Journal of Thermal Analysis, Vol. 31 (1986) 559–566

PHASE TRANSFORMATIONS IN Cu—Al AND Cu—Zn—Al ALLOYS

J. Kwarciak

INSTITUTE OF PHYSICS AND CHEMISTRY OF METALS, SILEASIAN UNIVERSITY, 12 BANKOWA, 40–007 KATOWICE, POLAND

(Received July 18, 1985)

Phase transformations in Cu—12.4% Al and Cu—14.4% Zn—8.4% Al alloys were examined by DTA. The influence of the rate of temperature change on the sequence of phase transformations was studied. It was found that the rates of heating and cooling were the major factors determining the transformations which take place in these alloys.

In a simple Cu—Al system, several phase transformations may be observed. This circumstance, together with the fact that these alloys have been shown to exhibit a shape memory effect [1], is the reason why Cu—Al alloy and ternary Cu—Zn—Al base alloys have been investigated intensively for some years.

It is well known that during the slow cooling of Cu—Al alloy from the high-temperature β-phase, a eutectoid transformation occurs (Fig. 1). The α-phase is a solid solution of aluminium in copper; it transforms into the α_2-superstructure below 340° [2, 3]. These transformations are reversible during reheating, and the

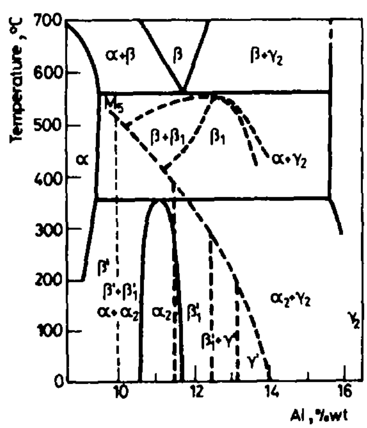

Fig. 1 Partial of phase diagram of Cu—Al system

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

sequence of transformation is then $\alpha_2+\gamma_2 \leftrightarrow \alpha+\gamma_2 \leftrightarrow \beta$. On rapid cooling of the β-phase (quenching in ice-water), a martensitic transformation occurs. First, however, ordering to the β_1-phase takes place. These transformations are reversible during rapid reheating, i.e. $\beta \leftrightarrow \beta_1 \leftrightarrow \beta'_1$, and this is connected with the shape memory effect in Cu—Al alloy [4]. However, if β'_1-martensite is slowly heated, it transforms into the β-phase and next into a eutectoid mixture. The sequence of transformations is then $\beta'_1 \rightarrow \beta_1 \rightarrow \alpha+\gamma_2 \rightarrow \beta$ [5, 6].

For rates of heating and cooling intermediate between very slow and rapid, it may be expected that these transformations will overlap. Hence, there are several phase transformations in Cu—Al alloy, depending on the rates of cooling and heating and on the chemical composition. The ternary Cu—Zn—Al alloys are important, because by varying the chemical composition it is feasible to change the characteristic temperatures of the transformations, and it is then possible to control the temperature at which the shape memory effect occurs.

The main object of the studies reported here was to examine the influence of the rates of heating and cooling on the phase transformations which take place in Cu—12.4 wt. % Al and Cu—14.4 wt. % Zn—8.4 wt. % Al, using DTA and X-ray methods.

Experimental procedure

The Cu—Al and Cu—Zn—Al alloys were prepared from 99.97% Cu, 99.95% Al and 99.95% Zn by induction melting. Polycrystal samples were homogenized at 800° in a helium atmosphere. Investigations were performed with a Mettler TA 1 Thermoanalyser and a Philips diffractometer. The heating and cooling runs, from 25° to 600°, were carried out in a protective helium atmosphere. Pure copper was used as standard. To determine the temperatures of phase transformations, cylindrical samples with a bored aperture were positioned directly at the end of the thermoelement. To determine the heats of transformations, samples were placed in a crucible, thereby simulating the conditions under which the calibration curve of the thermoelement was obtained. The calibration coefficient K, from the equation $\Delta H = KA$, where ΔH is the heat of the process and A is the area under the peak, was calculated over the range 100–600°. For a macro-DTA holder (DTA 20, ME 93523 Mettler crucible holder), with a Pt–PtRh thermocouple, using Al_2O_3 crucibles, the temperature-dependence of K is $K = a+bT^3$, where $a = 4.94$ and $b = 15.00$.

Additionally, phase analysis of specimens was performed with a Philips X-ray diffractometer. Filtered CuK_α radiation was used.

Results

A. Phase transformation during cooling

During the linear cooling of Cu—Al alloy at a rate below 2 deg/min, the high-temperature β-phase transforms into a eutectoid $\alpha+\gamma_2$-phase mixture (Fig. 2). Below 300°, the α-phase transforms into the α_2-superlattice. These transformations are seen as exothermic effects in the DTA curves. When the cooling rate was

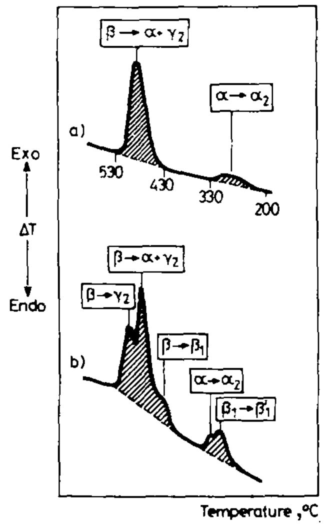

Fig. 2 DTA curves for Cu—12.4% Al alloy, obtained at the cooling rate (a) 2 deg/min and (b) 10 deg/min

between 4 and 25 deg/min, five exothermic DTA effects were found. Three of these overlap in the temperature interval 530–430°. These peaks are due to transformation of the β-phase into γ_2 and next into an $\alpha+\gamma_2$-phase mixture. The third effect is connected with the ordering process of that part of the β-phase which had not undergone eutectoid transformation, into the β_1-superlattice. In the temperature range 330–200°, two overlapping exothermic peaks are found, connected with the ordering process of the α-phase and martensitic transformation of the β_1-phase into β'_1. The results of X-ray measurements (Fig. 3) indicated that, after cooling of Cu—Al alloy at a rate of 2 deg/min, eutectoid $\alpha+\gamma_2$-phases with ordered α_2-phase were obtained [4].

After cooling at a rate of 10 deg/min, the eutectoid and martensite mixture was obtained. After cooling at a rate of 25 deg/min, mainly martensite β'_1 was obtained.

For Cu—Zn—Al alloy, no change was observed in the form of the $\beta\rightarrow\alpha+\gamma_2$

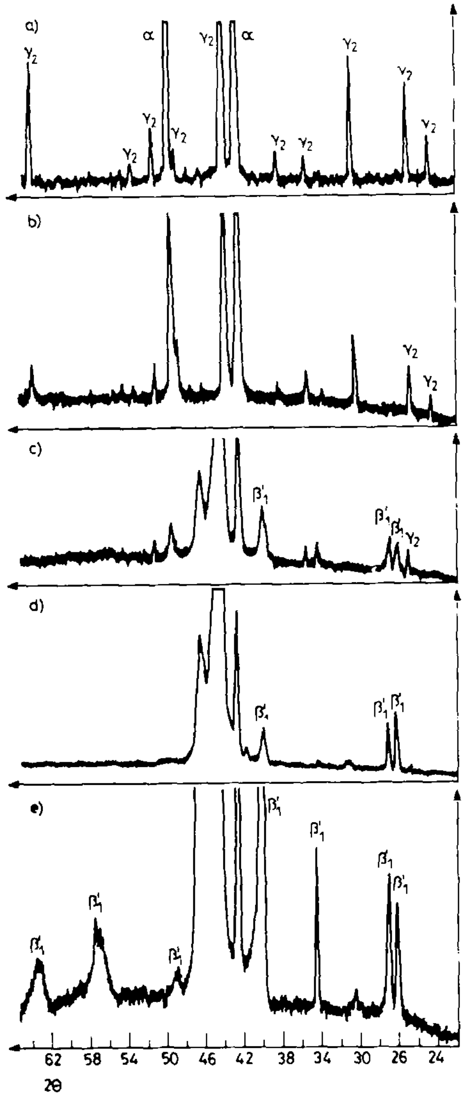

Fig. 3 X-ray diffraction pattern obtained for Cu—12.4% Al alloy after cooling the samples at the rates (a) 2 deg/min, (b) 6 deg/min, (c) 10 deg/min, (d) 25 deg/min, (e) after quenching from 700° into ice-water. The same results obtained for Cu—14.4% Zn—8.4% Al alloy

transformation DTA effect with increase in the cooling rate (Fig. 4). However, with increasing cooling rate, ordering of the β-phase takes place and next the martensitic transformation occurs, as is indicated by the DTA peaks and X-ray measurements (Figs 3 and 4).

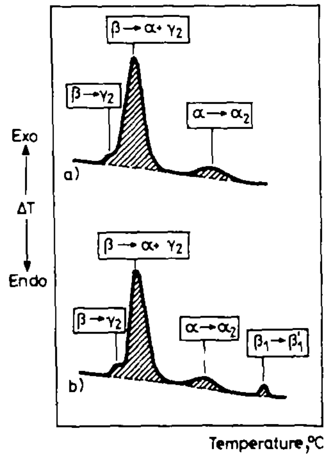

Fig. 4 DTA curves for Cu—14.4% Zn—8.4% Al alloy obtained at the cooling rate (a) 2 deg/min and (b) 10 deg/min

For both investigated alloys, the characteristic temperature of the eutectoid transformation decreases when the cooling rate is increased. Moreover, as obtained from thermal effect areas, the heat of eutectoid transformation in Cu—Al alloy decreases when the cooling rate increases (Fig. 5). The reason for this effect is the fact that part of the β-phase does not change into eutectoid, but passes to ordered β_1-phase and next into martensite β'_1.

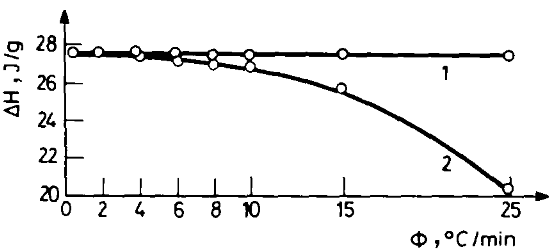

Fig. 5 Thermal effects values obtained for $\alpha + \gamma_2 \rightarrow \beta$ (curve 1) and $\beta \rightarrow \alpha + \gamma_2$ (curve 2) transformations after different rates of heating and cooling

This effect could explain the different values of the heat of eutectoid transformation given in the literature [7–10]. During reheating of Cu—Al alloy, a stable value of the heat of the $\alpha + \gamma_2 \rightarrow \beta$ transformation may be obtained. For Cu—Zn—Al alloy, no change was observed in the area of the DTA effect when the cooling rate was increased, and the heat of the $\beta \rightarrow \alpha + \gamma_2$ transformation was 16.5 J/g. For this alloy, the $\beta \rightarrow \alpha + \gamma_2$ and $\beta \rightarrow \beta_1$ transformations take place simultaneously, as is evidenced by the single DTA peak. It is difficult to separate the heats of the two overlapping transformations.

B. Phase transformations during heating

After cooling of the investigated copper alloys at different rates, different phase compositions were obtained. Because of this, various phase transformations occurred during reheating. When the Cu—Al alloy was cooled at a rate of 2 deg/min, during reheating two endothermic effects were observed in the DTA curve (Fig. 6). These effects are associated with disordering of the α_2-phase and the $\alpha+\gamma_2 \rightarrow \beta$ transformation. For a sample previously cooled at a rate of 10 deg/min, a small but distinct effect was also observed at 510°, associated with transformation of the β_1-phase into β. The martensite β'_1 changes into the β_1-phase in the same temperature interval (280–350°) as the disordering process of the α_2-phase. Next,

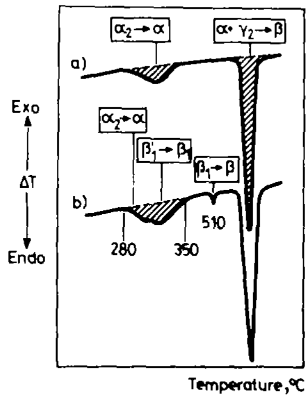

Fig. 6 DTA curves obtained during reheating of the Cu—12.4% Al after cooling at the rates (a) 2 deg/min and (b) 10 deg/min. The rate of heating 6 deg/min

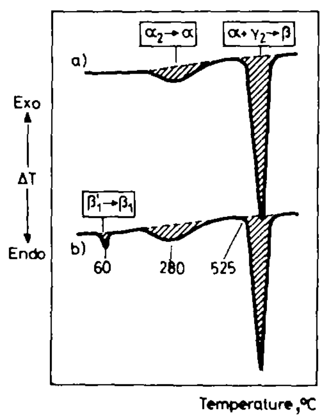

Fig. 7 DTA curves obtained during reheating of the Cu—14.4% Zn—8.4% Al alloy after cooling at the rate (a) 2 deg/min and (b) 10 deg/min. The rate of heating 6 deg/min

the β_1-phase transforms into the β-phase at 510°, and the $\alpha+\gamma_2$ mixture transforms into the β-phase at 560°. A similar phase transformation sequence was observed for a sample previously cooled at 25 deg/min.

In ternary Cu—Zn—Al alloy, the reverse martensitic transformation and disordering process of the α_2-phase take place in different temperature intervals (Fig. 7). The phase transformation sequence, however, was, similar to that found in Cu—Al alloy.

The phase transformations which take place during heating of the martensite of Cu—Al and Cu—Zn—Al alloys are presented in [11, 4].

Conclusions

The rate of heating and/or cooling is the major factor determining the transformations which take place in the investigated copper—base shape memory alloys. During heating and cooling of the alloys at a rate below 2 deg/min, the sequence of phase transformations is $\beta \leftrightarrow \alpha+\gamma_2 \leftrightarrow \alpha_2+\gamma_2$. For rates of cooling higher than 2 deg/min, two competitive transformations of the β-phase overlap, i.e. $\beta \rightarrow \alpha+\gamma_2 \rightarrow \alpha_2+\gamma_2$ and $\beta \rightarrow \beta_1 \rightarrow \beta'_1$. If the rate of cooling increased, the latter of the two competitive transformations starts to predominate.

These transformations are reversible during reheating of the alloys, i.e. the reverse martensitic transformation, disordering of the α_2-phase and β-phase formation take place.

References

1 H. Warlimont and L. Delaey, Martensitic Transformation in Copper-Silver and Gold—based Alloys, Pergamon Press, 1974.
2 W. Gaudig and H. Warlimont, Z. Metallkde, 60 (1969) 488.
3 W. Gaudig and H. Warlimont, Acta Met., 26 (1978) 1023.
4 J. Kwarciak, Z. Bojarski and H. Morawiec, to be published in Journal of Material Science.
5 A. B. Greninger, Trans. AIME, 133 (1939) 204.
6 G. Occampo, Sur la décomposition thermique après trempe de la β phase de l'alliage Cu—10.1% Al—influence du nickel et du fer, Thesis, Paris 1980.
7 D. Cheetham and N. Ridley, Met. Trans., 4 (1973) 2549.
8 S. D. Kulkarni, Acta Met., 21 (1973) 1539.
9 S. D. Kulkarni, Acta Met., 21 (1973) 1461.
10 D. Cheetham and F. R. Sale, Acta Met., 23 (1975) 1479.
11 J. Kwarciak, Proceedings of the 8th International Conference on Thermal Analysis, Bratislava, Czechoslovakia, August 19–23, 1985, p. 665.

Zusammenfassung — Phasenübergänge in den Legierungen Cu – 12,4% Al und Cu – 14,4% Zn – 8,4% Al wurden thermoanalytisch untersucht. Der Einfluß der Geschwindigkeit der Temperaturänderung auf die Reihenfolge der Phasenübergänge wurde untersucht. Aufheiz- und Abkühlgeschwindigkeit sind die wichtigsten Faktoren, von denen die Phasenübergänge in diesen Legierungen abhängen.

Резюме — Методом ДТА исследованы фазовые превращения сплавов медь — 12,4% алюминия и медь – 14,4% цинка – 8,4% алюминия. Изучено влияние скорости изменения температуры на последовательность фазовых превращений. Найдено, что скорости нагрева и охлаждения являются главными факторами, определяющие происходящие в этих сплавах превращения.