PHASE TRANSFORMATIONS IN THE Cu–Al ALLOY WITH Ag ADDITION

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The effect of Ag addition on the phase transformations that occur in the Cu–10% Al alloy was studied using differential thermal analysis, scanning electron and optical microscopies and energy dispersive X-ray analysis. The results indicated that Ag addition is responsible for the separation of the reverse martensitic transformation in two stages, and for the refinement of the α-phase grains. The relative amount of the β_1' martensitic phase, retained on slow cooling (above 2 K min^{-1} of cooling rate), and the relative fraction of phase α_2 are increased. The solubility limit of Ag in the matrix is close to 6 mass% and at this concentration the maximum stability of the β-phase is reached.

Keywords: Ag addition, Cu–Al alloys, phase transformations, thermal behavior

Introduction

During slow cooling of Cu–Al alloys from the high-temperature β-phase an eutectoid reaction occurs. The α-phase is a solid solution of aluminum in copper and transforms into the ordered α_2 below 340°C [1]. These transformations are reversible during reheating, and the sequence is then $\alpha_2+\gamma_1 \rightarrow \alpha+\gamma_1 \rightarrow \beta$ [2].

Silver additions to the Cu–Al alloys improve some of its properties, as hardness [3] and stress corrosion [4], without appreciable modification on its workability and plasticity. Cu–Al–Ag alloys are regarded as promising new materials because of its good mechanical properties, conductivity and appearance, high corrosion resistance in different media [5, 6] and ease of manufacture. Such alloys are applied in electronics, dentistry and also for ornamental purposes.

In this work the thermal behavior of the Cu–10% Al alloy, with and without Ag addition, was studied using classical differential thermal analysis (DTA), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) to analyze the influence of Ag additions on the phase transformations and on the stability of the β-phase.

Experimental

Cu–10% Al, Cu–10% Al–4% Ag, Cu–10% Al–6% Ag, Cu–10% Al–8% Ag and Cu–10% Al–10% Ag alloys were prepared in an induction furnace under argon atmosphere using 3N7 copper, 3N5 aluminum and 3N8 silver as starting materials. Results obtained from chem-

ical analysis indicated that the final alloy composition is very close to the nominal one.

Small cylinders of about 10 mm length and 5.0 mm diameter were used for DTA analysis and flat square samples of about 10 mm were obtained for metallography. These samples were initially annealed for 120 h at 850°C for homogenization and after annealing some of them were equilibrated for one hour at 850°C and quenched in iced water. After the heat treatments the flat samples were polished, etched and examined in a Leica DMR optical microscope and in a Jeol JSM T330A scanning electron microscopy with a Noran energy dispersive X-ray (EDX) microanalyser.

Results and discussion

Figure 1 shows the DTA curves obtained for the Cu–10% Al, Cu–10% Al–4% Ag, Cu–10% Al–6% Ag, Cu–10% Al–8% Ag and Cu–10% Al–10% Ag alloys, at a heating rate of 20 K min^{-1}, for annealed samples. In curve 1a, corresponding to the Cu–10% Al alloy, six endothermic peaks were observed: P$_1$, at about 175°C, may be associated to the beginning of the α_2-phase disordering; P$_2$, at about 265°C can be ascribed to the second stage of the α_2-phase disordering; P$_3$, at about 338°C, is due to the order–disorder transition $\alpha+\alpha_2 \rightarrow \alpha+\gamma_1$ [2]. Peak P$_4$, at about 395°C, is related to the dissolution of the α_2-phase precipitates formed during slow cooling [7]. Peak 5, at about 514°C, is associated to the transformation of the β_1-phase to the β-phase [8]. The martensitic β_1'-phase, retained on slow cooling, changes into the β_1-phase in the same temperature interval as the α_2-phase disordering process and

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then, at about 514°C, the β_1-phase changes into the β-phase. P_6, at about 571°C, is due to the $\alpha+\gamma_1\rightarrow\beta$ transformation [9], as expected from the Cu–Al phase diagram shown in Fig. 2. In curve 1b, corresponding to the Cu–10% Al–4% Ag alloy, it is possible to observe that the peak ascribed to the order–disorder transition was shifted to higher temperatures, and probably may be oc-

curring at about 380°C (peak P_4), together with the α_2-phase precipitates dissolution. An additional endothermic peak was observed at about 95°C in curve 1c (corresponding to the Cu–10% Al–6% Ag alloy), which can be due to the first stage of the reverse martensitic transformation [10]. In curves 1d and 1e (corresponding to the Cu–10% Al–8% Ag and Cu–10% Al–10% Ag al-
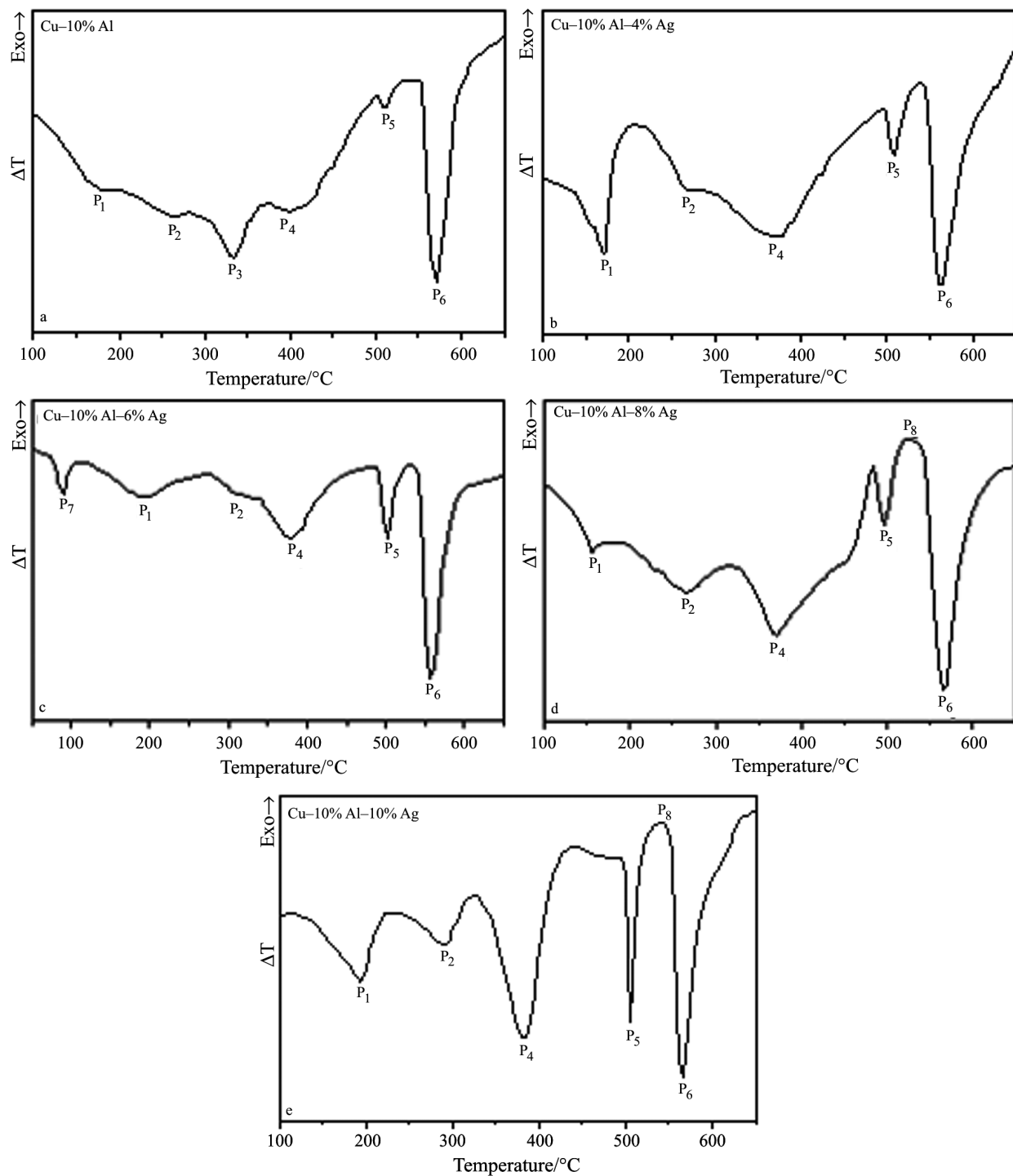

Fig. 1 DTA curves obtained for the annealed samples; β=20 K min^{-1}
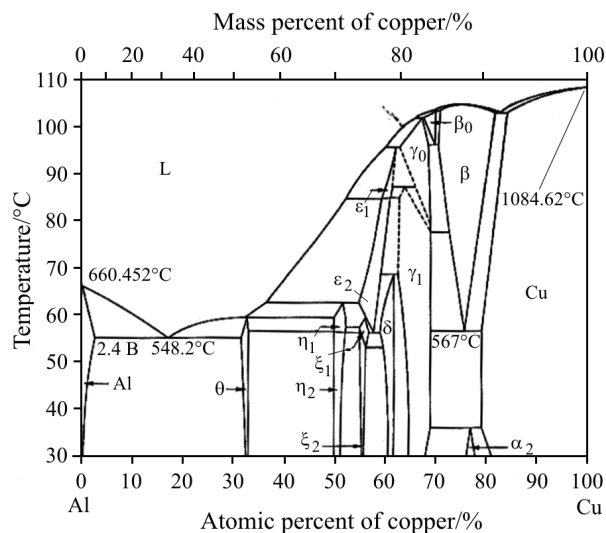
Mass percent of copper/%

Fig. 2 Cu–Al phase diagram [9]

loys, respectively) an additional exothermic peak was observed, in the temperature range of 530–540°C. This peak can be related to the α-phase precipitation, which precedes the $\alpha+\gamma_1\rightarrow\beta$ transition. The formation of the γ_1(Al_4Cu_9)-phase, from the β_1-phase decomposition, causes a decrease of solved aluminum atoms concentration in the matrix. This change of chemical composition causes the precipitation of the copper-rich solid-solution α-phase, which is evident from an exothermic effect in the temperature range of 530–540°C in curves 1d and 1e [11]. The starting point of the DTA curves corresponds to the ($\alpha+\alpha_2$) phase in the presence of Ag, as shown in Fig. 3.

In the micrographs of Fig. 3 it can be observed that the presence of Ag seems to introduce a refinement in the α-phase grains and that it is more pronounced with the higher silver content. This grain refinement in Cu–Al–Ag alloys may be explained by a similar mechanism proposed by Shewmon [12]. 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 less 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 the curves of Fig. 1 it is also possible to observe that the peaks due to the order-disorder transition, in the temperature range of 100–450°C, are changed when it is compared to the samples without Ag additions [2, 13]. In curve 1a, in the temperature range of 100–450°C, the DTA peaks are smaller than in the other curves. In curve 1b the peak between 150–200°C is more intense than the corresponding peak in curve 1a. It indicates that the amount of α_2-phase is increasing with Ag content and is evidenced by the more intense thermal effect in this temperature range (peak P_1 in Fig. 1b). In curve 1c one can observe a peak at 95°C, which is not detected in 1a, 1b, 1d and 1e curves. When Cu–Al alloys, with 9 and 13% Al content, are cooled at a rate above 2 K min^{-1}, part of the martensitic phase is retained at lower temperatures [2]. During slow reheating, this martensitic phase undergoes reverse transformation giving the β_1 parent phase prior to the eutectoid mixture, in the same temperature range of α_2-phase disordering. In this way, with the addition of 6% Ag to the Cu–10% Al alloy, these reactions take place in two well separated stages. The first one, at about 95°C, corresponds to parent phase formation and the second one, at higher temperatures, to the decomposition of the parent phase [10].

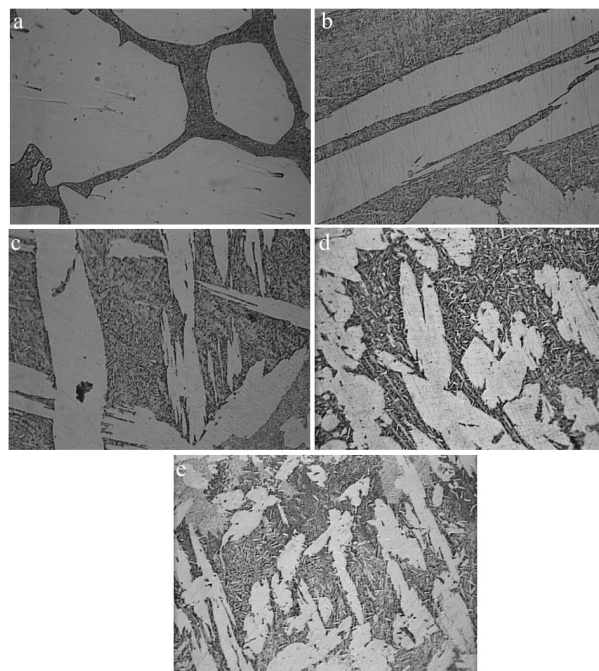From curves 1d and 1e in Fig. 1 (alloys with 8% and 10% Ag, respectively) it is possible to observe

Fig. 3 Optical micrographs (N=500) obtained for the annealed samples: a – Cu-10%Al, b – Cu–10% Al–4% Ag, c – Cu–10% Al–6% Ag, d – Cu–10% Al–8% Ag and e – Cu–10% Al–10% Ag

that the position of peaks corresponding to the α_2-phase disordering is yet not modified, indicating that the influence of Ag addition on this transition is effective up to 6% of silver content. Ag precipitates, shown in Fig. 4, are now interfering in the intensity of the peak corresponding to its dissolution, which occurs together with the dissolution of the α_2-phase, at about 380°C.
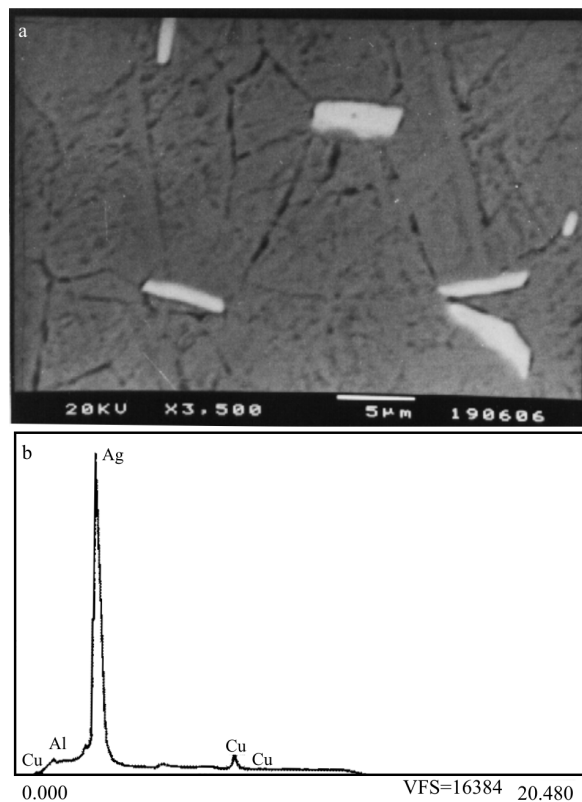

Fig. 4 a – Scanning electron micrograph obtained for the Cu–10% Al–8% Ag alloy annealed and then quenched from 650°C, b – EDX spectrum from the precipitates (white)

The peaks between 450 and 650°C seem also to be influenced by Ag concentration. In Fig. 5 (the enlarged part of Fig. 1), in this temperature range, it is possible to observe that the first peak, due to the $\beta_1 \rightarrow \beta$ transformation increases with Ag concentration and the second peak, due to the $\alpha + \gamma_1 \rightarrow \beta$ transition increases and then decreases. These results indicated that the presence of Ag increases the relative amount of the β_1' martensitic phase retained on slow cooling above 2 K min^{-1}. It also increases the amount of β_1-phase to be decomposed, thus increasing the pearlite fraction formed, which increases the DTA peak due to the $\alpha + \gamma_1 \rightarrow \beta$ transition. It is also observed that from 8% Ag, the $\beta_1 \rightarrow \beta$ transition starts to be more effective than the $\alpha + \gamma_1 \rightarrow \beta$ transition. It indicates that from this concentration the $\beta_1 \rightarrow \alpha + \gamma_1$ decomposition
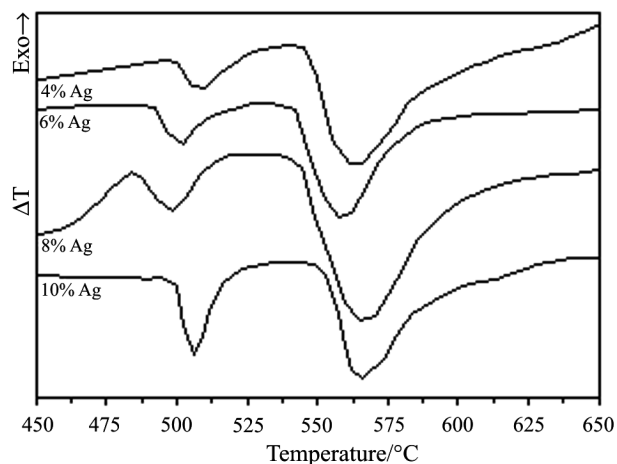

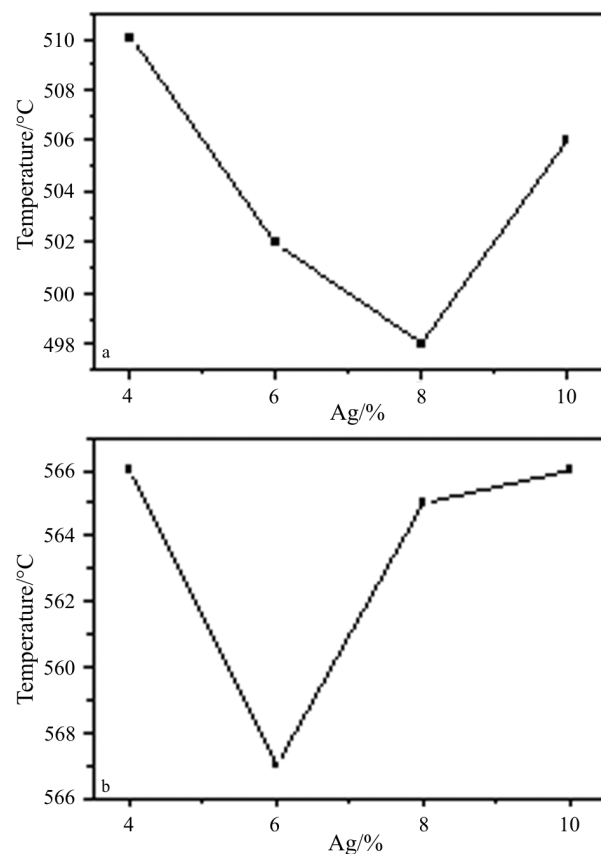Fig. 5 Enlarged part of Fig. 1, in the temperature range of 450–650°C

Fig. 6 Peak temperature change *vs*. Ag concentration for the a – $\beta_1 \rightarrow \beta$, b – $\alpha + \gamma_1 \rightarrow \beta$ transitions

rate is slower. All these thermal events are shifted to lower temperatures than those observed for samples without silver [2].

The increase in the Ag content causes the return of the transition temperature to a value close to that corresponding to the sample without silver, thus indi-

cating that higher Ag concentrations will not change the peak temperatures in this temperature range. This is corroborated by the plots in Fig. 6, which show the peak temperature change *vs*. Ag concentration for the $\beta_1 \rightarrow \beta$ transition (Fig. 6a) and for the $\alpha + \gamma_1 \rightarrow \beta$ transition (Fig. 6b). In these plots one can see that peak temperature decreases with Ag concentration down to 8% for the $\beta_1 \rightarrow \beta$ transition, and to 6% for the $\alpha + \gamma_1 \rightarrow \beta$ transition. It shows that Ag addition changes intensively the β_1-phase decomposition from 8% Ag. For the $\alpha + \gamma_1 \rightarrow \beta$ transition, this temperature change can be due to the α-phase precipitation, which is attributed to Ag solution treated in the matrix, indicating that the solubility of silver is limited in the matrix and is close to 6%. It also indicates that, at this concentration, the maximum stability of the β-phase is reached.

Conclusions

The results indicated that the presence of Ag is responsible for a new thermal event, due to the separation of the reverse martensitic transformation into two stages. The increase in the Ag addition introduces a refinement in the grains of the α-phase and this effect is more pronounced with higher silver content. The phase transformation sequence, expected from the Cu–Al phase diagram, is not affected by Ag addition, but it increases the relative amount of the β_1' martensitic phase retained on slow cooling above 2 K min^{-1}, and also the relative fraction of α_2-phase. It was also verified that the maximum silver solubility in the matrix is about 6%, at which the maximum stability of the β-phase is reached.

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