Positron Annihilation Study of Secondary Ageing in AlCu

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Abstract

Positron annihilation spectroscopy (PAS) was used to investigate on the structural evolution of Al-4 wt. % Cu taking place during secondary ageing (at temperatures up to 65°C) after the standard solution treatment and preliminary heating at 150°C. Two PAS techniques were employed: lifetime spectroscopy was used to monitor the presence of open volume defects (vacancies and misfit regions at precipitate-matrix interfaces) and coincidence Doppler broadening spectroscopy was adopted for detecting the association of these defects to solute atoms.

1. Introduction

Precipitation stages in AlCu alloys have extensively been investigated in the last decades. The decomposition of a supersaturated solid solution of Al containing a few per cent of Cu takes place via a complex sequence of precipitation, which is often condensed [1] in the formula

$$\text{supersaturated solid solution} \rightarrow \text{GPI} \rightarrow \text{GPII } (\theta'') \rightarrow \theta' \rightarrow \theta, \qquad (1)$$

where GP stands for Guinier-Preston zones (ordered aggregates of solute, coherent with the matrix lattice), θ' is a metastable precipitate and θ is the equilibrium Al_2Cu incoherent phase. In fact formula (1) is a simplification. Depending on the temperature, the decomposition sequence may or may not progress through all the stages, or some stages are partially overlapped [2]. It has also been realised that the possible forms of coherent aggregates are more than just two. According to [3], the list of possibilities is: a) pre-GP zones (three-dimensional atom clusters); b) GPI (pure Cu or Cu-rich monolayers); c) GPII-2 (two Cu-rich layers separated by two Al-rich layers); d) GPII-3 (two Cu-rich layers separated by three Al-rich layers); e) multi-layered GPII-2 or GPII-3 (sometimes indicated as θ'').

In the present work, secondary precipitation was studied for the classic composition Al-4 wt. % Cu by means of positron annihilation spectroscopy (PAS). Secondary precipitation is the microstructural evolution that occurs at moderate temperature after a primary heating stage at a temperature high enough to produce the formation of semicoherent or incoherent particles

This situation is interesting in view of the recent discovery of the beneficial effects that a dwell period at temperatures from 20°C to 70°C, between two ageing stages at higher temperatures, can have on the mechanical properties of most age-hardenable aluminium alloys, including Al-Cu [4, 5]. The use of PAS, which is a technique with unique sensitivity to open volume defects and to their chemical environment, puts in special focus the role of vacancies associated to solute atoms.

2. Materials and Methods

The alloy was prepared from high purity pure elements; the composition Al-4 wt.% Cu corresponds to Al-1.74 at. % Cu. The samples were solution treated at 520°C for 30 minutes and quenched in ice water. As-quenched samples were immediately aged at 150°C in a glycerine bath, quenched again in water at RT, and left to dwell at temperatures up to 65°C for various periods of time.

Two variants of PAS were applied, namely positron lifetime spectroscopy and coincidence Doppler broadening spectroscopy (thereafter, LS and CDB respectively). CDB measurements were performed via two intrinsic Ge detectors in timing coincidence. Coincidence events at energies E_1 and E_2 of the detected annihilation γ-rays were collected in a 512 x 512 matrix, with about 6 x 10^6 counts accumulated in 24 hours. The coincidence events located on a thin strip (~1.4 keV wide) centred on the $E_1+E_2=2\ m_0\ c^2$ matrix diagonal were used for obtaining the one-dimensional distribution ρ of the longitudinal component of the momentum of the electron-positron (*e-p*) pair $p_L = (E_1-E_2)/c$. The resulting peak-to-background ratio was 10^5:1. Reference spectra were obtained for well-annealed Al and Cu single crystals (Figure 1). The analysis of the reference spectra gave Fermi wave vectors k_F of 0.96 atomic units and 0.74 atomic units, for Al and Cu respectively, in fair agreement with the free electron model values. Other spectra were taken for cold-rolled Al and Cu: these spectra are needed to mimic the effect of positron trapping in open volume defects on the high-momentum tails of the spectrum.

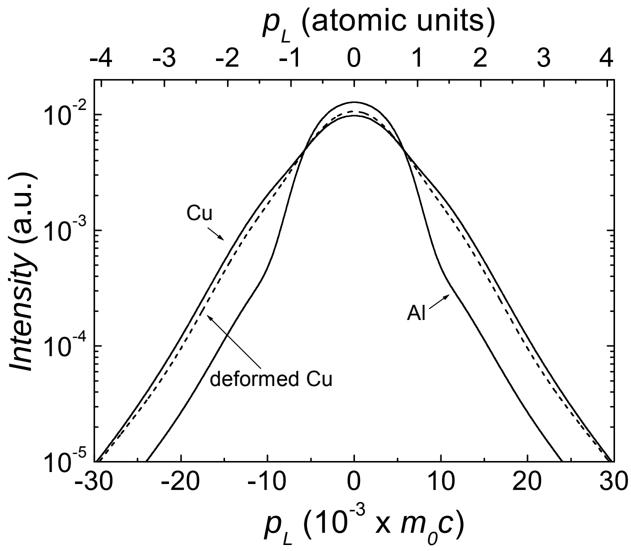

Figure 1: Measured CDB profile of the annihilation energy (511 keV) in Al, Cu and deformed Cu as a function of longitudinal momentum.

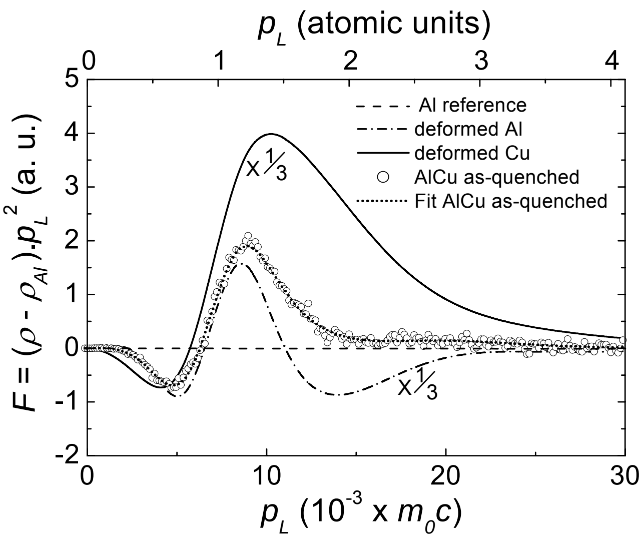

Figure 2: *F*-function for Al (horizontal dashed line), deformed Al (dash-dotted line), deformed Cu (solid line) and for the AlCu alloy (open circles) as-quenched after solution treatment (the dotted line is a fit with Eq. 2 [6]).

In Figure 2 the *e-p* momentum densities ρ_i are subtracted by the pure Al spectrum ρ_{Al} and weighted by the factor p_L^2, according to the transformation $F_i = (\rho_i - \rho_{Al})\, p_L^2$. This presentation is suitable to highlight features at high p_L related to the chemical environment of the annihilation site. For a quantitative interpretation, the CDB experimental data were fitted by linear combinations of the momentum distributions of the reference samples

$$\rho_{AlCu} = w_{Al}\rho_{Al} + w_{Al*}\rho_{Al*} + w_{Cu*}\rho_{Cu*} \;, \tag{2}$$

were w_i are the weights of Al, deformed Al and deformed Cu, constrained by the normalization condition $\sum_i w_i = 1$. According to [7], when the positron trapping at open volume defects is near to saturation, the w_{Cu*} coefficient can be taken as a fair approximation of the average Cu atomic ratio at the annihilation site (when positrons are not trapped at open volumes, w_{Cu*} overestimates the Cu ratio by ~40%).

Positron lifetime spectra (LS) were performed at RT for artificial aged samples and *in-situ* during secondary ageing. The data were accumulated for ~1 h with a standard fast-fast time spectrometer (coincidence rate: ≈170 counts/s; FWHM of the prompt curve: 250 ps). After subtraction of the source component, the spectra were analysed as a single component exponential using the Positronfit program [8]. Since the spectra can be a superposition of unresolved components, the positron lifetime obtained by the single component analysis is to be considered as an effective parameter associated with this type of data treatment.

3. Results and Discussion

The primary aim of this work is to present details of the microstructure in the studied alloy under the effect of secondary ageing after two different times of artificial ageing at 150°C (1 min and 2.5 h). The starting point, however, is a brief discussion of the state of the alloy at the beginning of secondary ageing.

3.1. Preliminary heating at 150°C

Artificial ageing at 150°C was studied in Al-4 wt. % Cu by means of positron techniques (LS and CDB) in Ref. 6.
Figure 3 shows the positron lifetime τ as a function of the ageing time at 150°C. The initial value obtained in as-quenched samples (0 h) is about 200 ps. This value is characteristic of positron trapped at vacancies associated to isolated solute atoms. A rapid decrease of τ is observed in the first minutes of ageing. The τ value obtained in a sample aged 1 min is about 178 ps (as obtained on averaging eight independent measurements; the rather large error bar shown for this point in Figure 3 comes

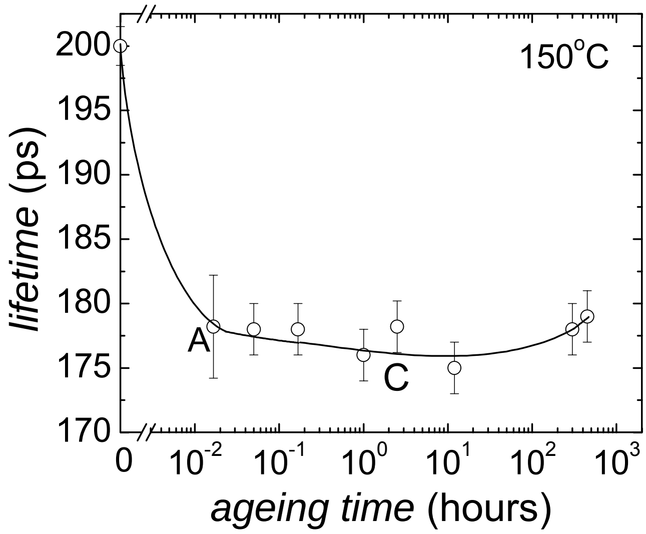

Figure 3: Positron lifetime evolution during artificial ageing at 150°C after solution treatment and quenching [6]. The solid line is a visual guide. Letters A and C label the points at the beginning of secondary ageing.

from imperfect reproducibility of very short heat treatment). This value is in good agreement with the result obtained for Al-4 wt. % Cu- 0.3 wt. % Mg [9]; it can be taken as an indication of the inclusion of vacancies in the small three-dimensional aggregates of Cu that are presumably formed in the very first ageing stages. One can see in Figure 3 that the lifetime remains near 177 ps for about 10 hours. The small lifetime increment observed above 300 h, if real, might hint incipient loss of coherence (the semicoherent θ' phase is expected as a final product of the precipitation sequence in this alloy aged at 150°C [3]). Lumley et al. [10] obtained in the same alloy the peak hardness (132 VHN) after ~100 h at 150°C (T6 treatment), in this situation they observed that the microstructure contains θ" and θ' precipitates. However, the absence in the data of Figure 3 of a marked lifetime increase, which is expected when positron trapping at misfit interfaces becomes dominant, suggest that peak hardness is attained without an important loss of coherency. Similar results were recently obtained in the commercial alloy 2024 and in Al-Cu-Mg-Ag [11]. The correlation of the new information obtained in this work and in [10] shows, in an important academic alloy, that the so-called intermediate phase present in the peak hardness has no significant misfit. This behaviour is not general in Al-based alloys; for example, in Al-Zn-Mg alloys hardening is concomitant with the loss of coherency [12].

3.2. Secondary ageing

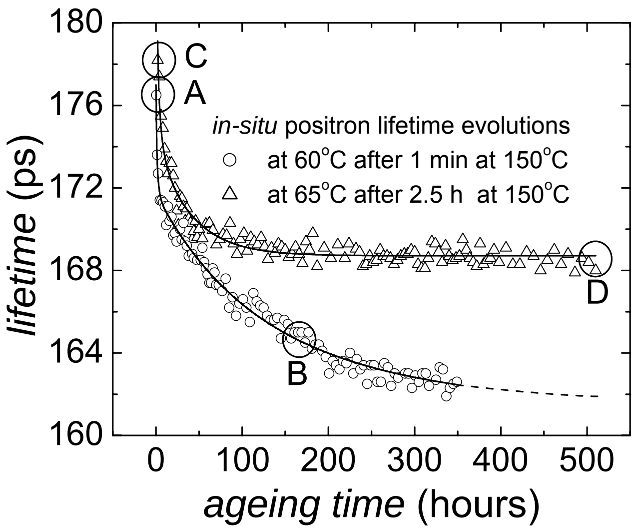

Figure 4: Positron lifetime as a function of the ageing time. The solid lines are best-fit curves calculated (see text). Labels A, B, C, D show the points corresponding to the curves in Figure 5

Figure 4 shows the results of lifetime measurements obtained *in-situ* during secondary ageing at 60°C and 65°C after 1 min and 2.5 h of ageing at 150°C, respectively. The solid lines through the experimental point represented in Figure 4 are the result of a fitting based on a trapping-model calculation discussed in Ref. [9]. This model implies that the initial stage of rapid variation of positron lifetime is determined by the loss of vacancies by aggregates of Cu atoms, while the slower part comes from a progressive atomic reorder. It is worth mentioning that the evolution of τ observed in this binary alloy is entirely different from the non-monotonic curves that were obtained for Al-Cu-Mg alloys with similar Cu content (0.3 to 1.8 Mg at. %) [9, 13, 14]. This comparison is consistent with ascribing the non-monotonic trend to fast aggregation of Mg to pre-existing vacancy-Cu clusters, followed by further aggregation of Cu taking place with a slower kinetics [9].

Figure 5 shows CDB results obtained at different stages of secondary ageing for samples aged 1 min (panel 5.a) and 2.5 h at 150°C (panel 5.b). Curves A and C, that correspond to the points labelled with the same letters in Figs. 3 and 4, were taken immediately after quenching from 150°C; thus these curves represent the conditions at the beginning of secondary ageing. Curves B and D, also corresponding to similarly labelled points in Figure 4, are for samples that were aged respectively 167 h at 60°C and 510 h at 65°C. The high momentum peaks near to $p_L = \pm 10^{-2}\ m_0c$ (~±1.3 atomic units) in Figure 5 are the signature of positron annihilation in the Cu *d-sell* and core electrons. The Cu contribution is enhanced when positrons are trapped near Cu atoms (see Figure 2). The solid curves through the experimental points of the CDB distributions represent the best fit with the linear combination mentioned in Section 2. The best-fit w_i coefficients are reported in Table I. The value of the relative weight assigned to the Cu distribution (w_{Cu*}) is practically the same for samples aged 1 min or 2.5 h at 150°C. The decrease of w_{Cu*} during secondary ageing indicates progressive reduction of positron traps adjacent to Cu atoms.

The following scenario is consistent with the combination of the above LS and CDB results:

- *1 min dwell time at 150°C*. At the beginning of secondary ageing (points A in Figure 3 and 4 and curve A in Figure5.a) there is a substantial concentration of vacancy-rich Cu clusters (VRC); on the average, the Cu atomic concentration at the annihilation site is near to 12%. After partial secondary ageing, most of the tree-dimensional Cu aggregates rich in vacancies have been transformed in GPI zones (Cu monolayers with no vacancies); thus the majority of positrons annihilates from a bulk state (the lifetime curve asymptotically converges to the lifetime observed for bulk Al and the effective Cu concentration at the annihilation site is clearly diminished).

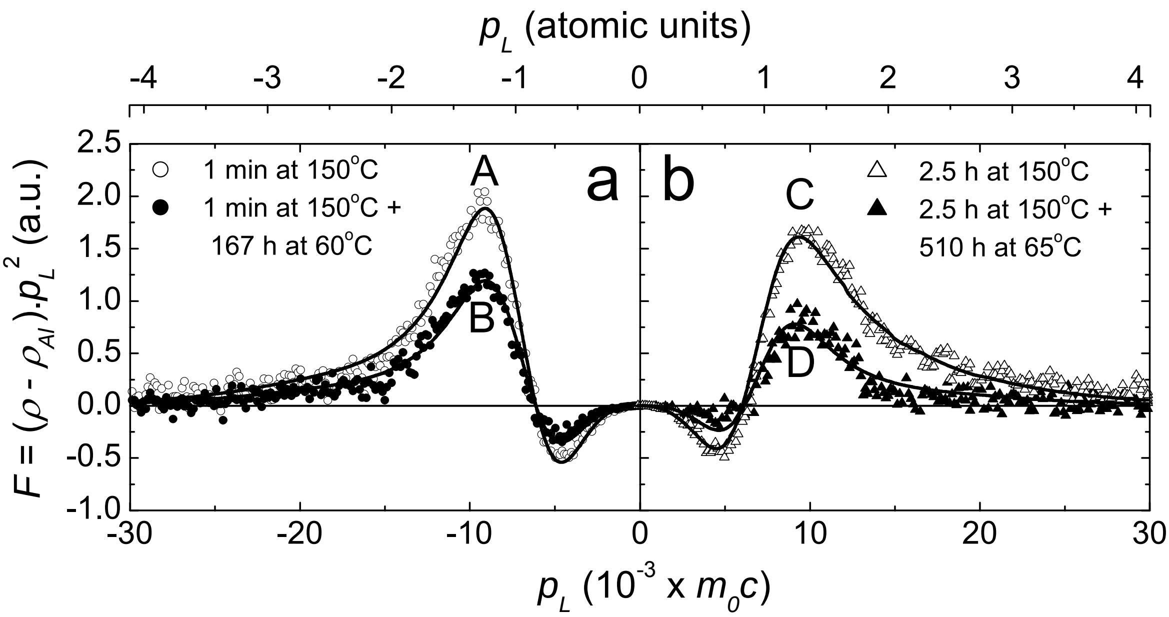

Figure 5: CDB *F*-function versus longitudinal momentum p_L. The solid lines represent a linear combination fit (see Section 2).

Table I: Weights of the linear combination fitting of CDB data. The uncertainty is of the order of 0.3 %.

Thermal treatment	w_{Al} (%)	w_{Al}*(%)	w_{Cu}*(%)
1 min at 150°C	7.5	13.1	11.6
1 min at 150°C + 167 h at 60°C	8.4	8.8	7.2
2.5 h at 150°C	8.1	7.2	11.5
2.5 h at 150°C + 510 h at 65°C	8.9	5.6	4.8

- *2.5 hours dwell time at 150°C*. At the beginning of secondary ageing (points C in Figs. 3 and 4, curve C in Figure 5.b) VRC are again the dominant species of positron traps; however, partial re-ordering leading to the formation of multi-layered GP zones and, possibly, of a small amount of θ' particles has taken place. This statement is not deducted from the data in Figure 3, where only small lifetime changes are observed for hundreds of hours, but is supported by TEM observations [3]. In any case, the formation of additional precipitates after 2.5 h at 150°C becomes evident after secondary ageing (point D in Figure 4), when trapping at VRC is strongly suppressed and, conversely, the new precipitates become the dominant positron traps (according to Figure 4, the corresponding positron lifetime is expected to be around 169 ps). The additional and completely new information comes from the low value of the Cu concentration at the positron annihilation sites: this result shows that the phase surviving after secondary ageing does not contain vacancies in contact with Cu. It is worth mentioning that theoretical predictions demonstrate that positrons can be trapped by defect-free θ' particles [15] and that this prediction can be reasonably assumed to hold also for similar coherent structures.

4. Conclusions

At the end of secondary ageing the situation is the following:

- with a brief period of artificial ageing (1 min at 150^{o}C), the final product are monolayer GPI zones containing no vacancies;
- after a more extended ageing (2.5 h at 150^{o}C), multi-layered GPII zones are already formed and survive to secondary ageing; thus, the final structure is given by a mixture of two species of GP zones;
- vacancies are absent in all forms of well-developed GP zones; however, defect-free multilayered GP zones are able to trap positrons whereas trapping cannot occur in monolayer GPI zones.

On the basis of the above conclusions, hardening effects produced by secondary ageing can be unambiguously attributed to the formation of GPI zones, which originates from residual supersaturation and from re-ordering of VRC without affecting more complex forms of GP zones that appear on holding at 150°C.

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