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EFFECT OF Ag CONCENTRATION ON THE THERMAL BEHAVIOR OF THE Cu–10 MASS% Al AND Cu–11 MASS% Al ALLOYS

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In this work the effect of Ag concentration on the thermal behavior of the Cu–10 mass% Al and Cu–11 mass% Al alloys with additions of 4, 6, 8 and 10 mass% Ag was studied using differential scanning calorimetry (DSC), in situ X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The results showed that for the Cu–10 mass% Al alloy Ag addition induce the β'_1 phase formation and for the Cu–11 mass% Al alloy these additions increase the amount of martensite formed on quenching and decrease the stability range of this phase on heating.

Keywords: *Ag addition, Al addition. thermal behavior*

Introduction

Copper-based alloys constitute a class of materials that have a number of applications due to their high thermal and electrical conductivities. They also have good resistance to corrosion and can exhibit the shape memory effect within a certain composition range in which the disordered β phase is stable at high temperature [1]. On fast cooling the β phase presents two successive ordering transitions and then transforms martensitically either to β'_1, (β'_1+γ') or γ' phase, depending on Al concentration [2]. Alloys in which a high-temperature bcc β phase is transformed into martensite during quenching were the subject of several researches [3–6]. It is known that silver additions to Cu–Al alloys increase its hardness, improve their resistance to stress corrosion in steam [1] and change the stability range of the martensitic phase [7].

In this work the effect of Ag concentration on the thermal behavior of the Cu–10 mass% Al and Cu–11 mass% Al alloys was studied using differential scanning calorimetry (DSC), in situ X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

Experimental

The alloys with concentration shown in Table 1 were prepared in an induction furnace under argon atmosphere using 99.95% copper, 99.97% 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). Cylindrical samples with 2.0 cm diameter and 6.0 cm length were cut in disks of 2.0 mm thickness. The disks were cold rolled and flat squares samples of 1.0 mm thickness and about 5.0 mm length were obtained. The samples were annealed for 120 h at 1173 K for homogenization and after annealing they were kept at 1173 K for one hour and quenched in iced water. Scanning electron micrographs and X-ray diffraction patterns were obtained to identify the phases present in the alloys at the different quenching temperatures. The micrographs were obtained using a Jeol JSM T330A scanning electron microscope and the in situ high-temperature X-ray diffraction experiments were performed using D10B-XPD X-ray diffraction beam line of the Brazilian Synchrotron Light Laboratory/MCT with solid (not powdered) samples, λ=1.746671 Å for the Cu–10 mass% Al–*X* mass% Ag alloys and λ=1.54984 Å for the Cu–11 mass% Al–*X* mass% Ag alloys. The DSC curves were obtained using a DSC Q20 TA Instruments at different heating rates.

Table 1 Concentration of alloys

Alloys*X*	0	4	6	8	10
Cu–10 mass% Al–*X* mass% Ag	I	II	III	IV	V
Cu–11 mass% Al–*X* mass% Ag	VI	VII	VIII	IX	X

Results and discussion

Figure 1 shows the DSC curves obtained for the alloys I, II, III, IV and V at a heating rate of 10 K min^{-1}, from samples solution treated at 1173 K and cooled in iced water at 273 K to produce the martensitic phase. In the

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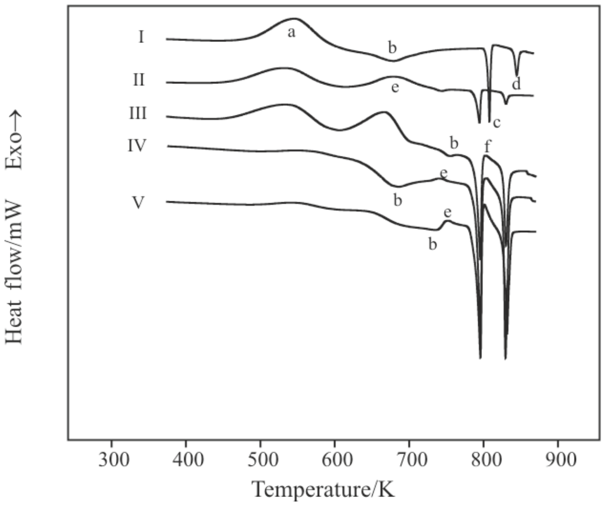

Fig. 1 DSC curves obtained with heating rate of 10 K min^{-1} for samples initially quenched from 1173 K

DSC curve corresponding to the alloy I four thermal events were detected. The exothermic peak a, at about 543 K is attributed to the $\beta' \to \beta_1'$ martensite ordering reaction [8] whereas the endothermic peak b around 680 K is due to $\beta_1' \to \beta_1$ reverse martensitic reaction followed by $\beta_1 \to (\alpha + \gamma_1)$ decomposition reaction of a β_1 phase fraction. The endothermic peak c at about 803 K is associated with the $\beta_1 \to \beta$ transition and peak d observed around 843 K is related to the $(\alpha + \gamma_1) \to \beta$ reaction [2]. In the DSC curve corresponding to alloy II a new exothermic peak e was observed around 680 K and attributed to the Ag precipitation reaction, from Ag dissolved into martensitic phase on quenching. The DSC curve obtained for the alloy III shows an additional exothermic peak f at about 803 K due to the α phase precipitation reaction that precedes the β phase formation from $(\alpha + \gamma_1)$ phase at high temperature. The γ_1 phase formation causes a decrease in the Al content dissolved in the matrix. This change in chemical composition leads to the precipitation of α phase from Cu-rich phase [2], which is evident from the exothermic effect peak f. In Fig. 1 the α phase precipitation reaction was detected only for alloy III.

In the DSC curves of Fig. 1 it is possible to notice that peak a decreases its intensity when Ag content is increased. This effect is related to a shift of equilibrium concentration to higher Al concentration [8] where a martensitic structure more ordered than that verified at lower Ag content is produced, thus decreasing the intensity of the peak corresponding to the ordering reaction. Peak e associated with Ag precipitation reaction is shifted to higher temperatures with the increase of Ag concentration. This indicates that the precipitation process is slower when the amount of Ag is increased. This is probability due to the Ag–Al pair interaction which decreases the diffusion rate of Ag and shifts its transition temperature to higher values.

The $\beta_1' \to \beta_1$ reverse martensitic transition followed by $\beta_1 \to (\alpha + \gamma_1)$ decomposition reaction are associated with peak b in Fig. 1. This thermal event does not appear in the DSC curve corresponding to the alloy II because Ag precipitation reaction occurs in the same temperature range and is the dominant effect. In the curve obtained for the alloys II and III Ag precipitation (peak e) appears before the consecutive reactions corresponding to peak b, the reverse martensitic transformation followed by decomposition reaction, while for alloys IV and V these consecutive reactions occur before Ag precipitation. This inversion seems to be related both to the Ag solubility limit in the α-Cu-rich matrix phase of the Cu–Al system, about 6 mass% Ag [9] and to Al concentration. On quenching for alloys with up to 6 mass% Ag (alloys II and III) almost all Ag is dissolved in the α matrix and a very little part in the martensitic phase. With additions of 8 and 10 mass% Ag (alloys IV and V) and the shift of equilibrium concentration to higher Al content a larger amount of martensitic phase is obtained and, consequently, the $(\alpha + \gamma_1)$ relative fraction also increases. This will enhance Ag solubility in the martensitic phase and decrease the Ag amount available for precipitation. In this way, $\beta_1' \to \beta_1$ reverse martensitic transition followed by $\beta_1 \to (\alpha + \gamma_1)$ decomposition reaction are intensified and precede Ag precipitation.

Figure 2 shows the in situ X-ray diffraction patterns obtained for samples initially quenched from 1173 K. This result confirms the proposed reactions sequence and also that Ag precipitation occurs in the same temperature range of the reverse martensitic transformation in alloy II. Figure 3 shows the scanning electron micrographs (BEI) obtained for samples quenched from 1173 K. In Fig. 3a it is possible to see the characteristic structure of the martensitic phase in Cu–Al alloys consisting of needle-shaped platelets. As addition of silver increases Ag precipitates are observed above 6 mass% Ag (Fig. 3b, white region) suggesting that Ag solubility limit in the alloy I is around this silver concentration. It is also possible to observe that the α phase formation onto the martensitic phase occurs from 6 mass% Ag indicating that, with the shift of equilibrium concentration to higher Al content there is a depletion of Al from the α-(Cu–Al) matrix which increases the Cu relative fraction causing α phase precipitation.

Figure 4 shows the DSC curves obtained at a heating rate of 10 K min^{-1} for alloys VI, VII, VIII, IX and X quenched from 1173 K in iced water to produce the martensitic phase. It is possible to observe that peak e

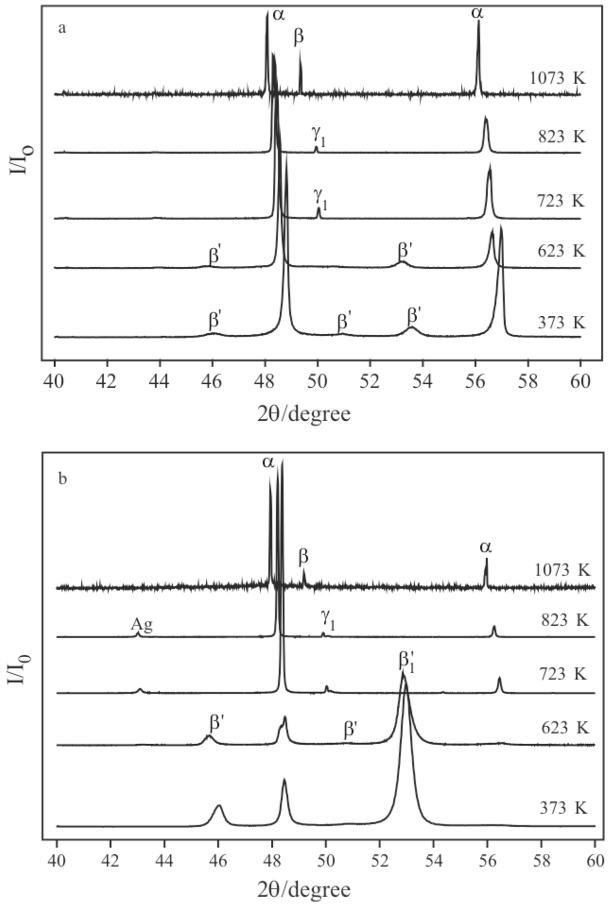

Fig. 2 In situ X-ray diffraction patterns obtained for samples initially quenched from 1173 K: a – alloy I; b – alloy II

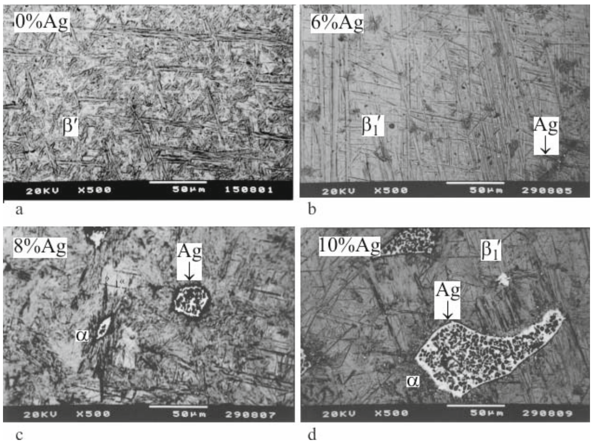

Fig. 3 Scanning electron micrographs (BEI) obtained for samples quenched 1173 K

related to the Ag precipitation reaction is not detected for the alloys with Ag additions compared to Fig. 1.

In the DSC curves of Fig. 4 it is also possible to verify that peak a at about 543 K and related to the martensitic phase ordering is not pronounced. As it has already been mentioned this suggests that the martensitic phase produced in the Cu–11 mass% Al alloy with and without Ag additions is close to the maximum degree of ordering. It is known [2] that Cu–Al alloys with Al concentrations lower than 10.8 mass% Al present a β' disordered martensitic structure which can evolve into a β'_1 ordered structure on heating while alloys with Al concentrations higher than 10.8 mass% Al will show a β'_1 ordered structure just after quenching. It is important to notice that the DSC curves obtained for the Cu–10 mass% Al alloys with additions of Ag higher than 6 mass% (Fig. 1) and those obtained for the Cu–11 mass% Al alloy with and without Ag additions (Fig. 4) all do not present the $\beta' \to \beta'_1$ ordering reaction thus confirming that Ag additions above 6 mass% to alloy I shift the equilibrium concentration from the β' phase stability field to that associated with the β'_1 ordered phase.

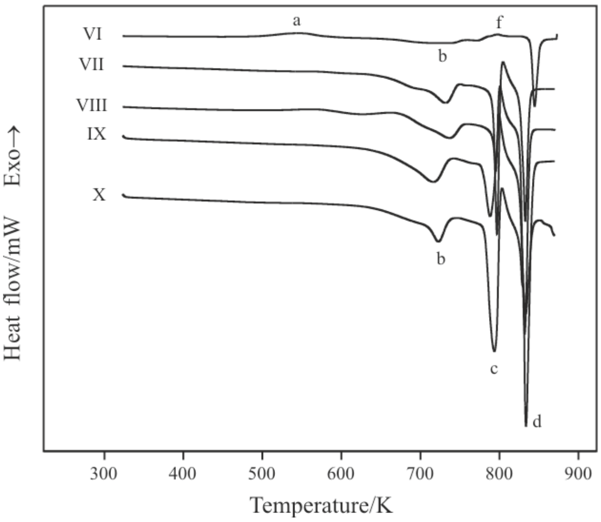

Fig. 4 DSC curves obtained at a heating rate of 10 K min^{-1} for initially quenched from 1173 K

In the DSC curves of Fig. 4 one can still observe that peak b due to the reverse martensitic and β_1 phase decomposition reactions is more evident and shifted to lower temperatures with the increase of Ag content. This indicates that crescent additions of Ag to the Cu–11 mass% Al alloy increase the martensitic phase relative fraction produced on quenching and consequently the $(\alpha+\gamma_1)$ phase amount is also increased but the stability of the martensitic phase is decreased.

Peak c attributed to the $\beta_1 \to \beta$ transition is not detected in the DSC curve corresponding to alloy VI (Fig. 4) whereas this same thermal event is very pronounced in the DSC curve obtained for the alloy I (Fig. 1). This can be associated with the increase in the $(\alpha+\gamma_1)$ phase relative fraction formed during β_1 phase decomposition which produces a significant increase in the α phase amount precipitated at high temperatures peak f, and decreases the β_1 phase fraction able to produce β, peak c. The absence of the $\beta_1 \to \beta$ transition in alloy VI is now probably due to

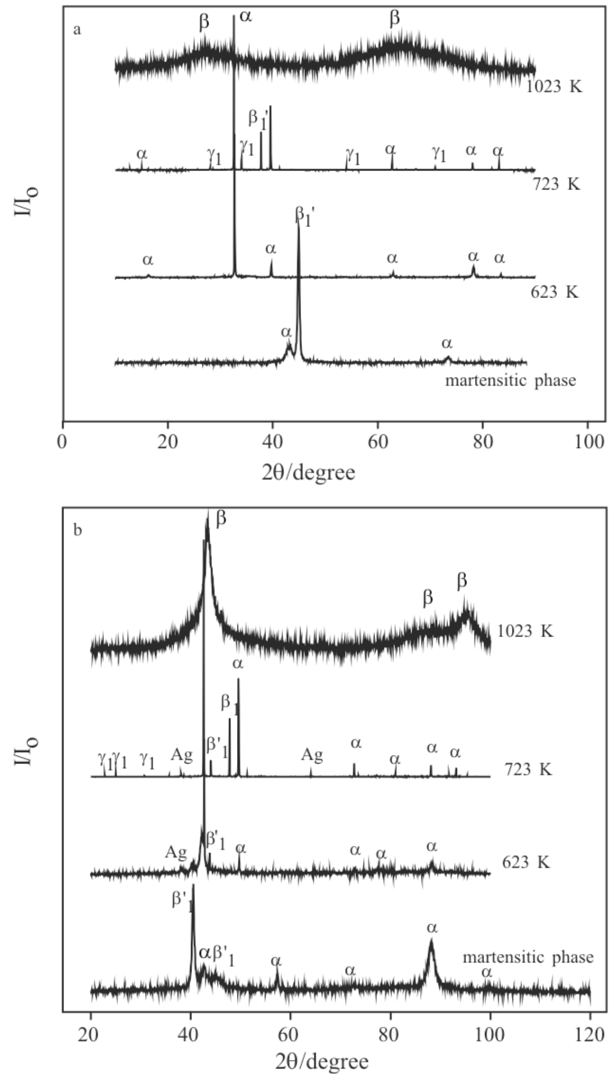

Fig. 5 In situ X-ray diffraction patterns obtained for samples initially quenched from 1123 K: a – alloy VI; b – alloy VII

the fact that peaks c and f are occurring in the same temperature range and the resultant effect is the sum of the reaction enthalpies of an endothermic (peak c) and an exothermic (peak f) event.

In the DSC curves of Figs 1 and 4 peak d is due to the $(\alpha+\gamma_1)\rightarrow\beta$ reverse eutectoid reaction. In these figures is possible to notice an increase in the intensity of this peak with the increase of Ag content. This effect is caused by Ag dissolution, which contributes to the increase in the Al atoms relative fraction available to produce the γ_1 phase and also shifts the equilibrium to higher Al concentration.

The transition sequence proposed in the above discussion for Fig. 4 is confirmed by the in situ X-ray diffraction patterns shown in Fig. 5. Figure 5a shows the X-ray diffraction patterns obtained for alloy VI, initially quenched to produce the martensite phase and then heated at 623, 723 and 1023 K, respectively, with a constant heating rate of 10 K min^{-1}. The starting point in this figure corresponds to the β_1' martensitic phase. On heating at 623 K one may observe an increase in the reflections of the α phase, suggesting a precipitation of this phase and at 723 K the reflections due to the γ_1 phase, resulting from the β_1 phase decomposition reaction. At 1023 K only the β phase is observed but with very large peaks. It is known that with the linear increase in the heating rate, the diffraction peaks become sharper and are shifted to lower angles [10]. This peak enlargement in Fig. 5a is probably related to the formation of very small crystals of the β phase. In Fig. 5b, obtained for the alloy VII in the same conditions of Fig. 5a, it is possible to observe the same reflections already mentioned and the presence of an additional peak at about 623 and 723 K, due to the Ag-rich phase formation. When the in situ X-ray diffraction patterns, in Figs 2 and 5, are compared it is possible to observe that the peak enlargement at high temperatures is only detected for the Cu–11 mass% Al alloys with and without Ag additions, suggesting that this effect is related to the change on the Al concentration.

Conclusions

The results showed that Ag additions to the Cu–10 mass% Al alloy induce the β_1' phase formation and to the Cu–11 mass% Al alloy increase the martensitic phase amount formed on quenching but decrease its stability range during heating. The martensite ordering reaction peak observed at about 563 K for all studied alloys is more intense for the Cu–10 mass% Al alloy with additions of Ag lower than 6 mass% indicating that the Cu–11 mass% Al alloy is near the ordering limit for this system. The results also showed that the dissolution of Ag precipitates enhanced the α phase formation at high temperature and that the increase in the Al concentration from 10 to 11 mass% Al interferes in the β phase crystal size.

Acknowledgments

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