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Reverse martensitic transformation in the Cu-10 wt% Al-6 wt%Ag alloy

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The reverse martensitic transformation in the Cu-10 wt%Al-6 wt%Ag alloy was studied by classical differential thermal analysis (DTA), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD). The results indicated that the presence of Ag in the Cu-10%Al alloy is responsible for the separation of the competitive reactions that occur during the reverse martensitic transformation and is also associated to an increase in the disordering degree at high temperatures, when compared with alloys without Ag addition. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Many Cu-based alloys have been developed envisaging better properties than pure copper for particular applications. A great number of these alloys exhibit on cooling a martensitic transformation from the β (bcc) phase towards a close-packed structure [1]. They are Hume-Rothery [2] alloys for which the phase stability is controlled by the average number of conduction electrons per atom. In general, in these alloys the β phase is only stable at high temperatures but it can be retained in a metastable state at lower temperatures by means of a fast quench [3], when the β phase transforms into the β' martensitic phase [4, 5]. Due to the diffusionless nature of the martensitic transformation the atom distribution on the lattice sites is inherited from the high temperature β phase [6]. Cu-Al alloys containing 9 to 14 wt%Al are among those showing a martensitic transformation on rapid cooling from high temperatures. During the heating of martensite, a reverse martensitic transformation, $\beta_1' \rightarrow \beta_1$, takes place in the temperature range 340 to 400°C in hypoeutectoid Cu-Al alloys. Afterwards, during slow heating the β_1 phase transforms into a eutectoid $(\alpha + \gamma_1)$ phase mixture [7]. At the temperature of 565°C, the β phase formation reaction occurs from the $(\alpha + \gamma_1)$ phase mixture [8–10]. Cu-Al-Ag alloys are regarded as promising new materials because of its good mechanical properties, conductivity and appearance [11], high corrosion resistance in different media [12, 13] and ease of manufacture. Such alloys find applications in electronics, odontology and also for ornamental purposes. The equilibrium diagram and some characteristics of the Cu-Al-Ag system have been reported [14, 15]. In this work the effect of 6 wt%Ag addition on the thermal behavior of the Cu-10%Al alloy was studied with the sample in the quenched condition (retained martensite on fast cooling), to analyze the reverse martensitic transformation and influence of Ag on it.

2. Experimental procedure

The Cu-10 wt%Al-6 wt%Ag alloy 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, with Pb, Fe, and Mn as main impurities (concentration less than 100 ppm).

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 and X-ray diffractometry. 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. XRD spectra were obtained using a Siemens D5000 X-ray diffractometer. After the heat treatments the flat samples were polished, etched and examined in a Jeol JSM T330A scanning electron microscopy with a Noran energy dispersive X-ray (EDX) microanalyser.

The DTA curves were obtained using a sample holder with two Ni/Cr-Ni/Al thermocouples, one of which was introduced in the sample and the other in a pure copper cylinder with the same sample dimensions. The sample holder, inside a Vycor tube, was introduced in a furnace and the thermocouples terminals were connected to a HP 34404A multimeter. The heating rate and the data acquisition were controlled using a MQ 112 Micro-Química interface.

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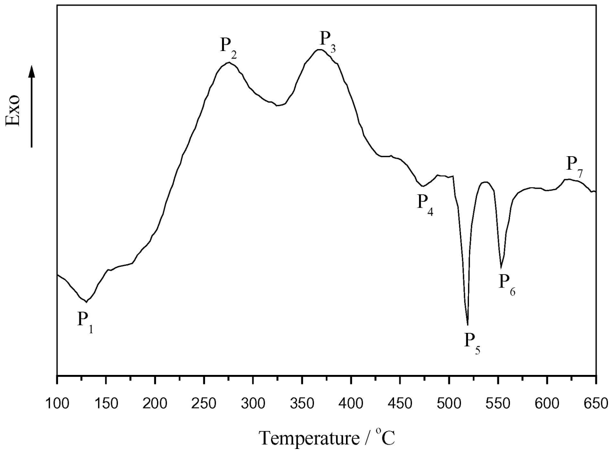


Figure 1 DTA curve obtained for the alloy quenched from 850°C. Heating rate 10°C min^{-1}.

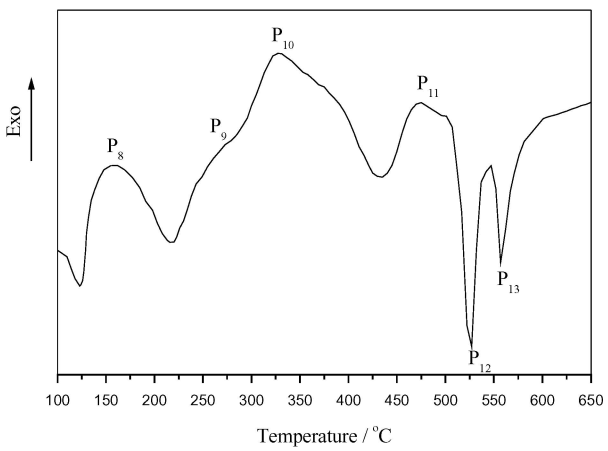
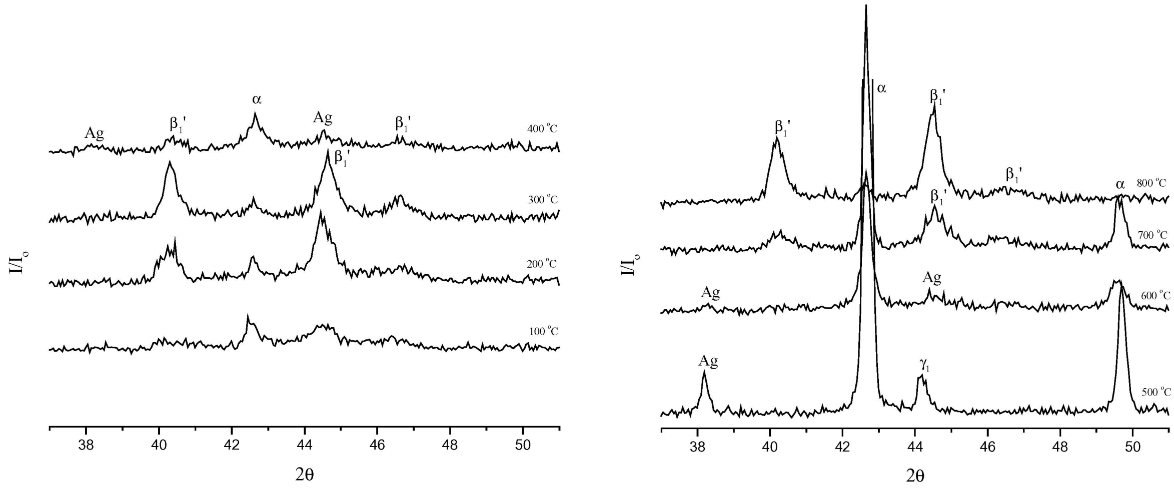


Figure 3 DTA curve obtained for the alloy quenched from 850°C. Heating rate 20°C min^{-1}.

3. Results and discussion

Fig. 1 shows the DTA curve obtained for the sample quenched from 850°C in iced water, with a heating rate of 10°C min^{-1}. In Fig. 1, the endothermic peak P_1 at about 130°C may be attributed to the first stage of the reverse martensitic transformation $\beta_1' \rightarrow \beta_1$ from part of the β_1' martensitic phase [16]. P_2, at about 280°C, is an exothermic event related to the $\beta_1' \rightarrow \beta_1''$ martensitic ordering reaction [7]. The exothermic peak P_3, at about 370°C, is associated to the Ag precipitation reaction [17] and the endothermic peak P_4, at about 475°C, to the second stage of the reverse martensitic transformation. This transition is a combination of two competitive reactions, the $\beta_1'' \rightarrow \beta_1$ disordering reaction [9] and the partial β_1 decomposition giving the eutectoid mixture [18]. P_5, at about 520°C, is an endothermic peak due to the transition $\beta_1 \rightarrow \beta$ from part of the β_1 phase remnant from the transformation at 475°C. The endothermic peak P_6 is related to the $(\alpha + \gamma_1) \rightarrow (\alpha + \beta)$ reaction [15] and P_7, at about 620 °C, is an exothermic event associated to the $(\alpha + \beta) \rightarrow \beta$ transition. The X-ray diffraction patterns shown in Fig. 2 confirm the proposed transformations sequence, which is in good agreement with that found in the literature for hypoeutectoid Cu-Al alloys with additions of a third element [16].

In the Cu-9 wt%Al and Cu-10 wt%Al alloys, the reverse martensitic transformation is observed at about 370°C [9, 19]. In Fig. 1 it is possible to see that with 6%Ag addition this transformation occurs in two distinct stages, well separated on the temperature scale. Partial reverse transformation of the total amount of martensite occurs in the temperature range from 100 to 160°C. The reverse transformation of the rest of the martensite takes place at about 475°C. The high-temperature stage of the reverse transformation is, however, not related directly with the decomposition of β-phase. Kustov [16] observed the same behavior in a Cu-10.4 wt%Al-0.47 wt%Be alloy and ascribed the low-temperature part of the reverse transformation to the formation of the bulk parent phase β_1. The mechanism of the high-temperature stage of the reverse transformation is a nucleation of fine lamellae of parent phase inside variants of martensite. The parent phase retransformed at this high-temperature stage of the reverse transformation decomposes rapidly after the transformation.



(a) (b)

Figure 2 X-ray diffraction patterns obtained for the Cu-10 wt%Al-6 wt%Ag alloy quenched from 850°C and then quenched from: (a) 100, 200, 300 and 400°C; (b) 500, 600, 700 and 800°C.

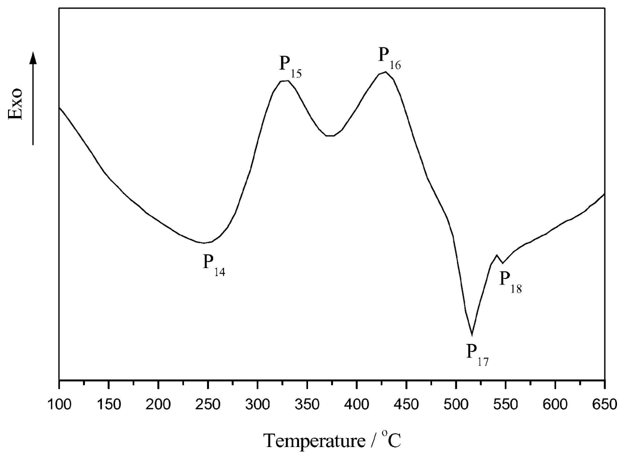
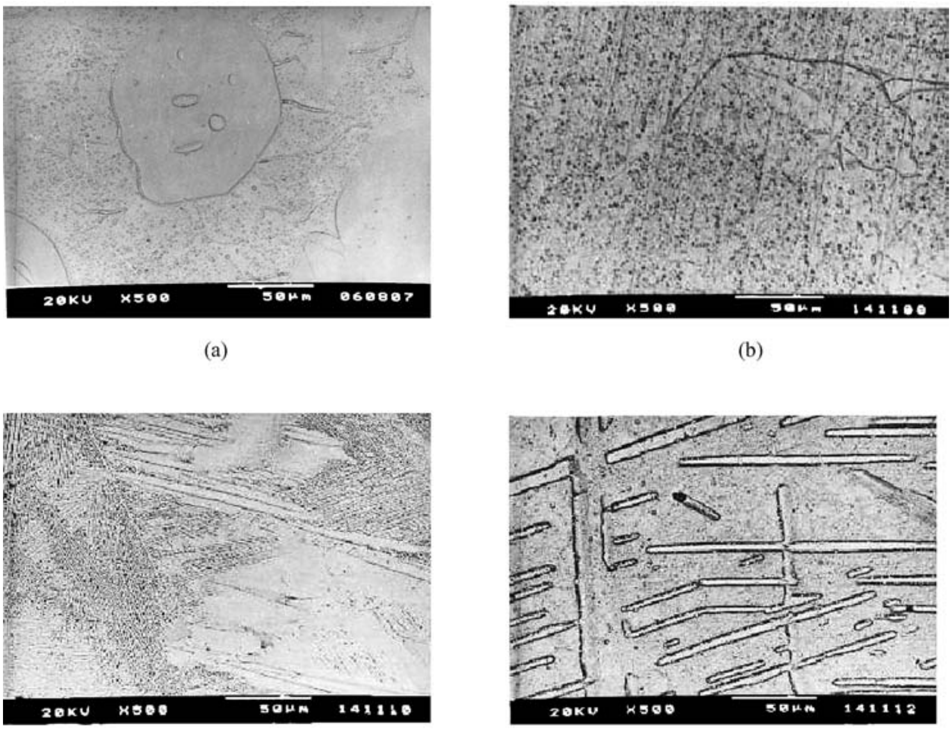


Figure 4 DTA curve obtained for the alloy quenched from 850°C. Heating rate 30°C min^{-1}.

Fig. 3 shows the DTA curve obtained for the sample quenched from 850°C in iced water, with a heating rate of 20°C min^{-1}. In this figure it is possible to observe the presence of two additional peaks P_8 and P_{11}, when compared with Fig. 1. P_8, at about 160°C, was ascribed to the $\alpha \rightarrow \alpha_2$ ordering process [9] and P_{11}, at about 470°C, to the precipitation of the α disordered phase [7]. The formation of the γ_1 phase (Al_4Cu_9) from the β_1 parent phase (peak P_4 in Fig. 1) causes a decrease in the concentration of solute aluminum atoms 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 [7], peak P_{11} in Fig. 3. In this way, it is possible to observe that with a heating rate of 20°C min^{-1} the transitions related to the α phase are better defined. The peaks associated to the reverse martensitic transformation were not observed in this curve. When compared with Fig. 1, one can observe that peaks P_9, P_{10}, P_{12} and P_{13}, in Fig. 3, are related to the thermal events P_2, P_3, P_5 and P_6, respectively.

Fig. 4 shows the DTA curve obtained for the sample quenched from 850°C in iced water, with a heating rate of 30°C min^{-1}. In this curve one can observe that peaks P_{14}, P_{15}, P_{16}, P_{17} and P_{18} correspond to peaks P_1, P_2, P_3, P_5 and P_6 respectively, in Fig. 1. The peak associated to the first stage of the reverse martensitic transformation, P_4, is now observed, and increasing the heating rate to 30°C min^{-1} this peak is shifted to higher temperatures.



(a)

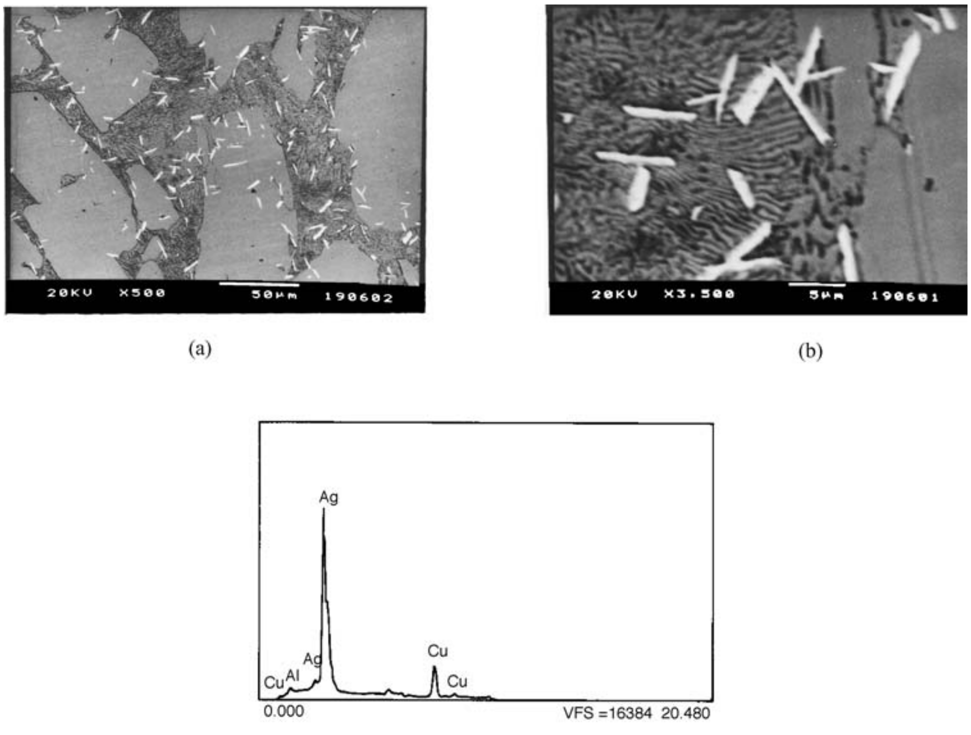
(b)

(c)

(d)

Figure 5 SEM micrographs obtained for the Cu-10 wt%Al-6 wt%Ag alloy (a) quenched from 850°C and then quenched from: (b) 300°C; (c) 400°C; (d) 500°C.

As already pointed out, in the transformations involving the β_1 phase two competitive reactions occur: part of the β_1 phase transforms into the eutectoid phase and the other part into the high-temperature β phase (peaks P_5, P_{12} and P_{17} in Figs 1, 3 and 4, respectively). With the increase of the heating rate and the presence of Ag one can observe, in Fig. 4, that the $\beta_1 \rightarrow \beta$ transformation is the dominant reaction. This is evidenced by the increase in the height of peak P_{17} ($\beta_1 \rightarrow \beta$) and the reduction of peak P_{18} ($\alpha + \gamma_1 \rightarrow \beta$), when compared with Figs 1 and 3 and with the results obtained for the Cu-10%Al alloy [9]. This seems to indicate that Ag precipitation (peaks P_3, P_{10} and P_{16} in Figs 1, 3 and 4, respectively) decreases the decomposition reaction rate. This effect may be associated to the presence of the γ_1 phase, which has a complex body-centred cubic structure with a lattice parameter about three times that of the corresponding body-centred cubic metal [20] and enhances the Ag precipitation reaction. This precipitated Ag will interfere in the Al diffusion process due to the greater Ag-Al electrochemical affinity and



(a)

(b)

(c)

Figure 6 (a), (b): SEM micrographs obtained for the Cu-10 wt%Al-6 wt%Ag alloy after annealing; (c) EDX spectrum from the white region on (b).

part of the Al atoms will be dissolved in the Ag-rich solid solution, thus decreasing the Al amount available for the $(\alpha + \gamma_1)$ phase formation. Hence, the stability range of the β_1' martensitic phase is increased.

The starting point of the DTA curves in Figs 1, 3 and 4 corresponds to the martensitic phase, as shown by the micrograph in Fig. 5a. It is known [21] that alloys with less than 10.8 wt%Al show the β' type martensitic phase and that for higher Al concentrations the observed martensitic phase is the β_1'. The micrographs in Fig. 5 show the characteristic structure of the β_1' martensitic phase [22], instead of the β' structure. It seems to indicate that the addition of 6 wt%Ag to the Cu-10 wt%Al alloy shifts the equilibrium concentration to higher Al contents. In Fig. 5 it is not possible to observe the characteristic structure of the $(\alpha + \gamma_1)$ phase, which is shown in Fig. 6 for the annealed sample, indicating that the amount of martensitic decomposition up to 500°C is very little, thus confirming that the presence of Ag is disturbing the formation of the $(\alpha + \gamma_1)$ phase.

In Fig. 4, the increase in the heating rate causes the increase of peak P_{14}, which corresponds to the first stage of the reverse martensitic transformation, $\beta_1' \rightarrow \beta_1$, and the absence of the peak corresponding to the second stage of this transformation, $\beta_1 \rightarrow (\alpha + \gamma_1)$. It seems to confirm that the reverse martensitic transformation in the Cu-10 wt%Al-6 wt%Ag occurs in two stages and that the second stage corresponds to a slower reaction. Hence, the presence of Ag is responsible for the separation of the competitive reactions that occur during the reverse martensitic transformation.

The high temperature events in Figs 1, 3 and 4 are shifted to lower temperatures in relation to those observed for the Cu-9 wt%Al and Cu-10 wt%Al alloys [9, 19]. It is known that the main effect of quenching is to retain a certain amount of atomic disorder and an excess of vacancies [23] and that the rate of free energy changes with temperature is proportional to the negative of the molar entropy of the system [24]. In this way, the increase in the number of vacancies with the heat treatment and the presence of Ag may change the entropy, as well as the Gibb's free energy of the system. So, the presence of Ag can be contributing to the increase in the disordering degree of the Cu-10 wt%Al-6 wt%Ag alloy at high temperatures and to the consequent decrease in the Gibbs free energy, thus increasing the relative stability of the product phase and disturbing the transformation temperature.

4. Conclusions

The heating rate is the main factor determining the transformations that take place in the Cu-10 wt%Al-6 wt%Ag alloy. The presence of Ag shifts the equilibrium concentration to higher Al contents and is responsible for the separation of the two competitive reactions, which occur during the reverse martensitic transformation. The first stage of this transformation, at low temperatures, is due to the disordering reaction of part of the martensitic phase retained by quenching. The second stage, at high temperatures, is associated with the β_1 phase decomposition reaction. The presence of Ag is also associated to changes in the transformation temperature.

Acknowledgments

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