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Thermal behavior of the Cu–22.55 at.%Al alloy with small Ag additions

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Abstract In this study the effect of Ag additions on the thermal behavior of the Cu–22.55 at.%Al alloy was studied using electrical resistivity measurements, in situ X-ray diffractometry, differential scanning calorimetry, and optical microscopy. The results indicated that Ag additions do not change the phase transformations sequence in the studied alloys, but modify its critical temperatures due to a change on entropy of system. It was verified that at the cooling rate of 10 K/min the decomposition of β phase into ($\alpha + \gamma_1$) is incomplete, but for lower cooling rates than 1.0 K/min this reaction is completed.

Keywords A. alloys · D. phase transitions

Introduction

The Cu–Al system shows a disordered bcc β phase, stable at high temperatures. The stability range becomes smaller at lower temperatures, showing a eutectoid point at 830 K for around 24 at.% Al. At temperatures below the β stability range the equilibrium phases are: α, a low Al fcc structure and γ_1, a higher Al Cu_9Al_4 phase [1, 2]. The equilibrium phases can be partially or totally suppressed increasing the cooling rate from high temperature and β phase is retained at temperatures below its stability region. During this process, the disordered β phase orders to a DO_3 structure (β_1) and at lower temperature transforms martensitically to an 18R structure. The martensitic transformation is responsible for the shape-memory properties exhibited by Cu–Al alloys.

Phase transitions in alloys are known to be accompanied by changes in their physical properties. One of the properties that are most sensitive to these processes is the electrical resistivity, whose variation allows to establish the temperatures of the onset and completion of the structural phase transition [3, 4]. This study involves an examination of the electrical resistivity evolution during cooling/heating of the metastable β phase of hypoeutectoid Cu–Al polycrystalline alloys with small additions of Ag, up to 1.55 at.%. The solid–solid phase transformations were also monitored by differential scanning calorimetry, optical microscopy, and in situ X-ray diffraction.

Experimental details

The alloys were prepared in an induction furnace under argon atmosphere using 99.95% copper, 99.97% aluminum, and 99.98% silver as starting materials. The alloys composition is shown in Table 1.

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). Samples of 30 mm length and 2.0 mm^2 area were cut for electrical resistivity measurements. In situ

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Table 1 Alloys composition/at.%Al

Cu	Al	Ag
77.45	22.55	0
76.86	22.63	0.51
76.26	22.71	1.03
75.66	22.79	1.55

X-ray diffraction patterns were obtained to identify the phases present in the alloys at different temperatures, using 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. Changes in the microstructure were followed by optical microscopy examinations at room temperature (RT) of specimens quenched from selected temperatures, T_Q, along the cooling curves. In this case, the continuous cooling rate between 1073 K and T_Q was 10 K/min. For optical microscopy (OM) observations, the samples were electropolished in a saturated solution of chromium trioxide in phosphoric acid at ~4 V. Some of them were suspending a few seconds in a solution of ferric chloride in order to reveal phase microstructure details.

Results and discussion

Figure 1 shows the curves of electrical resistivity changes with temperature for three of the tested samples: Cu–22.55 at.%Al, Cu–22.55 at.%Al–0.51 at.%Ag, and Cu–22.55 at.%Al–1.55 at.%Ag alloys. The samples were initially heated up to around 1073 K, in the range of β phase stability, after which the electrical resistivity curves were registered upon cooling and then on heating under temperature rump of 10 K/min. Therefore, each pair of curves was obtained first on cooling (←) and then on heating (→).

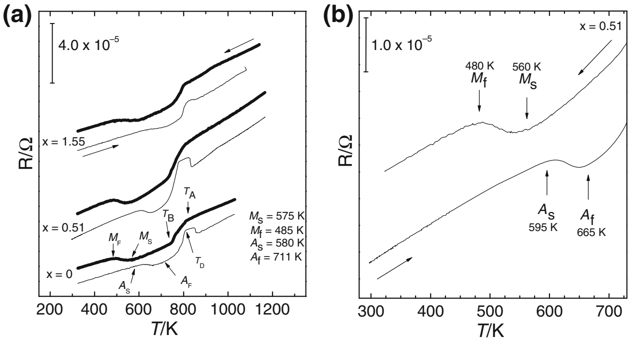

Fig. 1 **a** Phase transformations followed by electrical resistivity on heating and cooling. **b** Details of the forward and reverse martensitic transformation. The alloys were identified by Ag content (X = at.% Ag)

On cooling of the sample corresponding to the alloy without Ag additions three stages can be identified. According to the Cu–Al phase diagram [5] for higher temperatures than 900 K only the β phase is stable. When the temperature is decreased, the $\beta/(\beta + \alpha)$ boundary is reached at 870 K and the α phase formation is started. In this first stage, in the temperature range between 820 K (T_A) and 870 K, coarse plates of α phase are formed. In second stage, in the temperature range between 820 K (T_A) and 770 K (T_B), complex $(\alpha + \gamma_1)$ pearlitic phase is produced, suggesting that the $\beta \rightarrow (\alpha + \gamma_1)$ eutectoid decomposition occurs. In the temperature range from 770 K (T_B) to room temperature (RT), third stage, the sample is slowly cooled and the $(\alpha + \gamma_1)$ eutectoid phase is formed. It is also possible to notice that the martensitic transformation occurs in the temperature range from 575 K (M_s) to 485 K (M_f) in the presence of the $(\alpha + \gamma_1)$ eutectoid phase. This indicates that at the cooling rate of 10 K/min the decomposition of β phase into $(\alpha + \gamma_1)$ is incomplete.

During heating of the sample corresponding to the alloy without Ag additions it is possible to identify the reverse phase transformations. In the temperature range between 580 and 711 K the reverse martensitic transformation takes place, starting at the A_s temperature and finishing at the A_f temperature. Figure 1b shows details of the forward and reverse martensitic transformation obtained for the Cu–22.55 at.%Al 0.51 at.%Ag alloy. With further heating, a marked step around 800 K (T_D) indicates a phase dissolution. According to the Cu–Al equilibrium phase diagram [5], it corresponds to the reverse transformation of the $(\alpha + \gamma_1)$ eutectoid phase and consequently the formation of the $(\beta + \alpha)$ phase. The Cu–Al equilibrium phase diagram shows the $(\beta + \alpha)/\beta$ boundary at about 870 K, but this transition is not observed, indicating that the dissolution of the α phase is not detected by electrical resistivity measurements. This has been observed in other Cu–Al alloys like Cu–Al–Be [6], suggesting that the conduction electron mean path is similar for β and α phases.

The electrical resistivity curves obtained for the Cu–22.55 at.%Al alloy during cooling and heating are similar to those verified for alloys with Ag additions. For samples with Ag additions the only change is on the characteristic temperatures of the phase transitions, as seen in Fig. 2, which shows the critical transformation temperatures for the four studied alloys. The formation and dissolution temperatures of the $(\alpha + \gamma_1)$ eutectoid phase are lowered with Ag additions. It is known that the configurational entropy of solids system is a determining factor for the phase transitions temperatures [7]. Ag additions increase the entropy of the system, due to the possibility of two new pairs of atoms interaction, Cu–Ag and Al–Ag, thus decreasing the formation and dissolution temperatures of

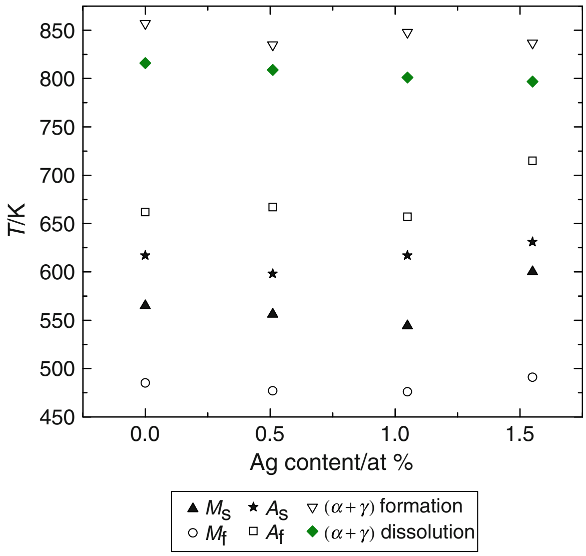

Fig. 2 Phase transformation critical temperatures determined from the electrical resistivity curves of Fig. 1

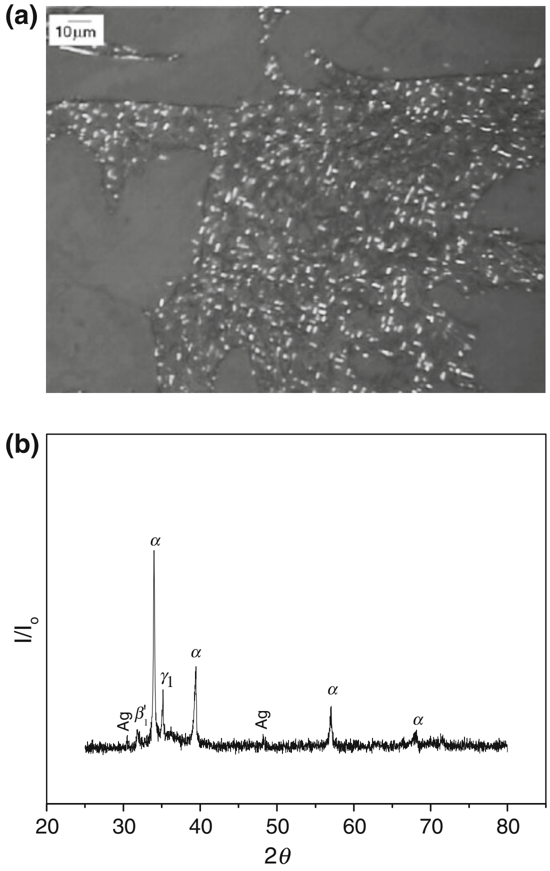

Fig. 3 **a** Precipitates (*white region*) observed in the Cu–22.79 at.%Al–1.55 at.%Ag alloy at the room temperature (RT) and **b** X-ray diffraction patterns obtained for the Cu–22.79 at.%Al–1.55 at.%Ag alloy

the $(\alpha + \gamma_1)$ eutectoid phase. It is also possible to observe that the characteristics temperatures of forward and reverse martensitic transition are increased when 1.5 at.% Ag is reached. This effect is associated with the presence of Ag precipitates in the Cu–22.55 at.%Al–1.55 at. % Ag alloy. These precipitates are formed at about 750 K on slow cooling and dissolved at about 1050 K on heating, hence the forward and reverse martensitic transitions always occur in the presence of silver precipitates. This Ag-rich phase decreases the mobility of martensite plates, thus requiring more energy for a new phase to be produced and consequently increasing the transitions characteristic temperatures.

Figure 3a shows that small Ag precipitates develop a lath form and are oriented in two perpendicular preferential directions. The in situ X-ray diffraction pattern shown in Fig. 3b confirms the presence of the silver precipitates on the $(\alpha + \gamma_1)$ pearlitic phase. These ones could be Widmanstatten type γ-AgAl precipitates with an (hcp) crystal structure [8]. In Fig. 3b it is also possible to notice the presence of the martensitic phase together with $(\alpha + \gamma_1)$ eutectoid phase, confirming that at the cooling rate of 10 K/min the decomposition of β phase into $(\alpha + \gamma_1)$ is incomplete. Besides, Ag-rich precipitates have been observed inside the eutectoid phase in the Cu–12.84 wt%Al–1.98 wt%Ag alloy [9]. This effect seems to be related to the diffusion of Ag in the $(\alpha + \gamma_1)$ pearlitic phase. The γ_1 phase has an open bcc type structure, and the Ag diffusion coefficient is appreciable greater in it than in the fcc α-(Cu) phase [10]. This seems to indicate that the pearlitic phase intensifies the formation of Ag-rich precipitates in the studied Cu–Al–Ag alloys.

Owing to the sluggishness of the eutectoid reaction, the β phase can be retained metastably and, on fast cooling, undergoes a martensitic transformation to a ordered β_1' phase at higher 10.8 wt% Al content. The ordering reaction $\beta \leftrightarrow \beta_1$ precedes the martensitic transformation [11]. A martensitic transformation is a diffusionless first-order phase transition in which the atom distribution does not change and only the distances between the atoms are modified [12]. Hence, considering that the martensitic phase inherits the atomic distribution of β phase, it is possible to obtain, by optical microscopy, some information about the reaction sequence above proposed.

Figure 4 shows the optical micrographs obtained for the samples quenched from different temperatures. The optical micrographs shown in Fig. 4 confirm the transformations sequence proposed in the discussion of Fig. 1. In the micrograph of Fig. 4I-a, corresponding to the sample quenched from 920 K, it is possible to observe that the initial structure of the Cu–22.63 at.%Al–0.51 at.%Ag alloy corresponds to the martensitic phase, consisting of needle-shaped platelets. As the temperature decreases (770 K, Fig. 4I-b), there is an increase in the amount of the α phase

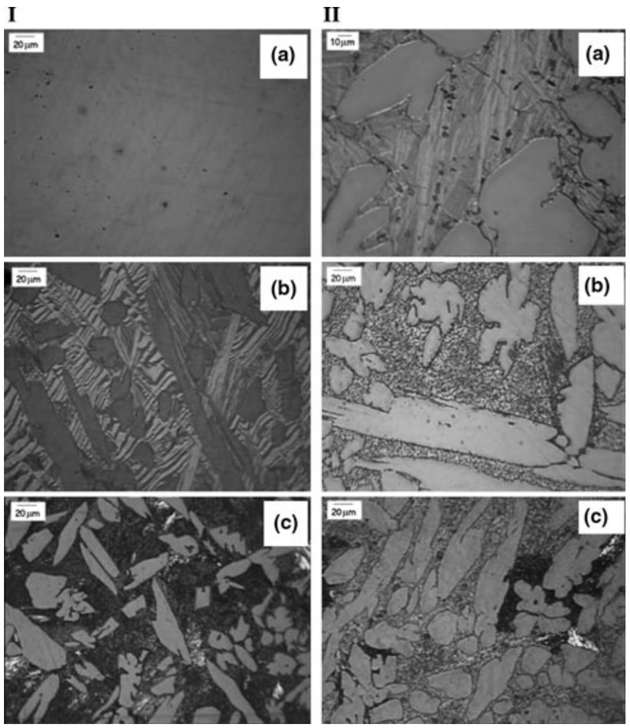

Fig. 4 Optical micrographs showing the sequence of the microstructural development during continuous cooling: (*I*) Cu–22.63 at.%Al–0.51 at.%Ag alloy quenched from 920 K (**a**), 770 K (**b**), and RT (**c**). (*II*) Cu–22.79 at.%Al–1.55 at.%Ag alloy quenched from 790 K (**a**), 720 K (**b**), and RT (**c**)

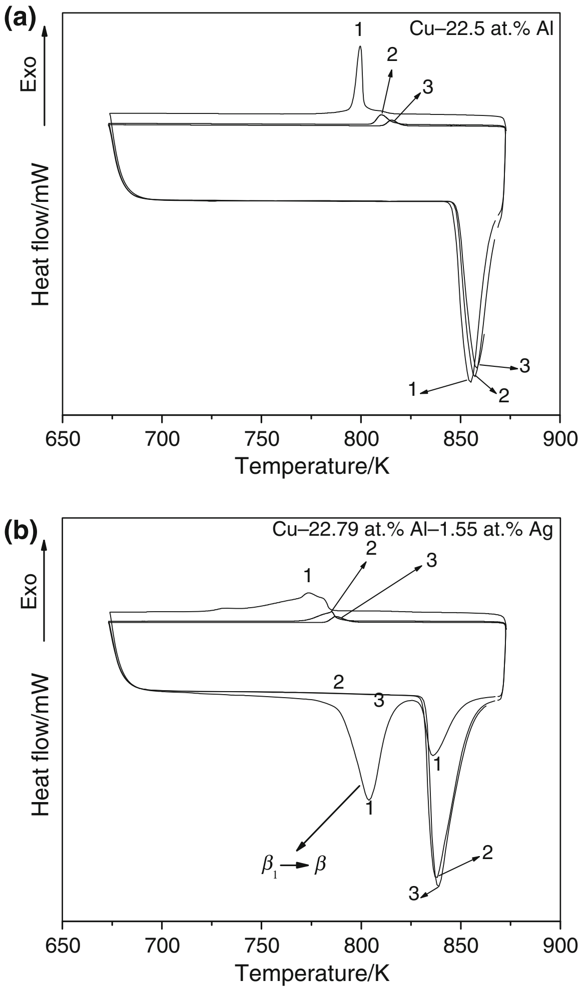

Fig. 5 **a** DSC curves obtained for the studied alloys: *(1)* Initially cooled at 10 K/min and then heated at 30 K/min, *(2)* cooled at 1.0 K/min and then heated at 30 K/min, *(3)* cooled at 0.5 K/min and then heated at 30 K/min

and ($\alpha + \gamma_1$) phase formation is started. At lower temperatures (room temperature, Fig. 4I-c), the ($\alpha + \gamma_1$) pearlitic phase fills the grain boundaries of the α phase plates.

In the micrograph of Fig. 4II-a, corresponding to the sample quenched from 790 K, it is possible to observe that the initial structure of the Cu–22.79 at.%Al–1.55 at.%Ag alloy corresponds to the martensitic phase with α phase plates and small precipitates in the matrix phase. As the temperature decreases (720 K, Fig. 4II-b), there is an increase in the amount of α phase and ($\alpha + \gamma_1$) phase is observed. At lower temperatures (room temperature, Fig. 4II-c), one can see that a low amount of eutectoid phase is produced. This confirms that the complete decomposition of β phase into ($\alpha + \gamma_1$) does not occur for the Cu–22.79 at.%Al–1.55 at.%Ag alloy.

The microstructural observations can be linked to the electrical resistivity–temperature evolution. In the first stage during cooling, corresponding to an almost linear decrease of electrical resistivity, α phase nucleates and growths when the β phase stability point is overcome. The α phase formation cannot be detected by any resistivity break [6]. The second stage is marked by a change in the slope of the electrical resistivity–temperature curve which corresponds to the ($\alpha + \gamma_1$) eutectoid phase formation. In the third stage, the martensitic transformation takes place in the temperature range from 575 to 485 K. It starts at the M_s and finishes at the M_f temperature. At lower cooling rates, it is possible to notice that the martensite is retained when the matrix phase has almost entirely transformed to ($\alpha + \gamma_1$) phase, as shown in Fig. 3b.

It is known [13] that when a sample of hypoeutectoid Cu–Al alloys is submitted to cooling rates higher than 2 K/min, the martensitic phase is retained and an endothermic peak due to the parent phase → β transition appears at about 800 K, during heating of the samples in DSC experiments. Figure 5a shows the DSC cycles obtained with three different cooling rates: 10, 1.0, and 0.5 K/min and only one heating rate of 30 K/min. On heating, the first endothermic peak (at about 800 K) is due to the martensitic phase retained on cooling. In this figure one can see that after a cooling rate of 1.0 K/min the peak attributed to the parent phase → β transition is not detected on heating, indicating that only for cooling rates equal or lower than

1.0 K/min the martensitic phase is not retained and also that the presence of Ag increases the martensitic phase stability.

Conclusions

The results indicated that Ag additions do not change the phase transformations sequence in the studied alloys, but modify its critical temperatures due to a change on entropy of system. It was verified that at the cooling rate of 10 K/min the decomposition of β phase into $(\alpha + \gamma_1)$ is incomplete, but for lower cooling rates than 1.0 K/min this reaction is completed. The results also showed that the dissolution of the α phase is not detected by electrical resistivity measurements for the studied alloys, suggesting that the conduction electron mean path is similar for β and α phases and that the pearlitic phase induces the formation of Ag-rich precipitates due to an increase of Ag diffusion rate in the pearlitic phase.

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