Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 629–635

THERMAL BEHAVIOR OF THE Cu–10 MASS%Al AND Cu–10 MASS%Al–4 MASS%Ag ALLOYS

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

Instituto de Química –Unesp, C. Postal 355, 14801-970 Araraquara-SP, Brazil

Abstract

The thermal behavior of the Cu–10 mass%Al and Cu–10 mass%Al–4 mass%Ag alloys was studied using classical differential thermal analysis (DTA), optical microscopy (OM) and X-ray diffractometry (XRD). The DTA curves were obtained for annealed and quenched samples. The results indicated that the presence of silver introduces new thermal events, associated to the formation of a silver-rich phase, to the shift of the equilibrium concentration to higher Al contents and to the decomposition of the silver-rich phase in the same temperature range of the β_1 phase decomposition.

Keywords: Cu–Al and Cu–Al–Ag alloys, phase transformation, thermal behavior

Introduction

The Cu–Al alloys show important characteristics, as chemical stability and good mechanical properties, depending on the aluminum content. Silver addition to the Cu–Al alloys improve some of their properties, as hardness [1] and stress corrosion [2] without appreciable modification in their workability and plasticity.

In this work, the thermal behavior of the Cu–10 mass%Al–4 mass%Ag alloy was studied using classical differential thermal analysis (DTA), optical microscopy (OM) and X-ray diffractometry (XRD) and compared with that of the Cu–10 mass%Al alloy.

Experimental

The Cu–10 mass%Al and Cu–10 mass%Al–4 mass%Ag alloys 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.

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 XRD. 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

* Author for correspondence: E-mail: atadorno@iq.unesp.br

1388–6150/2004/ $ 20.00
© 2004 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

quenched in iced water. The XRD diagrams 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.

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.

Results and discussion

Figure 1 shows the DTA curves obtained for the Cu–10%Al alloy (curve a) and Cu–10%Al–4%Ag alloy (curve b), at a heating rate of 10°C min^{-1} for annealed samples.

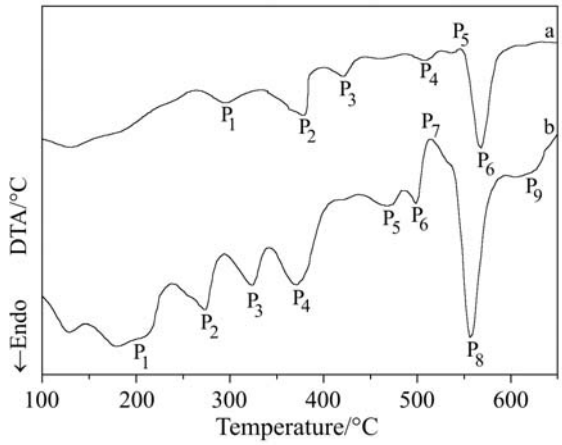

Fig. 1 DTA curves obtained for the alloys after annealing: a – Cu–10 mass%Al alloy; b – Cu–10 mass%Al–4 mass%Ag alloy. Heating rate 10°C min^{-1}

The starting point of these curves corresponds to the ($\alpha+\alpha_2$) phase, as shown in the optical micrographs of Fig. 2. In curve 1(a) one exothermic and five endothermic peaks were observed. Peak P_1, at 290°C, may be attributed to the beginning of the α_2 phase disordering. P_2, at about 380°C, corresponds to the order–disorder transition [3].

$$(Cu)\text{-}\alpha + \alpha_2 \rightarrow (Cu)\text{-}\alpha + (\alpha+\gamma_1)$$

Peak P_3, at about 420°C, may be associated to the dissolution of α_2 precipitates formed during slow cooling [4]. The peak P_4, at about 510°C, is due to the $\beta_1 \rightarrow \beta$ phase transformation. The martensitic phase β_1' change into the β_1 phase in the same temperature interval of the α_2 phase disordering process and at about 510°C the β_1 phase transforms into the β phase [3]. The exothermic peak P_5, at about 535°C, is associated to the precipitation of the disordered α phase, which precedes the eutectoid transformation. The endothermic peak P_6 at about 575°C is due to the eutectoid transformation [5],

$$(Cu)\text{-}\alpha+(\alpha+\gamma_1)\rightarrow(Cu)\text{-}\alpha+\beta$$

as expected from the Cu–Al equilibrium diagram [6].

In curve 1(b) three additional peaks were observed, when compared with curve 1(a): P_1, P_6 and P_9. Peak P_1, at about 200°C, may be due to a combination of the ordered phase α_2 with Ag. Peak P_6, at about 500°C, is related to the formation of a silver-rich phase from the combination of Ag with part of the β phase. Peak P_9 may be related to the dissolution of the remaining Ag, as observed in the X-ray diffraction patterns of Fig. 3.

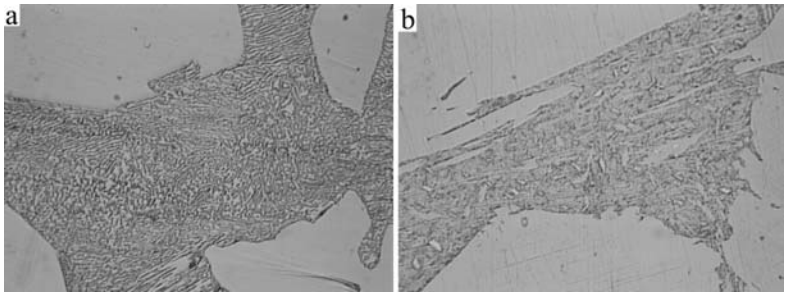

Fig. 2 Optical micrographs (500×) obtained for the annealed samples:
a – Cu–10 mass%Al alloy; b – Cu–10 mass%Al–4 mass%Ag alloy

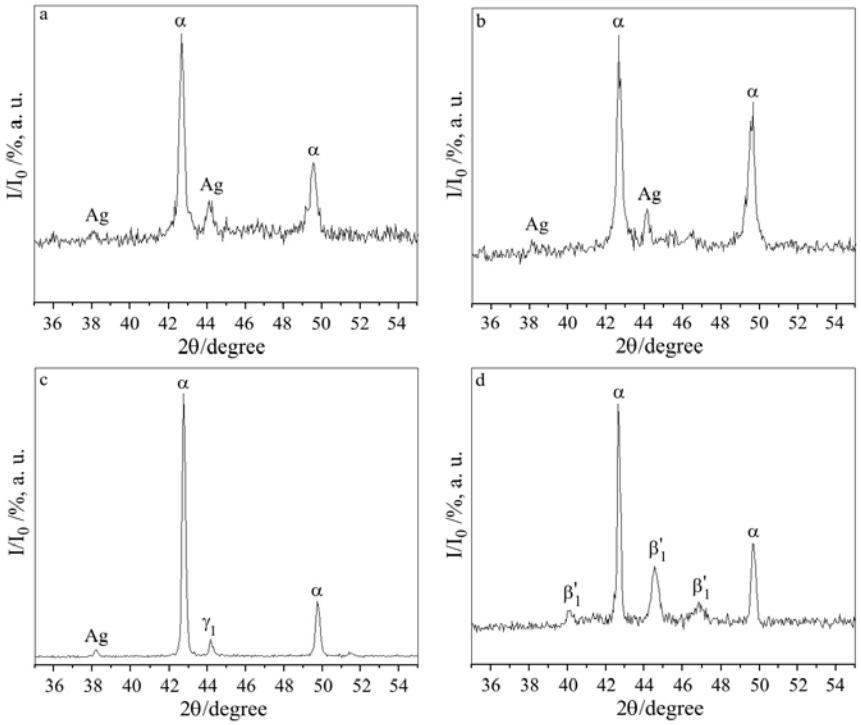

Fig. 3 X-ray diffraction patterns for Cu–10 mass%Al–4 mass%Ag alloy: a – annealed;
b – quenched from 300°C; c – quenched from 500°C; d – quenched from 700°C

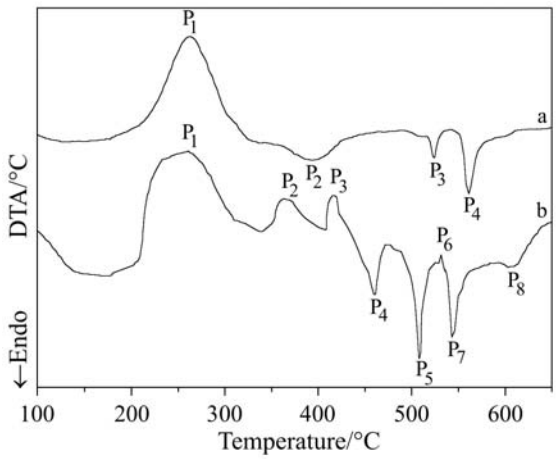

Fig. 4 DTA curves obtained for quenched samples: a – Cu–10 mass%Al alloy; b – Cu–10 mass%Al–4 mass%Ag alloy. Heating rate 10°C min^{-1}

Figure 4 shows the DTA curves obtained at a heating rate of 10°C min^{-1} for samples quenched from 850°C

In curve (a) in Fig. 4 four peaks are observed. The exothermic peak P_1, at about 290°C, may be attributed to the ordering of the β' martensitic phase ($\beta' \rightarrow \beta_1'$). The endothermic peak P_2, at about 410°C, is asymmetric and is associated to the reverse martensitic transformation $\beta_1' \rightarrow \beta_1 \rightarrow \beta$ and to the decomposition $\beta_1 \rightarrow (\alpha+\gamma_1)$ from part of the β_1 phase. The exothermic peak P_3, at about 530°C, is due to the $\beta_1 \rightarrow \beta$ transition from part of the remaining β_1 phase formed at 410°C. Peak P_4, at about 580°C, is associated to the $(\alpha+\gamma_1) \rightarrow \beta$ transformation [7]. In curve (b) in Fig. 4 one may observe four additional peaks, in comparison with curve (a). The exothermic peak P_2, at about 370°C, may be associated to an Ag precipitation [8], from the silver dissolved in the martensitic matrix (Fig. 5b). The exothermic peak P_3, at about 420°C, may be attributed to Ag precipitation from the silver-rich phase. The endothermic peak P_4, at about 470°C, may be due to the decomposition of the silver-rich phase, together with the reverse martensitic transformation and the decomposition of part of the β_1 phase. It is known that Ag diffusion in the γ_1 phase is greater than in the α phase, due to changes in the atomic density [9]. In this way, the Ag-rich phase decomposition must occur mainly on the perlitic phase resulted from the β_1 phase decomposition. Peak P_4 is shifted to a higher temperature, in relation to the corresponding peak on Fig. 4a, probably due to the presence of silver. In this way, the Ag addition seems to allow for a greater stability of the β_1' phase. It is possible to observe in curve 4b that peak P_5, at about 510°C and corresponding to the $\beta_1 \rightarrow \beta$ transition from the remaining part of the β_1 phase, is now better defined, probably due to a greater amount of β_1 phase available because of the decrease in the β_1 phase decomposition reaction rate, caused by the presence of the Ag-rich phase decomposition reaction in the same temperature range. The exothermic peak P_6, at about 530°C, may be associated to the precipitation of the α phase remaining from the $\beta_1 \rightarrow (\alpha+\gamma_1)$ decomposition reaction [7]. The endo-

thermic peak P_8, at about 610°C, is due to the dissolution of the remaining Ag. The results from the X-ray diffraction patterns showed in Fig. 6 indicated the presence of the β_1' phase. It is known that alloys with less than 10.8 mass%Al must show the β' type martensitic phase and that over this concentration the martensitic phase observed is the β_1' [10]. It seems to indicate that the addition of 4 mass%Ag shifts the equilibrium concentration to higher Al contents.

Figure 5 shows the optical micrographs obtained for quenched samples. In Fig. 5a it is possible to observe that the initial structure of the Cu–10%Al–4%Ag alloy is different from the Cu–Al alloy martensitic structure [11], consisting of small platelets instead of the acicular form showed by the Cu–Al alloys. With the increase of the temperature, this structure seems to change to an acicular one, probable due to a decomposition of the α_2 phase and of the Ag dissolved on it (Fig. 5b). For higher temperatures it is possible to observe the beginning of the perlitic ($\alpha+\gamma_1$) phase formation (400°C, Fig. 5c), and the disordered α phase precipitation on the perlitic phase (600°C, Fig. 5d). These results confirm what was proposed for the interpretation of the DTA curves in Fig. 4.

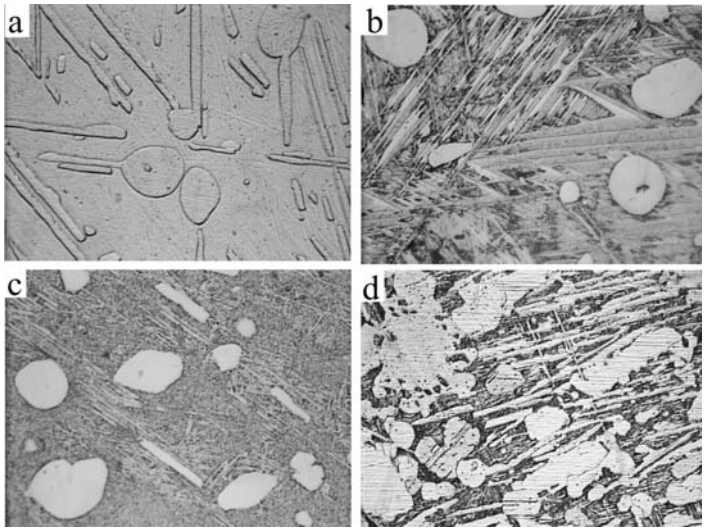

Fig. 5 Optical micrographs (500×) obtained for the Cu–10 mass%Al–4 mass%Ag alloy quenched from a – 850°C and then quenched from b – 300°C, c – 400°C, d – 600°C

Figure 7 shows the DTA curves obtained on cooling for the Cu–10 mass%Al (curve a) and Cu–10 mass%Al–4 mass%Ag (curve b) alloys, with a cooling rate of 2°C min^{-1} in the temperature range 800 to 200°C. Curve 7a shows only one exothermic peak, while in curve 7b it is possible to observe five thermal events. Peak P_3, at about 517°C in curve 7a and 498°C in curve 7b, is associated to the eutectoid reaction

$$\beta+(Cu)\text{-}\alpha \rightarrow (Cu)\text{-}\alpha+(\alpha+\gamma_1),$$

as expected from the Cu–Al equilibrium diagram [6].

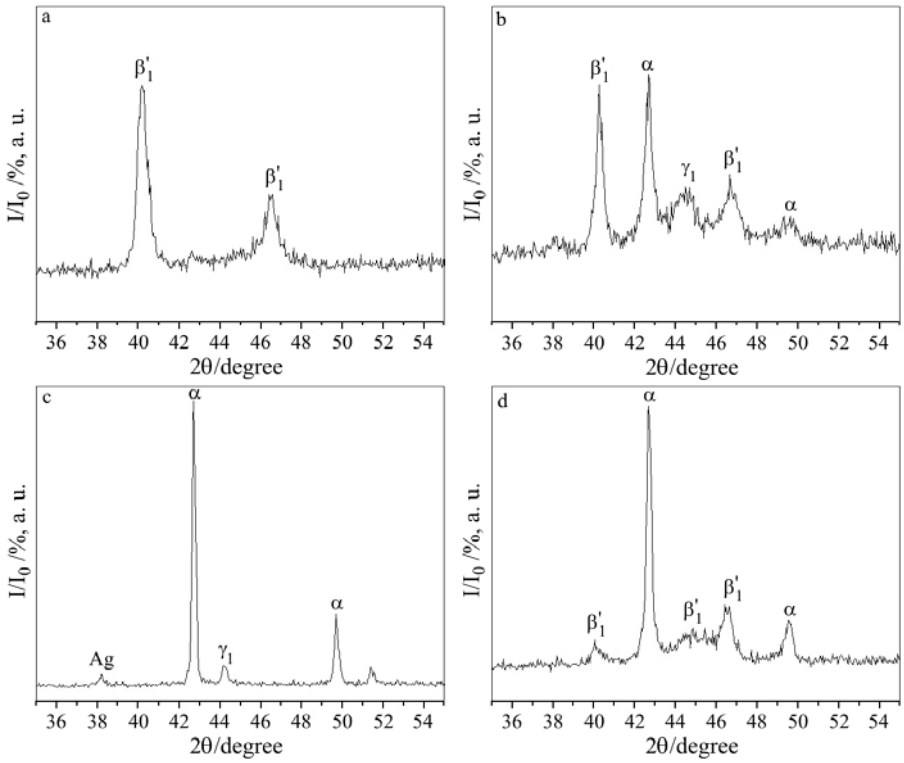

Fig. 6 X-ray diffraction patterns obtained for the Cu–10 mass%Al–4 mass%Ag alloy quenched from a – 850°C and then quenched from b – 400°C, c — 500°C and d – 600°C

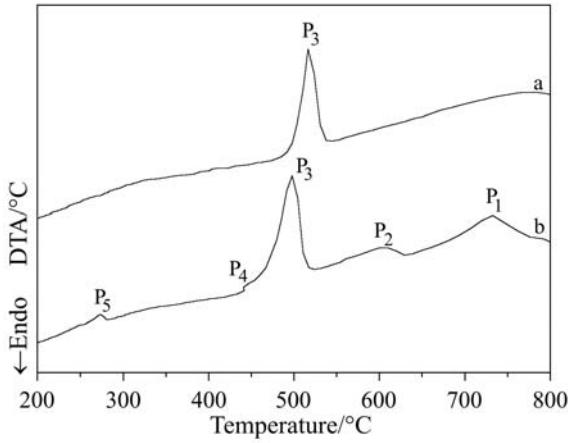

Fig. 7 DTA curves obtained on cooling for the Cu–10 mass%Al (curve a) and Cu–10 mass%Al–4 mass%Ag (curve b) alloys. Cooling rate 2°C min^{-1}

In curve 7b, P_1, at about 730°C, is attributed to the Ag precipitation. Peak P_2, at about 600°C, is due to the $\beta \rightarrow \gamma_1$ phase transformation from part of the β phase. P_4, at about 450°C, is related to the

$$\beta+(Cu)\text{-}\alpha \rightarrow \beta_1+(Cu)\text{-}\alpha$$

transition from the remaining part of the β phase. Peak P_5, at about 280°C, is associated to the ordering of the α phase [12]. These transitions are according to those reported for Cu–Al alloys with more than 10 mass%Al [3] and this is another evidence that the addition of 4 mass%Ag to the Cu–10 mass%Al alloy shifts the equilibrium concentration to higher Al content.

Conclusions

The results indicated that the presence of silver is responsible for new thermal events, corresponding to the formation of a silver-rich phase, to the shift of the equilibrium concentration to higher Al contents, to the increase in the stability range of the β_1' martensitic phase and to the decomposition of the silver-rich phase in the same temperature interval where the β_1 phase decomposition occurs.

* * *

The authors thank CNPq for financial support.

References

1 A. T. Adorno, M. Cilense and W. Gárlipp, J. Mat. Sci. Lett., 6 (1987) 163.
2 A. T. Adorno, M. R. Guerreiro and A. V. Benedetti, J. All. Comp., 268 (1998) 122.
3 J. Kwarciak, J. Thermal Anal., 31 (1986) 559.
4 W. Gaudig and H. Warlimont, Z. Metallk., 60 (1969) 488.
5 J. L. Murray, Int. Met. Rev., 30 (1985) 211.
6 T. B. Massalski, Ed., 'Binary Alloy Phase Diagrams' 2nd Ed., Vol. 1, pp. 141–143, American Society for Metals, Metals Park, Ohio 1992.
7 J. Kwarciak, J. Bojarski and H. Morawiec, J. Mat. Sci., 21 (1986) 788.
8 A. T. Adorno, M. R. Guerreiro, C. A. Ribeiro and C. T. R. Guerreiro, J. Therm. Anal. Cal., 64 (2001) 1141.
9 J. E. Ruzzantes, S. Kurokawa, E. A. Garcìa and F. Dyment, Acta Metall., 28 (1980) 699.
10 P. R. Swann and H. Warlimont, Acta Metall., 11 (1963) 511.
11 A. T. Adorno, M. R. Guerreiro and A. V. Benedetti, J. All. Comp., 315 (2001) 150.
12 A. T. Adorno and R. A. G. Silva, J. Therm. Anal. Cal., 73 (2003) 931.