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Ag-RICH PHASE PRECIPITATION IN THE Cu–9 MASS% Al ALLOY WITH Ag ADDITIONS

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The Ag-rich phase precipitation in the Cu–9 mass% Al was studied using differential scanning calorimetry (DSC), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The results indicated that Ag additions did not interfere on the metastable transitions sequence of the Cu–mass% Al alloy but Ag precipitation disturbs the β phase formation reaction and the martensitic phase decomposition reaction.

Keywords: *Ag additions, Cu–Al alloys, silver precipitation, thermal behavior*

Introduction

Copper-based alloys constitute a class of materials that have a number of applications due to their high thermal and electrical conductivity. They also exhibit good resistance to corrosion. The aluminium bronzes (Cu–Al) present good strength and are also corrosion resistant [1]. These copper-based alloys can also exhibit the shape memory effect within a certain range of compositions which have a disordered body center cubic structure (bcc), called β-phase, which are stable at high temperature [2–5]. They possess two successive ordering transitions during cooling treatment.

The Cu–9 mass% Al alloy when quenched from the β phase passes through a martensitic transformation to disordered β' phase. On heating this disordered martensitic phase undergoes an ordering reaction $\beta'\rightarrow\beta_1^{'}$ that precedes the martensitic decomposition reaction [6]. Ag additions to the Cu–Al system introduce some changes on the stability limit of the phases [7, 8], its microhardness [9], electrical resistivity [10] and in the eutectoid decomposition reaction [11].

In this work, the Ag-rich phase precipitation reaction in the Cu–9 mass% Al alloy was studied using differential scanning calorimetry (DSC), X-ray diffractometry (XRD) and scanning electron microscopy (SEM), to analyze the influence of Ag additions on the phase transformations in this alloy.

Experimental

Cu–9 mass% Al, Cu–9 mass% Al–6 mass% Ag, Cu–9 mass% Al–8 mass% Ag and Cu–9 mass% Al–10 mass% Ag 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 composition very close to the nominal one. The samples were annealed for 120 h at 850°C for homogenization. After this, some annealed samples were equilibrated at 850°C during 1 h and then quenched in iced water to reach the maximum dissolution of Ag. After the heat treatments the samples were polished, etched and examined by scanning electron microscopy (SEM) using a JEOL JSM T330A electron microscope. The X-ray diffraction (XRD) patterns were obtained using a Siemens D5000 4B diffractometer, CuK_α radiation and solid (not powdered) samples. DSC curves were obtained using a Q20 TA instrument, aluminum pan, nitrogen flux at about 50 mL min^{-1} and solid samples with diameter of 3.0 mm.

Results and discussion

Figure 1 shows the DSC curves obtained with a heating rate of 10°C min^{-1} for the Cu–9 mass% Al, Cu–9 mass% Al–6 mass% Ag, Cu–9 mass% Al–8 mass% Ag and Cu–9 mass% Al–10 mass% Ag alloys initially quenched from 850°C. Curve 1a, obtained for the Cu–9 mass% Al shows five peaks: the exothermic peak P_1, at about 180°C is associated to the $\alpha\rightarrow\alpha_2$ ordering reaction [12] and the exothermic peak P_2, at about 280°C is due to the $\beta'\rightarrow\beta_1^{'}$ martensitic ordering reaction; the endothermic peak P_3, around 380°C corresponds to two consecutive reactions, the $\beta'\rightarrow\beta_1$ martensitic retransformation and the partial β_1 decomposition giving the $(\alpha+\gamma_1)$ eutectoid mixture;

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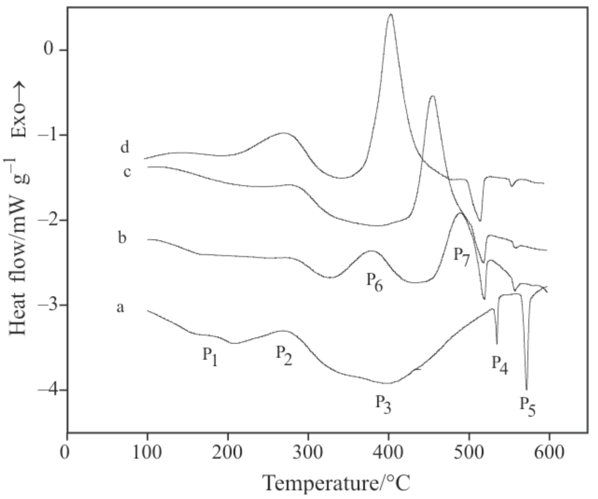

Fig. 1 DSC curves obtained for quenched alloys: a – Cu–9 mass% Al; b – Cu–9 mass% Al–6mass% Ag; c – Cu–9 mass% Al–8 mass% Ag and d – Cu–9 mass% Al–10 mass% Ag at a heating rate: 10°C min^{-1}

peak P_4, at about 540°C is associated with the $\beta_1\to\beta$ transition from the β_1 remnant part of the transition at about 380°C; and peak P_5, at about 570°C, is due to the $(\alpha+\gamma_1)\to\beta$ transition [6].

Comparing curve 1a, obtained for the Cu–9 mass% Al alloy, to curve 1b obtained for the Cu–9 mass% Al–6 mass% Ag alloy one can observe the presence of two additional exothermic peaks, P_6 and P_7. These peaks at about 350 and 500°C, respectively, are ascribed to Ag precipitation indicating that it occurs in two stages. The first stage observed at about the same temperature range where the two consecutive reactions $\beta'\to\beta_1$ and the partial $\beta_1\to(\alpha+\gamma_1)$ must occur. In this and in the other DSC curves obtained for alloys with Ag addition the exothermic peak P_1, associated to the $\alpha\to\alpha_2$ ordering reaction is not observed.

In curves 1c and 1d, obtained respectively for the Cu–9 mass% Al–8 mass% Ag and Cu–9 mass% Al–10 mass% Ag alloys it is possible to observe that Ag precipitation reaction is now occurring in just one stage. Another remarkable change can be observed in the intensity of peak P_5, which decreases with the increase in the Ag content indicating that Ag precipitation is disturbing the martensitic phase decomposition reaction and decreasing the amount of $(\alpha+\gamma_1)$ complex phase available for the β phase formation.

Figure 2 shows the X-ray diffraction patterns obtained for the Cu–9 mass% Al–6 mass % Ag and Cu–9 mass% Al–10 mass% Ag alloys quenched from 850°C and then quenched from 350°C (Figs 2a and b, respectively) and 450°C (Figs 2c and d, respectively). In these figures, one can observe that Ag diffraction peaks are easily noted in Fig. 2a but almost absent in Fig. 2b and that in Figs 2c and d the presence of Ag is evident. This seems to confirm what was observed in Fig. 1, that Ag precipitation before 450°C only occurs in the Cu–9 mass% Al–6 mass% Ag alloy, in a process with two stages.

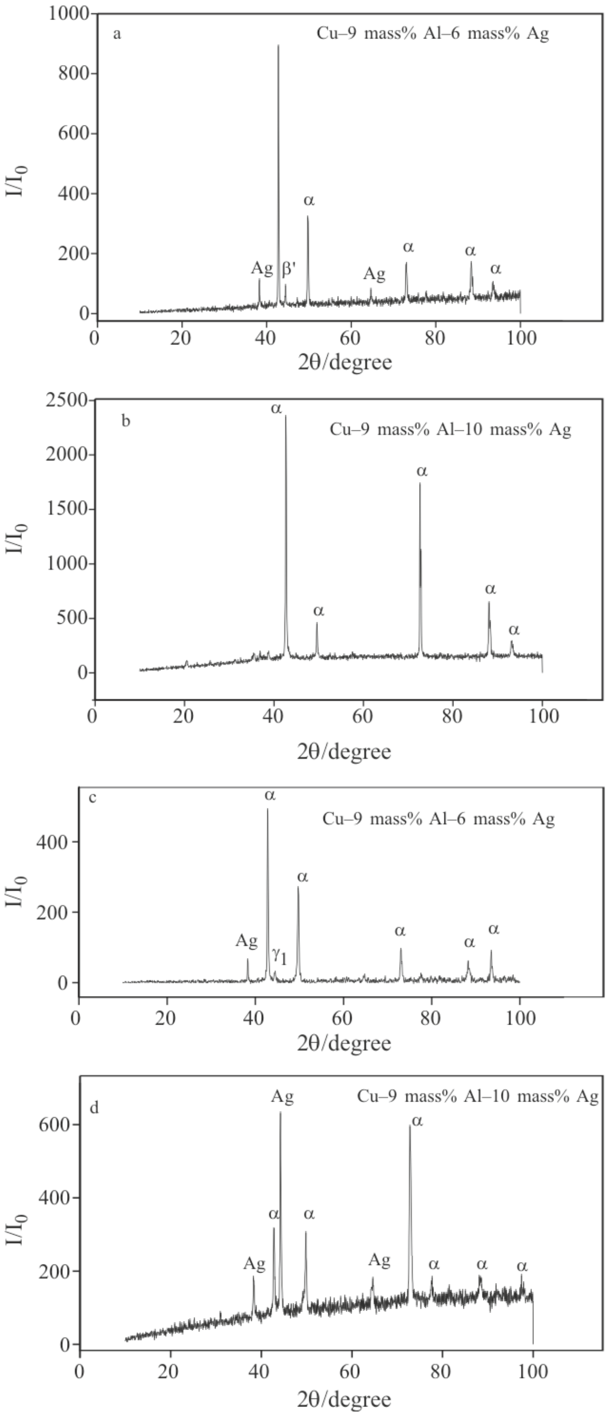

Fig. 2 X-ray diffraction patterns obtained for the Cu–9 mass% Al–6 mass% Ag and Cu–9 mass% Al–10 mass% Ag alloys, respectively: a, b – quenched from 350°C; c, d – quenched from 450°C

Figure 3 shows the scanning electron micrographs obtained for the Cu–9 mass% Al–6 mass% Ag and Cu–9 mass% Al–10 mass% Ag alloys. One can observe

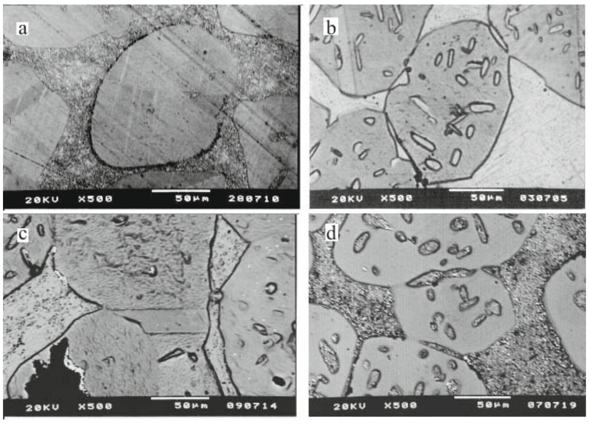

Fig. 3 Scanning electron micrographs (SEM) obtained for the Cu–9 mass% Al–6 mass% Ag and Cu–9 mass% Al–10 mass% Ag alloys, respectively: a, b – quenched from 350°C; c, d – quenched from 450°C

the presence of Ag-rich precipitates (white) at the grain boundaries and over the grains of the α-(Cu-rich) matrix for the Cu–9 mass% Al–6 mass% Ag alloy quenched from 350°C (Fig. 3a) and 450°C (Fig. 3c) and the presence of Ag-rich precipitates at the grain boundaries for the Cu–9 mass% Al–10 mass% Ag alloy quenched from 450°C (Fig. 3d), but not when it is quenched from 350°C (Fig. 3b). This confirms what was observed in Figs 1 and 2, where the Ag precipitation is occurring in two stages for the Cu–9 mass% Al–6 mass% Ag alloy (peaks P_6 and P_7) and in just one stage for the other alloys with Ag additions (peak P_7). In the scanning electron micrograph in Fig. 3b there is no Ag precipitates formed at 350°C for the Cu–9 mass% Al–10 mass% Ag alloy quenched from 350°C, suggesting that Ag precipitation process starts at higher temperatures. Data obtained for the Cu–9 mass% Al–8 mass% Ag indicated a very similar behaviour between this and the alloy with 10 mass% Ag.

The occurrence of Ag precipitation in two stages in the Cu–9 mass% Al–6 mass% Ag alloy and just in one stage on the alloys with additions of 8 and 10 mass% Ag is related to the $\beta_1 \rightarrow (\alpha + \gamma_1)$ decomposition reaction and to the influence of Ag on this transition. For the alloy with 6 mass% Ag the $\beta_1 \rightarrow (\alpha + \gamma_1)$ reaction is occurring in the same temperature range of the first stage of Ag precipitation, as observed from curves 1a and 1b. As it is stated in [13] the Ag solubility limit in the α-Cu-rich phase of the Cu–Al system is at about 6 mass% Ag and in this way the first stage of Ag precipitation in the Cu–9 mass% Al–6 mass% Ag must be related to dissolution and precipitation from the α phase and the second stage to the $\beta_1 \rightarrow (\alpha + \gamma_1)$ decomposition reaction. On quenching part of Ag atoms dissolved in the α-Cu-rich matrix phase and other part in the martensitic phase. The part of Ag in the α phase is less stable than that in the martensitic phase due to the larger Al amount in the latter than in the former and Ag solved in the α phase will precipitate first and the second Ag precipitation from the martensitic phase may occur from the saturated martensitic phase. This seems to be the case for the Cu–9 mass% Al–6 mass% Ag alloy, which is close to the Ag solubility limit. When the second stage occurs, the $\beta_1 \rightarrow (\alpha + \gamma_1)$ decomposition reaction already occurred and the presence of the γ_1 phase, with an open bcc type structure and a diffusion coefficient greater than that for the fcc α phase [14], catalyzes the Ag precipitation reaction. With the increase in the Ag content, this reaction is enhanced and the correspondent DSC peak is shifted to lower temperatures (Fig. 1). The increase and shift of the corresponding DSC peak will appear in the DSC curve as one and more intense exothermic peak indicating a process in just one stage.

From Fig. 1 it was also observed that the DSC peak corresponding to the $(\alpha + \gamma_1) \rightarrow \beta$ transition decreases with the increase in the Ag content. This must be also related with the second stage of Ag precipitation. With the increase in Ag concentration, Ag precipitation reaction is enhanced and disturbs the $\beta_1 \rightarrow (\alpha + \gamma_1)$ decomposition reaction, thus decreasing the $(\alpha + \gamma_1)$ amount available for the β phase formation.

Conclusions

The results indicated that Ag addition do not interfere on the metastable transitions sequence of the Cu–9 mass% Al alloy but introduce some changes on its thermal behavior. Peaks associated with the $(\alpha + \gamma_1) \rightarrow \beta$ reaction decrease in intensity with Ag concentration increases, suggesting that the presence of Ag decreases the $(\alpha + \gamma_1)$ complex phase relative fraction and disturbs the β phase formation reaction. The Ag precipitation reaction was observed in two steps for additions of 6 mass% Ag. The first one is related to Ag precipitation from the α–Cu-rich matrix phase and the second is associated with Ag precipitation from the martensitic phase. For Ag addition more than 8 mass% the first step was not observed and this was associated with the presence of the γ_1 phase, which catalyzes the second step of the Ag precipitation reaction.

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