Aging behavior in Cu−Al−Be shape memory alloy

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This article reports positron annihilation spectroscopy and calorimetric measurements of the aging behavior in a Cu−Al−Be shape memory alloy. An excess of single vacancies is retained in the alloy as a result of a quench. All vacancies in excess disappear after long aging time, and a migration energy $E_M = 1.0 \pm 0.1$ eV for this process has been found to be larger than in other Cu-based shape memory alloys. The good correlation found for the concentration of vacancies and the shift in the martensitic transition temperature demonstrates that, in Cu−Al−Be, changes in the transition after a quench are deeply related to the excess of vacancies. © *1999 American Institute of Physics.* [S0021-8979(99)02101-5]

I. INTRODUCTION

The martensitic transformation is a diffusionless structural transition between crystalline phases.[1] Due to the spontaneous symmetry breaking at the transition, a single crystal of the high temperature phase splits into several twin-related domains which configure a complex heterophase. Many characteristic features of martensites, including shape memory properties, are a direct consequence of the interplay between these domains.[2] Among the different materials displaying these peculiar thermomechanical properties, the Cu-based alloys are receiving increasing attention.[3] In the range of compositions of practical interest, in these systems the martensitic transition takes place from an ordered bcc phase (or β phase) to an 18R structure.[4] In general, the β phase is the equilibrium phase at high temperature but it can be retained as a metastable phase at low temperature by means of a quench.[4] During the quench, Cu-based alloys get configurationally ordered; the order–disorder transitions have been investigated in relation to the martensitic transition in a number of alloys.[4-6]

Among Cu-based shape memory alloys, Cu−Al−Be is the one that has been developed more recently and is unique because of its adaptability for high as well as low temperature actuator applications.[7] Indeed, this potentiality is the result of the drastic effect of a small addition of Be to the Cu−Al system, which strongly reduces the martensitic transition temperature and leaves practically unaltered the low temperature limit of stability of the β phase (eutectoid point), as well as the order–disorder transition line.[6,7]

Above room temperature, aging effects represent a serious limitation on the actual applications of shape memory alloys.[8] In several Cu-based alloys, such as the Cu−Zn−Al and Cu−Al−Ni systems, these effects have been extensively studied and are well understood in terms of ordering

processes.[9,10] On the contrary, in the case of the Cu−Al−Be alloy, only few works have been devoted to this problem which still remains unclear. Notwithstanding, very recent neutron diffraction experiments[11] have undoubtedly demonstrated that in this alloy the influence of aging on the martensitic transition cannot be attributed to changes in long range atomic order in the system. Moreover, it has been found that the concentration of vacancies is strongly dependent upon the quenching temperature.[12] These results suggest that aging effects in Cu−Al−Be could have their origin in the effect of vacancies on the martensitic transition. The goal of this article is to provide experimental evidence in support of such a statement.

Positron annihilation spectroscopy has been used for the study of vacancies. This is acknowledged to be the most powerful method for the study of point defects in metals and alloys.[13] In the present work, the positron lifetime technique is employed in order to characterize the properties of quenched-in vacancies in Cu−Al−Be. In addition to the significant interest in relation to the aging problem, the subject is also of fundamental importance since experimental information concerning vacancy migration energies in β-Cu-based alloys is still scarce.[14,15] On the other hand, the martensitic transition has been studied by differential scanning calorimetry measurements. This technique has been widely used in the characterization of this kind of transitions in shape memory materials.

II. EXPERIMENTAL PROCEDURE

The sample investigated was a single crystal of composition Cu-22.72 at % Al-3.5 at % Be, grown by the Bridgman method. The order–disorder (from a DO_3, space group $Fm3m$, to a disordered phase, space group $Im3m$) and nominal martensitic transition temperatures are 793 and 145 K, respectively. Samples of 15 mm diameter and 1.5 mm thickness for both positron lifetime measurements and calo-

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rimetry, were cut from the original rod using a low speed diamond saw. The damaged surface was etched away with a solution of 50% HNO_3 in water.

For positron annihilation spectroscopy measurements, two identical samples were sandwiched with a 20 μCi ^{22}NaCl positron source evaporated onto a 1.14 mg/cm^2 Kapton foil. The lifetime measurements were carried out using a fast–fast timing coincidence system with a time resolution of 255 ps in operating conditions. The lifetime spectra, each containing at least 10^6 counts accumulated in a time interval of 7200 s, were analyzed by the RESOLUTION and POSITRON-FIT computer programs.[16] After subtracting background and source contribution (the source contributes to the spectra with only one component, $\tau_S = 382$ ps, $I_S = 12.5\%$), all spectra could be fitted with one or two components, depending on the aging time. Prior to the measurements, the sample was maintained at 1073 K for 7200 s, and subsequently it was quenched into an ice–water mixture. This quenching temperature was chosen both to retain a high vacancy concentration and to minimize the time, after quenching, during which the positron signal remains in the saturation regime (when all positrons are annihilated in vacancies[12]). After the quench, the sample was isothermally aged at 323, 333, 343, 358, and 373 K for different aging times t_{aging}. In all cases the positron measurements have been performed at room temperature.

Calorimetric measurements have been carried out using a highly sensitive differential scanning calorimeter.[17] Immediately after the quench, the sample was mounted into the calorimeter, and a first calorimetric run was conducted. The time elapsed between the quench and the beginning of the cooling cycle was around 200 s. After this first run, the sample was annealed inside the calorimeter at a temperature of 323 K. Additional calorimetric runs were performed at selected aging times. We have not studied different aging temperatures because the experimental system was not prepared for working at higher annealing temperatures. In the cooling cycle, the calorimeter was cooled from 323 K down to liquid nitrogen temperature in less than 150 s. From this temperature, it was heated up to ~160 K at a rate ~1 K/min, and calorimetric data were acquired at ~1 Hz. The run was completed by heating the calorimeter as fast as possible (average rate 1 K/s) up to 323 K. Such an experimental procedure minimized the uncontrolled time spent by the sample at temperatures where thermally activated phenomena can occur, and hence it ensured that the measured aging time at 323 K was comparable to that measured in positron annihilation experiments.

III. RESULTS AND DISCUSSION

Positron annihilation results have been analyzed according to the procedure followed in previous studies.[12,18–20] First of all, we have obtained the aging time variation of the average positron lifetime $\langle \tau \rangle$ for different moderate aging temperatures T_{aging}. In general, $\langle \tau \rangle = I_1 \tau_1 + I_2 \tau_2$, where $I_1 + I_2 = 1$, I_1 and I_2 are the intensities of the first and second lifetime components, and τ_1 and τ_2, the short- and long-lived lifetimes, respectively. As mentioned above, in some

cases, depending on the aging time, a two terms decomposition was not appropriate and in these cases $\langle \tau \rangle$ has been considered to be the lifetime component. This is consistent with the standard trapping model: when short-lived lifetimes τ_1 are shorter than 40 ps and I_1 or I_2 are less than 10%, the fitting procedure cannot resolve a two-decomposition process.[21] The extreme cases correspond to a near free-defect annihilation regime ($I_1 \sim 1$) and to a saturation defect trapping regime ($I_2 \sim 1$).

In our experiments, in the whole range of the investigated aging temperatures and times, we have obtained, within the experimental scatter, a constant value of the long-lived lifetime τ_2. By averaging data corresponding to constrain-free analysis we obtained $\tau_2 = 170 \pm 1$ ps. Consequently, in all data analysis, the lifetime of the long-lived component has been fixed to this value. In all cases, the average lifetime value monotonously decreases with increasing aging time t_{aging} from its initial value of about 170 ps. After long enough aging time, the original bulk lifetime, $\tau_f = 119$ ps, is recovered. Besides, we have observed that the higher the aging temperature, the faster the decrease of $\langle \tau \rangle$. This behavior suggests that thermally induced point defects are frozen-in by the quench, and they anneal-out completely after aging. Moreover, it is worth mentioning that no detectable amount of precipitates of other phases within the β-matrix phase after the thermal treatment has been found.

Assuming that after a quench the retained defects are mainly single vacancies ($\tau_2 = \tau_v$) and according to the well-known standard trapping model (STM) (see Ref. 22), the product of the defect concentration C_v and the positron specific trapping rate μ_v can be determined from

$$\mu_v C_v = \frac{1}{\tau_f} \frac{\langle \tau \rangle - \tau_f}{\tau_v - \langle \tau \rangle}. \tag{1}$$

In Fig. 1 the values of $\mu_v C_v \tau_f$ are shown versus t_{aging} in a semilogarithmic plot for the five aging temperatures investigated. Since μ_v and τ_f can be considered to be constant, these plots are equivalent to C_v vs t_{aging} plots.

In β Cu-based alloys, the vacancy formation energy is estimated to be about 0.5 eV or higher,[23,24] therefore, the equilibrium vacancy concentration for the aging temperatures of this study can be considered negligible. Consequently, the variation of vacancy concentration during aging can be described by

$$dC_v/dt = -C_v \rho \nu_0 \exp(-E_M/kT_{aging}) \tag{2}$$

where C_v is the single vacancy concentration, ν_0 is the vibrational frequency, ρ is the atomic concentration of vacancy sinks, and E_M, an activation energy. When the atomic concentration of vacancy sinks is assumed to be constant in Eq. (2), a linear behavior of $\ln(C_v)$ as a function of aging time is expected for each constant T_{aging}. All curves in Fig. 1 show an initial fast decay followed by a crossover to a very slow regime. As can be observed in Fig. 1, a linear fit in the time interval in which the vacancy concentration falls, at least two orders of magnitude is quite satisfactory in all cases (see solid lines). In this case, it is important to point out that for all aging temperatures the first experimental points of $\mu_v C_v \tau_f$ corresponding to the almost saturation defect-
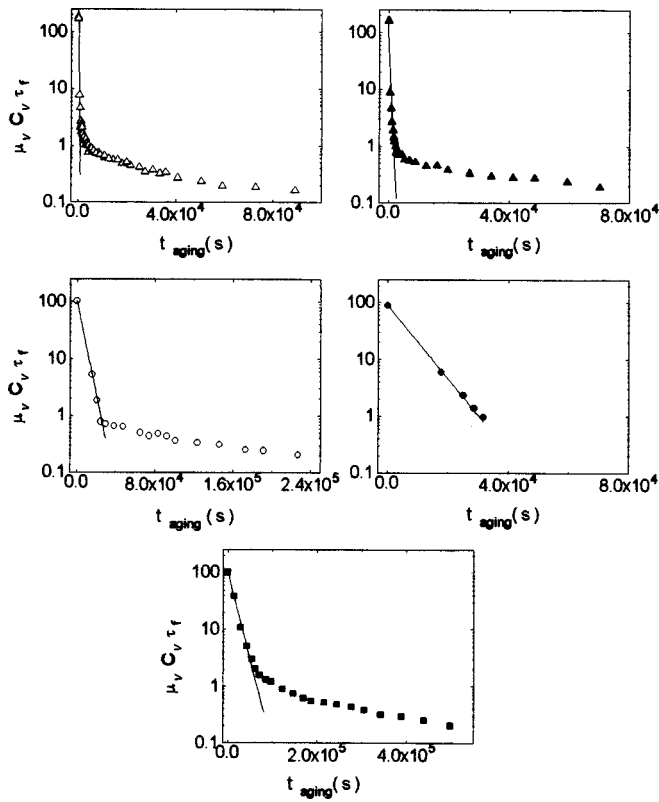
FIG. 1. Evolution of the vacancy concentration C_v in semilogarithmic scale as a function of aging time at 323 K (squares), 333 K (filled circles), 343 K (open circles), 358 K (filled triangles), and 373 K (open triangles). The solid line is a fit to the experimental data corresponding to short aging time.

FIG. 2. Arrhenius plot of the logarithm of the inverse of relaxation time θ as a function of $1/T$. The straight line is a least-square linear fit.

trapping regime, are affected by a significant error associated with the use of Eq. (1); however, the extrapolation of the solid lines corresponding to the linear fit in the region of the fast decrease of the experimental data, is in good agreement with the initial vacancy concentration data obtained for each aging temperature.

For this region of fast decrease shown in Fig. 1, the evolution of the vacancy concentration with the aging time can be described by

$$C_v \propto \exp(-t_{\text{aging}}/\theta), \tag{3}$$

where θ is an average relaxation time characterizing the time scale of the evolution towards equilibrium. We assume that θ is proportional to $\exp(E_M/kT)$, where E_M is an effective migration energy of vacancies. The logarithm of θ^{-1} as a function of $1/T$, is for all aging temperatures represented in Fig. 2. From the slope of a least-square straight line fit ($\ln \theta^{-1} = 26.47 - 11766/T$) the migration energy is obtained. The result of this calculation is $E_M = (1.0 \pm 0.1)\text{eV}$. It is worth noting that, in spite of the experimental scatter, the present E_M value is considerably higher than that obtained for β Cu–Zn–Al, $E_M = (0.65 \pm 0.03 \text{ eV})$[14] and for β Cu–Zn, $E_M = (0.61 \text{ eV})$.[15]

The thermal curves recorded during the reverse martensitic transition at different aging times are shown in Fig. 3(a). It is apparent from the figure that upon increasing the aging time, the transition shifts towards lower temperatures. We
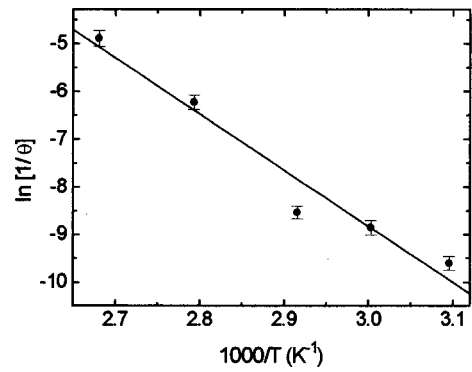
have used the temperature of the peak in the thermogram (T_A) as the characteristic temperature for the transition (the associated error is ± 0.2 K).

It is acknowledged that successive cycling of a shape memory alloy through the martensitic transition can result in a modification of the martensitic transition characteristics. Therefore, the temperature shift of the thermograms at different aging times can be affected by this phenomenon. In order to account for this effect, we have investigated the influence of thermal cycling in the same sample, after being quenched and annealed for a period of long enough time (~ 1 week) to reach the equilibrium state. The recorded thermograms are shown in Fig. 3(b). A slight shift in the transition temperature towards lower values on increasing the number of cycles is found. We have corrected the measured values of T_A at each aging time, by the shift associated with the corresponding number of cycle. In Fig. 4, we have plotted these corrected values of T_A and the concentration of vacancies as a function of aging time. We have used the value of the
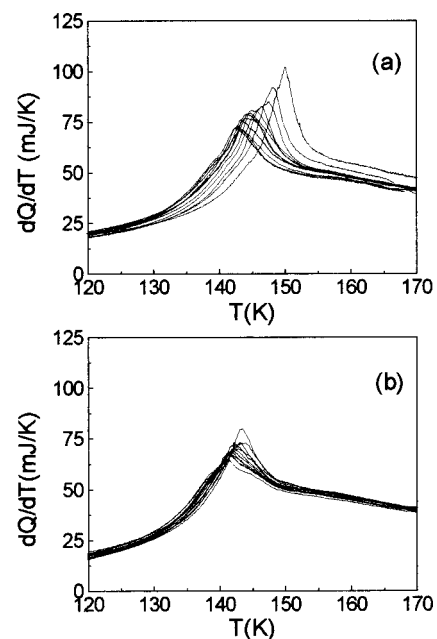

FIG. 3. Thermal curves recorded during the reverse martensitic transformation: (a) at different aging times ($T_{\text{aging}} = 323$ K), and (b) during successive thermal cycling of a long time aged sample.
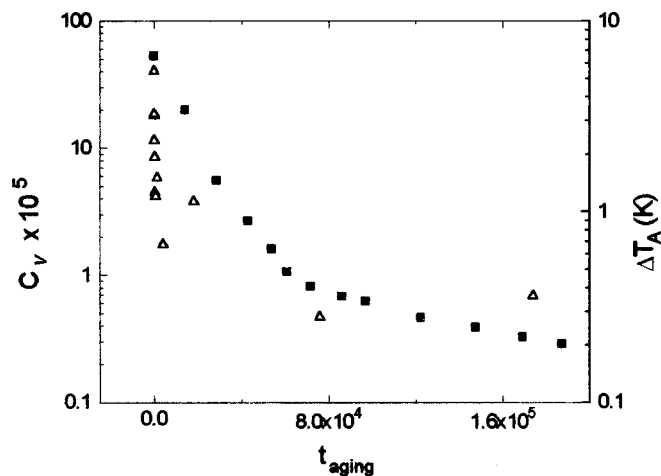
FIG. 4. Shift in the transition temperature (triangles), corrected from the effect of cycling, and concentration of vacancies (squares), as a function of aging time at $T_{aging} = 323$ K. C_v has been obtained using $\mu_v = 1.6 \times 10^{15}$ s^{-1}.

specific trapping rate $\mu_v = 1.6 \times 10^{15}$ s^{-1} recently obtained for the B2 structure FeAl.[25] The behavior of T_A with aging time seems to exhibit two different regimes: a fast initial decay, followed by a long tail. This is qualitatively similar to the dependence of the vacancy concentration with aging time. Nevertheless, the decay of the transition temperatures in the initial regime is faster than in the concentration of vacancies. Such a different behavior cannot be attributed to changes in the long-range atomic order;[11] it may be due to local atomic order rearrangements. In any case, the results presented here seem to indicate that in Cu–Al–Be, the most important source of the changes in the martensitic transition during aging is the evolution of the concentration of vacancies in the alloy. The results found for Cu–Al–Be are in contrast to the behavior observed for Cu–Zn–Al. In that alloy, changes in the transition temperature during aging arise from a variation in the degree of long-range order.[4,11] We argue that the influence of vacancies on the transition occurs via a modification of the effect of Be on the transition temperature. Actually, it has been proposed[26] that the strong effect of Be arises from a mass–disorder effect owing to the small mass of Be in comparison with that of Cu and Al. Since the excess of vacancies induces a decrease in the effective Be concentration, the change in the transition temperature during aging is expected to be proportional to this vacancy excess. This prediction is consistent with the results given in Fig. 4. From the data shown in the figure it is obtained that $\delta T_A / \delta C_v \approx 10^4$ K. This value conforms to the measured dependence of T_A with Be concentration.[7]

IV. SUMMARY AND CONCLUSIONS

In this article we have characterized the aging behavior of the Cu–Al–Be shape memory alloy by positron annihilation and calorimetric techniques. It has been shown that after the quench there is an elimination of quenched-in vacancies.

The migration energy of vacancies ($E_M = 1.0 \pm 0.1$ eV) has been found to be higher than in other Cu-based alloys. In addition, the correlation found for the concentration of vacancies and the shifts in the transition temperatures, is an experimental evidence that the concentration of vacancies has an important contribution in determining the evolution of the martensitic transition characteristics during the post-quench aging of Cu–Al–Be. This result shows that the physical origin of the aging phenomena observed in Cu–Al–Be is completely different from that in other Cu-based shape–memory alloys.

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