

Completeness of β -phase decomposition reaction in Cu–Al–Ag alloys

R. A. G. Silva · E. S. Machado · A. T. Adorno ·
A. G. Magdalena · T. M. Carvalho

Received: 3 June 2011 / Accepted: 20 July 2011 / Published online: 3 August 2011
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract The completeness of β -phase decomposition reaction in the Cu–11wt%Al– x wt%Ag alloys ($x = 0, 1, 2,$ and 3) was studied using differential scanning calorimetry (DSC), X-ray diffractometry (XRD), and optical microscopy (OM). The results indicated that β -phase transformations are highly dependent on cooling rate and on the presence of Ag. On slow cooling, the silver presence prevents the β - and β_1 -phase decomposition; thus, inducing the martensitic phase formation. After rapid cooling, a new thermal event is observed and the reverse martensitic transformation is shifted to lower temperatures.

Keywords Alloys · Phase transitions · Thermal behavior · β -phase decomposition

Introduction

Cu–Al base alloys quenched in iced water from the β -phase field can exhibit a thermoelastic martensitic transformation below the M_s temperature [1]. Since shape memory effect and high damping capacity of the alloys, in general, have been associated with the martensitic transformation, this one has interested many investigators [2]. M_s temperatures of these alloys are sensitive to the cooling rate during

quenching, because the cooling rate relates to the completeness of β -phase ordering followed by the decomposition of β and β_1 into α and γ_1 phases and vacancy concentration. It is known that quenching of a Cu–Al binary alloy could not completely prevent β - and β_1 -phase decomposition in the stable phases [1]. Therefore, an element, such as Mn and/or Ni, can be added into Cu–Al binary alloys as a third element to stabilize β - and β_1 -phases [1, 3] and increase the martensitic fraction after quenching. The purpose of this work is to analyze the effect of cooling rate on the β -phase transformations in the Cu–11%Al alloy with additions of 1, 2, and 3%Ag, correlating with the changes in the β -phase decomposition rate and in the concentration of Ag.

Experimental procedure

The Cu–11wt%Al, Cu–11wt%Al–1wt%Ag, Cu–11wt%Al–2wt%Ag, and Cu–11wt%Al–3wt%Ag alloys were prepared in an induction furnace under argon atmosphere using 99.95% copper, 99.97% aluminum, and 99.98% silver as starting materials. Cylindrical samples with 2.0 cm diameter and 6.0 cm length were cut in disks of 2.0 mm thickness. The disks were cold rolled and flat squares samples of 1.0 mm thickness and about 5.0 mm length were obtained. The samples were annealed during 120 h at 1,173 K for homogenization. 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) in annealed samples. After annealing, the samples were maintained at 1,173 K for 1 h and quenched in iced water. Optical micrographs and X-ray diffraction patterns were obtained to identify the phases present in the alloy at the different quenching

R. A. G. Silva (✉)
Departamento de Ciências Exatas e da Terra-UNIFESP,
Diadema, SP, Brazil
e-mail: galdino.ricardo@gmail.com

E. S. Machado
Campus Prof. Alberto Carvalho, UFS, Itabaiana, SE, Brazil

A. T. Adorno · A. G. Magdalena · T. M. Carvalho
Instituto de Química, UNESP, Araraquara, SP, Brazil

temperatures. The micrographs were obtained using a Leica DMR optical microscope and the in situ high-temperature X-ray diffraction experiments were performed at the D10B-XPD X-ray diffraction beam line of the Brazilian Synchrotron Light Laboratory/MCT with solid (not powdered) samples. The DSC curves were obtained using a DSC Q20 TA Instruments at different rates. The temperature and the heat flow were calibrated by measuring the melting temperatures and the heat of fusion of pure In. In the DSC measurements, the samples were initially heated with a rate of 50 K min^{-1} up to 873 K , cooled down to 658 K with a rate of 1.0 K min^{-1} and then again cooled down to 373 K with a rate of 20 K min^{-1} . In sequence, the samples were heated with a rate of 50 K min^{-1} . In the second moment, the samples were heated with a rate of 50 K min^{-1} up to 873 K , cooled down to 658 K with a rate of 50 K min^{-1} and then again cooled down to 373 K with a rate of 20 K min^{-1} . In sequence, the samples were again heated with a rate of 50 K min^{-1} . This procedure allows obtaining more precise information about the presence of martensitic phase formed from incomplete decomposition of β -phase on the slow cooling (1.0 K min^{-1} , from 873 to 658 K) and the behavior of this phase when rapidly cooled (50 K min^{-1} , from 873 to 658 K).

Results and discussion

The curves due to the thermal cycles were separated to facilitate the visualization and analyze of the results, as shown in Figs. 1, 3, and 6. Figure 1 shows the DSC curves obtained with a heating rate of 50 K min^{-1} for the Cu–11%Al, Cu–11%Al–1%Ag, Cu–11%Al–2%Ag, and Cu–11%Al–3%Ag alloys initially quenched from $1,173 \text{ K}$ in

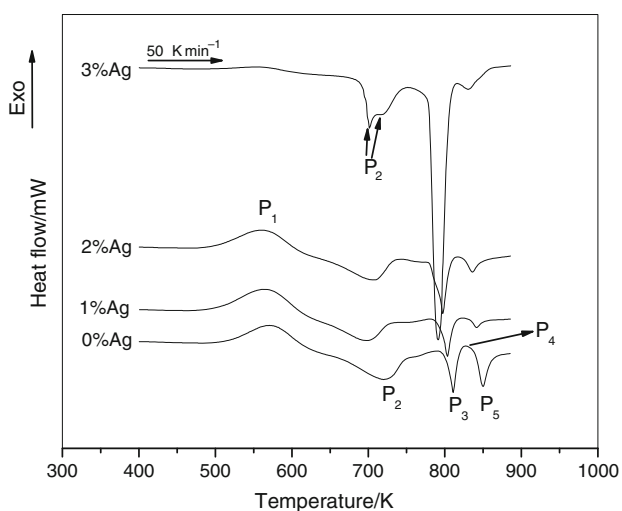


Fig. 1 DSC curves obtained for the Cu–11%Al– x %Ag alloys ($x = 0, 1, 2$ and 3) during first heating

iced water for producing the martensitic phase, as shown in the optical micrographs of the Fig. 2. In the DSC curve of Fig. 1, corresponding to the first heating of the Cu–11%Al alloy, five thermal events were detected: two exothermic peaks (P_1 and P_4) and three endothermic peaks (P_2, P_3 , and P_5). Peak P_1 was attributed to the $\alpha(\text{Cu})$ -rich phase precipitation reaction from martensitic phase produced on quenching. P_2 is related to the $\beta_1' \rightleftharpoons \beta_1 \rightleftharpoons (\alpha + \gamma_1)$ reaction, in which the first process corresponds to the reverse martensitic reaction and the second to the partial decomposition of β_1 -phase. Peak P_3 is associated with $\beta_1 \rightarrow \beta$ transition [4]. Peak P_4 , at about 840 K , is ascribed to the $\alpha(\text{Cu})$ -rich phase precipitation reaction that precedes the eutectoid reaction. The formation of the γ_1 (Al_4Cu_9) at P_2 causes a decrease in the Al content dissolved into the matrix. This change on the chemical composition of the alloy promotes the $\alpha(\text{Cu})$ -rich phase precipitation reaction at P_4 . Peak P_5 , at about 870 K , is related to the $(\alpha + \gamma_1) \rightleftharpoons \beta$ eutectoid reaction [4]. The DSC curves in Fig. 1, corresponding to the Cu–11%Al–1%Ag and Cu–11%Al–2%Ag alloys, show a thermal behavior similar to that observed for the Cu–11%Al alloy, without additional phase transitions, whereas in the curve associated with the Cu–11%Al–3%Ag alloy some modifications are observed. In this curve, it is possible to verify that peak P_2 , due to the $\beta_1' \rightleftharpoons \beta_1 \rightleftharpoons (\alpha + \gamma_1)$ transition, is now separated into two thermal events. The narrower peak, first thermal event, can be associated with the reverse martensitic transformation (faster process) and the second can be attributed to the β_1 -phase decomposition (slower process). It is also noticed that peak P_3 related to the $\beta_1 \rightarrow \beta$ reaction is quite intensified, suggesting that the β_1 -phase decomposition reaction at P_2 is delayed in the presence of 3%Ag. In the sequence, the samples were cooled as described for Fig. 3a.

Figure 3a shows the DSC curves obtained with a cooling rate of 1.0 K min^{-1} (down to 658 K) and with a cooling rate of 20 K min^{-1} (down to 373 K) for the studied alloys. The exothermic peak P_6 , associated with the $\beta \rightarrow (\alpha + \gamma_1)$ eutectoid reaction, was observed for all studied alloys, whereas the exothermic peak P_7 due to the martensitic transformation was only detected for the Cu–11%Al–3%Ag alloy. In Cu–Al–Ag alloys, when the $\beta \rightarrow (\alpha + \gamma_1)$ decomposition reaction is incomplete the remaining β -phase produces the β_1 -phase, in the same temperature range of the $\beta \rightarrow (\alpha + \gamma_1)$ eutectoid reaction, at P_6 and this β_1 -phase is transformed in the β_1' martensitic phase by a diffusionless process in the temperature range from 573 to 473 K . This transition is called forward martensitic transformation [5]. The absence of peak P_7 in the temperature range here considered indicates that the cooling rate of 1.0 K min^{-1} promotes the complete decomposition of β -phase into $(\alpha + \gamma_1)$ in the Cu–11%Al, Cu–11%Al–1%Ag, and Cu–11%Al–2%Ag alloys, as

Fig. 2 Optical micrographs obtained for alloys quenched from 1173 K in iced water: **a** Cu–11%Al–1%Ag and **b** Cu–11%Al–2%Ag

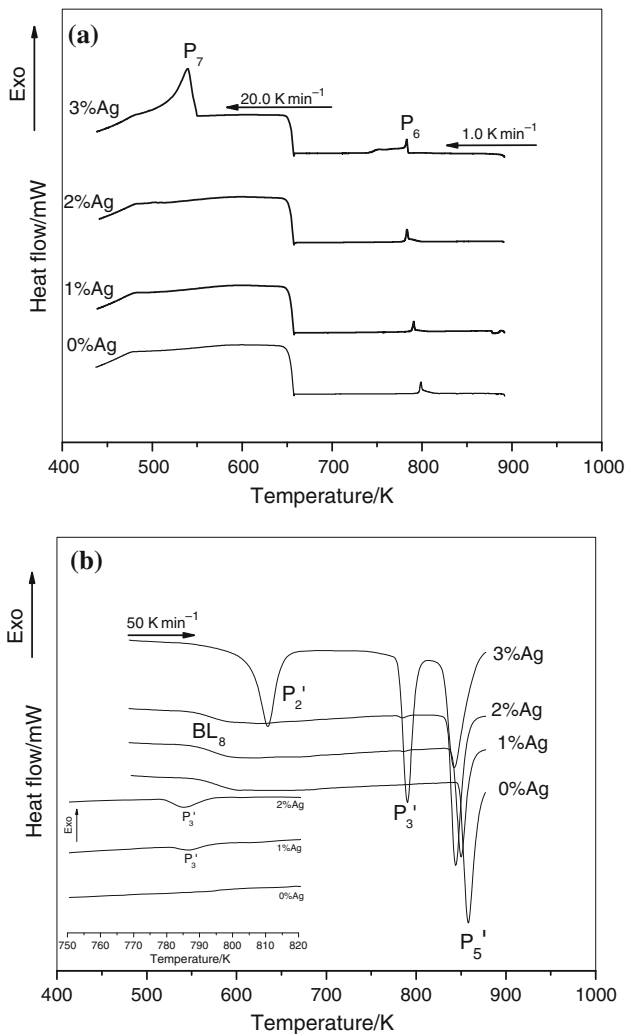
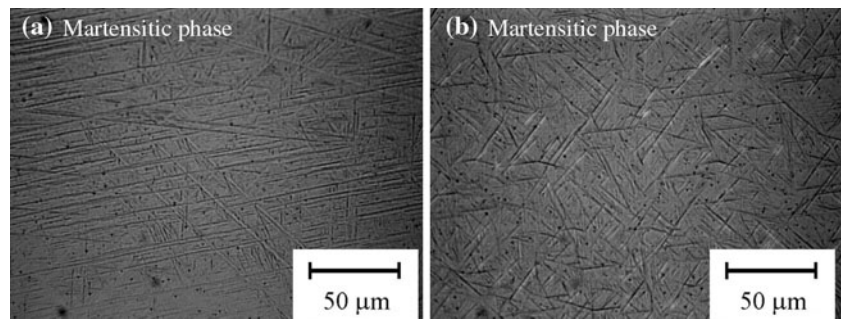


Fig. 3 DSC curves obtained for the Cu–11%Al– x %Ag alloys ($x = 0, 1, 2$ and 3): **a** on cooling and **b** on second heating

shown in the optical micrographs of Fig. 4. For the Cu–11%Al–3%Ag alloy, the presence of Ag seems to retard the β -phase decomposition reaction, thus contributing for the occurrence of the forward martensitic transformation in the temperature range from 550 to 490 K (peak P_7).

After the cooling shown in Fig. 3a, the samples were heated with a rate of 50 K min^{-1} and the obtained curves

are shown in Fig. 3b. Two thermal events were detected for the Cu–11%Al alloy: BL_8 , corresponding to a change on the baseline, is due to the α_2 -phase disordering reaction [6], whereas P_5' is associated with the reverse eutectoid reaction. The change in the intensity of P_5' , as compared with Fig. 1, is related to the increase of the β -phase relative fraction decomposed on slow cooling (peak P_6 , Fig. 3a). In the curves corresponding to the Cu–11%Al–1%Ag, Cu–11%Al–2%Ag, and Cu–11%Al–3%Ag alloys, the peak ascribed to the $\beta_1 \rightarrow \beta$ transition was observed (P_3'). This effect can be seen in Fig. 3b and in its enlarged portion in the temperature range from 700 to 820 K (inside Fig. 3b). This peak P_3' confirms that a small fraction of the martensitic phase was retained on slow cooling and that this fraction depends on Ag concentration. It also suggests that on slow cooling the β -phase decomposition reaction is incomplete in the presence of Ag. For the curve corresponding to the Cu–11%Al–3%Ag alloy, the peak P_2' due to the $\beta_1' \rightleftharpoons \beta_1 \rightleftharpoons (\alpha + \gamma_1)$ reaction is now observed at temperatures lower than those in the first heating of this sample (Fig. 1), suggesting that this reaction is disturbed by the cooling rate. Peak P_5' is ascribed to the eutectoid reaction, as already discussed for the Cu–11%Al alloy.

The X-ray diffraction patterns shown in Fig. 5a indicate that at the start of the heating curves in Fig. 1 the martensitic phase (β_1') appears in all alloys, whereas in Fig. 5b, corresponding to the start of second heating in Fig. 3b, the $(\alpha + \gamma_1)$ phase is dominant and the martensitic phase is only detected for the Cu–11%Al–3%Ag alloy. This confirms that in the presence of 3%Ag the β -phase decomposition is incomplete and the remaining β -phase transforms to martensite at lower temperatures. The martensitic phase is also formed in the alloys with 1 and 2%Ag, as shown in Fig. 3b and its enlarged portion (peak P_3' , associated with presence of the martensitic phase), but this phase is detected by X-ray diffraction only at the alloy with 3%Ag. Hence, the DSC apparatus allows the detection of small relative fractions of martensitic phase in the Cu–11%Al–1%Ag and Cu–11%Al–2%Ag alloys.

The samples were again quenched from 1,173 K in iced water and heated with a rate of 50 K min^{-1} up to 873 K. The obtained curves were similar to those shown in Fig. 1.

Fig. 4 Optical micrographs obtained at the end of the cooling curves in Fig. 3a: **a** Cu–11%Al–1%Ag alloy and **b** Cu–11%Al–2%Ag alloy

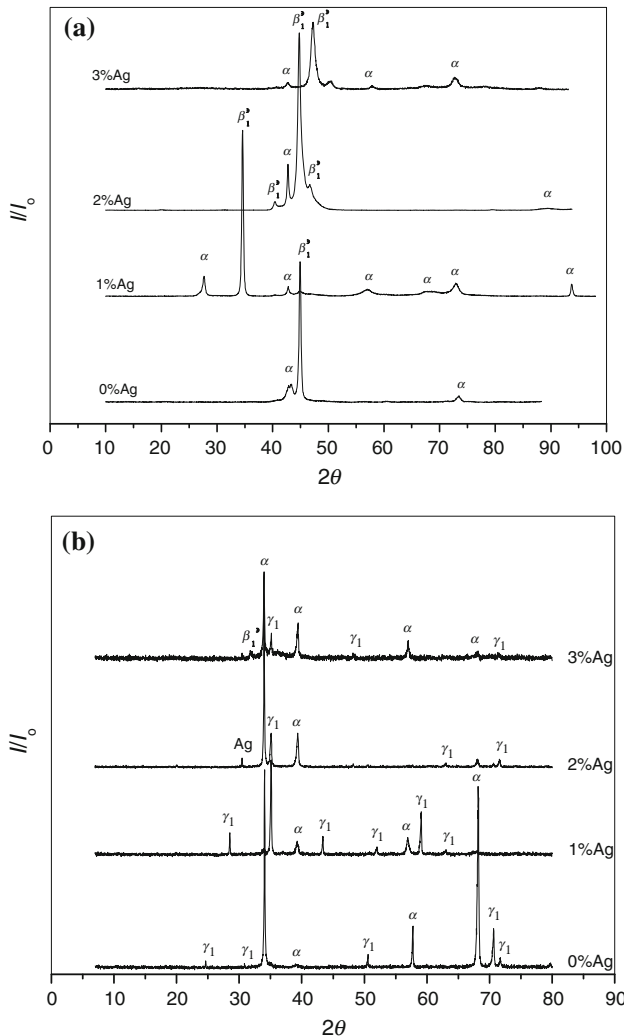
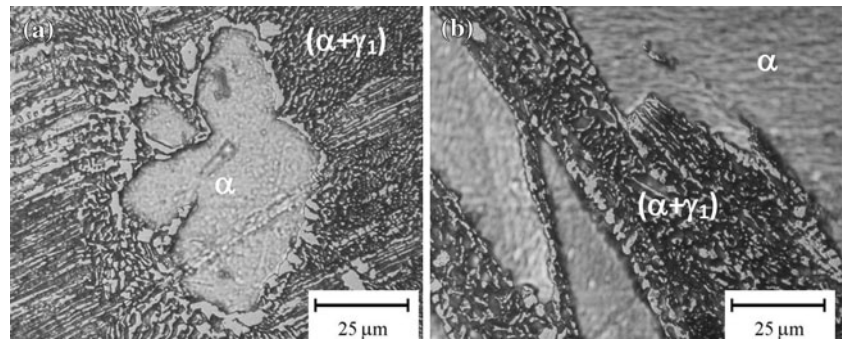


Fig. 5 X-ray diffraction patterns obtained for the studied alloys: **a** before the first heating and **b** before the second heating

In sequence, the samples were cooled down to 658 K with a rate of 50 K min^{-1} and down to 373 K with a rate of 20 K min^{-1} , as shown in Fig. 6a. On rapid cooling (at about 50 K min^{-1}), it is possible to see that peak P_6 is intensified while the forward martensitic transformation, P_7 , is detected for all alloys. P_6 was attributed to the

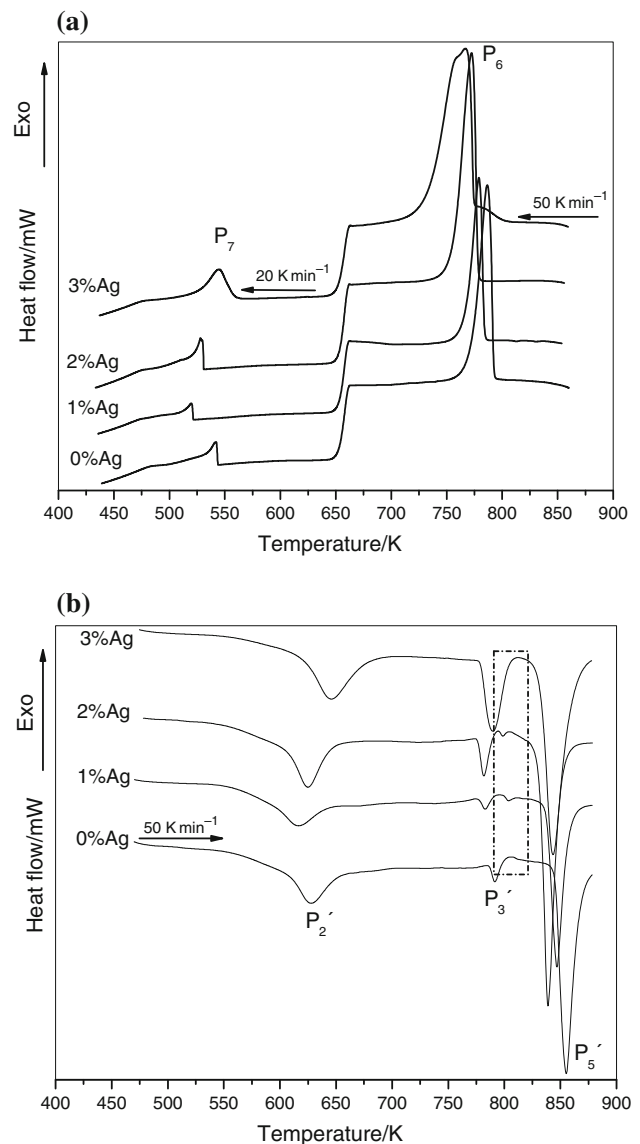


Fig. 6 DSC curves obtained for the Cu–11%Al– x %Ag alloys ($x = 0, 1, 2$ and 3): **a** on cooling and **b** on second heating

$\beta \rightleftharpoons \beta_1$ reaction. The increase in the amount of β_1 -phase for all alloys produces the forward martensitic transformation at lower temperatures, peak P_7 . When the β -phase

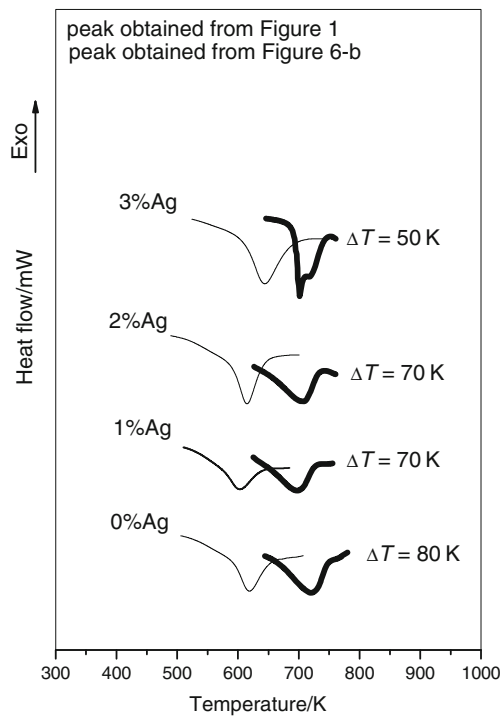


Fig. 7 Peak temperature changes for the reverse martensitic transformation due to the cooling rate

is cooled, two reactions can occur in the temperature range of peak P_6 ; the $\beta \rightarrow \beta_1$ ordering reaction and $\beta \rightarrow (\alpha + \gamma_1)$ decomposition reaction. The ordering reaction is a short-range process while the decomposition reaction is a diffusive process; therefore, the former must be faster than the latter. In this way, when samples are cooled with a rate of 50 K min^{-1} the ordering reaction is dominant in relation to the decomposition reaction and the produced β_1 -phase contributes for martensitic transformation at lower temperature, peak P_7 . In sequence, the samples were again heated with a rate of 50 K min^{-1} , as shown in Fig. 6b.

In the curves of Fig. 6b one can observe the presence of peaks P_2' , P_3' , and P_5' for all studied alloys. It is interesting to note that P_2' is now observed at lower temperatures, as compared with samples initially quenched from 1,173 K in iced water, Fig. 1. The changes in peak temperatures decrease with the increase in Ag concentration, as shown in Fig. 7. This variation can be associated with the lower vacancies content in samples cooled at about 50 K min^{-1} , as compared with those cooled in iced water, and to vacancies annihilation due to Ag.

Figure 6b also shows a new thermal event at about 800 K, which is only detected in alloys with additions of 1%Ag and 2%Ag. For the alloy with 3%Ag this peak seems to occur in the same temperature range of peak P_3' .

It is known [7] that Ag precipitation in Cu–Al–Ag alloys occurs at about 723 K during heating and that these precipitates dissolve preferentially in the $(\alpha + \gamma_1)$ phase [8], due to Al excess in this phase and to the Ag–Al interaction. Hence, this peak can be related with Ag precipitates dissolution in the $(\alpha + \gamma_1)$ phase, formed from the martensitic phase decomposition at P_2' .

Conclusions

The results obtained for samples initially cooled at 1.0 K min^{-1} showed that, in the absence of Ag, the thermal event associated with the forward martensitic transformation does not occur, indicating that the $\beta \rightarrow (\alpha + \gamma_1)$ decomposition reaction is completed. The increase of Ag concentration in the Cu–11%Al alloy decreases the β -phase decomposition reaction rate and induces the martensitic phase formation at slow cooling (1.0 K min^{-1}). For samples submitted to rapid cooling (50 K min^{-1}), the reverse martensitic transformation temperature is shifted to lower values. The samples with 0, 1, and 2%Ag showed a new thermal event, between the reverse eutectoid reaction and the β_1 -phase disordering reaction, which was attributed to the dissolution of Ag precipitates.

Acknowledgements The authors thank to CNPq, FAPESP, and LNLS.

References

1. Matsushita K, Okamoto T, Okamoto T. Effects of manganese and ageing on martensitic transformation of Cu–Al–Mn alloys. *J Mater Sci.* 1985;20:689–99.
2. Graczykowski B, Biskupski P, Mroz B, Mielcarek S, N6 ML, San Juan J. Elastic properties of Cu–Al–Ni shape memory alloys studied by dynamic mechanical analysis. *Smart Mater Struct* 2010;19:015010.
3. Cheniti H, Bouabdallah M, Patoor E. High temperature decomposition of the β_1 phase in a Cu–Al–Ni shape memory alloy. *J Alloys Compd.* 2009;476:420–4.
4. Kwarciac J. Phase transformation in Cu–Al and Cu–Zn–Al alloys. *J Therm Anal.* 1986;31:559–66.
5. Guilemany JM, Fernández J, Franch R, Benedetti AV, Adorno AT. A new Cu-based SMA with extremely high martensitic transformation. *J Physique IV (Colloque C2).* 1995;5:361–5.
6. Lelatto J, Kwarciac J, Bojarski Z, Morawiec H. The effect of cooling rate on α -phase ordering in Cu–12.4wt% Al alloy. *J Mater Sci.* 1985;20:3529–34.
7. Adorno AT, Silva RAG. Effect of Ag additions on the reverse martensitic transformation in the Cu–10 mass%Al alloy. *J Therm Anal Cal.* 2006;83:241–6.
8. Adorno AT, Silva RAG. Isothermal decomposition kinetics in the Cu–9%Al–4%Ag alloy. *J Alloys Compd.* 2004;375:128–33.