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INFLUENCE OF SILVER ADDITIONS ON THE THERMAL BEHAVIOR OF THE Cu–8 MASS% Al ALLOY

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Abstract

The influence of additions of 2, 4, 6, 8, 10 and 12 mass% Ag on the thermal behavior of the Cu–8 mass% Al alloy was studied using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD). The results indicate that the presence of silver introduces new thermal events, due to the formation of a silver-rich phase and, for additions of 10 and 12 mass% Ag, it is possible to verify the formation of the γ_1 phase (Cu_9Al_4) and the metastable transitions which are only observed in alloys with a minimum of 9 mass% Al.

Keywords: copper-based alloys, DSC, silver additions, thermal behavior

Introduction

The Cu–Al alloys present good mechanical properties, depending on the aluminum content and good chemical stability. Additions of Ag to the Cu–Al alloy improve its stress corrosion resistance [1], hardness [2] and introduce some changes in the microstructure [3], in the kinetics of eutectoid decomposition [4] and in the aging characteristics of the alloys [5]. The phases in the Cu–Al–Ag alloy are structurally analogous to those present in the binary systems, without ternary intermediate phases [6, 7].

In this work, the influence of additions of 2, 4, 6, 8, 10 and 12 mass% Ag on the thermal behavior of the Cu-8 mass% Al alloy was studied using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD), for annealed and quenched samples.

Experimental

The alloys were prepared in an induction furnace under argon atmosphere, using 99.97% copper, 99.95% aluminum and 99.98% silver as starting materials. Results from chemical analysis indicated a final alloy composition very close to the nominal one, with Pb, Fe and Mn as main impurities (concentration less than 100 ppm). Cylin-

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drical samples with 2.0 cm diameter and 6.0 cm length were cut in disks of 0.4 cm thickness and small square pieces of about 0.3 cm length were used as solid samples for DSC analysis. The disks were cold rolled for optical and scanning electron microscopy. The samples were annealed during 120 h at 850°C for homogenization. After annealing, some of them were equilibrated at 850°C for one h and then quenched in iced water.

DSC data were obtained using a TA 2910 thermal analyzer. After the heat treatments, the samples were polished, etched and examined by SEM using a Jeol JSM T330A. The XRD diagrams were obtained using a Siemens D5000 X-ray diffractometer with filtered CuK_α radiation and solid (not powdered) samples.

Results and discussion

Figure 1 shows the DSC curves obtained for the alloys studied, at a heating rate of 20°C min^{-1} for annealed samples. All curves show an endothermic peak at about 315°C which is associated with the disordering of the α_2 phase [8]. The curves for the alloys containing 10 and 12% Ag show another endothermic peak at about 570°C. As observed for Cu–Al alloys with more than 9% Al [9], this peak may be attributed to the (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation, but now in the presence of Ag. These results indicate that additions of about 10% Ag to the Cu–8 mass% Al alloy may induce the formation of the γ_1 phase (Cu_9Al_4) in this alloy, with a shift in the equilibrium concentration to the eutectoid range.

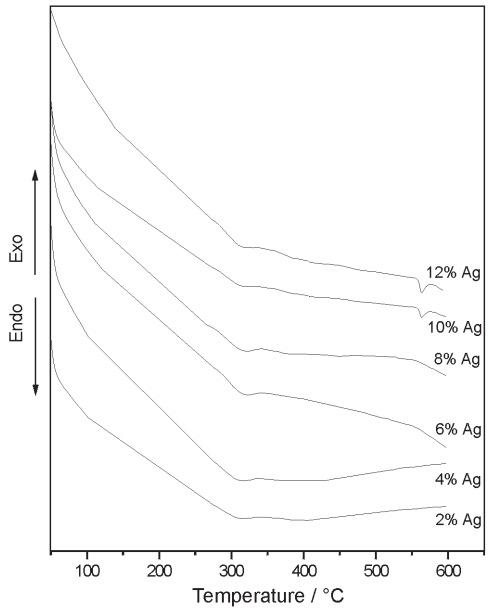

Fig. 1 DSC curves obtained for the alloys after annealing. Heating rate 20°C min^{-1}

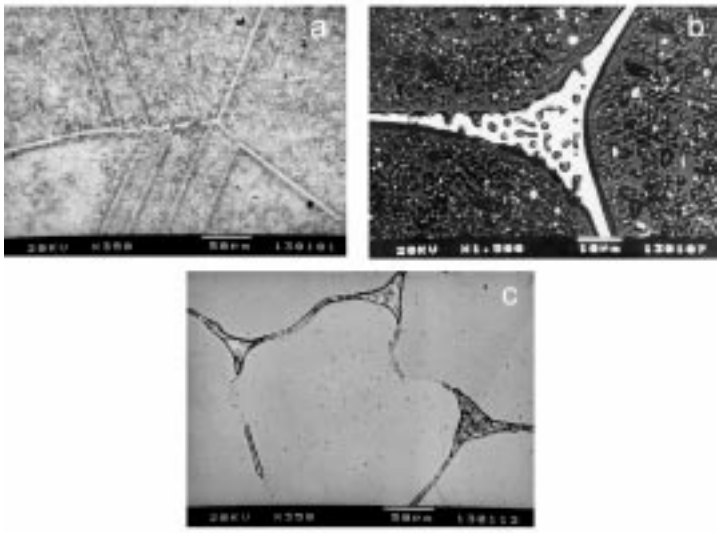

Fig. 2 Scanning electron micrographs obtained for the Cu–8 mass% Al–12 mass% Ag alloy: a – after annealing; b – after quenching from 315°C; c – after quenching from 800°C back-scattered electron imaging (BEI)

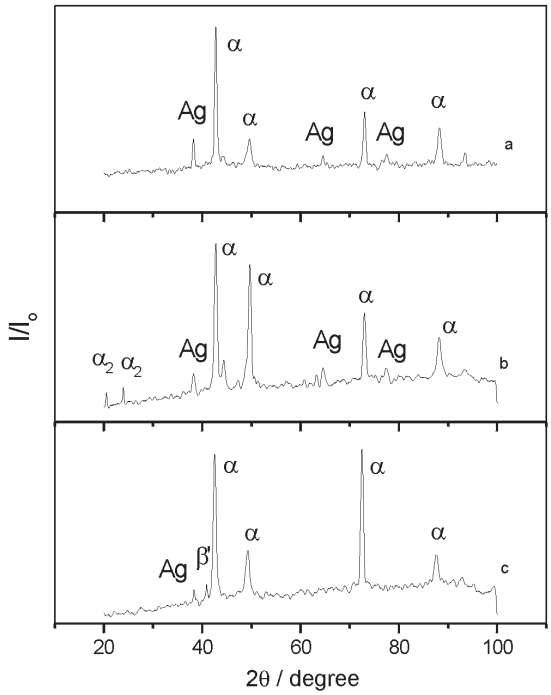

Fig. 3 X-ray diffraction patterns obtained for the Cu–8 mass% Al–12 mass% Ag: a – after annealing; b – after quenching from 315°C; c – after quenching from 800°C

Figure 2 shows the scanning electron micrographs obtained for the Cu–8 mass% Al–12 mass% Ag alloy after annealing (Fig. 2a) and after quenching from 315°C (Fig. 2b) and from 800°C (Fig. 2c) in iced water. It is possible to observe the silver-rich phase (white) in Fig. 2a and the presence of the α_2 phase in Fig. 2b and of the martensitic β' phase in Fig. 2c, together with the silver-rich phase.

Figure 3 shows the X-ray diffraction patterns obtained for the Cu–8 mass% Al–12 mass% Ag in the same conditions as in Fig. 2 and it is possible to observe that these data confirm what was proposed for the discussion of the results in Figs 1 and 2.

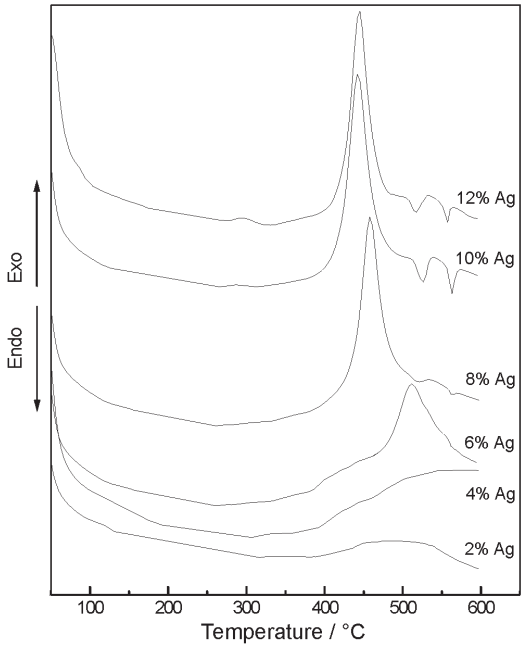

Fig. 4 DSC curves obtained for the alloys after quenching. Heating rate 20°C min^{-1}

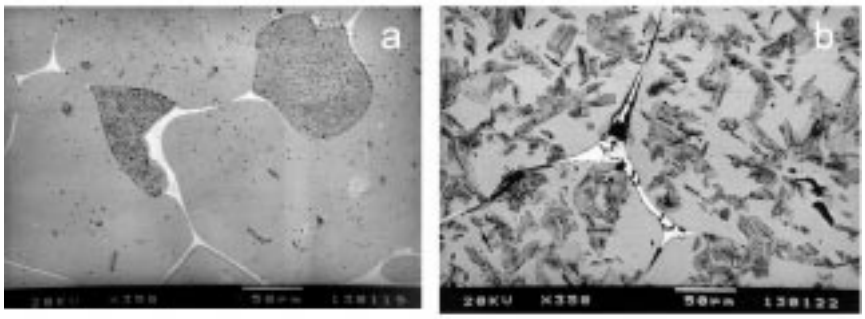

Fig. 5 Scanning electron micrographs obtained for the Cu–8 mass% Al–12 mass% Ag alloy after quenching from 800°C: a – quenched from 350°C; b – quenched from 450°C

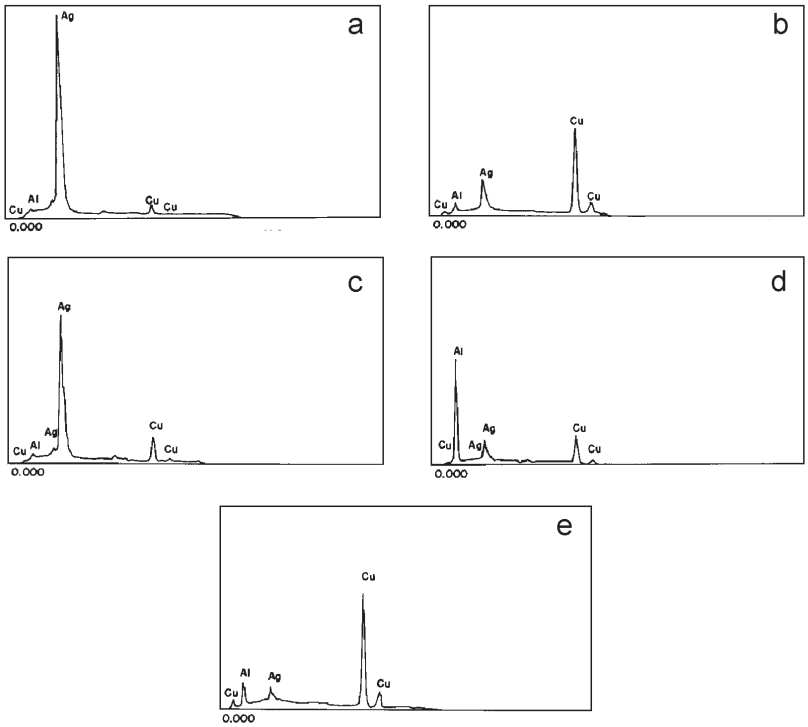

Fig. 6 EDX spectra obtained for the Cu–8 mass% Al–12 mass% Ag: a, b – after quenching from 350°C; c, d, e – after quenching from 450°C

Figure 4 shows the DSC curves obtained for the alloys quenched from 800°C in iced water before heating at 20°C min^{-1}. The curves obtained for the alloys with 10 and 12 mass% Ag show a very weak endothermic peak at about 300°C which may be ascribed to the ordering of α_2 phase. The curves for the alloys with 6, 8, 10 and 12 mass% Ag show an exothermic peak at about 500°C in the curve for the alloy with 6 mass% Ag and which is increased and shifted for lower temperatures with the increase of the silver concentration. This exothermic peak seems to be due to some transition related to the presence of Ag. The curves obtained for the alloys with 10 and 12 mass% Ag also show two endothermic peaks at about 520 and 560°C. The peak at 520°C may be related to the transition $\beta_1 \rightarrow \beta$ and the peak at 560°C is due to the $(\alpha+\gamma_1) \rightarrow \beta$ transformation [10]. The peaks corresponding to the ordering of the martensitic phase ($\beta' \rightarrow \beta'_1$) and to the reverse martensitic transformation ($\beta'_1 \rightarrow \beta_1$) are not observed, maybe due to the small quantity of the γ_1 phase formed in the alloys. It is also possible to observe that in the curve obtained for the alloy with 8% Ag the endothermic peaks at 520 and 560°C are very weak, indicating that the lower limit for Ag additions to form the γ_1 phase may be at about 8%.

Figure 5 shows the scanning electron micrographs obtained for the Cu–8 mass% Al–12 mass% Ag quenched from 800°C and then quenched from 350°C (Fig. 5a) and

from 450°C (Fig. 5b). Figure 6 shows the EDX spectra taken from the white part of Fig. 5a (Fig. 6a), the gray and black part of Fig. 5a (Fig. 6b), from the white part of Fig 5b (Fig. 6c), from the grey part of Fig. 5b (Fig. 6d) and from the black part of Fig. 5b (Fig. 6e). From these it is possible to see that at 350°C there is a silver-rich phase (white part of Fig. 5a – solid solution of Cu and Al in Ag) at the grain boundaries of the Cu matrix, together with another phase that is a solid solution richer in Al than the white one. At 450°C there is a segregation of Al at the boundaries and a split of the gray solid solution over the matrix grains. These changes may be responsible for the exothermic peak observed at about 450°C for the Cu–8 mass% Al–12 mass% Ag. The gray solid solution will be dissolved by the matrix and the Al segregated at the grain boundaries will be consumed in the $(\alpha+\gamma_1)\rightarrow\beta$ reaction.

Conclusions

The results indicate that additions of more than 8 mass% Ag to the Cu–8 mass% Al alloy may induce the formation of the γ_1 phase (Cu_9Al_4) in this alloy, with a shift in the equilibrium concentration to the eutectoid range and with the metastable transitions due to the presence of this phase, which are only observed in alloys with a minimum of 9 mass% Al. The presence of silver introduces a new thermal event, due to the formation of a silver-rich phase and to the segregation of Al in the grain boundaries of the Cu matrix.

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