J Therm Anal Calorim (2009) 97:117–121
DOI 10.1007/s10973-009-0253-7

Influence of Ag addition on the thermal behavior of the Cu-11 mass% Al alloy

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ICTAC2008 Conference

Abstract In this work the influence of Ag additions on the thermal behavior of the Cu-11 mass% Al alloy was studied using differential scanning calorimetry, in situ X-ray diffractometry and scanning electron microscopy. The results indicated that changes in the heating rate shift the peak attributed to α phase formation to higher temperatures, evidencing the diffusive character of this reaction. The activation energy value for the α phase formation reaction, obtained from a non-isotherm kinetic model, is close to that corresponding to Cu atoms self diffusion, thus confirming that this reaction is dominated by Cu atoms diffusion through the martensite matrix.

Keywords Thermal behavior · Cu–Al alloys · Ag addition

Introduction

Due to their high thermal and electric conductivity, copper-based alloys constitute a class of materials that have a number of applications. They also exhibit good resistance to corrosion. Cu–Al bronzes present good strength and are also corrosion resistant. Cu–Al alloys containing 9–14 mass% of Al among those showing a martensitic phase after the rapid cooling from high temperatures. When cooled to exhibit the martensitic phase, these alloys undergo disorder-order transitions and the supersaturation of quenched-in vacancies that is produced can favor subsequent diffusion controlled phenomena [1]. It has been shown that the addition of silver to Cu–Al alloys increases hardness and improves their resistance to stress corrosion in steam. 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]. In this work, the influence of Ag addition on the thermal behavior of the Cu-11 mass% Al alloy was studied using differential scanning calorimetry (DSC), in situ X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

Experimental procedures

The Cu-11 mass% Al, Cu-11 mass% Al-1 mass% Ag, Cu-11 mass% Al-2 mass% Ag and Cu-11 mass% Al-3 mass% Ag alloys were prepared in an induction furnace under argon atmosphere using 99.95% copper, 99.97% aluminum and 99.98% silver as starting materials. Results of 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 of diameter and 6.0 cm of length were cut in disks with 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 900 °C for homogenization and after annealing they were maintained at 900 °C for 1 h and quenched in iced water. Scanning electron micrographs and X-ray diffraction patterns were obtained to identify the phases present in the alloy at the different quenching temperatures. The micrographs were obtained

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using a Jeol JSM T330A SEM electron microscope with a Noran (EDX) micro-analyzer and the in situ high-temperature X-ray diffraction experiments were performed at the D10B-XPD X-ray diffraction beam line of the Brazilian Synchrotron Light Laboratory/MCT, with solid (not powdered) samples and $\lambda = 1.54984$ Å. The DSC curves were obtained using a DSC Q20 TA Instruments at different heating rates.

Results and discussion

Figure 1 shows DSC curves obtained for the Cu-11 mass% Al alloy at heating rates of 5, 10, 20, and 30 °C min^{-1}, from sample solutions treated at 900 °C and cooled in iced water at 0 °C to produce the martensitic phase. In the curve corresponding to the Cu-11 mass% Al alloy and obtained at a heating hate of 30 °C min^{-1}, five peaks are observed. P_1, at 291 °C is ascribed to α phase formation [3]. The endothermic peak P_2, at about 410 °C is associated with the reverse martensitic transformation $\beta_1' \rightarrow \beta_1$ followed by the decomposition reaction $\beta_1 \rightarrow (\alpha + \gamma_1)$ of β_1 phase fraction. P_3 is an endothermic peak that appears at about 535 °C due to the $\beta_1 \rightarrow \beta$ transition of β_1 remnant part formed at 410 °C. The endothermic peak P_4 at about 570 °C is related to the $(\alpha + \gamma_1) \rightarrow \beta$ transformation [4]. When the heating rate is decreased to 20, 10 and 5 °C min^{-1} the intensity of the peaks P_1, P_2 and P_5 is also decreased; P_3 is not detected, while P_4 is shifted to lower temperatures (see arrow).

In these curves is also possible to observe that the peak attributed to α phase formation (P_1) is shifted to higher temperatures when the heating rate is increased. This indicates that α phase formation is a diffusion-controlled process [4]. The peak at about 410 °C ascribed to the reverse martensitic transformation $\beta_1' \rightarrow \beta_1$ and the decomposition reaction $\beta_1 \rightarrow (\alpha + \gamma_1)$, increases its intensity with heating rate. It is known [5] that the reverse martensitic transformation $\beta_1' \rightarrow \beta_1$ is a diffusionless phase transition while decomposition reaction $\beta_1 \rightarrow (\alpha + \gamma_1)$ is a diffusive process; hence the increase on the heating rate must be contributing to the diffusionless phase transition. In this way, the dominant reaction in this temperature range depends on the heating rate. The peak P_3 at about 535 °C and associated with the $\beta_1 \rightarrow \beta$ structural change is not shifted with changes in the heating rate. Otherwise, peak P_4 attributed to the diffusive reaction due to α phase formation at high temperatures is shifted to higher temperatures with the increase in the heating rate and only in this condition this peak is detected. As it can be seen from Fig. 1 for heating rates lower than 30 °C min^{-1} a weak signal associated with α phase precipitation is observed probably because peaks P_3 and P_4 are occurring in the same temperature range and the resultant effect is the sum of the reaction enthalpies of an endothermic (P_3) and an exothermic (P_4) event.

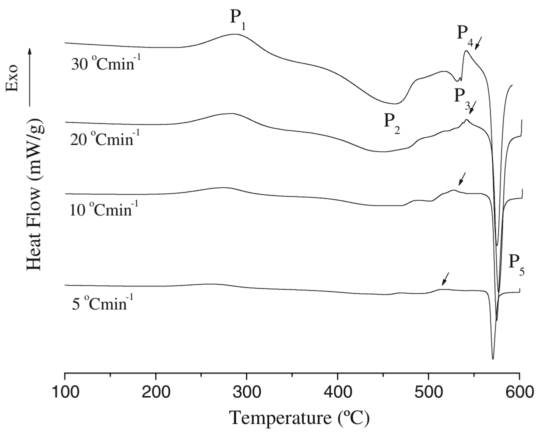

Fig. 1 DSC curves obtained for the Cu-11 mass% Al alloy

Figure 2 shows DSC curves obtained for the Cu-11 mass% Al-1 mass% Ag, Cu-11 mass% Al-2 mass% Ag and Cu-11 mass% Al-3 mass% Ag alloys at heating rates of 5, 10, 20, and 30 °C min^{-1}, from sample solutions treated at 900 °C and cooled in iced water at 0 °C to produce the martensitic phase. In the curve of Fig. 2a it is not observed any new thermal event, but in curves of Fig. 2b and c a new reaction at about 450 °C was verified, as compared with the curve obtained for the Cu-11 mass% Al alloy (Fig. 1). This new thermal event is ascribed to Ag-rich phase formation [6], suggesting that presence of Ag does not modify the reaction sequence observed in the Cu-11 mass% Al alloy but only introduces a new thermal event due to Ag precipitation retained during solution treatment.

It is important to notice that the endothermic peak P_3 at about 535 °C and attributed to $\beta_1 \rightarrow \beta$ transition is observed for the alloy with 3 mass% Ag addition at the lowest heating rate of 5 °C min^{-1}, while for the Cu-11 mass% Al alloy this peak is observed only at a heating rate of 30 °C min^{-1}. This is due to the β_1 phase relative fraction increase in the presence of Ag, which it is related with the decrease in the $\beta_1 \rightarrow (\alpha + \gamma_1)$ decomposition reaction rate. This result indicates that the presence of Ag interferes on the formation of the $(\alpha + \gamma_1)$ phase thus increasing the relative fraction of the β_1 phase available for the $\beta_1 \rightarrow \beta$ transition.

Figure 3 shows the scanning electron micrographs obtained for quenched samples. From Fig. 3a and b one can observe that the microstructure of the Cu-11 mass% Al-2 mass% Ag alloy is a little different from that of the Cu-11 mass% Al alloy, which shows small platelets in acicular form. With the increase of the temperature α phase precipitation occurs (Fig. 3c, d), probably due to a diffusive process into the martensitic phase. The microstructures shown in Fig. 3a and b are the starting point of the DSC curves in Figs. 1 and 2.

The transition sequence proposed in the above discussion for Figs. 1 and 2 was confirmed by the in situ X-ray

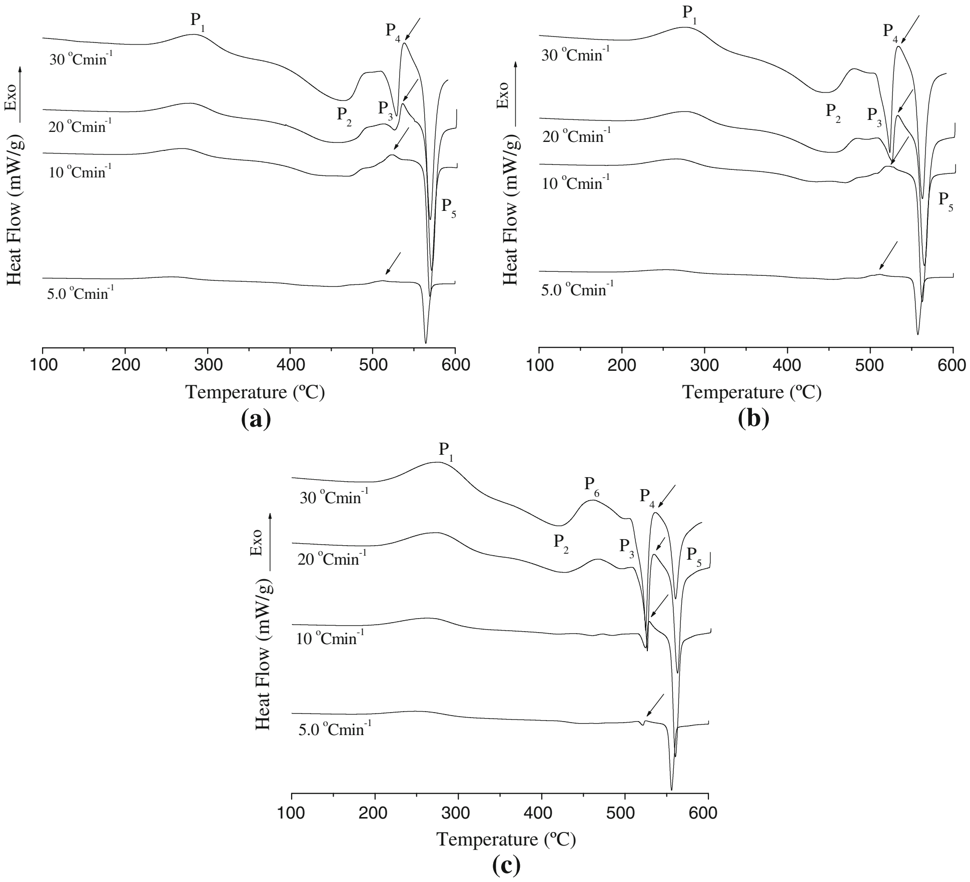

Fig. 2 DSC curves obtained for the (**a**) Cu-11 mass% Al-1 mass% Ag, (**b**) Cu-11 mass% Al-2 mass% Ag and (**c**) Cu-11 mass% Al-3 mass% Ag alloys

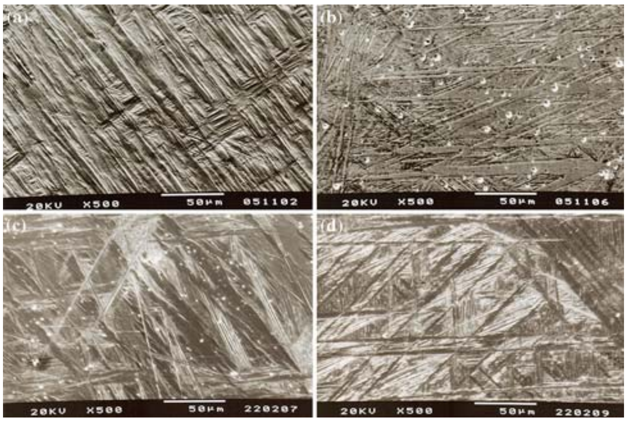

Fig. 3 Scanning electron micrographs obtained for the **a** Cu-11 mass% Al and **b** Cu-11 mass% Al-2 mass% Ag quenched from 900 °C and then **c** Cu-11 mass% Al and **d** Cu-11 mass% Al-2 mass% Ag quenched from 300 °C

diffraction patterns shown in Fig. 4. Figure 4a shows the X-ray diffraction patterns obtained for the Cu-11 mass% Al alloy initially quenched to produce the martensite phase and then heated at 350, 450 and 750 °C, respectively, with a constant heating rate of 10 °C min^{-1}. The starting point in this figure corresponds to the β_1' martensitic phase. On heating at 300 °C one may observe an increase in the reflections of α phase, suggesting a precipitation of this phase (Fig. 3c) and at 450 °C the reflections due to the γ_1 phase (Fig. 3d), resulting from the β_1 phase decomposition reaction. At 750 °C 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 temperatures [7]. This peak enlargement in Fig. 4a is probably related to the formation of very small crystals of the β phase and to the end of the A2 $\leftrightarrow$ B2 ordering reaction. In Fig. 4b obtained for the Cu-11 mass% Al-3 mass% Ag alloy in the same conditions of Fig. 4a it is possible to observe the same reflections already mentioned and the presence of an additional peak at about 450 °C due to the Ag-rich phase formation.

The α phase formation reaction at low temperatures (at about 270 °C) is responsible for the decrease of the shape memory capacity in Cu-based alloys [8]. In Figs. 1 and 2 peak P_1 associated with α phase formation reaction is shifted to higher temperatures with the increase of the heating rate for all analyzed alloys as shown in Fig. 5 and Table 1. This indicates that the α phase formation reaction is a diffusive process and can be associated with the diffusion of Cu atoms into the martensitic matrix. The shift of peak P_1 with different heating rates serve as a basis for determining the activation energies of this diffusion process using the linear relationships obtained from the Kissinger [9] method:

Fig. 4 In situ X-ray diffraction patterns obtained for the **a** Cu-11 mass% Al and **b** Cu-11 mass% Al-3 mass% Ag alloys initially quenched to produce the martensitic phase

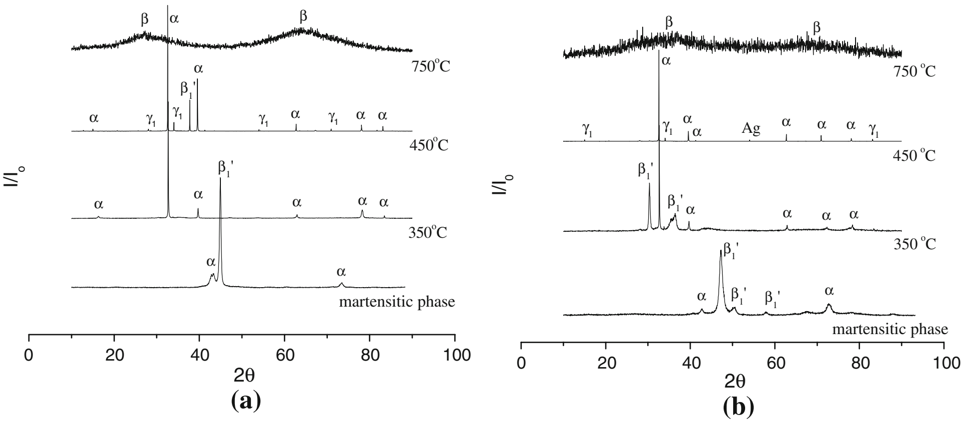

Fig. 5 Enlarged parts of Figs. 1 and 2: **a** Cu-11 mass% Al and **b** Cu-11 mass% Al-2 mass% Ag alloys

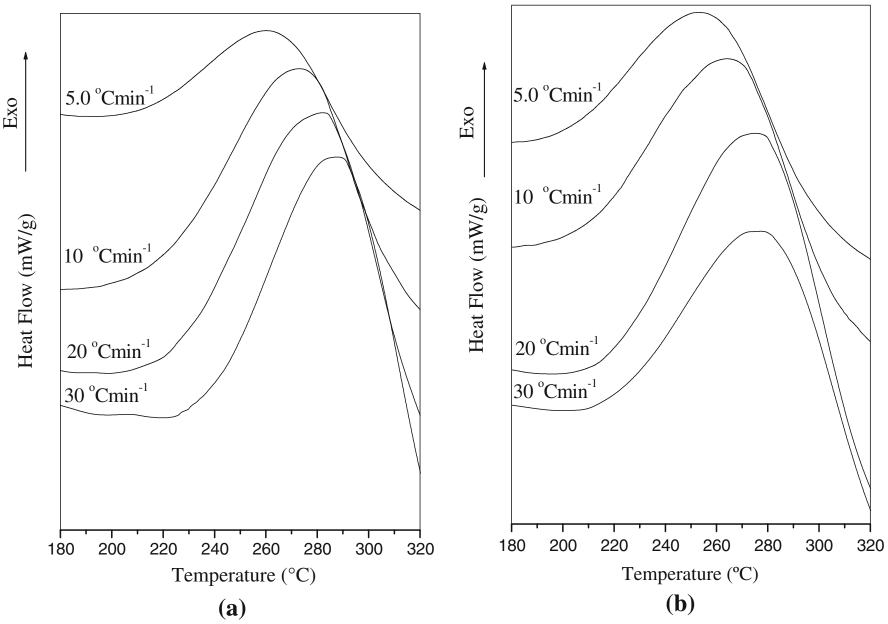

Table 1 Peak temperatures obtained from Fig. 5

ϕ/°C min^{-1}/ Alloys	Cu-11% Al	Cu-11% Al–1%Ag	Cu-11% Al–2%Ag	Cu-11% Al–3%Ag
5.0	266.5	262.7	260.0	255.5
10	274.9	272.0	269.2	266.3
20	284.0	280.5	279.8	276.1
30	291.3	287.8	281.7	279.6

$$\ln\left[\frac{\phi}{T_{\mathrm{p}}^{2}}\right] = C - \frac{E}{RT_{\mathrm{p}}} \quad (1)$$

where ϕ is the heating rate, T_{p} the maximum on the DSC peak, E the activation energy, R the universal gas constant and C is integration constant.

Figure 6 shows the plot of $\ln[\phi/T_{\mathrm{p}}^{2}]$ versus $1{,}000/T_{\mathrm{p}}$ for the Cu-11 mass% Al, Cu-11 mass% Al-1 mass% Ag,

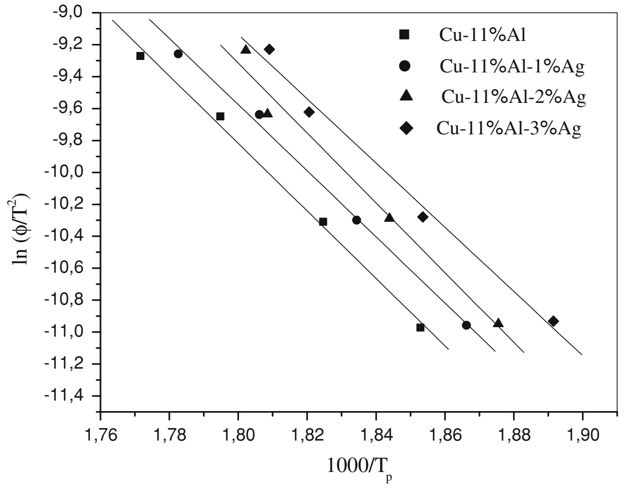

Fig. 6 ln (ϕ/T^{2}) vs. $1{,}000/T_{\mathrm{p}}$ plot

Table 2 Enthalpy values obtained from the α phase formation reaction

ϕ/°C min^{-1}	5.0	10	20	30
ΔH (Jg^{-1})	(−6.654 ± 0.018)	(−6.389 ± 0.123)	(−6.519 ± 0.165)	(−6.445 ± 0.191)

Cu-11 mass% Al-2 mass% Ag and Cu-11 mass% Al-3 mass% Ag alloys, where one can observe that the experimental points are aligned and these lines are almost parallel, thus indicating a similar basic mechanism for all alloys.

From the Arrhenius equation,

$$D = Ae^{\frac{-Q}{RT}} \quad (2)$$

it is found that the activation energy mean value, obtained from the slope of these straight lines is $E = (174.2 \pm 3.0)$ kJ mol^{-1}, which correlates well with the activation energy for self-diffusion of Cu atoms ($E = 194.0$ kJ mol^{-1}) [10].

In this way the results suggest that the activation energy value obtained from Fig. 6 is associated with Cu diffusion into the martensitic matrix at about 290 °C. The presence of Ag has little influence on this diffusion process due to its lower concentration and weaker chemical interaction with Cu atoms but Ag solution treated is distributed into martensitic phase and increases the transition entropy, since the transition enthalpy is constant for all alloys, as it can be seen from Table 2. As a consequence, the α phase formation reaction occurs at lower temperature in the presence of Ag (see Table 1).

Conclusions

The results indicated that Ag addition to the Cu-11 mass% Al alloy decreases the $\beta_1 \rightarrow (\alpha + \gamma_1)$ decomposition reaction rate. The activation energy value for the α phase formation confirmed that this reaction is dominated by diffusion of Cu atoms through the martensite matrix. The DSC peak corresponding to this reaction is shifted to lower temperatures with the increase in the Ag content thus suggesting that the decrease in the peak temperature may be related to the increase in the entropy of the system due to the addition of a third alloy element.

Acknowledgements The authors thank the support of FAPESP (Project no. 2006/04718-0), LNLS-Brazilian Synchrotron Light Laboratory/MCT and CNPq.

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