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Vacancy-solute aggregates in Al-Cu-Mg alloys studied by positron annihilation techniques

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Vacancy-solute aggregates formed in the alloy Al-Cu (4.38 wt %)-Mg (1.62 wt %) were studied by two different positron annihilation techniques (lifetime spectroscopy and two-detectors Doppler broadening spectroscopy) and by differential scanning calorimetry (DSC). The results show that the concentration of Cu in the environment of a vacancy increases when the temperature of aging is raised from 20 to 60 °C. Structural transformations, which produce a reordering of the chemical species in contact with vacancies and an energetic stabilization of the solute aggregates, are observed to occur at room temperature after aging at 180 °C through effects on the kinetics of the average positron lifetime as well as on DSC thermograms.

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Alloys, initially prepared in the form of supersaturated solid solutions (SSS), tend to decompose by forming a dissemination of solute aggregates of different morphology [in sequence: clusters, Guinier-Preston (GP) zones, precipitates]. The phenomenon, which is referred to as aging, critically affects the mechanical properties. It depends on the composition of the alloy and can be controlled, to a certain extent, by thermal and mechanical treatments. Its technological interest promotes an intense research activity, carried out with the help of a variety of experimental techniques.[1]

Vacancies play an important role in aging. They assist the migration of the solute and favor its aggregation by lowering the mechanical stress when there is a size difference between solute and matrix atoms. Existing information on the association of vacancies with solute aggregates is scarce and almost always indirect, as empty atomic sites are not resolved even by the most powerful imaging techniques at atomic resolution. One technique with specific sensitivity to vacancies is positron annihilation spectroscopy (PAS).[2] This technique has been frequently adopted for studies concerning Al-based alloys.[3] Most recently, PAS was adopted by Somoza *et al.*[4,5] for investigating the role of vacancies in the decomposition kinetics of Al-Cu-based alloys with Mg and Ag as trace elements. The results of the above studies led the authors to conclude that: (a) the chemical environment of vacancies retained in the solute aggregates (GP zones), which are formed after long aging at temperatures below 70 °C, depends on the aging temperature; (b) the chemical environment of the vacancies surviving in the material after aging at 180 °C (i.e., above the solvus of the GP zones) evolves at room temperature (RT) with a complicated kinetics determined by the duration of the aging at 180 °C and by the composition of the alloy. The aim of the present work is to verify these conclusions, which are somewhat surprising, by means of a wider choice of experimental methods and with an Al-Cu-Mg alloy with simpler decomposition features.

Three different experimental techniques were adopted: (a) positron annihilation lifetime spectroscopy (PALS), which is the same technique used in Refs. 4 and 5; (b) two-detector Doppler broadening ($2d$-DB) positron annihilation spectroscopy, a technique specifically sensitive to the chemical composition around the annihilation site;[6,7] and (c) differential scanning calorimetry (DSC), a powerful method for the study of phase transformations that has become a classic technique in the field of physical metallurgy.

The same positron source (5.5×10^5Bq of ^{22}Na deposited between two 7.5-μm-thick Kapton foils) was used for PALS and $2d$-DB experiments. The PALS setup was a commercial fast-fast ORTEC system equipped with BaF_2 detectors; in the condition of the present experiment, the full width at half maximum of the resolution function was 185 ps, with a typical counting rate of 250 coincidences per second. To monitor the rapid evolution of the alloy, 45-min-long acquisitions were adopted, allowing the accumulation of $\sim7\times10^5$ counts in each spectrum. The spectra were analyzed by means of the POSITRONFIT program.[8] Since multicomponent analyses were impossible without forcing the fit by some kind of constraint, the lifetime results given below are the results of one-exponential analyses (reduced $\chi^2\approx1$) and may have the meaning of an average over several unresolved components.

The $2d$-DB experiment was performed by means of two intrinsic germanium detectors in timing coincidence. The energy resolution was ~1.85 keV at the sum energy of 1022 keV. Coincidence events at energies E_1 and E_2 of the detected annihilation γ rays were collected in a 512×512 matrix, with overall 6×10^6 counts accumulated in 24 h. Only the coincidence events located on a thin strip (~ 1.4 keV wide) centered on the matrix diagonal ($E_1+E_2=2\,m_0c^2$) were used for obtaining the one-dimensional distribution of the longitudinal component of the momentum of the electron-positron pair $\rho(p_L)$ [with $p_L=(E_1-E_2)/c$], deprived of all the coincidence events affected by incomplete charge collection in the detectors. The resulting peak-tobackground ratio was 10^5:1 (about 10^2 times higher than in the single-detector mode). The experimental data were analyzed in terms of the relative difference $\Delta = (\rho - \rho_{\mathrm{Al}})/\rho_{\mathrm{Al}}$, where ρ_{Al} is the Al reference distribution. This analysis is suited to highlight features related to the chemical environment of the annihilation site over a wide range of momenta. Reference spectra were produced by measuring well-annealed aluminum and copper single crystals. The analysis of the reference spectra gave Fermi wave vectors k_F of 0.96 a.u. and 0.74 a.u, for Al and Cu, respectively, in fair agreement with the free-electron model values.

Calorimetric scans were performed by means of a DuPont 2000 analyzer with a plug-in 910 cell, under a protective argon atmosphere, at a scanning rate of 20 K/min. Repeated runs were performed for ensuring the reproducibility of the features discussed below.

The composition of the alloy studied in the present work was Cu 4.38 wt % (1.9 at %), Mg 1.62 wt % (1.83 at %), and Al to balance. Within the concentration limits of the above composition, having an almost equal number of atoms of Cu and Mg, a possible decomposition sequence should yield mostly clusters and/or Guinier-Preston-Bagaryatski (GPB) zones evolving into the semicoherent orthorhombic $S'(\mathrm{Al_2CuMg})$ phase.[9] In comparison to the alloys studied in Refs. 4 and 5, where the low-Mg content implies that the phase θ' (composition $\mathrm{Al_2Cu}$) would also be present, this condition leaves less ambiguity in interpreting the mechanism of any compositional effect. The material was produced by induction melting of high-purity elements. After a preliminary homogenizing treatment for 10 h at 500 °C, samples for PAS and DSC measurements were cut in the form of discs of 8 and 5 mm in diameter, respectively, and 1 mm in thickness. A further solution treatment (520 °C for 1 h, followed by quenching in water at room temperature) was performed prior to any aging. Artificial aging was made in a silicon oil bath at 180 ± 2 °C. Different sequences of natural and artificial aging were adopted, as specified below. After the chosen heat treatment, the samples were maintained at about −17 °C prior to DSC measurements.

The first PALS experiment addressed the evolution of the average positron lifetime τ during natural aging at room temperature (RT = 22 °C). The results are presented in Fig. 1. In accordance with the procedure of Refs. 4 and 5, the data were fitted by a Kohlrausch stretched exponential, as given by the equation $\tau = \tau_\infty + (\tau_0 - \tau_\infty)\exp\lfloor -(t/t^*)^\beta \rfloor$, where $\tau_0 = 210\,\mathrm{ps}$ and $\tau_\infty = 191\,\mathrm{ps}$ are the lifetimes extrapolated at $t \to 0$ and $t \to \infty$, respectively. The other parameters of the curve shown in Fig. 1 are $\beta = 0.74$, $t^* = 864\,\mathrm{ks}$. The physical implications of this kinetics will be discussed elsewhere.[10] Here it can be recalled that a similar decay, observed for a series of four different Al-Cu-based alloys, was attributed to the progressive change, associated with the formation of solute aggregates, of the chemical environment of the vacancies where positrons are trapped and annihilated.[4,5]

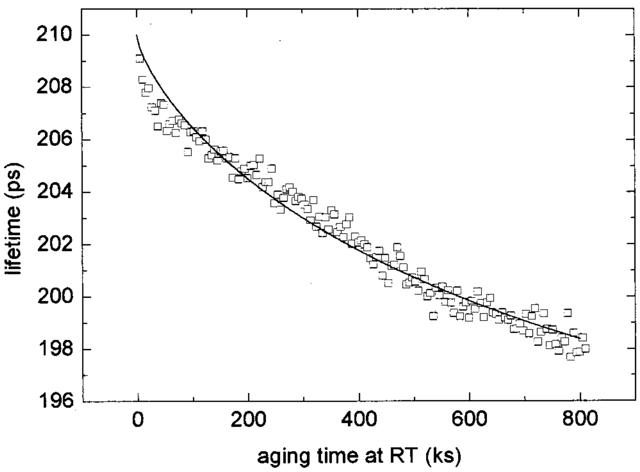

FIG. 1. Average positron lifetime in Al-Cu-Mg vs RT aging time (experimental errors ≈0.5 ps). The curve through the experimental points is a Kohlrausch stretched exponential.

The above-mentioned interpretation of the positron lifetime change during aging, proposed in Ref. 4, was essentially based on a comparison of the measured values with those available for other Al alloys. In the present work, the 2*d*-DB experiment was designed as a direct check of the effect of the aging temperature on the chemical environment of the vacancies after prolonged aging. The results are shown in Fig. 2 in terms of Δ curves. The data points refer to two samples aged for 1 week, respectively at RT (open circles) and at 60 °C (open triangles). To highlight the details of the Δ curves pertaining to the alloy, the figure also shows (broken lines) replicas of Δ curves measured for Cu (i.e., $\Delta_{\mathrm{Cu}} = (\rho_{\mathrm{Cu}} - \rho_{\mathrm{Al}})/\rho_{\mathrm{Al}}$), made to merge with the alloy points at high p_L through scaling by an appropriate factor. The positive values of Δ_{Cu} in this region are due mainly to annihilations with *d* electrons. As the functional dependence of the Δ curves for the two Al alloys is very similar to that of the reference curve Δ_{Cu}, we attribute it to annihilations in proximity of Cu sites. However, the Δ curves show an additional peak at ≈ 1.5 a.u. Most probably, this is the effect of positron trapping at vacancies, a structural effect, which is visible

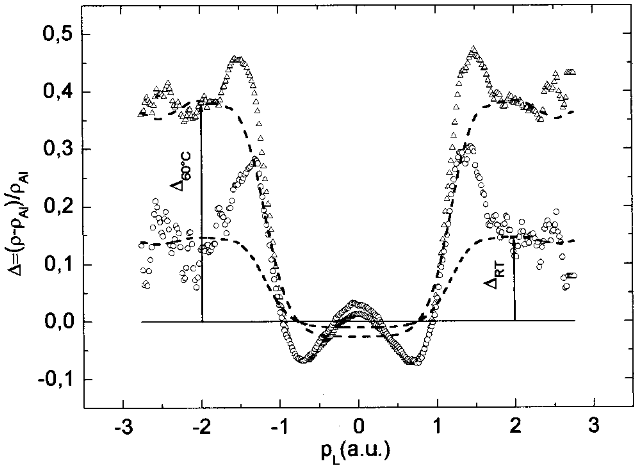

FIG. 2. 2*d*-DB results in terms of relative differences △ of distributions (reference is pure Al) versus the momentum component p_L. Open triangles: Al-Cu-Mg alloy, 7 days aging at 60 °C; open circles: Al-Cu-Mg alloy, aged 7 days at RT. Broken curves are smoothed and scaled replicas of the Cu curve.

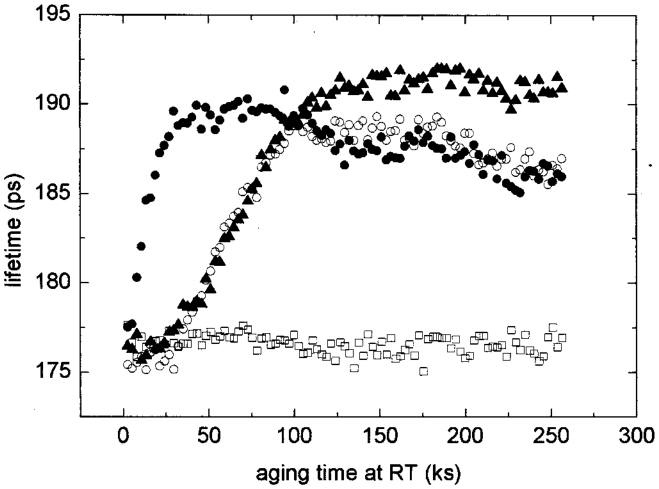

FIG. 3. Average positron lifetime evolution occurring at RT for Al-Cu-Mg samples aged for (a) 30 s at 180 °C (solid circles); (b) 2 min at 180 °C (open circles); (c) 12 min at 180 °C (solid triangles); and (d) 24 h at RT+ 12 min at 180 °C (open squares) (experimental errors ≈ 0.5 ps).

also in the case of pure metals in the region of low p_L.[6] The separation of chemical and structural effects is beyond the purposes of the present work; however, Fig. 2 suggests assuming, as an approximation, that the effects of trapping become negligible where the broken curves merge with the alloy data (at ≈ 2 a.u.). According to this approximation, the ratio $\Delta_{60\,°\mathrm{C}}/\Delta_{\mathrm{RT}}$ taken at 2 a.u. (see vertical arrows in Fig. 2) would coincide with the ratio of Cu concentration at the annihilation sites in the two samples. This estimate gives 2.6 times more Cu in the case of aging at 60 °C than for RT aging.

The second PALS experiment addressed the RT evolution of the alloy structure occurring after artificial aging at 180 °C for 30 s, 2 min and 12 min. The results shown in Fig. 3 are similar to those reported in Refs. 4 and 5 in the following aspects: (a) immediately after the artificial aging, the positron lifetime τ takes its lowest value (≈ 176 ps, almost identical to the value of 177 ps reported in Ref. 4); and (b) during post-aging at RT τ has a rapid increase, followed by a plateau or by a slowly decreasing stage. Additional information obtained in the present work is that this complex kinetics disappears if a pre-aging of 24 h at RT is applied before the heat treatment at 180 °C (open squares in Fig. 3) and, in a few cases, even without any intentional pre-aging. This unstable behavior, which is probably related to accidental differences in the thermal history of the samples, shows that the conditions that determine the kinetics are rather critical.

The variation of the mean lifetime, equivalent to more than 20 times its statistical uncertainty, is much larger than what was reported in a previous lifetime study of the age-hardening process in a very similar alloy.[11] To our best knowledge, in the scientific literature regarding Al alloys there are no other examples of evolution occurring at RT after a heat treatment at a considerably higher temperature. To understand whether this effect was attributable to a positional rearrangement involving solute and vacancies we performed DSC experiments.

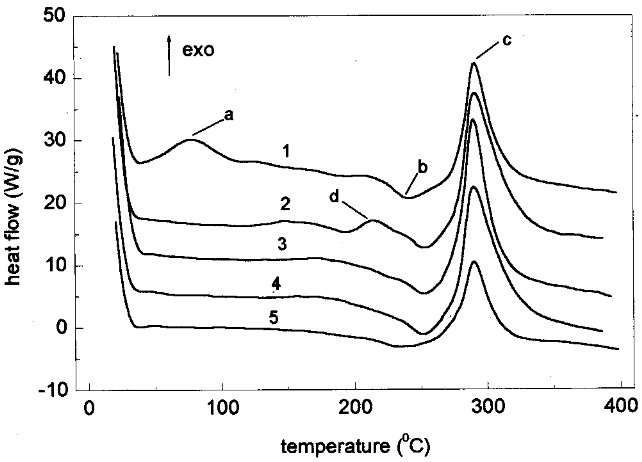

FIG. 4. DSC thermograms for Al-Cu-Mg samples with different heat treatments. Curve 1: as quenched. Curve 2: 12 min at 180 °C. Curve 3: 12 min at 180 °C+48 h at RT . Curve 4: 24 h at RT +12 min at 180 °C . Curve 5: 24 h at RT+12 min at 180 °C +48 h at RT. Scan rate 20 K/s.

Thermograms obtained for samples with different thermal histories are shown in Fig. 4. Curve 1 refers to a solution-treated (as-quenched) sample. Curves 2–5 refer to samples artificially aged at 180 °C for 12 min after the solution treatment, plus RT aging stages as follows: curve 2—no RT aging; curve 3—48 h at RT after the treatment at 180 °C; curve 4—24 h at RT before the treatment at 180 °C; curve 5—24 h at RT before and 48 h at RT after the treatment at 180 °C. The most evident features of curve 1 (marked with letters *a–c* in Fig. 4) are: (a) an exothermic peak at ≈ 75 °C; (b) an extended endothermic stage determining a minimum at ≈ 250 °C; (c) a strong exothermic stage peaked at ≈ 290 °C. Feeble signals are visible between peak *a* and minimum *b*. In accordance with accepted views on the sequence of transformations occurring in Al-Cu-Mg with Cu/Mg atomic ratios close to 1, the above structures can be attributed as follows: (a) formation of coherent solute aggregates (clusters and GPB zones); (b) partial dissolution (reversion) of the less stable aggregates; and (c) precipitation of the semicoherent phase S'. The feeble signals between *a* and *b* probably are the consequence of the structural evolution (increase in size, reordering of different chemical species) of the coherent aggregates. In curves 2–5, minimum *b* and peak *c* are clearly visible; on the contrary, peak *a* is absent. This shows that the solute aggregation, which in the as-quenched sample (curve 1, peak *a*) occurs during the DSC heating ramp, in the other cases (curves 2–5) has already taken place during the artificial aging at 180 °C, i.e., before the DSC scan. However, the aggregates formed in the aged samples are not identical: this is shown by an exothermic stage at ≈ 220 °C (marked *d*) in curve 2, which is perhaps present as a hump also in curve 1, but is clearly absent in curves 3–5. This means that an RT treatment, applied before or after artificial aging, produces more stable structures than simply heating at 180 °C. Thus the interpretation of the PAS results as the indication of a real structural transformation is fully supported by the present DSC data. It must also be noted that RT pre-aging does not suppress the effect of additional RT aging after heating at 180 °C, as one would have concluded observing no positron lifetime variations in the pre-aged sample (open squares in Fig. 3). On the contrary, the combination of two RT aging stages reinforces the stabilizing effect on the coherent species, as demonstrated by partial filling of the reversion minimum b in curve 5.

In conclusion: (i) $2d$-DB results give the first direct proof of the presence of Cu in the environment of the vacancies surviving in Al-Cu-Mg alloys after aging; (ii) differences in $2d$-DB curves show that the Cu enrichment of the vacancy environment increases if the aging temperature is raised from 20 to 60 °C; (iii) the complex kinetics of the positron lifetime, observed at RT after aging at 180 °C for alloys with high Cu/Mg ratio,[4,5] is confirmed to exist also for an alloy with a Cu/Mg atomic ratio near to 1; and (iv) DSC measurements show that RT treatments combined with aging at 180 °C are responsible of structural changes that not only affect the positron lifetime but also have energetic effects.

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