THERMAL BEHAVIOR OF α-(Cu–Al–Ag) ALLOYS

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Thermal behavior of α-(Cu–Al–Ag) alloys, i.e. alloys with composition less than about 8.5 mass% Al, was studied using differential scanning calorimetry (DSC), differential thermal analysis (DTA), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD). The results indicated that the presence of silver introduces new thermal events ascribed to the formation of a silver-rich phase and, after addition higher amounts than 8 mass% Ag to the Cu–8 mass% Al alloy it is possible to observe the formation of the γ_1 phase (Al_4Cu_9), which is only observed in alloys containing minimum of 9 mass% Al. These results may be attributed to some Ag characteristics and its interaction with Cu and Al.

Keywords: *Ag–Al interaction, copper-based alloys, silver additions, thermal behavior*

Introduction

Cu–Al alloys present good mechanical properties, depending on the aluminum content and good chemical stability. The solubility of Al in Cu up to about 8.5 mass% is complete and obviously, it is not possible to submit these alloys to an age hardening treatment. Addition of Ag to Cu–Al alloys improve its stress corrosion resistance [1], hardness [2] and causes some changes in the microstructure [3] in the kinetics of eutectoid decomposition [4] and in the aging characteristics of the alloys [5]. Phases in Cu–Al–Ag alloys are structurally analog to those present in the binary systems, without ternary intermediate phases [6, 7].

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

Experimental

The alloys were prepared in an induction furnace under argon atmosphere, using copper, aluminium and silver with 99.97, 99.95, 99.98% purities, respectively as starting materials. Results from chemical analysis indicated a final alloy composition very close to the nominal one. Cylindrical samples with 20 mm of diameter and 60 mm of length were cut in disks of 4.0 mm thickness and small square pieces of about 3.0 mm length were used for DSC and DTA analyses. 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 heated at 850°C for 1 h and then quenched in ice–water bath.

DTA data were obtained using a TA 2960 system and DSC data were obtained using TA 2910 thermal analyzer. After the heat treatments the samples were polished, etched and examined by scanning electron microscopy (SEM) using a Jeol JSM T330A apparatus. The XRD patterns were obtained using a Siemens D5000 X-ray diffractometer with filtered CuK_α radiation in solid (not powdered) samples.

Results and discussion

Figure 1 shows the DTA curves obtained for the Cu–2 mass% Al–*X* mass% Ag, Cu–4 mass% Al–*X* mass% Ag, Cu–6 mass% Al–*X* mass% Ag and Cu–8 mass% Al–*X* mass% Ag alloys, where *X*=2, 4, 6, 8, 10 and 12, at a heating rate of 20°C min^{-1}. An endothermic peak appeared about 800°C in these curves. This thermal event becomes more intense with the increase of Ag content, indicating that this transition can be attributed to the maximum dissolution of Ag in the matrix [8]. This was confirmed by the SEM micrographs in Fig. 2 and by the EDX spectra in Fig. 3, showing that after annealing (Fig. 2a) the grain boundaries of the sample become filled with silver (white), and from 800°C there are few silver pre-

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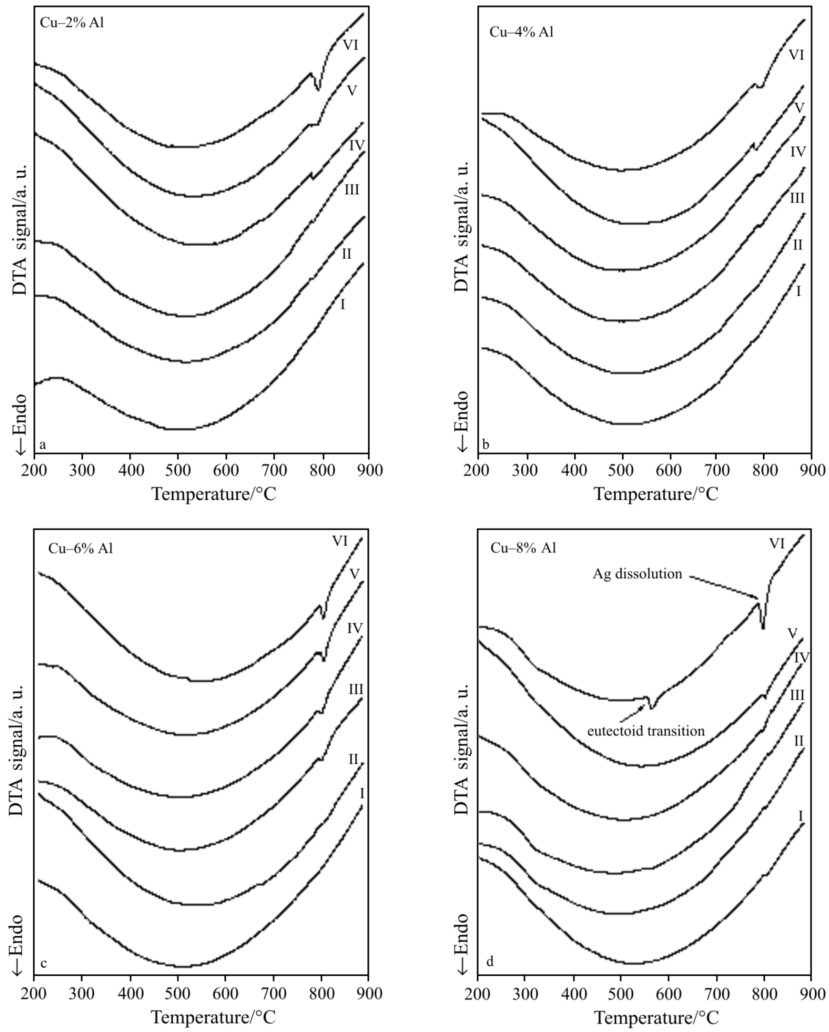

Fig. 1 DTA curves obtained from α-(Cu–Al) alloys with: I – 2% Ag, II – 4% Ag, III – 6% Ag, IV – 8% Ag, V – 10% Ag and VI – 12% Ag additions

cipitates. In curve VI of Fig. 1d it is possible to observe the presence of an additional peak at about 565°C. As observed for Cu–Al alloys with more than 9% Al [9], this peak may be attributed to the $(\alpha+\gamma_1)\rightarrow\beta$ transformation, but now in an alloy with 8 mass% Al and 12 mass% Ag. These results indicate that additions of Ag may induce the formation of the γ_1 phase (Al_4Cu_9) in this alloy, in annealed samples, shifting the equilibrium concentration to the eutectoid range.

Figure 4 shows the DSC curves obtained at a heating rate of 20°C min^{-1}, for the alloys quenched from 850^{o}C in ice-water bath. The curves obtained for the Cu–8% Al alloy with additions of 10 and 12% Ag (curves V and VI, Fig. 4d) show a very weak endothermic peak at about 300°C which may be attributed to the ordering of the α_2 phase. All exothermic peaks ob-

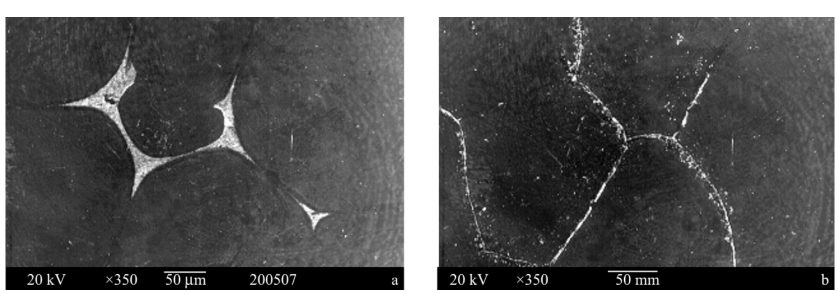

Fig. 2 Scanning electron micrographs obtained for the Cu–6% Al–6% Ag alloy: a – annealed, b – quenched from 800°C

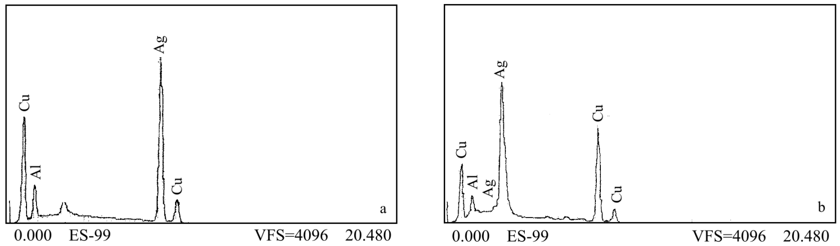

Fig. 3 EDX spectra taken from a – middle of the grain and b – grain boundary (silver-rich white portions) of Fig. 2a

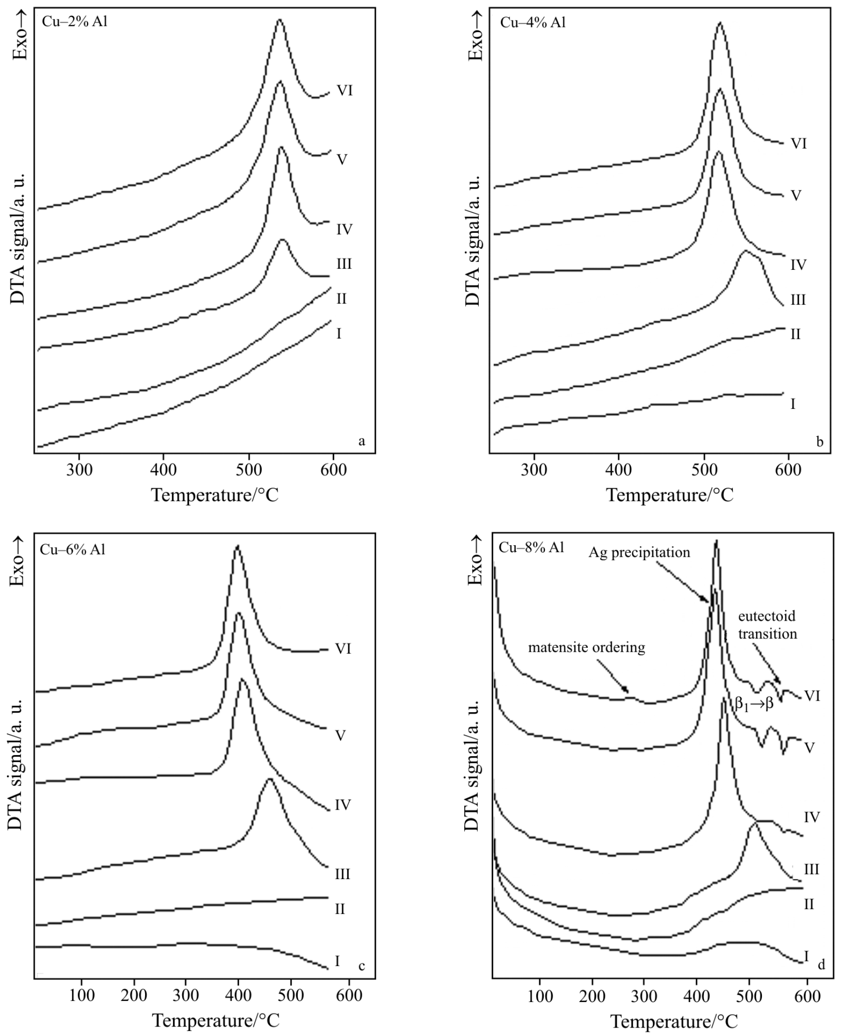

Fig. 4 DSC curves obtained from α-(Cu–Al) alloys with: I – 2% Ag, II – 4% Ag, III – 6% Ag, IV – 8% Ag, V – 10% Ag and VI – 12% Ag additions

served at about 550°C are increased and shifted to lower temperatures with the increase of the aluminum and silver concentrations. These exothermic peaks are due to Ag precipitation from matrix, as it can be seen in the X-ray diffraction patterns of Fig. 5. The curves obtained for the Cu–8% Al alloy with 10 and 12% Ag also show two endothermic peaks at about 520 and 560°C. The peak at 520°C maybe due to the $\beta_1 \rightarrow \beta$ transition and the peak at 560°C is for 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 γ_1 phase formed in the alloys. It is also possible to observe that in the curve obtained for the Cu–8% Al–8% Ag alloy (curve IV, Fig. 4d) the endothermic peaks at 520 and 560°C are very weak, indicating that the lowest limit of Ag addition to form the γ_1 phase may be at about 8% Ag in the Cu–8% Al alloy.

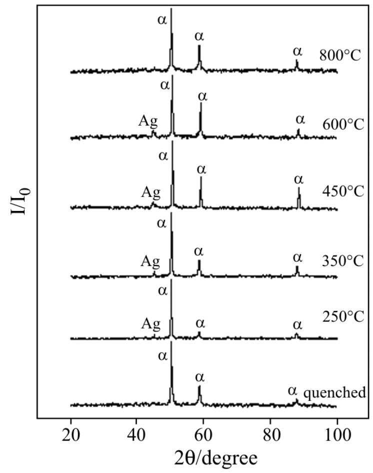

Fig. 5 X-ray diffraction patterns obtained for the Cu–2% Al–8% Ag alloy (quenching temperatures chosen from Fig. 4)

The shift in the equilibrium concentration, observed in these alloys, may be attributed to some Ag characteristics and its interaction with Cu and Al. During quenching, the Ag atoms are retained in the Cu-rich α phase. On heating, Ag diffusion from bulk to grain boundaries of the α phase to produce the Ag-rich precipitates and the redistribution of the remaining Ag atoms at the bulk will result a lowering of the Gibbs energy of the system.

The Cu-rich α phase of Cu–Al–Ag alloys is a f.c.c. solid solution of Al and Ag in copper [6]. At elevated temperatures this phase is disordered and, on cooling, there is a tendency to ordering, due to a more favorable number of Cu–Al pairs. The copper-silver miscibility gap in the Cu–Ag system results from the excessive disparity between Cu and Ag atoms (large size factor) while the Ag–Al system is an example of a very small size factor [6]. In this way, Ag solubility may be larger at higher Al content and the Ag–Al interaction will enable even with larger number of Cu–Al pairs. This Ag–Al interaction disturbs the Al equilibrium in the α phase and increases the relative fraction of Al available to interact with Cu, thus shifting the equilibrium concentration to higher Al content.

Conclusions

Ag addition to the Cu–8% Al alloy introduce a new thermal event ascribed to the formation of a silver-rich phase. Addition of more than 8 mass% of Ag induce the formation of the γ_1 phase (Al_4Cu_9) in this alloy with a shift in the equilibrium concentration to the eutectoid range and the metastable transitions due to this phase, which are only observed in alloys with a minimum of 9 mass% Al. These effects may be attributed to some Ag characteristics and its interaction with Cu and Al.

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