Effect of Ag addition on the martensitic phase of the Cu–10 wt.% Al alloy

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Abstract

Thermal analysis and compression tests at room temperature have been carried out for Cu–10 wt.% Al and Cu–10 wt.% Al–10 wt.% Ag alloys samples. The results indicate that the decomposition reaction of the (β_1) parent phase is decreased suppressed and a martensite stabilization effect can be induced by Ag addition. The Cu–Al–Ag alloy shows some degree of shape memory capacity.
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1. Introduction

Copper-based alloys are widely used in many fields because of their good combination with high thermal and electrical conductivity and high strength. In particular, Cu base alloys with high performance are required in the field of electronic materials, such as substrate and lead frame in the printed board, interconnection and so on, because the electronic packaging has a tendency to miniaturization [1]. Some Cu-based alloys can exhibit the martensitic phase on the fast cooling, which is connected with the shape memory effect (SME). This effect has been attracted considerable attention in various industrials fields such as orthodontic arch wire, brassieres for women, eyeglass frame, antennas for cellular phones and recently as material for medical devices such as guides for catheters, stents and so on [2]. Cu–Al alloys containing 9–14 wt.% Al are among those showing a martensitic phase after the rapid cooling from high temperatures. The martensite ageing in these Cu–Al alloys leads to formation of the eutectoid ($\alpha + \gamma_1$) phase and the presence of an interposing order–disorder reaction, substitutional type parent and product phases, makes the eutectoid reaction in this system distinguishable from other ones [3]. Silver additions

to Cu–Al alloys increase its hardness, influence the nucleation rate and the activation energy of the eutectoid decomposition reaction [4]. In this work the thermal and mechanical behavior of Cu–10 wt.% Al and Cu–10 wt.% Al–10 wt.% Ag alloys were analyzed using differential scanning calorimetric (DSC), scanning electron microscopy (SEM), optical microscopy (OM), high temperature X-ray diffractometry (XRD) and compression tests.

2. Experimental procedure

Cu–10 wt.% Al and Cu–10 wt.% Al–10 wt.% Ag polycrystalline 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, with Pb, Fe, and Mn as main impurities (concentration less than 100 ppm).

Flat square samples of about 1.0 mm thickness and 5.0 mm length were obtained for metallography and X-ray diffractometry. These samples were initially annealed for 120 h at 850 °C for homogenization and after annealing they were equilibrated for 1 h at 850 °C and quenched in iced water in order to obtain the martensitic phase. After the heat treatments the samples were mechanically polished and electropolished in a solution of trioxide of chromium in phosphoric acid, etched and examined in
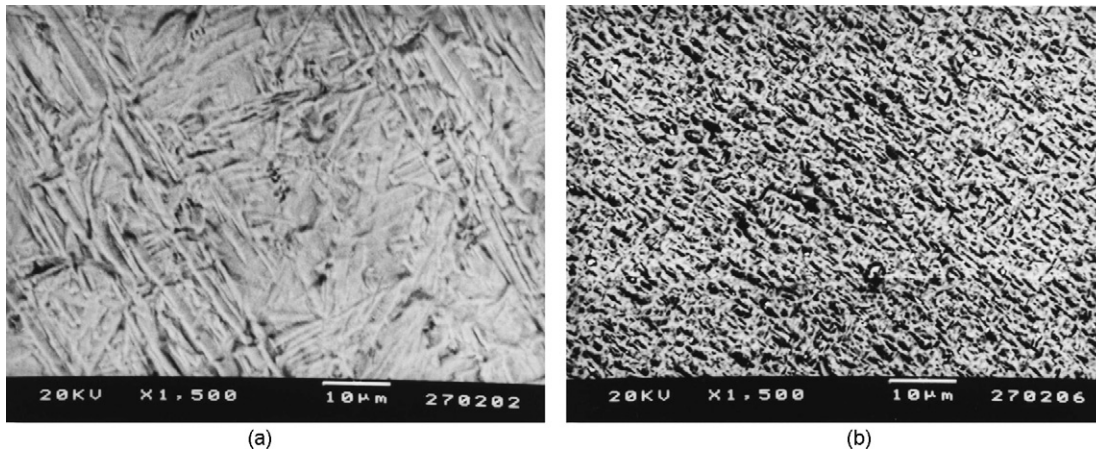
Fig. 1. Scanning electron micrographs obtained for the Cu–10 wt.% Al (a) and Cu–10 wt.% Al–10 wt.% Ag (b) alloys quenched from 850 °C.

an Riechter Mef optical microscope and in a Jeol JSM T330A scanning electron microscopy.

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 $\lambda = 1.746617$ Å and 7098.6 eV. Calorimetric data were obtained using a Rheometric Scientific DSC SP differen-

tial scanning calorimeter. The samples used were thin slices (1–1.5 mm thick and mass 20–100 mg), annealed at 950 °C for 30 min and followed by quenching into iced water. A Shimadzu Autograph-DSS-10T-S deformation universal machine was used for compression tests at room temperature and a constant cross-head speed of 0.5 mm min^{-1}. The stress–strain measurements were recorded and stored for further compu-
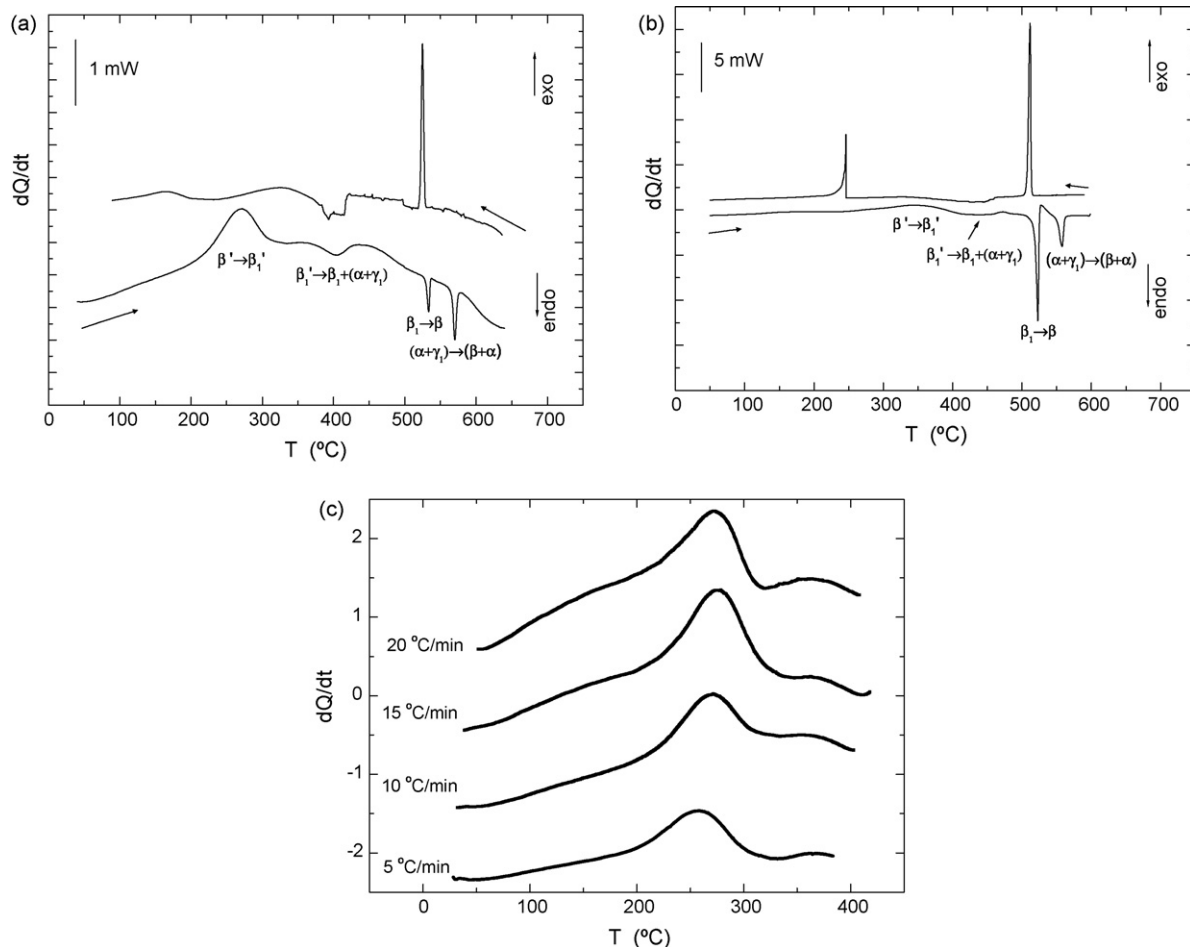

Fig. 2. DSC curves obtained for the Cu–10 wt.% Al alloy (a) and Cu–10 wt.% Al–10 wt.% Ag alloy (b) with heating and cooling rates of 10 °C min^{-1}; (c) DSC curves obtained for the Cu–10 wt.% Al alloy with different heating rates.

tation using a high speed digital acquisition system with compression–train compliance compensation. To reduce the friction during the tests, the end faces were covered with a thin Teflon film and lubricated with grease. Square section samples for compression test were obtained, with around 9.5 mm length and 14 mm^2 section. Previous the mechanical tests, the Cu–Al and Cu–Al–Ag samples were thermal treated at 800 and 940 °C (T_β), respectively, and quenched in a mix of water and ice. In this way the samples were in martensitic state.

3. Results and discussion

The scanning electron micrographs obtained for the Cu–10 wt.% Al and Cu–10 wt.% Al–10 wt.% Ag alloys quenched from 850 °C are shown in Fig. 1. In the micrograph of Fig. 1a one can observe the initial structure of the Cu–10 wt.% Al alloy which corresponds to β′ martensitic phase found in alloys with less than 10.8 wt.% Al [5]. In Fig. 1b it is possible to notice that, with Ag addition, there is a change on the alloy microstructure and one can observe the presence
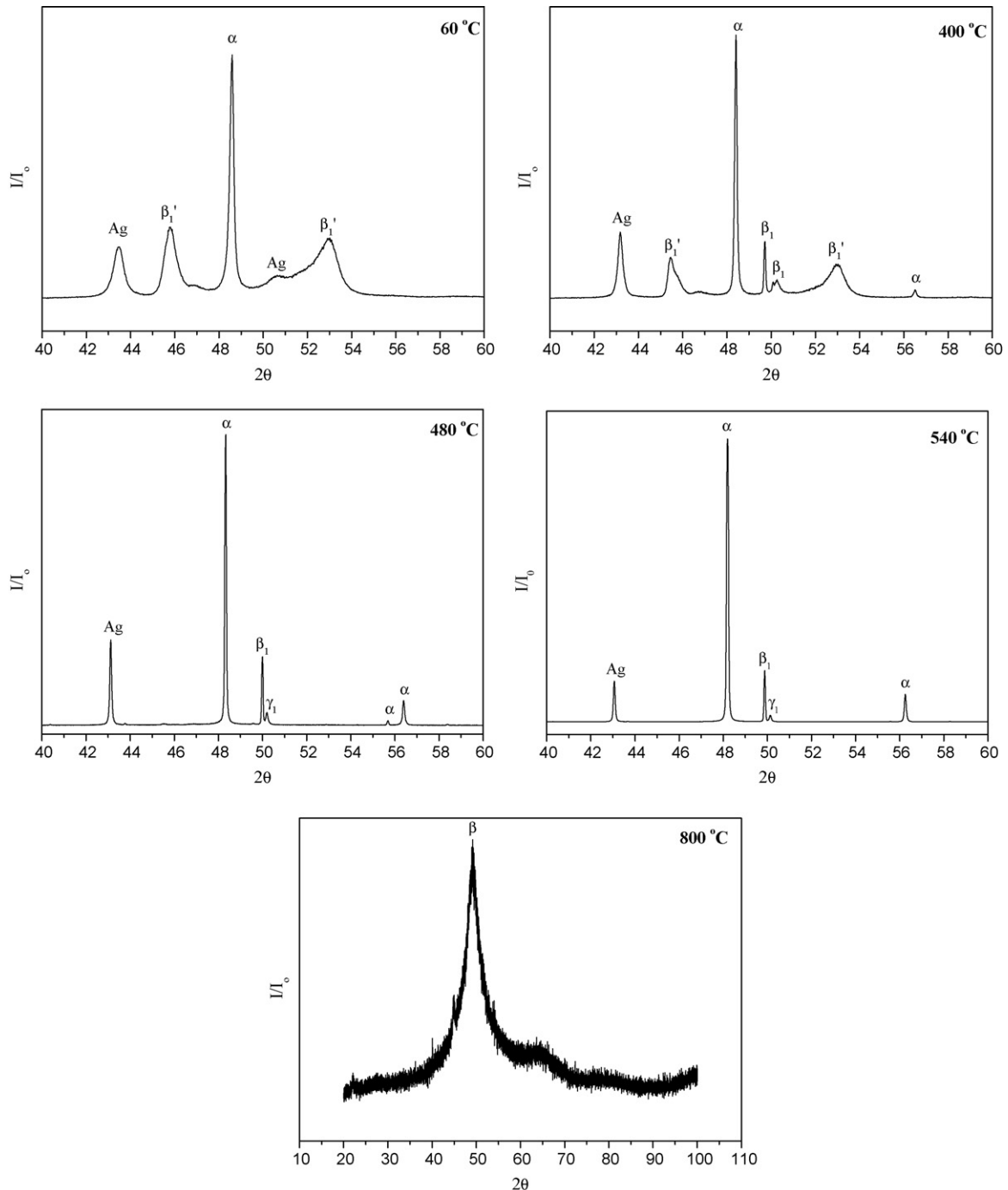

Fig. 3. X-ray diffraction patterns obtained in situ for the Cu–10 wt.% Al–10 wt.% Ag alloy initially quenched from 850 °C.

of a large amount of α phase (white) over the martensitic matrix.

Fig. 2a shows the DSC curves obtained for the Cu–10 wt.% Al alloy quenched from 850 °C in iced water, with heating and cooling rates of 10 °C min^{-1}. On heating, the exothermic peak at about 265 °C is related to $β' → β'_1$ martensitic ordering reaction. The endothermic peak at about 400 °C is ascribed to a combination of two consecutive reactions, the $β'_1 → β_1$ reverse martensitic transformation and the partial $β_1$ decomposition giving the eutectoid mixture. The endothermic peak at about 525 °C is due to the $β_1 → β$ ordering transition from part of the $β_1$ phase remnant from the transformation at 400 °C. The endothermic peak at about 564 °C is related to the $α + γ_1 → β + α$ reaction [6]. On cooling, only the $β → β_1$ ordering reaction is detected.

Fig. 2b shows the DSC curves obtained for the Cu–10 wt.% Al–10 wt.% Ag alloy quenched from 950 °C in iced water, with heating and cooling rates of 10 °C min^{-1}. On heating it is possible to see that the calorimetric signal is weak for the two first peaks compared with those corresponding to the Cu–10 wt.% Al alloy. The peak ascribed to the $(β'_1 → β_1)$ reverse martensitic transformation is now observed at around 450 °C. This increase in the reverse martensitic transformation temperature indicates that the martensite stabilization effect can be induced by Ag addition in the Cu–10 wt.% Al alloy. It is also possible to observe that the peak related to $α + γ_1 → β + α$ transition decreases for the alloy containing Ag, suggesting that the $β_1$ parent phase decomposition reaction rate is decreased, thus decreasing the $(α + γ_1)$ content able to produce the β phase. On cooling, it is possible to observe the peak for the $β → β_1$ ordering reaction at about 520 °C and an exothermic peak at 250 °C which is not observed in Fig. 2a, indicating that the presence of Ag is responsible for this new thermal event. This peak may be attributed to the $β_1 → β'_1$ martensitic reaction, probably enhanced by the superposition of the α-phase ordering reaction [6,7]. This indicates that the relative fraction of $β_1$ produced during cooling is greater in the alloy with Ag. It is known that on cooling at 10 °C min^{-1} of the Cu–9 wt.% Al alloy the $β → α + γ_1$ decomposition reaction is observed, but in the Cu–12.4 wt.% Al alloy all the following reactions are observed: $β → γ_1$, $β → α + γ_1$, $β → β_1$, $α → α_2$ and $β_1 → β'_1$ [8,9]. In this way, the presence of an exothermic peak at about 250 °C in the DSC curve obtained for the Cu–10 wt.% Al–10 wt.% Ag alloy indicates that Ag addition is shifting the equilibrium concentration to higher Al content and disturbing the $β → γ_1$ and $β → (α + γ_1)$ reactions, increasing the β phase amount available for the $β → β_1$ reaction and thus enhancing the peak corresponding to the $β_1 → β'_1$ reaction.

It is interesting to note that the exothermic peaks attributed to the martensitic ordering reaction and observed at about 265 and 350 °C, respectively, for the Cu–Al and Cu–Al–Ag alloys, are in the same range (200–400 °C) at where the bainitic transformation by low temperature ageing has been reported in the Cu–Al–Ni-based and Cu–Al–Mn alloys with low Al content [2,10]. There is a similarity between analysis of DSC peaks whose shape are dominated by reaction kinetics and those whose shapes are dominated by the thermodynamics of the reaction,

since DCS is a rising temperature experiment and both situations can occur [11]. In process governed by reaction kinetics, increasing the imposed heating rate causes the peaks to occur at systematically higher temperatures; an example of this is the particle formation or dissolution on precipitate phases [12]. In contrast to this behavior, same peaks do not shift significantly with the imposed heating rate; this reactions occurs at the same temperature regardless of the imposed heating (cooling) rate. This reactions are dominated by its temperature thermodynamic equilibrium.

It has been observed that order–disorder transitions in β brass shown a behavior similar to reactions dominated by its equilibrium thermodynamic temperature. If the processes of precipitation and order–disorder reactions at different heating rates are compared, small modifications in the heating rate produce very different effects in both processes. Increasing the heating rate, the temperature of order reaction does not change significantly, while the precipitation peaks are observed at higher temperatures [13]. Fig. 2c shows the DSC curves obtained for the Cu–10 wt.% Al alloy at heating rates of 5, 10, 15, and 20 °C min^{-1}. As can be seen, the exothermic peak does not move with the change of the heating rate. This strongly suggests that the signal corresponds to a order reaction and not to a process of bainitic transformation.

Fig. 3 shows the high temperature X-ray diffraction patterns obtained for the Cu–10 wt.% Al–10 wt.% Ag alloy initially quenched from 850 °C in iced water. These results confirm what was observed in the DSC curve on Fig. 2b. The $β_1$ phase formation starts at about 400 °C and between 400 and 480 °C the $β'_1 → β_1$ transition occurs. From 540 to 800 °C only the β phase is observed.

The mechanical properties have been evaluated under compressive load. Fig. 4 shows the stress–strain curves obtained for both alloys. On loading, the curves are linear at first, a smooth slope change follows, and a new almost linear regime is reached as the deformation proceeds. The first linear part corresponds to the elastic regime of the martensitic phase, while the linearity deviation is associated with the martensite deformation start.
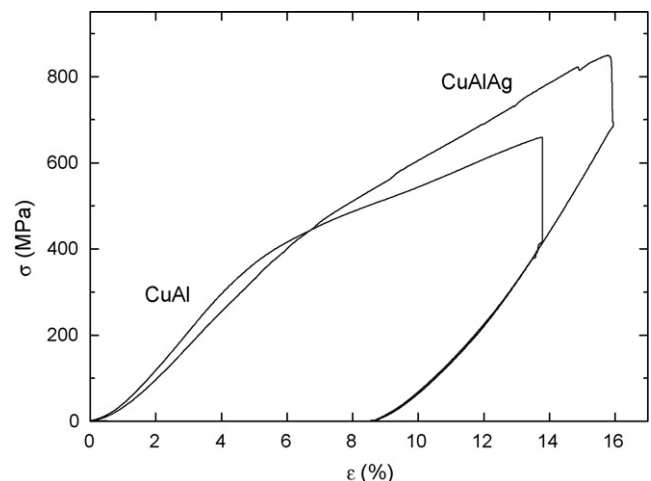

Fig. 4. Compression curves obtained for the Cu–Al and Cu–Al–Ag alloys.

The stress corresponding to the end of the initial lineal part will be referred as the critical martensite deformation stress, σ_d. The final almost constant stress–strain slope corresponds to the progress of the martensite deformation; this slope will be called the deformation slope, DS.

No significant difference in σ_d is observed between both alloys, being around 360 MPa for Cu–Al alloy, and around 380 MPa for Cu–Al–Ag alloy. The strain hardening, denoted by the DS, is higher for the Cu–Al–Ag alloy with $d\sigma/d\varepsilon$ of around 44 MPa/%, while for Cu–Al alloy is around 33 MPa/%. The measured maximum strain without sign of failure was around 9% for both alloys, at a maximum stress of 850 MPa for Cu–Al–Ag alloy and 650 MPa for Cu–Al alloy. Once overcome that strain, grains decohesion is observed. The presence of Ag is then responsible for a strengthening of the martensitic phase. Fig. 5 shows the materials surface at different deformation levels.

Two processes can occur when a load higher than σ_d is applied; martensite variants growth at expenses of another ones, or/and plastic deformation of the martensite. The strain resulting from the first one is reversible by heating above the critical reverse transformation temperature, giving rise to the one-way shape memory effect. Plastic deformation is not reversible by heating. In order to distinguish which one is acting, stress–strain cycles with increasing applied maximum load were done, heating the sample up to 800 °C after each cycle. The length of the samples was measured before the compression test (l_0), after compression (l_f), and after the heating (l_f'). Compression tests have the great advantage to permit the determination of the samples length changes directly and with great accuracy. In this case, a digital caliper with precision $\pm 10^{-2}$ mm was used. The strains of interest here are ε_{ret}, the strain retained on unloading, and ε_{TT}, the strain retained after the thermal treatment, being $\varepsilon_{ret} = (l_0 - l_f)/l_0$, and $\varepsilon_{TT} = (l_0 - l_f')/l_0$ where ε_{TT} is the irreversible strain associated to plastic deformation, and the difference between ε_{ret} and ε_{TT} is the strain due to martensite variants growth.
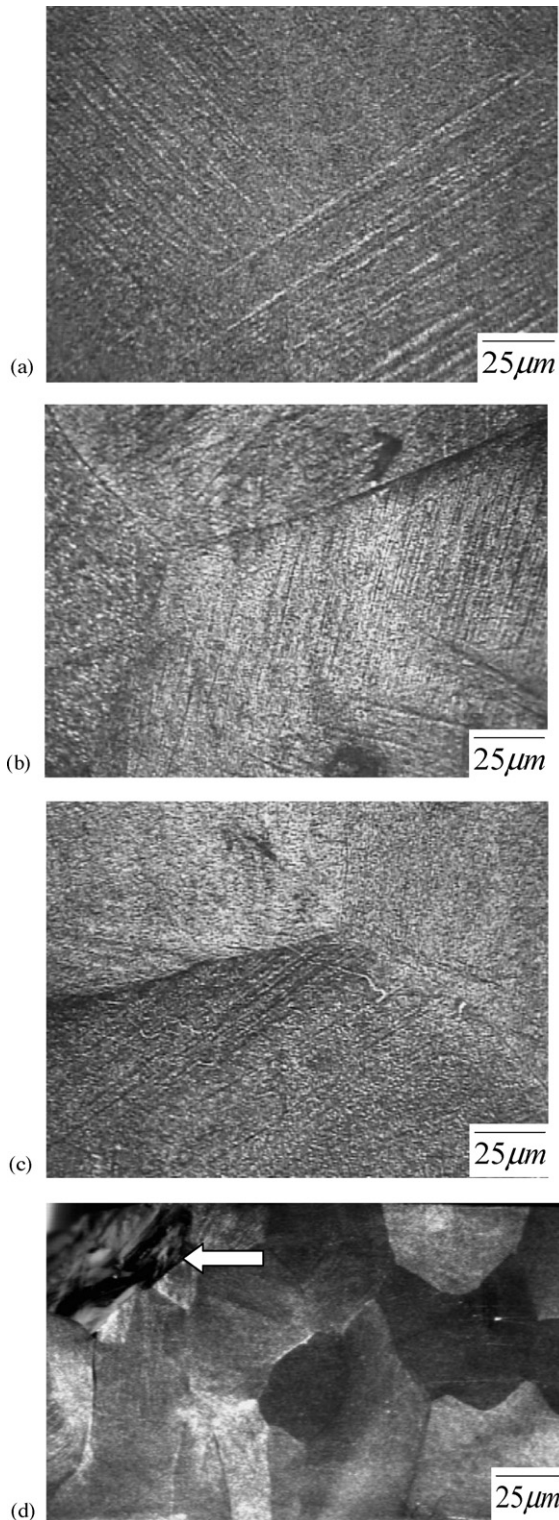

Fig. 5. Optical micrographs obtained for the Cu–10 wt.% Al–10 wt.% Ag alloy. (a) Martensite needles without deformation; (b) with 3% deformation: deformation marks are seen; (c) with 5.7% deformation: deformation marks inside and at the grain boundaries are seen; (d) with 9% deformation: deformation marks inside and at the grain boundaries are seen; failure by grain decohesion is indicated.
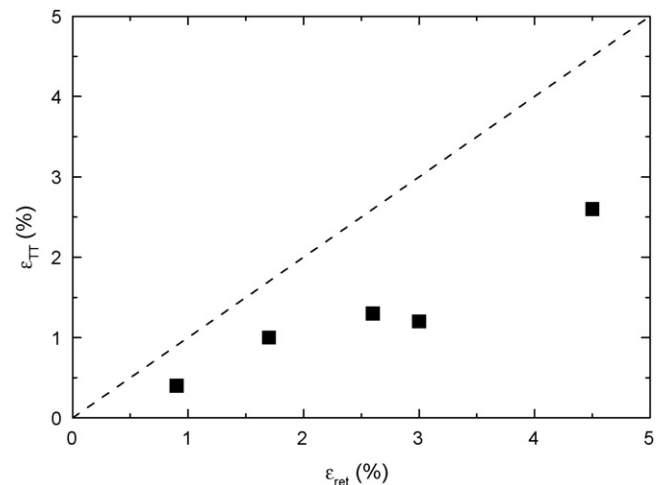
Fig. 6. Strain retained after the thermal treatment (ε_{TT}) as a function of the strain retained on unloading (ε_{ret}). Dotted line corresponds to $\varepsilon_{TT} = \varepsilon_{ret}$.

Samples of Cu–Al alloy do not change its length after heating, $\varepsilon_{TT} = \varepsilon_{ret}$ was measured denoting only plastic deformation of martensite occurs. Samples of Cu–Al–Ag alloy show some degree of recovering. Fig. 6 shows this behavior. As can be seen, the ε_{TT} is always smaller than ε_{ret}, indicating both mentioned processes are acting in Cu–Al–Ag alloy. In this way, Cu–Al–Ag alloy shows some degree of shape memory capacity, while Cu–Al alloy does not.

4. Conclusions

The results from DSC on heating indicate that a martensite stabilization effect can be induced by Ag addition and the (β_1) parent phase decomposition reaction is decreased. On cooling, the presence of an exothermic peak at about 250 °C indicates that Ag addition is shifting the equilibrium concentration to higher Al content and enhancing the peak corresponding to the $\beta_1 \rightarrow \beta_1'$ martensitic transition.

From compression tests at room temperature the mechanical behavior of the martensitic phase was analyzed. The critical stress for deformation is similar for both alloys, but a higher strain hardening is shown by the Cu–Al–Ag alloy. Pure plastic deformation occurs in the Cu–10%Al alloy. In the Cu–10%Al–10%Ag alloy two processes occurs: martensite variants growth and plastic deformation. In this way, Cu–Al–Ag alloy exhibits some degree of shape recovery, associated with some shape memory capacity.

Acknowledgements

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