24 h after the heat treatment.

A flow multicell calorimeter measuring the differential signals (Δ*T*) by MELCOR FC06-32-06L thermobatteries made up of 32 thermocouples was used, the work temperature range was from −150 to 100 °C. The temperature was measured by Pt-100 standard sond. All the signals were digitalized by multichannel and stored on the computer. The sensitivity of the differential signal detectors was 400 mV W^{-1} at room temperature. The uncertainty in entropy values was less than 5% and that of the temperatures was 0.5 K. The heating–cooling rate was 1 °C min^{-1} [8, 9]. The system allowed the measurement of the characteristic temperatures. The entropy was obtained by integration of the corrected thermal power divided by the instantaneous temperature.

The entropies of martensitic transformation *vs.* the electron-to-atom ratio are shown in Fig. 1. The rela-

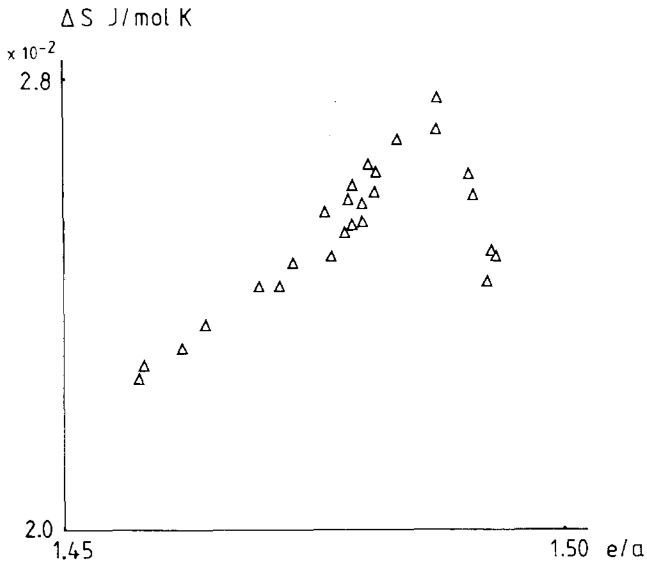

Fig. 1. Entropy values in relation to electron-to-atom ratio.

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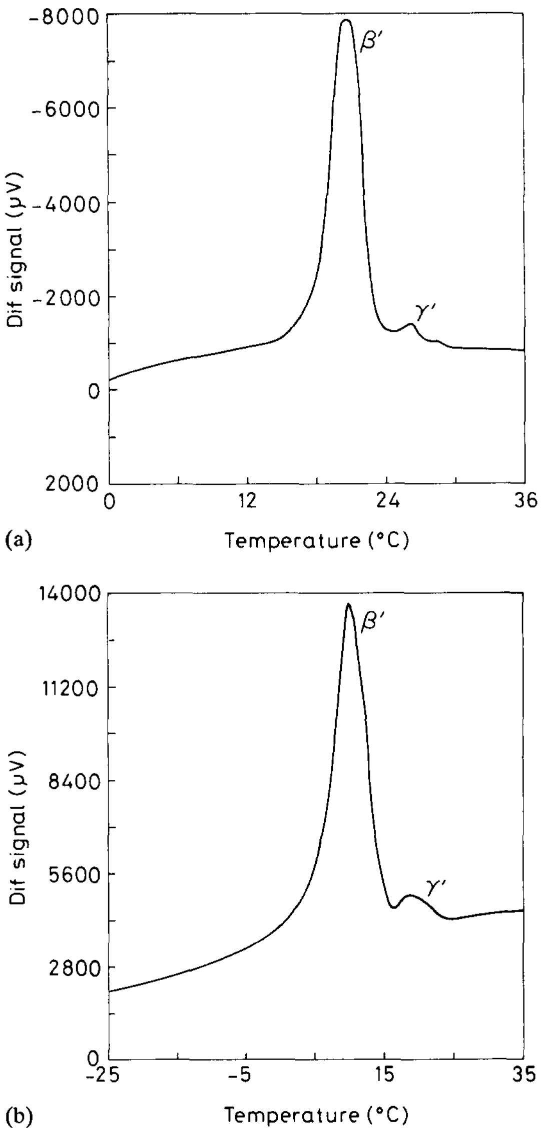

Fig. 2. (a) Calorimetric register of the heating cycle; (b) Calorimetric register of the cooling cycle.

tionship is increasing linear up to an electron-to-atom ratio of 1.485. From this point, the entropy values decrease. This change in behaviour is due to the appearance of the γ' martensite. The coexistence of the β' and γ' martensites provokes a greater disorder in the system and therefore an increase in the entropy value. Since the relative stability of γ' compared with β' martensite decreases with decreasing Al concentration [10], this double stage transformation must be associated with the thermally induced formation of two martensite types in the same specimen during cooling, and their separate reversion to the parent phase during heating. The coexistence of two types of martensite is shown in Fig. 2; these correspond to the calorimetric registers (heating and cooling cycles) for an alloy with an electron-to-atom ratio of 1.49, with two peaks of each type of martensite. The electron-to-atom ratio increases with Al content, producing a high disorder in the β structure being the more unstable martensitic transformation [11].

Acknowledgments

The present research was supported by the Comisioń Interministerial Cientifico y Técnico project MAT 92-1025-C02-02.

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