JOURNAL OF MATERIALS SCIENCE **32** (1997) 6299–6303

Influence of silver additions on the structure and phase transformation of the Cu–13 wt % Al alloy

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The influence of silver additions on the structure and phase transformation of the Cu–13 wt % Al alloy was studied by differential thermal analysis, X-ray diffraction, scanning electron microscopy and energy dispersive analysis of X-rays. The results indicate that the presence of silver modifies the phase-stability field, the transition temperature and the structure of the alloy. These effects are more pronounced for silver concentrations up to 8 wt %.

1. Introduction

The Cu–Al alloys present good mechanical properties, depending on the aluminium content and good chemical stability. For compositions near to 13 wt % Al, the β (Cu_3Al) phase is stable from 567 °C, and for lower temperatures, the alloy shows two phases, α (solid solution of aluminium in copper) and γ (Al_4Cu_9) [1]. The rates of heating and cooling affect the transformations that occur in this alloy [2]. During rapid quenching from the temperature range where the β phase is stable the diffusion processes required for the formation of the equilibrium phases are suppressed, and the β-phase transforms to the β′ acicular martensitic phase [3].

The addition of silver to the Cu–Al alloy modifies its mechanical properties and the stability of the β-phase. The hardness of the alloy is increased, probably due to the presence of silver precipitates [4, 5]. It also affects the electrical resistivity of the alloy. Some inflections in the electrical resistivity versus temperature curves have been attributed to the dissolution and coalescence of silver precipitates [6]. Recently, it has been shown that the addition of silver improves shape-memory properties, giving martensitic transformation temperatures well above 200 °C [7].

In this work, the influence of silver concentration on the thermal behaviour of the Cu–Al–Ag alloy was examined by differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDX). The results obtained in Cu–Al–Ag alloys with 13 wt % Al and 2, 4, 6, 8, 10, 12, 14 and 16 wt % Ag, were compared with those obtained in a Cu–13 wt % Al alloy.

2. Experimental procedure

The Cu–Al and Cu–Al–Ag alloys were prepared from 99.97% Cu, 99.95% Al and 99.98% Ag by induction melting in an argon atmosphere. Thermal investigations were performed with a Perkin–Elmer 1700 Thermoanalyser using powder samples. The heating runs, from 200–900 °C and 20 °C min^{-1}, were carried out in a compressed air atmosphere. The identification of the phases was made using an HZG-4B diffractometer and a Jeol JSM-T330A SEM with a Noran energy dispersive X-ray microanalyser.

The samples for metallographic examination were annealed at 850 °C for 120 h for homogenization, and water quenched after 2 h annealing at each temperature.

3. Results and discussion

Fig. 1 shows the DTA curves obtained for the Cu–13 wt % Al alloy (A) and for the Cu–13 wt % Al–Ag alloys (B = 2 wt % Ag; C = 4 wt % Ag; D = 6 wt % Ag; E = 8 wt % Ag; F = 10 wt % Ag; G = 12 wt % Ag; H = 14 wt % Ag; I = 16 wt % Ag). Curve (A) shows only one peak (peak 1, endothermic), at about 560 °C, due to the α + γ → β eutectoid transformation as expected from the binary phase diagram [1]. Curve B shows, in addition to the peak shown by curve A, another peak (peak 2, exothermic), at about 300 °C. This exothermic peak diminishes in intensity as the silver concentration is raised, as can be clearly seen on curves B–D, but with decreasing intensity in this order. The presence of this endothermic peak seems to indicate some structural change which is related to the silver concentration. It is interesting to

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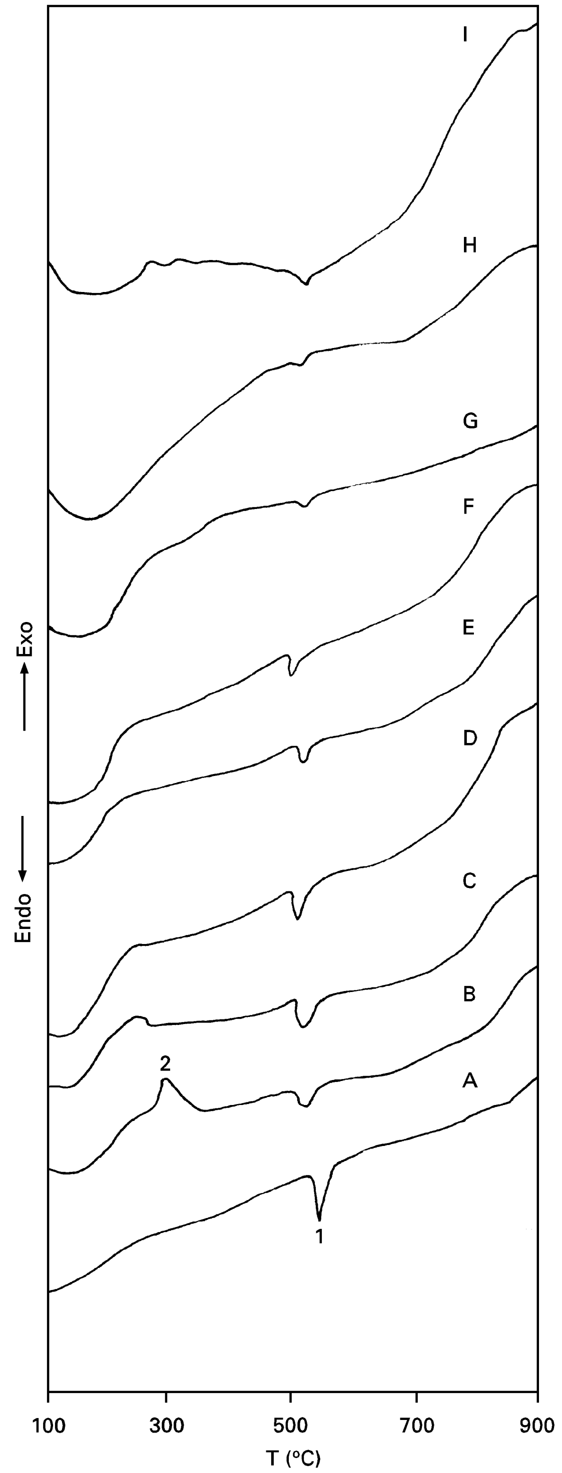

Figure 1 DTA curves for the nine studied alloys, showing two peaks for alloys B (2 wt % Ag), C (4 wt % Ag), D (6 wt % Ag), E (8 wt % Ag) and F (10 wt % Ag), and just one for alloys A (0 wt % Ag), G (12 wt % Ag), H (14 wt % Ag) and I (16 wt % Ag).

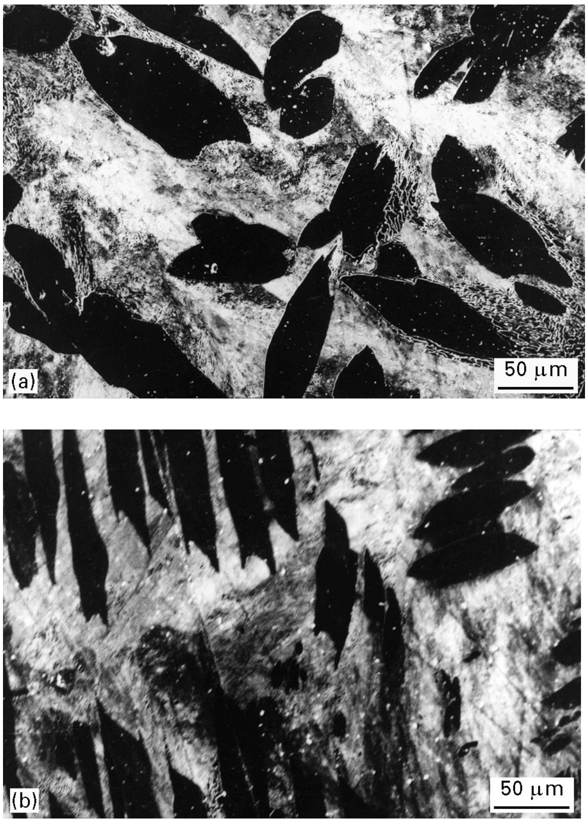

Figure 2 Scanning electron micrographs of alloy A (Cu–13 wt % Al): (a) annealed at 850 °C for 120 h, and (b) quenched from 300 °C. The black grains are the γ-(Al_4Cu_9) and the matrix corresponds to the eutectoid structure.

note that for silver concentrations greater than 8%, peak 2 completely disappears, as shown on curves G–I. The presence of peak 2 has been previously found by the authors [7] using a DSC with higher energy resolution. Thus, it may be possible that the DTA is not capable of detecting the energy released involved during the transformation for these curves.

The position of peak 1 on curves B–F is almost the same at about 530 °C and a little different from curve A (≈ 560 °C). On curves G–I, this peak is at about 550 °C. Based on these results, the position of peak 1 also seems to be influenced by the silver concentration. It should be noted that the presence of peak 2 and the shift of peak 1 both are verified at the same silver concentration range.

Fig. 2a shows the scanning electron micrograph for the alloy with Cu–13 wt % Al (alloy A) after annealing and for the same alloy after quenching from 300 °C (Fig. 2b).

Fig. 3a shows the scanning electron micrograph for the alloy with Cu–13 wt % Al–2 wt % Ag (alloy B) after annealing and for the same alloy after quenching from 300 °C (Fig. 3b). On these micrographs, the dark phase is γ (Al_4Cu_9) and the matrix is the eutectoid $\alpha + \gamma$, α being a solid solution of aluminium in copper. It is possible to see that the phases on Figs 2 and 3 are similar, but when silver is added to the alloy, the size of the γ phase is modified at 300 °C (Fig. 3b), compared with the same phase in the alloy without silver (Fig. 2b). The grains of the γ-phase become smaller in the alloy with silver and remain almost unchanged in the alloy without silver.

Fig. 4 shows the X-ray diffraction pattern obtained for the alloy A after annealing (Fig. 4a) and after quenching from 300 °C (Fig. 4b) and 600 °C (Fig. 4c). Fig. 5(a–c) show the X-ray diffraction patterns obtained for alloy B under the same conditions. It can be seen that the only phase change verified on both alloys is the $\beta \leftrightarrow \alpha + \gamma$ eutectoid transformation.

These results seem to indicate that the presence of silver modifies the stability range of the β-(Cu_3Al)

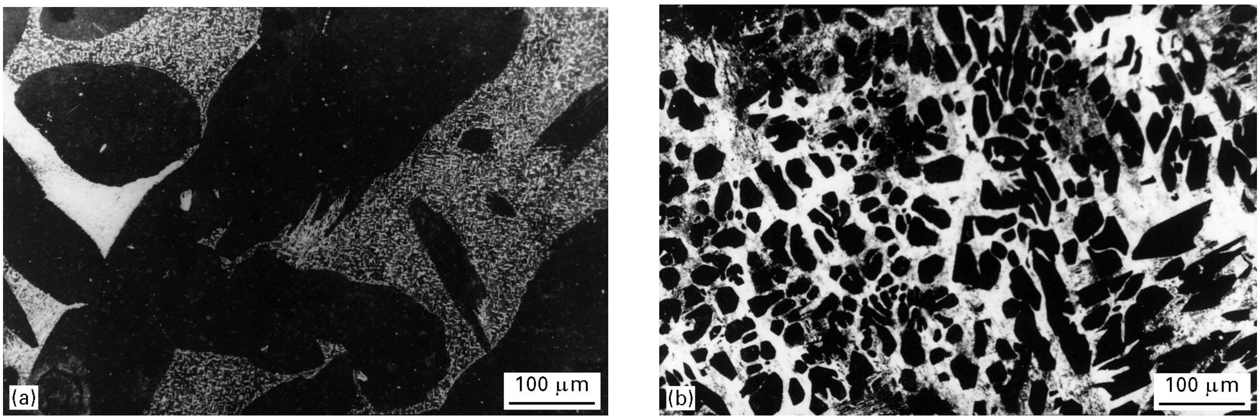

Figure 3 Scanning electron micrographs of alloy B (Cu–13 wt % Al–2 wt % Ag): (a) annealed at 850 °C for 120 h, and (b) quenched from 300 °C, showing the refinement of the γ-phase grains.

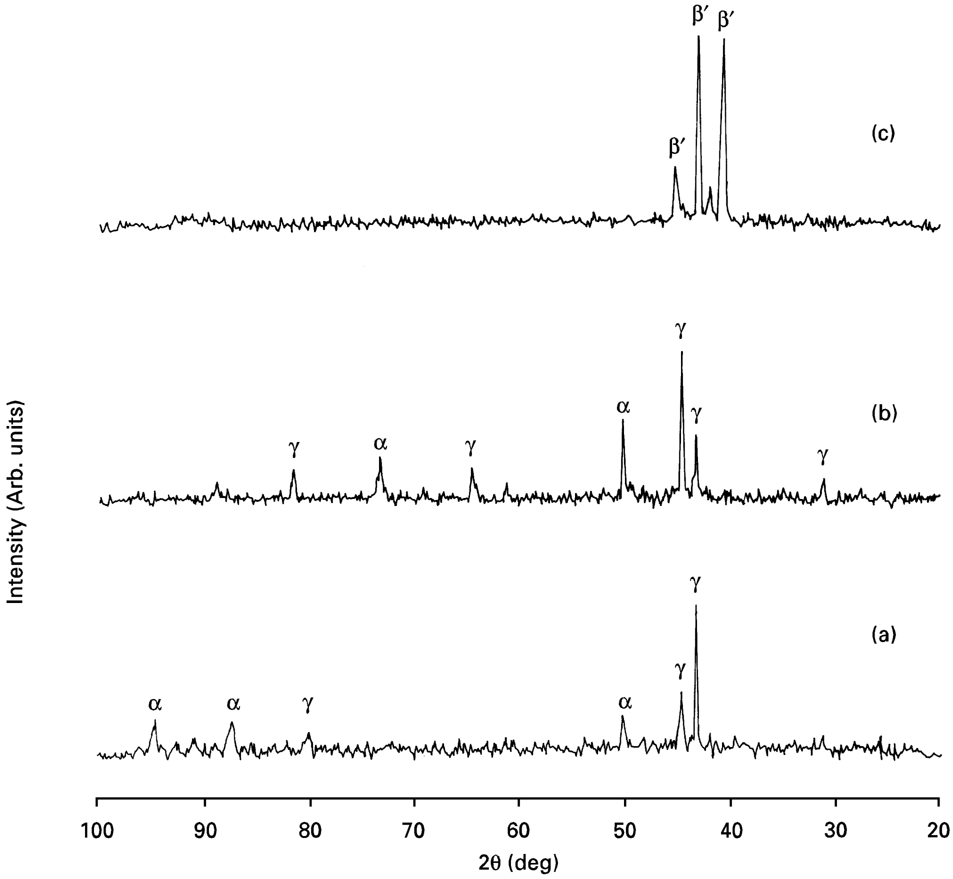

Figure 4 X-ray diffraction pattern obtained for alloy A: (a) annealed, (b) quenched from 300 °C, and (c) quenched from 600 °C. The diffractograms indicate that the α + γ ↔ β eutectoid transformation is the only phase change occurring.

phase. The eutectoid transformation occurs at a temperature slightly lower than that verified for the Cu–13 wt % Al alloy. This change is more evident for silver contents up to 6 wt % Ag. For additions higher than 8 wt %, the beginning of the transformation occurs in a temperature close to that verified for the Cu–Al alloy, as shown by the position of the peak between 500 and 600 °C (peak 1) on the DTA curves of Fig. 1.

As can be seen in Fig. 6a and b for alloy B, the γ-phase seems to be dissolved in the matrix as the temperature is raised. In Fig. 6a, corresponding to the alloy quenched from 600 °C, it is possible to see the grains of the γ-phase and the β-phase martensitically transformed, on quenching, from the β-phase, as already detected by XRD (see Fig. 5c). When this alloy is quenched from 700 °C (Fig. 6b), the eutectoid reaction is already completed and only a martensitic structure can be seen. So, this reaction must be occurring with the consumption of the γ-phase. If the grains become smaller with silver addition, the surface area where the reaction occurs increases and the free energy per unit volume associated with the grain boundaries also increases, favouring the reverse transformation α + γ → β, thus increasing the stability of the β-phase. This could account for the decrease of the temperature

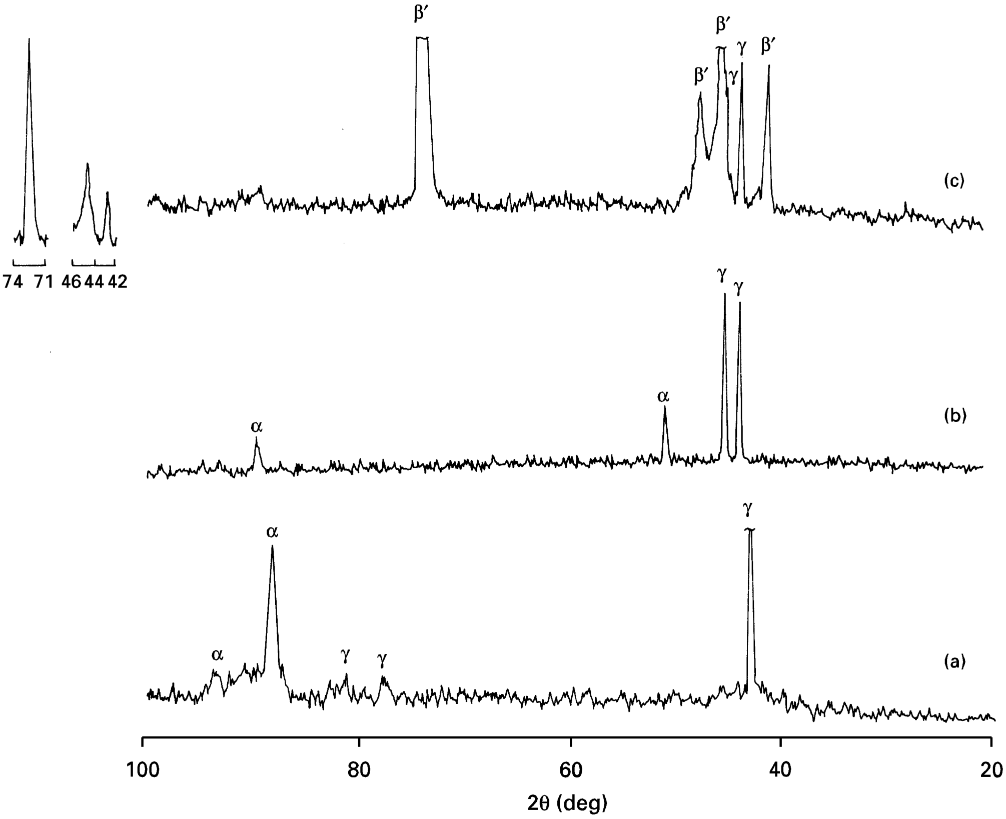

Figure 5 X-ray diffraction pattern obtained for alloy B under the same conditions as Fig. 4, and showing the same transformation.

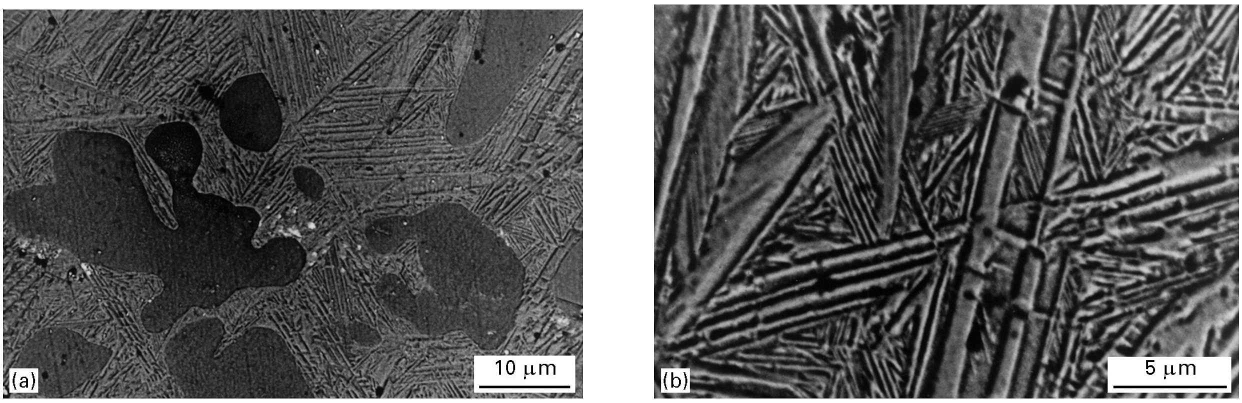

Figure 6 Scanning electron micrographs of alloy B: (a) quenched from 600 °C, showing the grains of the γ-phase and β′-phase (which has martensitically transformed) as the matrix, and (b) quenched from 700 °C, showing only the martensitic structure.

for the eutectoid reaction in alloys with silver concentration lower than 8 wt %.

The presence of peak 2 on DTA curves seems to be due also to the addition of silver to the Cu–Al alloy. This second peak is more evident at lower silver contents and is not clearly observed for compositions above 6 wt % Ag. Peak 2 is produced by the reverse martensitic transformation [7] on heating due to the stability of the β-phase at lower temperatures, as has been previously reported [8]. When the alloy has a higher amount of martensite, the exothermic peak exhibits a high energy released and, on the other hand, as there is a lower amount of $\alpha + \gamma$ phases, the peak of the re-transformation to β-phase is small. On increasing the silver content, the presence of α_2 phase (solid solution of aluminium in silver) reduces the amount of $\alpha + \gamma \rightarrow \beta$ transformation (Fig. 7a), decreasing the height of the endothermic peak.

The presence of silver seems to introduce a refinement of the γ-phase grains, at about 300 °C. Data obtained from BEI and EDX for alloy E (Fig. 7b) show the presence of small silver-rich precipitates on the grain boundaries of the γ-phase. The refinement is more pronounced for lower silver contents and seems to disappear when this content is higher than 8 wt % Ag, when a new silver-rich phase is observed in the range of temperatures considered in this work.

This refinement of the grains on the Cu–Al–Ag alloys with silver content up to 6% may be explained by a mechanism similar to that proposed by Shewmon

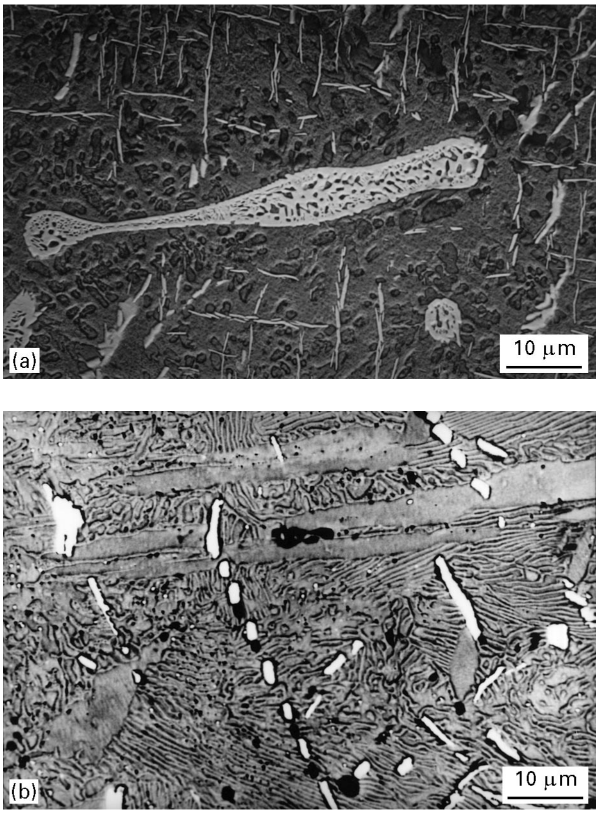

Figure 7 Scanning electron micrographs (BEI) of (a) alloy H (14 wt % Ag) quenched from 850 °C, and (b) alloy E (8 wt % Ag) quenched from 500 °C, showing the silver-rich precipitates (white) on the matrix.

[9]. In a pure metal, all boundaries have the same mobility, and any differences in the interface velocity are due to impurity adsorption at grain boundaries, that is, the impurity atoms are "bound" to the boundary. In an alloy in which the solute segregates to the boundary, this solute must be dragged along by the boundary and this decreases substantially the mobility of the boundary. The major factors that influence the boundary mobility are temperature, impurity concentration, relative orientation of the grains, and to a lesser extent, the orientation of the boundary itself. The reduced effect of impurities at high temperatures is due to its lower concentration. If the alloying element forms a fine precipitate it can have a more pronounced effect on grain-growth inhibition. At higher temperatures, the precipitate will often coarsen and/or go into solution. Thus, up to a given temperature the precipitate will inhibit grain growth and keep the grain size small. At some critical temperature, the particles will partially dissolve and grain growth starts again.

In this work, the temperature and the silver concentration seem to be the main factors related to the production of a grain refinement.

4. Conclusion

The addition of silver to the Cu–13 wt % Al alloy up to 10 wt % Ag makes the $\alpha + \gamma \leftrightarrow \beta$ eutectoid transformation start at about 530 °C, instead of 565 °C, as for the Cu–13 wt % Al alloy, hence, the stability range of the β (Cu_3Al) phase is increased in the alloys with silver. Above 10 wt % Ag, the situation is closer to that for the alloy without silver.

The presence of silver seems to produce a refinement of the γ-phase at about 300 °C. The presence of silver is also responsible for a second DTA peak on heating, which is related to martensitic re-transformation.

The relationship between the changes of the eutectoid transformation temperature, and the change in structure of the alloys with the addition of silver indicate that the dissolution of silver is more effective up to 8 wt % Ag, and for higher silver contents the presence of silver-rich phase, as verified by X-ray diffraction and EDX, gives the alloy a behaviour closer to that of the Cu–13% Al alloy.

Acknowledgement

The financial support from FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) is greatly appreciated.

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Received 25 March 1996
and accepted 18 April 1997