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EFFECT OF 4 MASS% Ag ADDITION ON THE THERMAL BEHAVIOR OF THE Cu-9 MASS% Al ALLOY

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Abstract

The effect of 4 mass% Ag addition on the thermal behavior of the Cu-9 mass% Al alloy was studied using differential scanning calorimetry (DSC), optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD). The results showed that the presence of silver causes (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation to occur in two stages. In the first one, part of the produced β phase combines with the precipitated Ag to give a silver-rich phase and in the second one the transformation is completed. The formation of this silver-rich phase seems to be enhanced at very low cooling rates.

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

Introduction

In the Cu-9 mass% Al alloy, the β phase undergoes a martensitic transformation on rapid cooling from high temperatures, giving β' fcc disordered martensite after the ordering to β_1 phase. $\beta_1\rightarrow\beta$ transition occurs at about 520°C and the heating rate is determinant in the observation of the endothermic peak corresponding to this transition. During the slow cooling from the high temperature β phase, an eutectoid transformation occurs. These transformations are reversible during reheating and, depending on the rates of heating and cooling, some of these transformations may overlap. The rate of heating and cooling is the major factor determining the transformations which take place in Cu-rich Cu–Al alloys with Al concentration in the eutectoid range. For samples cooled at a rate equal or lower than 2°C min^{-1}, during re-heating only two endothermic effects were observed, the disordering of α_2 phase and (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation. The presence of an endothermic peak at about 520°C depends on an incomplete (Cu)-α+$\beta\rightarrow$(Cu)-α+(α+γ_1) transformation, which retains a small fraction of the martensitic phase [1]. Additions of a third element to Cu–Al alloys in the eutectoid range change the characteristics of its martensitic transformations [2, 3]. Silver additions to Cu–Al alloys may shift the equilibrium concentration to higher Al contents and induce the formation of a silver-rich phase [4].

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In this work, the thermal behavior of the Cu-9 mass% Al alloy with 4 mass% Ag addition was studied on heating and on cooling, to analyze the effect of Ag addition in (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation.

Experimental

Cu-9 mass% Al alloy with 4 mass% Ag addition was 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 alloy composition very close to the nominal one.

Small pieces of about 40 mg were used for DSC analysis and flat square samples of about 10 mm length and 1.0 mm of thickness were obtained for metallography and X-ray diffractometry. The samples were initially annealed for 120 h at 850°C for homogenization. DSC curves were obtained from an annealed sample cooled at a rate of 4°C min^{-1} before heating at 20°C min^{-1} and cooling at a rate of 1°C min^{-1}. In sequence, the sample was reheated at a rate of 20°C min^{-1}.

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. DSC data were obtained using a TA 2910 instrument. XRD diagrams were obtained using a Siemens D5000 X-ray diffractometer.

Results and discussions

Figure 1 shows the DSC curves obtained for Cu-9 mass% Al alloy with 4 mass% Ag addition and Figs 3, 5, 6 and 7 show the enlarged portion of these curves. In the DSC curve of Fig. 3, obtained for a sample heated at 20°C min^{-1} after cooling at about 4°C min^{-1}, it is possible to observe the expected transformations from the Cu–Al equilibrium diagram [5] shown in Fig. 2. In Fig. 3, peak 1, at about 300°C, corresponds to the α_2 phase disordering. Peak 2, at about 380°C, corresponds to the disso-

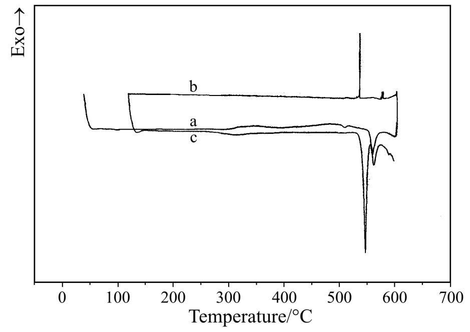

Fig. 1 DSC curves obtained for the Cu-9 mass% Al alloy with 4 mass% Ag addition; a – heating at 20°C min^{-1} after cooling at about 4°C min^{-1}; b – cooling at 1°C min^{-1}; c – heating at 20°C min^{-1}

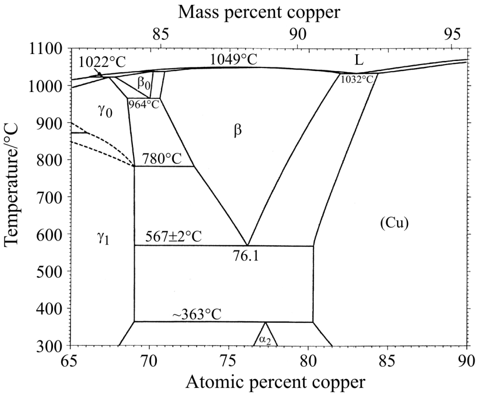

Fig. 2 Cu-rich region of the Cu–Al phase diagram [5]

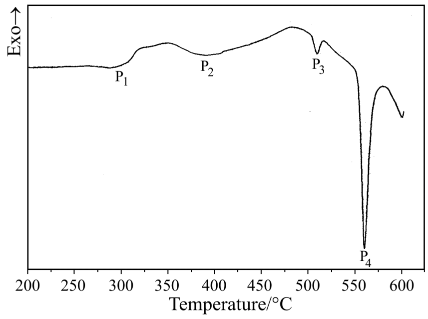

Fig. 3 DSC curve obtained for the Cu-9 mass% Al alloy with 4 mass% Ag addition on heating, after cooling at 4°C min^{-1}. Heating rate 20°C min^{-1}

lution of α_2 precipitates [6]. Peak 3, at about 510°C, is due to the transformation of the β_1 phase into the β phase. The β_1' martensitic phase changes into the β_1 phase in the same temperature interval as the disordering process of the α_2 phase and at 510°C $\beta_1 \rightarrow \beta$ transformation occurs. Peak 4, at about 560°C, is associated to the $\alpha+(\alpha+\gamma_1) \rightarrow \alpha+\beta$ transformation [7]. Peaks 3 and 4 are shifted to lower temperatures, in relation to those observed for Cu-19 at.% Al alloy [8].

Peaks 1 and 2 have a shape that is more like that observed for Cu-21 at.% Al alloy [6]. This seems to indicate a shift of the equilibrium concentration to higher Al concentrations, due to the Ag addition. The shift of peak 3 to lower temperatures may also be related to this shift of the equilibrium concentration, considering that at higher Al concentrations the β phase is easily formed from the β_1 phase [9].The shift of peak 4 to lower temperatures may be due to the Ag dissolution which increases the relative fraction of the α phase and allows the early formation of the β phase.

Figure 4 shows the X-ray diffraction patterns obtained for the alloy quenched from 500°C (Fig. 4a) and 600°C (Fig. 4b). In this figure it is possible to observe that the diffraction peak corresponding to a silver-rich phase is detected at 600 but not at

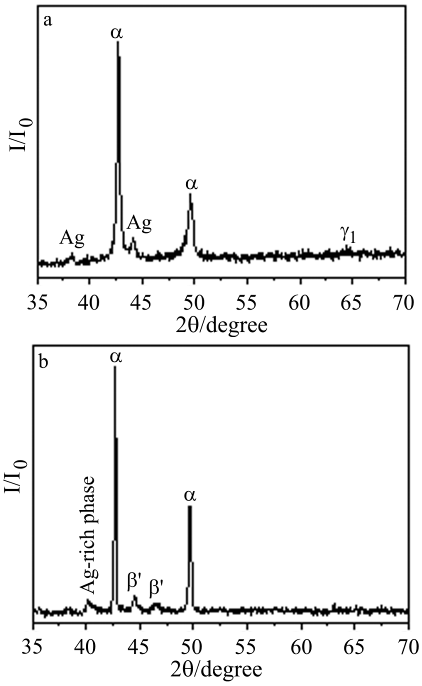

Fig. 4 X-ray diffraction patterns obtained for the sample quenched from; a – 500; b – 600°C

500°C. This seems to indicate that the formation of this silver-rich phase is connected to the presence of the β phase.

After heating at 20°C min^{-1} (Fig. 3), the sample was cooled at 1°C min^{-1} and the obtained DSC curve is shown in Fig. 5. Figure 6 shows three parts of Fig. 5, corresponding to the temperature ranges of 585 to 540°C (Fig. 6a), 540 to 534°C (Fig. 6b) and 534 to 510°C (Fig. 6c). In Fig. 6a it is possible to observe six exothermic peaks, respectively at about 580 (P_1), 579 (P_2), 578 (P_3), 576 (P_4), 575 (P_5) and 561°C (P_6). Peak P_1 may be attributed to Ag precipitation and P_2 to the precipitation of the disordered α phase from the β phase. P_3 may be attributed to the $\beta\to\beta_1$ transformation from part of the β phase, P_4 to the $\beta\to\gamma_1$ and P_5 to the $\beta\to\alpha$ transitions. Peak P_6 corre-

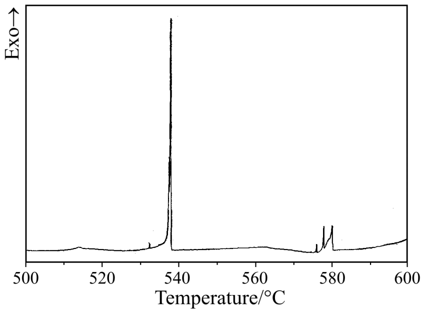

Fig. 5 DSC curve obtained on cooling. Cooling rate 1°C min^{-1}

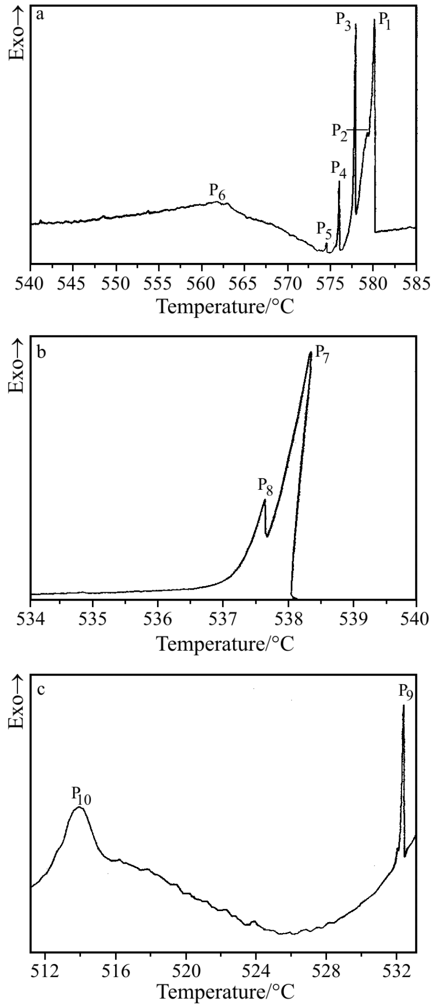

Fig. 6 DSC curve of Fig. 5 in the temperature ranges; a – 585 to 540°C; b – 540 to 534°C; c – 534 to 510°C

sponds to the (Cu)-α+$\beta$$\rightarrow$(Cu)-$\alpha$+($\alpha$+$\gamma_1$) transformation. In Fig. 6b two exothermic peaks are observed, respectively at about 538°C (P_7) and 537°C (P_8). Peak P_7 may be attributed to the (Ag-rich phase)$\rightarrow$$\beta$ transition and peak P_8 to Ag precipitation from (Ag-rich phase). In Fig. 6c peak P_9, at about 532°C, may be due to $\beta_1$$\rightarrow$$\beta$ transformation and peak P_{10}, at about 532°C, may correspond to $\beta$$\rightarrow$($\alpha$+$\gamma_1$) transition.

In sequence, the sample cooled at 1°C min^{-1} was reheated at 20°C min^{-1} and in the obtained DSC curve shown in Fig. 7, four endothermic peaks are observed, respectively at about 320, 548, 563 and 589°C. The peak at 320°C (P_1), is due to the α_2 phase disordering and the peak at 563°C (P_3) to the (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation. It was expected from literature [8] that for cooling rates equal or lower than 2°C min^{-1}, in which the martensitic phase is not retained, the endothermic peak at about 510°C should not be observed. In the curve obtained for Cu-9 mass% Al alloy with 4 mass% Ag addition, the peak at 563°C (P_3) decreases and the peak at 548°C is the most intense, indicating that this is the dominant reaction. This peak at 548°C may be attributed to the formation of the Ag-rich phase. The formation of this phase, as pointed out in the discussion of Fig. 4, seems to depend on the presence of the β phase. In this way, peak P_2 could correspond to $\alpha+(\alpha+\gamma_1)\rightarrow\alpha+\beta$ and $\beta+\mathrm{Ag}\rightarrow(\mathrm{Ag\text{-}rich\ phase})+\alpha$ transitions and explain its higher intensity. Peak P_4, at about 589°C, may be related to the dissolution of the remaining Ag.

From Figs 3 and 7 it is possible to observe that the peak attributed to the formation of the Ag-rich phase was not detected in the first heating run (Fig. 3) but is the most intense in the second (Fig. 7). This seems to indicate that the formation of the silver-rich phase is enhanced at very low cooling rates. In the first run the β phase formed from $\beta_1\rightarrow\beta$ transition may be combined with Ag to form a few of the Ag-rich phase. In the second heating run, in the absence of $\beta_1\rightarrow\beta$ transition, the Ag dissolution increased the relative fraction of the α phase and allowed the early formation of the β phase. The combination of β phase with Ag seems to occur in sequence and both transformations give the thermal event corresponding to peak P_2 in Fig. 7.

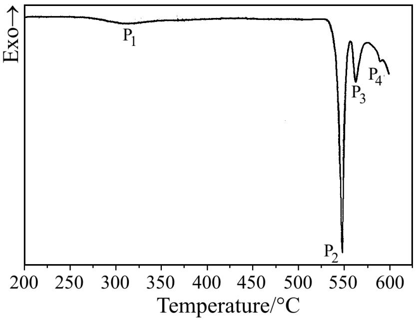

Fig. 7 DSC curve obtained after cooling at 1°C min^{-1}. Heating rate 20°C min^{-1}

Figure 8 shows the optical micrographs obtained for the Cu-9 mass% Al alloy with 4 mass% Ag addition quenched from 500°C (Fig. 8a) and from 600°C (Fig. 8b). In Fig. 8b it is possible to observe the presence of some precipitates on the grain boundary. These precipitates may be better observed in the scanning electron micrograph shown in Fig. 9a and from the EDX spectrum of Fig. 9b it is possible to see that

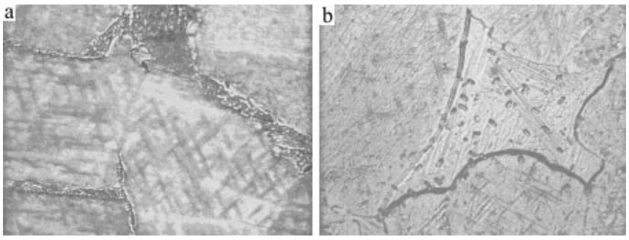

Fig. 8 Optical micrographs (500×) obtained for the alloy quenched from; a – 500°C; b – 600°C

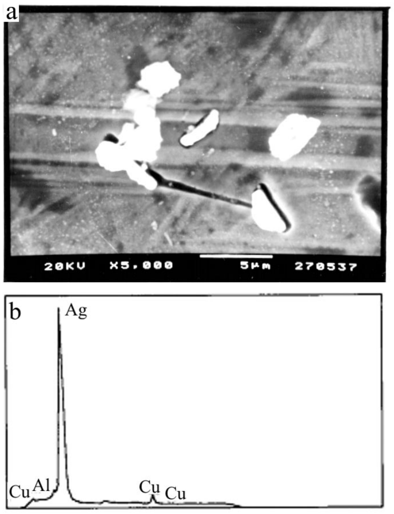

Fig. 9 a – Scanning electron micrograph obtained for the alloy quenched from 600°C;
b – EDX spectrum from the precipitates

they are silver-rich precipitates. These results seem to confirm what was proposed for peak P_2 in Fig. 7, i.e., this peak corresponds to the formation of a silver-rich phase.

Conclusions

The results showed that the presence of Ag strongly modifies the thermal behavior of Cu-9 mass% Al alloy and causes (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation to occur in two stages. In the first one, part of the produced β phase combines with the precipitated Ag to give a silver-rich phase and in the second one the transformation is completed. As expected [8] for cooling rates equal or lower than 2°C min^{-1}, at which the martensitic phase is not retained, the endothermic peak at about 510°C, corresponding to $\beta_1\rightarrow\beta$ phase transformation was not observed in the curve obtained for Cu-9 mass% Al alloy with 4 mass% Ag addition. However, in this curve the peak at about 563°C, corresponding to (Cu)-α+(α+γ_1)$\rightarrow$(Cu)-α+β transformation decreases and the endothermic peak at 548°C is the most intense, indicating that this is the dominant reaction. This peak at 548°C is attributed to the formation of a silver-rich phase, as observed from the X-ray diffraction patterns. This new phase seems to be formed from the combination of β phase with the precipitate Ag and its formation is enhanced at very low cooling rates.

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