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# Martensite aging kinetics in the Cu-10 wt.%Al and Cu-10 wt.%Al-10 wt.%Ag alloys

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**Abstract** The martensite aging kinetics in the Cu-10 wt.%Al and Cu-10 wt.%Al-10 wt.%Ag alloys was studied using microhardness measurements, classical differential thermal analysis (DTA), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and in-situ high-temperature X-ray diffractometry (XRD). The results for the Cu-10%Al alloy indicated a process dominated by the martensite ordering assisted by migration of quenched-in vacancies and followed by the consumption of the α phase. For the Cu-10%Al-10%Ag alloy the dominant process is the consumption of the α phase associated with a decrease in the ordering degree of the martensitic phase.

## Introduction

When an alloy is aged in the martensitic state the reverse transformation finish temperature increases with aging time to a saturated value, a phenomenon known as martensite stabilization. Martensitic stabilization processes are responsible for some anomalies that damage shape memory phenomena such as changes in the transformation temperature and others [1]. Main mechanisms of stabilization are the pinning of interfaces by quenched-in vacancies, martensitic structure modification, and changes in the degree of order inherited from the austenite. Cu-based alloys, when cooled to exhibit the martensitic phase, undergo disorder–order transitions and the supersaturation of quenched-in vacancies that is produced can favor subsequent diffusion controlled phenomena [2, 3].

Cu–Al alloys containing 9–14 wt.%Al are among those showing a martensitic phase after the rapid cooling from high temperatures. The martensite aging 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 [4]. Silver additions to Cu–Al alloys increase its hardness, influence the nucleation rate and the activation energy of the eutectoid decomposition reaction [5]. In this work, the martensite aging kinetics in the Cu-10 wt.%Al and Cu-10 wt.%Al-10 wt.%Ag alloys was studied using microhardness measurements, classical differential thermal analysis (DTA), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and in-situ high-temperature X-ray diffractometry (XRD).

## Experimental procedure

The Cu-10 wt.%Al and Cu-10 wt.%Al-10 wt.%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. 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).

Cylindrical samples with 2.0 cm diameter and 6.0 cm length were cut in disks of 0.4 cm 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 850 °C for homogenization and after annealing they were maintained

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at 850 °C for 1 h and quenched in iced water. The Vickers microhardness measurements were made with a Buehler Micromet 2003 Microhardness Tester using a load of 0.5 kg. Scanning electron micrographs and X-ray diffraction patterns were obtained to identify the phases present in the alloy at the different quenching temperatures. The micrographs were obtained using a Jeol JSM T330A SEM electron microscope with a Noran (EDX) micro-analyzer 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 and $\lambda = 1.39313$ Å. 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(a) shows the DTA curve obtained with a heating rate of 10 °C min$^{-1}$ for the Cu-10 wt.%Al alloy initially quenched from 850 °C in iced water. The exothermic peak at about 265 °C is related to two exothermic ordering reactions occurring in the same temperature range, $\beta' \rightarrow \beta_1'$ and $\alpha \rightarrow \alpha_2$ [6]. The endothermic peak at about 380 °C is ascribed to a combination of two consecutives reactions, the $\beta_1' \rightarrow \beta_1$ retransformation of the martensite and the partial $\beta_1$ decomposition giving the eutectoid mixture. The endothermic peak at about 525 °C is due to the transition $\beta_1 \rightarrow \beta$ from part of the $\beta_1$ phase remnant from the transformation at 380 °C. The endothermic peak at about 564 °C is related to the $(\alpha + \gamma_1) \rightarrow \alpha + \beta$ reaction [7].

Figure 1(b) shows the DTA curve obtained with a heating rate of 10 °C min$^{-1}$ for the Cu-10 wt.%Al-10 wt.%Ag alloy quenched from 850 °C in iced water. The observed peaks in this figure correspond to the same transformations verified in Fig. 1(a). The first exothermic peak, at about 300 °C is enlarged and shifted to a higher temperature. It is interesting to note that the curve in Fig. 1(b) was obtained for an alloy with addition of 10 wt.%Ag and the peak associated with Ag precipitation was not observed, in opposition to what could be expected from similar thermal data obtained with Ag additions less than 10 wt.% to the Cu-10 wt.%Al alloy. In Cu-10 wt.%Al alloys with 4, 6, and 8 wt.%Ag, silver precipitation was observed in the temperature range between 350 and 450 °C [8]. This indicates that, in the Cu-10 w.%Al-10 wt.%Ag alloy, this considerable Ag amount is, in some way, dissolved in this alloy and is not precipitating in the expected temperature range. If there is some Ag precipitation, this must be occurring together with the martensite ordering reaction or it is dissolved in the α phase. Besides, the reverse martensitic transformation is now observed at about 480 °C, what seems to indicate that Ag addition is increasing the stability of the martensitic phase. The peak corresponding to the ($\beta_1 \rightarrow \beta$) transition, at about 540 °C, is now more intense, showing that the $\beta_1$ phase decomposition reaction is disturbed by the presence of Ag. It is also possible to verify that the peak related to the $(\alpha + \gamma_1) \rightarrow \alpha + \beta$ transition, at about 550 °C, is decreased, indicating that the decomposition reaction rate of the ($\beta_1$) parent phase is decreased, thus decreasing the $(\alpha + \gamma_1)$ content able to produce $\beta$.

The shift of the reverse martensitic transformation to a higher temperature with Ag addition was confirmed by in-situ high-temperature X-ray diffractometry. Figure 2(a) shows the X-ray diffraction pattern obtained at room temperature for the Cu-10 wt.%Al-10 wt.%Ag alloy initially quenched from 850 °C. In this figure one can observe the expected starting phases α, Ag-rich and $\beta_1'$ martensitic phase. The sample was then heated at a heating rate of 10 °C min$^{-1}$ and the in-situ X-ray diffraction patterns obtained at 400, 450, and 500 °C are shown, respectively, in Fig. 2(b, c, and d).

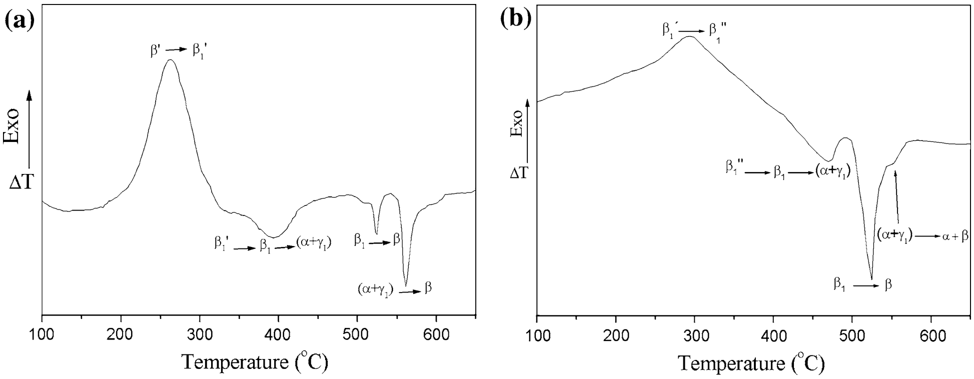
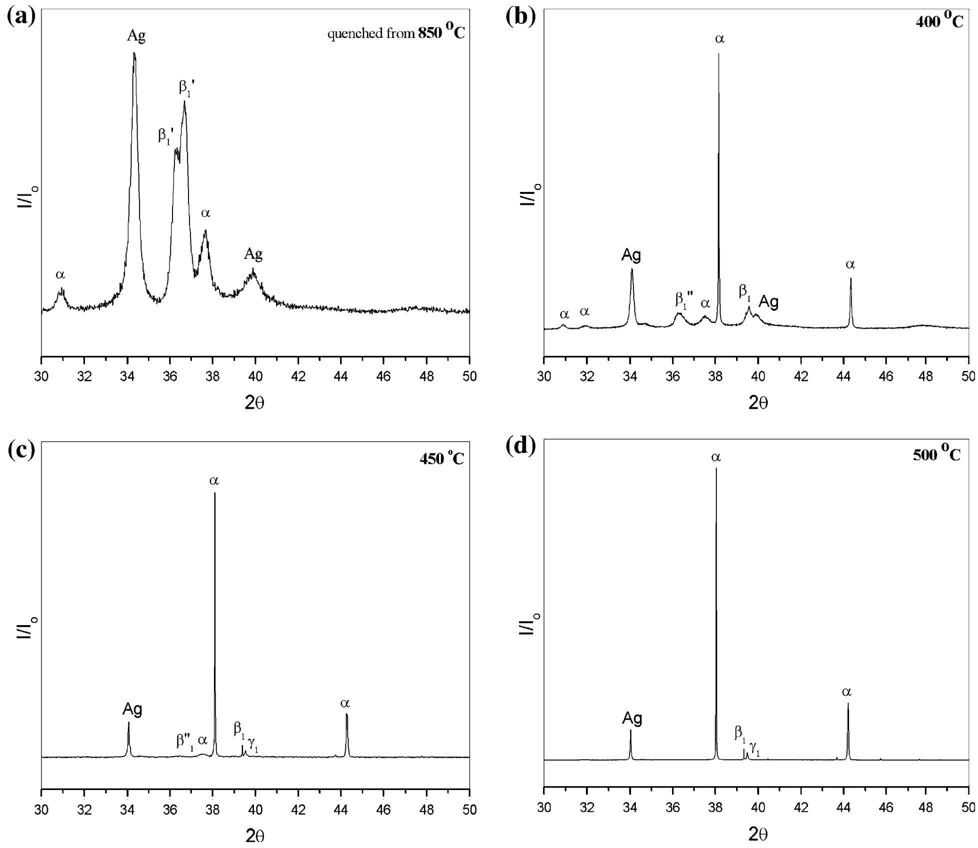


**Fig. 1** DTA curves obtained for samples initially quenched from 850 °C, with a heating rate of 10 °C min$^{-1}$: (**a**) Cu–10%Al alloy and (**b**) Cu-10%Al-10%Ag alloy

**Fig. 2** In situ X-ray diffraction patterns obtained for the Cu-10 wt.%Al-10 wt.%Ag alloy initially quenched from 850 °C



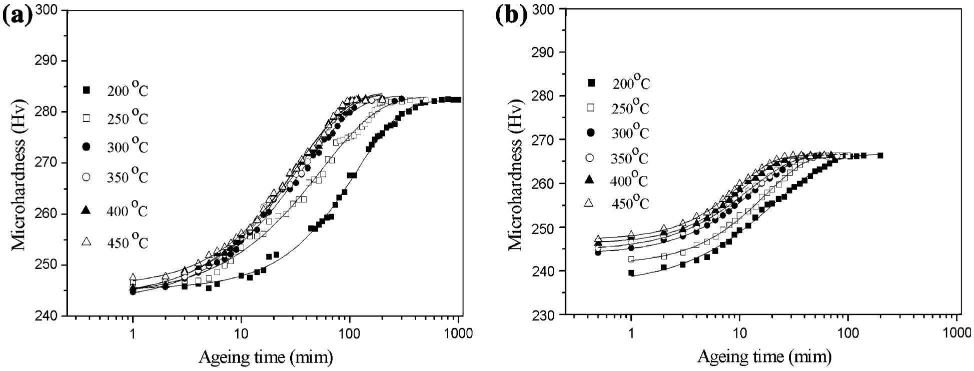
In Fig. 2(b), obtained at 400 °C, it is possible to observe the presence of α, Ag-rich and $\beta_1{}'$ phases together with the $\beta_1$ phase formed from the ($\beta_1{}'' \rightarrow \beta_1$) reverse martensitic transformation, $\beta_1{}''$ being the ordered Cu–Al–Ag martensitic phase. In Fig. 2(c), obtained at 450 °C, it is possible to notice a decrease in the intensity of the $\beta_1{}'$ diffraction peak and the presence of the peak corresponding to the $\gamma_1$ phase, together with the $\beta_1$ phase peak. At 500 °C (Fig. 2(d)) it is possible to observe that the ($\beta_1{}'' \rightarrow \beta_1$) reaction is completed.

The results obtained from DTA and in-situ XRD confirm that the presence of Ag is increasing the stability range of the $\beta_1{}'$ martensitic phase. In the Cu-10 wt.%Al alloy the $\beta_1$ decomposition reaction is completed at about 380 °C while in the Cu-10 wt.%Al-10 wt.%Ag alloy it occurs at about 480 °C. This corresponds to an extremely increase in the temperature of the reverse martensitic reaction enhanced by Ag addition.

In order to analyze the influence of Ag in the martensite aging kinetics in the Cu-10 wt.%Al and Cu-10 wt.%Al-10 wt.%Ag alloys, six aging temperatures were chosen in the range 200–450 °C determinate from Fig. 1.

Figure 3 shows the isothermal microhardness versus aging time curves obtained for alloys aged at the chosen temperatures (200, 250, 300, 350, 400, and 450 °C). In these curves one can see that the final hardness values are

**Fig. 3** Plots of microhardness change versus aging time: (**a**) Cu-10 wt.%Al alloy; (**b**) Cu-10 wt.%Al-10 wt.%Ag alloy



the same for all aging temperatures, but the initial ones are a little different for the alloy with Ag. This difference in the values for lower aging temperatures may be associated with the presence of a greater amount of the $\alpha$ phase, which decreases the alloy hardness. This is confirmed by the micrographs and EDX spectra shown in Fig. 4, where it is possible to note the presence of the $\alpha$ phase for the alloy aged at 200 °C for 1 min (Fig. 4(a, b)), and a decrease in the $\alpha$ phase amount for the alloy aged at 200 °C for 200 min (Fig. 4(c, d)). Figure 4(b and c) were taken with a greater magnification, for a better visualization of the microstruture. The final hardness values for the Cu-10%Al-10%Ag are lower than those observed for the Cu10%Al alloy at the plateau of the curves. This may be due to the presence of Ag precipitates (white). After quenching, part of Ag atoms is dissolved in the martensitic matrix and the other part in the $\alpha$ phase. On aging, during the martensite ordering reaction, the $\alpha$ phase is dissolved in the martensitic matrix, increasing the Cu relative fraction and consequently decreasing the Al relative fraction in the martensitic phase. The Ag dissolved in the $\alpha$ phase is released onto the martensite surface, as seen in Fig. 4(d). The decrease in the Al relative fraction in the martensitic phase also decrease the number of different atoms pairs Cu–Al [9], thus decreasing the ordering degree of the $\beta_1' \rightarrow \beta_1''$ ordered martensite. From the EDX spectra shown in Fig. 4(e and f), obtained at the $\alpha$ phase of the Cu–Al–Ag alloy, it is possible to observe a decrease in the Cu and Ag relative fraction and an increase in the Al relative fraction, thus confirming the Cu consumption in the martensitic phase.

Figure 5(a and b) show the X-ray diffraction patterns obtained for the Cu-10 wt.%Al (Fig. 5(a)) and Cu-10 wt.%Al-10 wt%Ag (Fig. 5(b)) alloys aged at 200 °C for different aging times. In these figures it is possible to observe that at the plateau of curves in Fig. 3 the final product corresponds to $\beta_1'$ and $\alpha$ phases, with Ag precipitated when it is added, indicating that there is no martensite decomposition on aging. In this way, the martensite

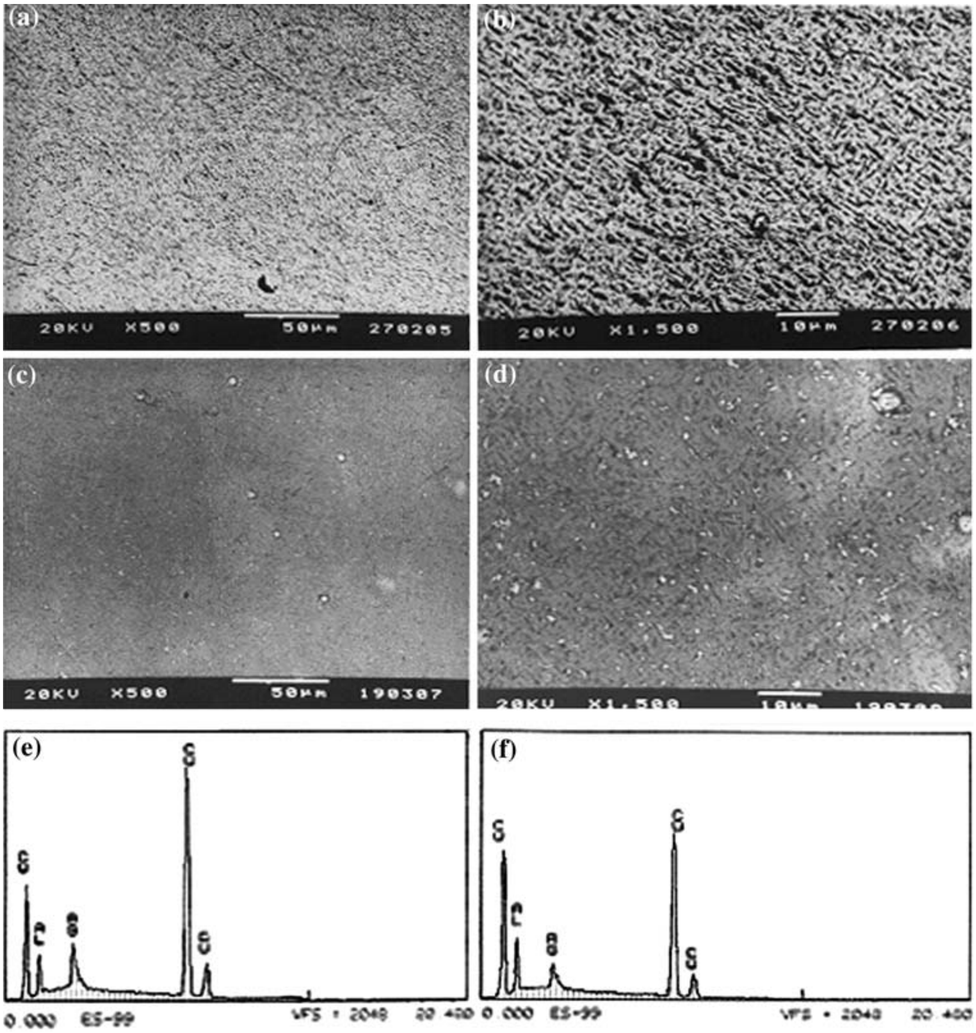


**Fig. 4** Scanning electron micrographs obtained for the Cu–Al–Ag alloy aged at 200 °C for: (**a**) and (**b**) 1 min; (**c**) and (**d**) 200 min. EDX spectra obtained for the alloy aged for (**e**) 1 min and (**f**) 200 min

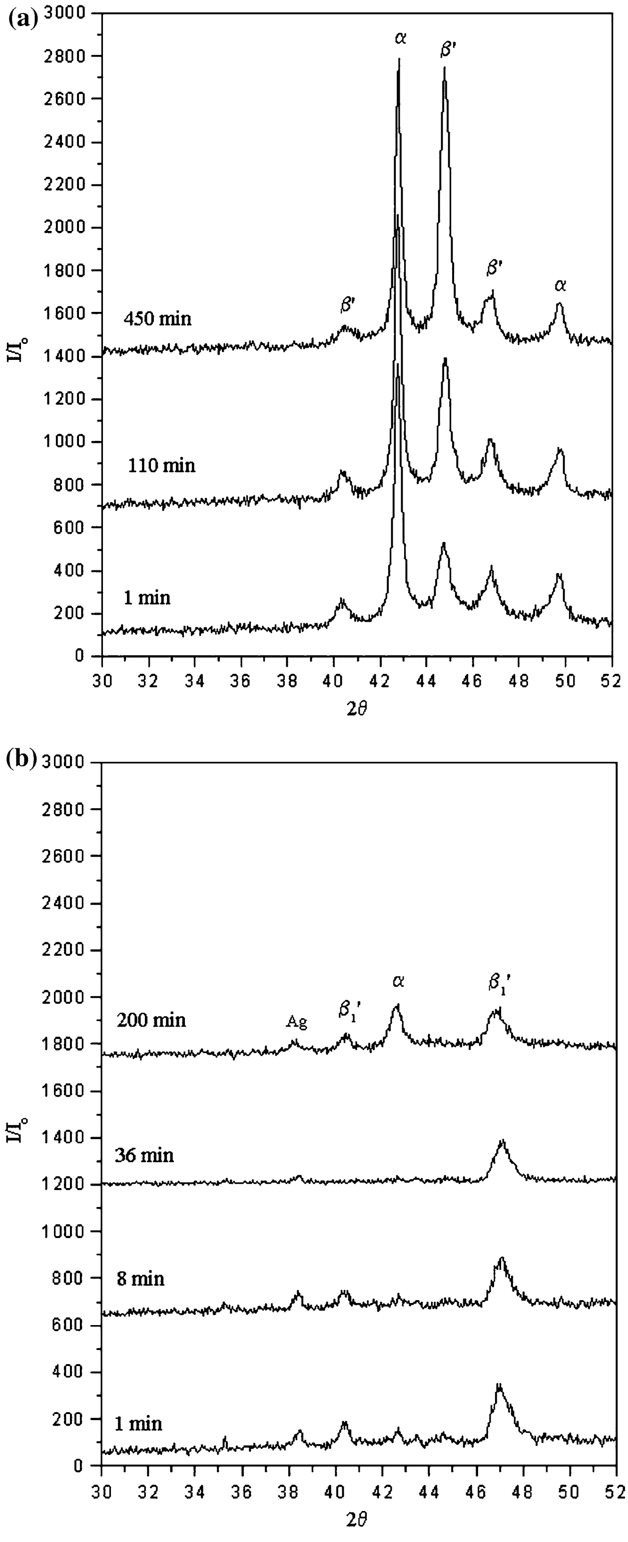


**Fig. 5** X-ray diffraction patterns obtained for samples aged at 200 °C for different aging times: (**a**) Cu-10 wt.%Al alloy; (**b**) Cu-10 wt.%Al-10 wt.%Ag alloy

decomposition reaction, expected from DTA results, did not occurred on aging, in the time and temperature ranges here considered.

Considering the transformed fraction defined by the relation

$$y(t) = \frac{Hv_{(t)} - Hv_{\mathrm{o}}}{Hv_{\infty} - Hv_{\mathrm{o}}} \tag{1}$$

where *y(t)* is the transformed volume fraction at a given temperature, $Hv_{\infty}$ is the hardness value when the considered reaction is completed, $Hv_{\mathrm{o}}$ the initial hardness, and $Hv_{(t)}$ the hardness value at a given time $t$, plots of the transformed fraction versus aging time may be obtained from Fig. 3. Figure 6 shows these plots and, as $y$ and $t$ are functionally related, it is possible to choose $t$ instead of $y$ as the dependent variable and then the rate equation,

$$\frac{\mathrm{d}y}{\mathrm{d}t} = kf(y) \tag{2}$$

may be written in the form

$$\mathrm{d}t = k^{-1}f^{-1}(y)\mathrm{d}y \tag{3}$$

and the time $t_{1/2}$, required for half of the reaction to occur is

$$t_{1/2} = k^{-1}\int_{y=0}^{y=\frac{1}{2}} (y)\mathrm{d}y \tag{4}$$

The kinetics of martensite aging was studied at a series of temperatures, and the time $t_{1/2}$ was measured at each aging temperature for $y = ½$, all others experimental variables maintained constant. The martensite aging effect is developed by a diffusion mechanism as a thermal activation process [10] and, considering that $t_{1/2}$ is proportional to the martensite aging rate, the activation energy for the process can be obtained from the Arrhenius equation,

$$k = A_{\mathrm{A}}e^{-\frac{E_{\mathrm{A}}}{KT}} \tag{5}$$

where $A_{\mathrm{A}}$ is the pre-exponential factor, $E_{\mathrm{A}}$ is the activation energy for the process and $K$ is the Boltzmann constant.

Since the function *f(y)* does not change in the temperature range considered, the integral in eq. (4) has a constant numerical value and, therefore,

$$t_{1/2} \propto k^{-1} \tag{6}$$

$$t_{1/2} = A_{\mathrm{A}}^{-1}e^{\frac{E_{\mathrm{A}}}{KT}} \tag{7}$$

and

$$\ln t_{1/2} = -\ln A_{\mathrm{A}} + \frac{E_{\mathrm{A}}}{K}\left(\frac{1}{T}\right) \tag{8}$$

So, a linear relationship between ln $t_{1/2}$ and 1/T is expected and the value of $E_{\mathrm{A}}$ for the process can be obtained from the slope of this straight line [11].

Figure 7 shows the linear relationship between ln $t_{1/2}$ and 1/T, which corresponds to two processes for the

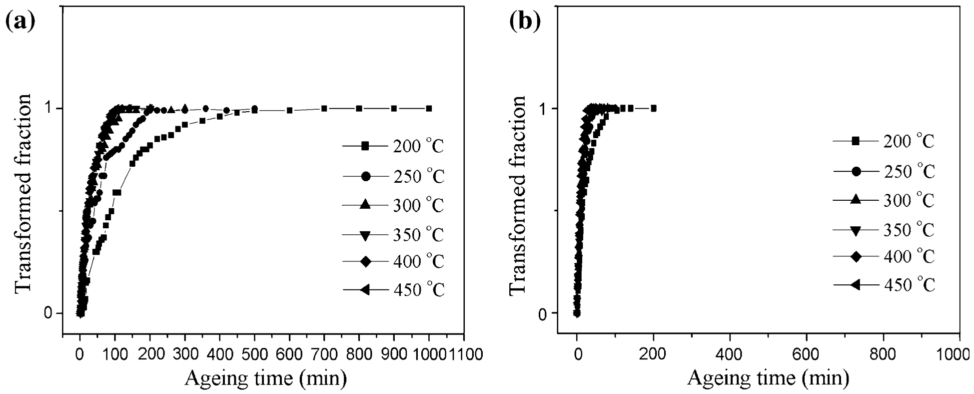


**Fig. 6** Plots of transformed fraction versus aging time for the alloys: (**a**) Cu-10%Al and (**b**) Cu-10%Al-10%Ag

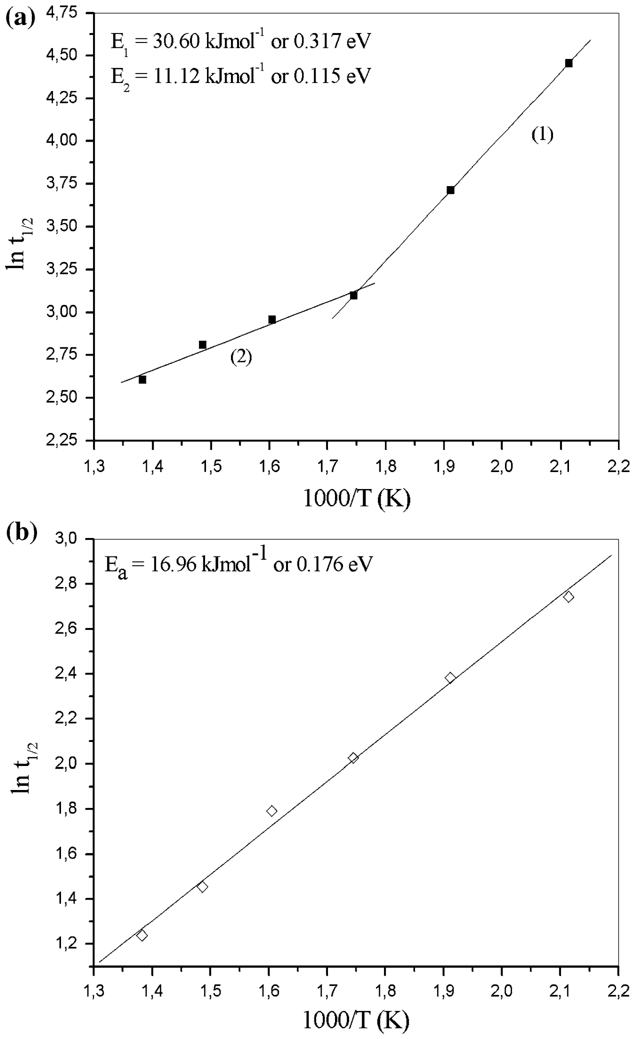


**Fig. 7** Plots of ln $t_{1/2}$ vs. 1,000/T: (**a**) Cu-10%Al alloy and (**b**) Cu-10%Al-10%Ag alloy

Cu-10%Al alloy and only one for the Cu-10%Al-10%Ag alloy. From the results obtained for the Cu-10%Al alloy, the activation energy value for the temperature range 200–300 °C is 0.317 eV and for the range 350–450 °C is 0.115 eV. The activation energy value obtained for the Cu-10%Al-10%Ag alloy is 0.176 eV.

The activation energy value found in the literature for the migration of a vacancy in Au-Cd martensites, i.e., the activation energy for a jump of a vacancy, which is the rate determinant process for the aging of martensite, is $E' = 0.44$ eV [10]. This indicates that the activation energy value obtained for the Cu-10%Al alloy in the temperature range between 200 and 300 °C may be associated with the martensite ordering reaction assisted by migration of quenched-in vacancies and the value obtained in the range 350–450 °C may be ascribed to the consumption of the $\alpha$ phase in the martensitic phase.

The activation energy value obtained for the Cu-10%Al-10%Ag alloy corresponds to the consumption of $\alpha$ phase in the presence of Ag. This is now the dominant step in the martensite aging process when Ag is present, instead of the martensite ordering reaction, as observed for the Cu-10%Al alloy. As already pointed out in the discussion of Figs. 3 and 4, on aging, during the martensite ordering reaction, the $\alpha$ phase is dissolved in the martensitic matrix, increasing the Cu relative fraction and consequently decreasing the Al relative fraction in the martensitic phase. This decrease in the Al relative fraction also decreases the number of different atoms pairs Cu–Al [9], thus decreasing the ordering degree of the $\beta_1' \rightarrow \beta_1''$ ordered martensite. In this way, the martensite aging process is now determinate by the consumption of $\alpha$ phase.

## Conclusions

The analyzes of martensite aging kinetics in the Cu-10%Al alloy indicated a process dominated by the martensite ordering assisted by migration of quenched-in vacancies followed by the consumption of the $\alpha$ phase. For the Cu-10%Al-10%Ag alloy the dominant process is the consumption of the $\alpha$ phase associated with a decrease in the ordering degree of the martensitic phase.

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## References

1. Ahlers M (1996) Proceeding of the ICOMAT86, Japan Institute of Metals, p 786
2. Gonzalez CH, De Araújo CJ, Quadros NF, Guénin G, Morin M (2004) Mater Sci Eng A 378:253
3. Otsuka K, Ren X (2004) Scripta Mater 50:207
4. Kulkarni SD (1973) Acta Metall 21:1461
5. Adorno AT, Silva RAG (2004) J Alloys Comp 375(1–2):128
6. Adorno AT, Guerreiro MR, Benedetti AV (2001) J Thermal Anal Cal 65:221
7. Kwarciak J, Bojarski Z, Morawiec H (1986) J Mater Sci 21:788. doi:10.1007/BF01117355
8. Adorno AT, Silva RAG (2006) J Therm Anal Calorim 414:241
9. Pelegrina J, Ahlers M (2004) Scripta Mater 50:213
10. Murakami Y, Nakajima Y, Otsuka K, Ohba T, Matsuo R, Oshima K (1997) Mater Sci Eng A 237:87
11. Burke J (1965) The kinetics of phase transformations in metals. Pergamon Press, Oxford