Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 1, 241–246

EFFECT OF Ag ADDITIONS ON THE REVERSE MARTENSITIC TRANSFORMATION IN THE Cu–10 MASS% Al ALLOY

A. T. Adorno[*] *and R. A. G. Silva*

Departamento de Físico-Química, Instituto de Química-Unesp, Caixa Postal 355, 14801-970 Araraquara SP, Brazil

The effect of Ag additions on the reverse martensitic transformation in the Cu–10 mass% Al alloy was studied using differential thermal analysis (DTA), optical (OM) and scanning electron microscopies (SEM) and X-ray diffractometry. The results indicated that Ag additions to the Cu–10 mass% Al alloy shift the equilibrium concentration to higher Al contents, allow to obtain both β_1' and β' martensitic phases in equilibrium and that Ag precipitation is a process associated with the perlitic phase formation.

Keywords: *Ag additions, Cu-based alloys, reverse martensitic transformation*

Introduction

A martensitic transformation is a first order diffusionless phase transition in which the atom distribution does not change and only the distances between the atoms are modified. This makes it different from the diffusion-controlled transformation in which the redistribution of atoms permits to get to the equilibrium phase with the lowest possible Gibbs free energy [1]. Copper–aluminum alloys containing 9 to 14 mass% Al are among those showing a martensitic transformation on rapid cooling from high temperatures [2].

The martensitic transformation in alloys of the Cu–Al system has a number of distinguishing features. The interposing order–disorder reaction, substitutional type parent and product phases make the eutectoid reaction in this system distinguishable from other ones [3]. According to the Cu–Al equilibrium diagram [4], the b.c.c. β solid solution is stable as a high temperature phase at 70.6–82 at% Cu. A two-phase (Cu)+β field exists between the eutectic temperature and the eutectoid reaction $\beta \leftrightarrow \gamma_1$+(Cu) at 840±2 K. Because the sluggishness of the eutectoid reaction, the β phase can be retained metastably. During quenching, metastable β alloys undergo a martensitic transformation to a disordered β′ phase at low Al content and the ordering reaction $\beta \leftrightarrow \beta_1$ precedes the martensitic transformation. During heating of the martensite a reverse martensitic transformation $\beta' \leftrightarrow \beta_1$ takes place in the temperature range from 613 to 673 K. Afterwards, on slow heating the β_1 phase transforms into the eutectoid ($\alpha+\gamma_1$) phase. At the temperature of 838 K, the β phase formation occurs from the α and γ_1 mixture. Silver additions to Cu–Al alloys increase its hardness [5] and influence the nucleation rate and the activation energy of the eutectoid decomposition reaction [6]. The aim of this paper is to discuss the influence of Ag additions on the martensitic reverse transformation in the Cu–10 mass% Al alloy.

Experimental

Cu–10 mass% Al–*X* mass% Ag polycrystalline alloys (with *X*=0, 4, 6, 8 and 10) were 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 1123 K for homogenization and after annealing they were equilibrated for one hour at 1123 K and quenched in iced water in order to obtain the martensitic phase. 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 Leica DMR optical microscope and in a Jeol JSM T330A scanning electron microscopy.

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 in-

* Author for correspondence: atadorno@iq.unesp.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

troduced 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.

Results and discussion

Figure 1 shows the DTA curve obtained for the Cu–10 mass% Al alloy quenched from 1123 K, with a heating rate of 20 K min^{-1}. In this curve one may observe five peaks, which are in agreement with what was expected from the literature for hypoeutectoid Cu–Al alloys: P_1, at about 453 K, is a low intensity exothermic peak associated with the α phase ordering process; P_2, another exothermic peak at about 573 K, corresponds to the $\beta' \rightarrow \beta'_1$ ordering reaction of the martensitic phase [7]; the endothermic peak P_3, at about 698 K is asymmetric and is associated with the $\beta'_1 \rightarrow \beta_1 \rightarrow \beta$ transformations and also with the $\beta_1 \rightarrow \alpha+\gamma_1$ decomposition reaction from part of the β_1 phase; the endothermic peak P_4, at about 813 K, is attributed to the $\beta_1 \rightarrow \beta$ transition from part of the remaining β_1 phase formed at 698 K; finally, the endothermic peak P_5, at about 843 K, is due to the $\alpha+\gamma_1 \rightarrow \beta$ transition [8].

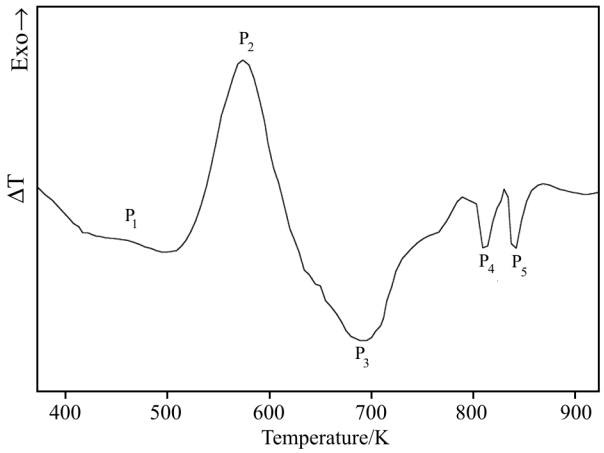

Fig. 1 DTA curve obtained for the Cu–10 mass% Al alloy quenched from 1123 K; heating rate 20 K min^{-1}

The optical micrographs shown in Fig. 2 confirm the sequence of transformations proposed in the discussion of Fig. 1. In the micrograph of Fig. 2a it is possible to observe the initial structure of the Cu–10 mass% Al alloy, corresponding to the Cu–Al β' martensitic phase found in alloys with less than 10.8 mass% Al [9, 10] and consisting of needle-shaped platelets. As the temperature increases, there is an increase in the amount of the α phase, probably due to the beginning of the ordered α_2 phase decomposition (Fig. 2b). At higher temperatures (673 K, Fig. 2c), the $\alpha+\gamma_1$ perlitic phase formation starts and at 823 K (Fig. 2d) the precipitation of the disordered α phase occurs in the perlitic phase, preceding the $\alpha+\gamma_1 \rightarrow \beta$ transition.

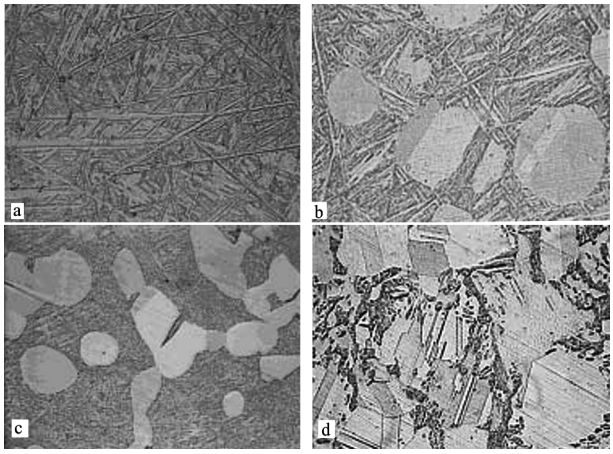

Fig. 2 Optical micrographs (×500) obtained for the Cu–10 mass% Al alloy quenched from a – 1123 and then quenched from: b – 573, c – 673 and d – 823 K

Figure 3 shows the DTA curves obtained for the Cu–10 mass% Al alloy with additions of 4, 6, 8 and 10 mass% Ag (Figs 3a–d, respectively), quenched from 1123 K. In Fig. 3a it is possible to observe an additional peak P_6, at about 683 K, when compared with Fig. 1 (sample without Ag). This peak is associated with Ag precipitation from the supersatured solution formed during quenching [11]. In Fig. 3b, peak P_6 is observed at about 603 K and another peak P_7 is now observed at about 743 K, which is associated to the α phase precipitation that precedes the $\alpha+\gamma_1 \rightarrow \beta$ transition [12]. In Fig. 3c peak P_6 is observed at about 653 K and peak P_3 at about 733 K. In Fig. 3d the peak corresponding to Ag precipitation was not detected and peak P_3 is observed at about 743 K. It is interesting to observe that peak P_3, associated with the $\beta'_1 \rightarrow \beta_1 \rightarrow \beta$ transformations and also with the $\beta_1 \rightarrow \alpha+\gamma_1$ decomposition reaction from part of the β_1 phase, was not observed in Fig. 3a; furthermore, peak P_1 is now better defined and its intensity increases with the increase of Ag up to 6 mass% and then decreases for higher Ag additions.

The scanning electron micrographs in Fig. 4 show the microstructure of the alloys with and without Ag additions, for samples quenched from 1123 K. When compared with the micrographs in Fig. 2, one can observe that there are some changes in the martensitic microstructure, caused by the presence of Ag. The microstructure of these alloys does not show the α-phase grains and the lamellas of the martensitic phase seem to be thicker than those of the alloy without Ag. These structures are quite similar to those corresponding to the β'_1 martensitic phase [13], and this was

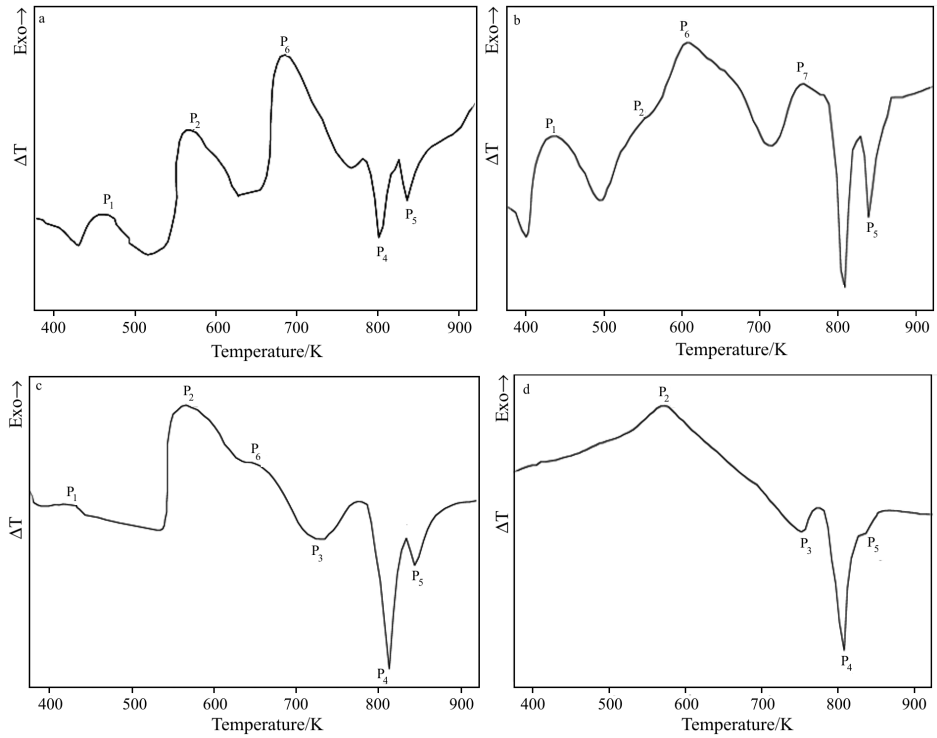

Fig. 3 DTA curves obtained for the Cu–10 mass% Al with Ag additions, quenched from 1123 a – 4% Ag, b – 6% Ag, c – 8% Ag and d – 10% Ag; heating rate: 20 K min^{-1}

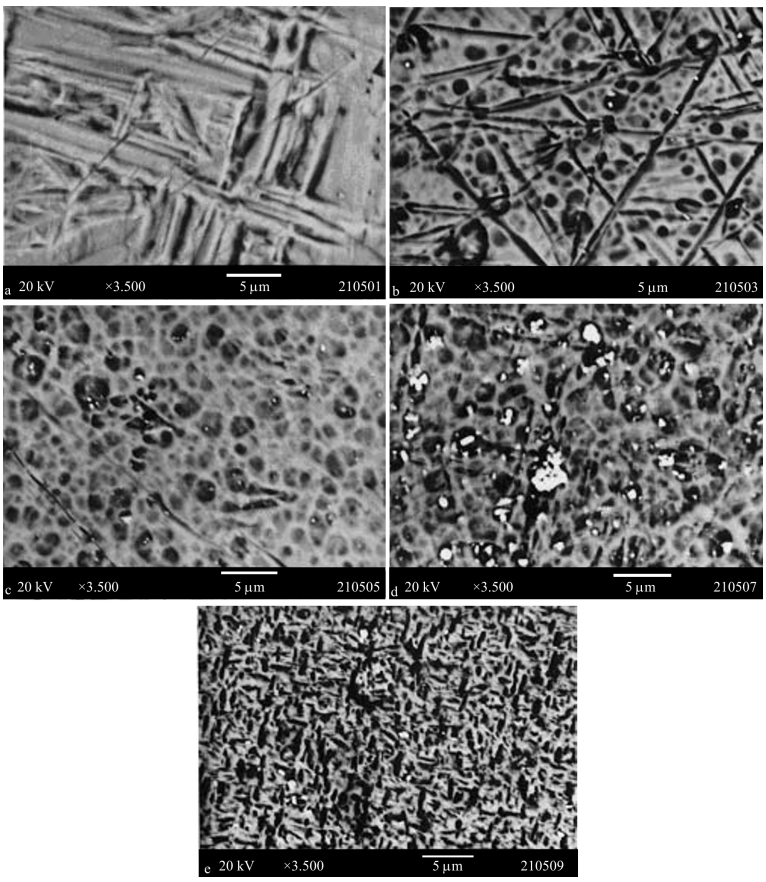

Fig. 4 Scanning electron micrographs obtained for the alloys quenched from 1123 K: a – Cu–10% Al, b – Cu–10% Al–4% Ag, c – Cu–10% Al–6% Ag, d – Cu–10% Al–8% Ag and e – Cu–10% Al–10% Ag

confirmed by the X-ray diffraction patterns shown in Fig. 5. The presence of the β_1' martensitic phase indicates that Ag additions to the Cu–10 mass% Al alloy seems to promote the formation of a phase that is characteristic of higher Al concentrations.

The results in Figs 1 and 3 indicate that the presence of Ag strongly modifies the transitions that occur in the range of temperatures from 373 to 773 K, in the Cu–10 mass% Al alloy. As already observed, peak P_1, associated with the α-phase ordering process, increases its intensity up to 6 mass% Ag and then decreases with the increase of Ag content. It seems to indicate that Ag additions up to 6% must increase the α-phase relative fraction due to Ag dissolution, thus enhancing the $\alpha \rightarrow \alpha_2$ transition. From 8% Ag this effect is not so intense, indicating that the limit for Ag dissolution in the Cu–10 mass% Al is at about 6%. This is confirmed by the micrographs in Fig. 4, where one may observe Ag-rich precipitates on the martensitic matrix (Figs 4d and e), and by the X-ray diffraction patterns in Fig. 5.

The peak associated with the ordering of the β' martensitic phase seems not to be influenced by the addition of 4% Ag; with 6% Ag this peak is not well defined and appears like a 'shoulder' at about 553 K, but with 8% Ag it is better defined and with 10% Ag it is a large peak. It seems to indicate that it is possible to obtain both β' and β_1' martensitic phases in equilibrium in the Cu–10% Al alloy with 4 and 6 mass% Ag additions, and that Ag precipitation is the dominant effect in the temperature range from 373 to 773 K. With additions of 8 and 10% Ag the dominant effect turns to be the $\beta' \rightarrow \beta_1'$ transition in this temperature range, indicating that additions from 8% Ag do not shift the phase equilibrium concentration to higher Al content. It is also possible to observe that the $\beta' \rightarrow \beta_1'$ transition becomes slower from 8% Ag, thus making larger the peak associated with this transformation. The peak associated with the $\beta_1' \rightarrow \beta_1 \rightarrow \beta$ transformations and also with the $\beta_1 \rightarrow \alpha + \gamma_1$ decomposition reaction from part of the β_1 phase, was observed at about 698 K in the DTA curve

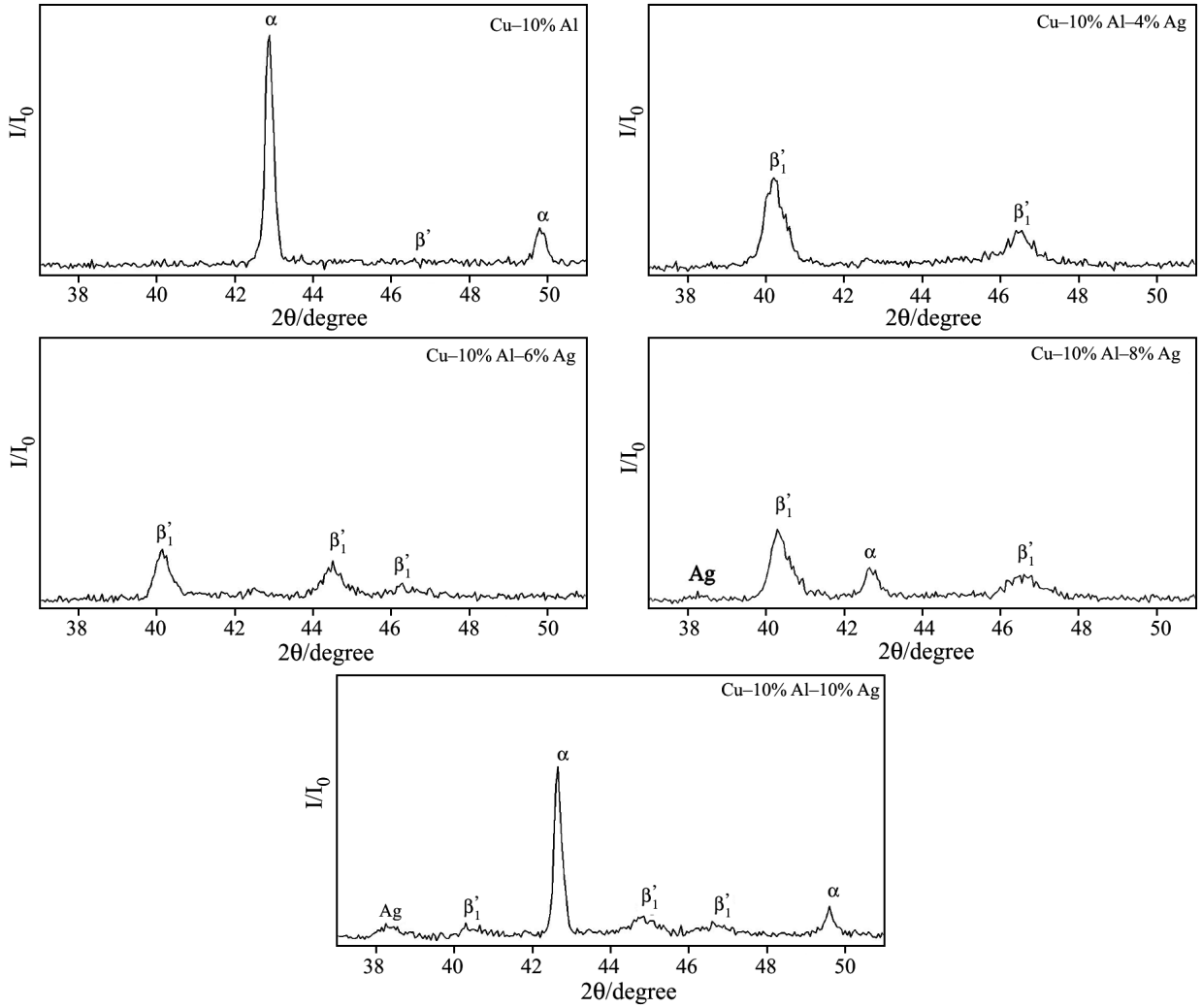

Fig. 5 X-ray diffraction patterns obtained for the alloys quenched from 1123 K

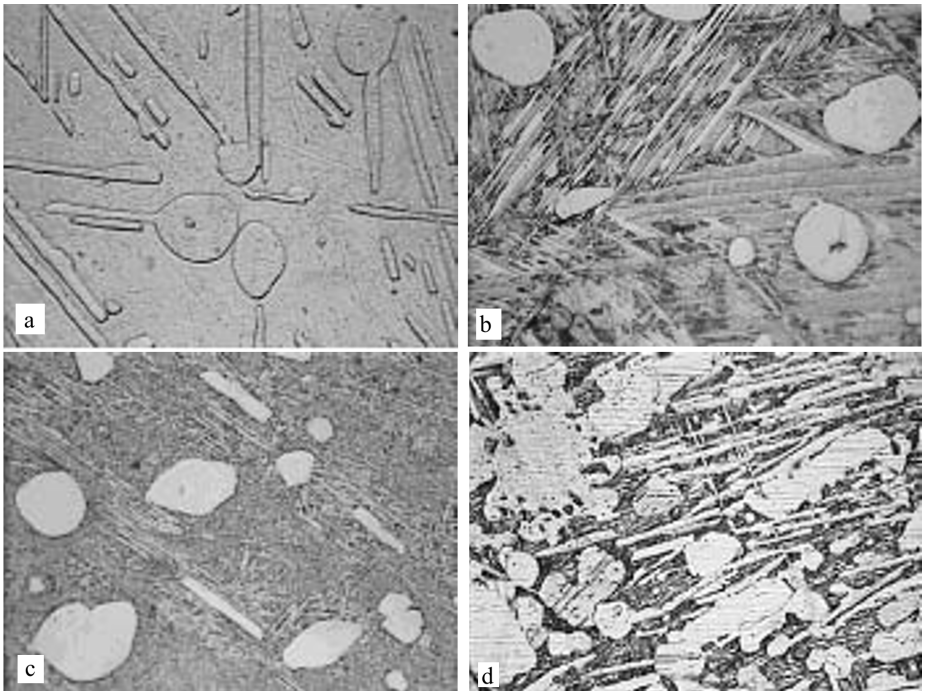

Fig. 6 Optical micrographs (×500) obtained for the Cu–10 mass% Al–4 mass% Ag alloy quenched from a – 1123, and then quenched from: b – 573, c – 673 and d – 823 K

obtained for the Cu–10 mass% Al alloy and was not detected for the Cu–10 mass% Al–4 mass% Ag and Cu–10 mass% Al–6 mass% Ag alloys; for the other alloys, with 8 and 10 mass% Ag, this thermal event was observed, respectively, at 733 and 743 K.

Figure 6 shows the optical micrographs obtained for the alloy with 4% Ag previously quenched from 1123 K (Fig. 6a) and then quenched from 573 K (Fig. 6b), 673 K (Fig. 6c) and 823 K (Fig. 6d), to obtain the microstructures corresponding to the transformations assigned to the peaks in Fig. 3. In these micrographs it is possible to observe the beginning of the perlitic phase formation (Fig. 6c), which occurs by the decomposition of the β_1 phase. This seems to indicate that the $\beta_1' \rightarrow \beta_1 \rightarrow \beta$ transformations and the $\beta_1 \rightarrow \alpha + \gamma_1$ decomposition reaction from part of the β_1 phase are occurring together with Ag precipitation and that Ag precipitation is the dominant process in the temperatures range considered, being the only of these transitions that is detected.

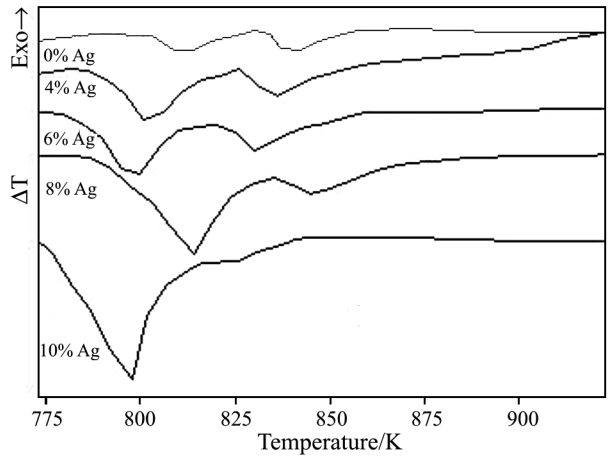

Fig. 7 Enlarged portion of Figs 1 and 3, in the temperature range from 773 to 923 K

With the increase in the Ag content, the peak corresponding to the $\beta_1' \rightarrow \beta_1 \rightarrow \beta$ transformations and the $\beta_1 \rightarrow \alpha + \gamma_1$ decomposition reaction from part of the β_1 phase is shifted to higher temperatures, indicating a decrease in the rate of these reactions and, consequently, an increase in the stability range of the β_1' martensitic phase. This increase in the martensite stability range with the increase of Ag additions may be associated with an increase in the concentration of point defects and its reconfiguration [14].

In the DTA curve obtained for the Cu–10% Al–10% Ag, the peak corresponding to Ag precipitation was not detected and the peak corresponding to the $\alpha + \gamma_1 \rightarrow \beta$ transition is extremely small, indicating that the amount of the perlitic phase available for this transition is also small. This seems to confirm that the presence of Ag is responsible for a delay in the β_1 decomposition reaction rate and to indicate that Ag precipitation is connected to the $\alpha + \gamma_1$ perlitic phase formation.

The presence of Ag also changes the position of the thermal events in the range from 773 to 923 K, as shown in Fig. 7, which corresponds to the enlarged portion of Figs 1 and 3 in this temperature range. The first peak in Fig. 7, associated to the $\beta_1 \rightarrow \beta$ transition, increases its intensity with the increase of Ag concentration and the second peak, associated to the $\alpha+\gamma_1 \rightarrow \beta$ transition, increases its intensity up to 6 mass% Ag and then decreases with Ag increase, almost disappearing for 10 mass% Ag. The first effect may be attributed to the increase in the β_1 phase stability range and the second seems to indicate that this increase in the stability range is more pronounced from 6 mass% Ag; in the alloy with 10 mass% Ag the β_1 phase decomposition reaction is practically suppressed.

Conclusions

The results indicated that Ag additions to the Cu–10 mass% Al alloy shift the equilibrium concentration to higher Al contents, allow to obtain both β_1' and β' martensitic phases in equilibrium and increase its stability range. Addition of 10% Ag suppresses the β_1 decomposition reaction and Ag precipitation is a process associated with the perlitic phase formation.

References

1 M. Ahlers, Mater Sci. Eng., A 349 (2003) 120.
2 J. Kwarciac, Z. Bojarski and H. Morawiec, J. Mater. Sci., 21 (1986) 788.
3 S. D. Kulkarni, Acta Metall., 21 (1973) 1461.
4 T. B. Massalski, Ed., Binary Alloys Phase Diagrams, Vol. 1, ASM International, Ohio 1992, p. 141.
5 A. T. Adorno, M. R. Guerreiro and A. V. Benedetti, J. Alloys Compd., 268 (1998) 122.
6 A. T. Adorno and R. A. G. Silva, J. Alloys Compd., 375 (2004) 128.
7 A. T. Adorno, M. R. Guerreiro and A. V. Benedetti, J. Therm. Anal. Cal., 65 (2001) 221.
8 J. Kwarciak, J. Thermal Anal., 31 (1986) 559.
9 A. T. Adorno, M. R. Guerreiro and A. V. Benedetti, J. Alloys Compd., 315 (2001) 150.
10 P. R. Swann and H. Warlimont, Acta Metall., 11 (1963) 511.
11 A. T. Adorno, M. R. Guerreiro, C. A. Ribeiro and C. T. R. Guerreiro, J. Therm. Anal. Cal., 64 (2001) 1141.
12 A. T. Adorno and R. A. G. Silva, J. Therm. Anal. Cal., 79 (2005) 445.
13 P. R. Swann and H. Warlimont, Acta Metall., 10 (1962) 903.
14 K. Otsuka and X. Ren, Scripta Mater., 50 (2004) 207.

Received: March 20, 2005
In revised form: June 28, 2005

DOI: 10.1007/s10973-005-6986-z