

Vacancy–solute interactions during multiple-step ageing of an Al–Cu–Mg–Ag alloy

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Small additions of Ag and Mg stimulate nucleation of the Ω phase in artificially aged Al–Cu alloys, after which these elements segregate to the Ω /matrix interfaces. In this work, positron spectroscopy results show that vacancies accompany the Ag (and Mg) atoms at the interface during precipitate formation, after which they are released back into the matrix and facilitate secondary ageing at ambient temperature.

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Al–Cu alloys containing small additions of Mg and Ag show an enhanced response to age hardening [1]. Strengthening of these Al–Cu–Mg–Ag alloys in the T6 temper is attributed to the presence of the orthorhombic phase Ω together with smaller amounts of the tetragonal phase θ' [2]. The Ω phase precipitates as thin plates on the $\{111\}_\alpha$ planes [3,4] and appears to maintain close coherency with the matrix [5]. This may account for its morphological stability at temperatures up to approximately 200 °C [5,6], which enhances the creep resistance of a range of Al–Cu–Mg–Ag alloys [2,7].

Recent work has shown that creep resistance may be further improved if the above alloy is tested in the underaged (UA) condition (e.g. 2 h at 185 °C) rather than in the fully hardened T6 temper [7,8]. A common feature of UA aluminium alloys is that secondary precipitation (and hardening) may occur if the alloys are held for extended periods at temperatures around 25–65 °C [9]. This phenomenon is associated with the formation of coherent solute aggregates (clusters or Guinier–Preston zones) originating from the residual supersaturation of

solute atoms retained in the matrix after underaging [9–12].

Secondary precipitation in aged aluminium alloys can be clearly observed by positron annihilation lifetime spectroscopy (PALS) [10,13,14]. For the Al–5.6Cu–0.45Mg–0.45Ag–0.3Mn–0.18Zr (wt%) alloy, which is the object of this study, hardness measurements and PALS consistently show secondary precipitation, although this phenomenon begins only after an incubation period of 24 h or more (see Figure 1) [7,15,16].

An incubation period prior to the onset of secondary ageing has been observed before in a range of alloys [7,16,17], but the reason for its existence has not so far been elucidated. A tentative explanation for this behaviour in the Al–Cu–Mg–Ag alloy is that the incubation period corresponds to a re-ordering process within the Ω plates, during which entrapped vacancies diffuse to the precipitate/matrix interfaces before eventually being released into the still supersaturated matrix [15], thereby facilitating atomic transport of solute atoms and leading to secondary precipitation. The fact that Mg and Ag atoms do partition to the precipitate/matrix interfaces has been confirmed by microanalysis [4], atom probe [18,19] and atomic resolution Z-contrast microscopy [5]. Since it is also known that Ag atoms trap vacancies during the early stages of ageing of Al–Cu–Mg alloys

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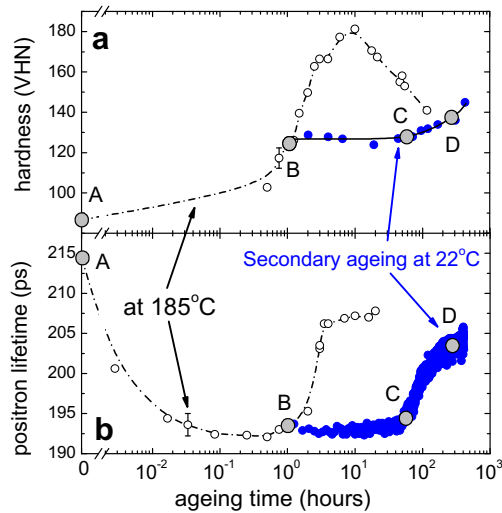


Figure 1. Evolution of the Vickers hardness (a) and of the positron lifetime (b) during ageing at 185 °C (open black circles) and during secondary ageing at ambient temperature after underageing 1 h at 185 °C (blue circles). Labels *A*, *B*, *C*, *D* correspond approximately to the ageing stages selected for CDB measurements (after Ref. [15]) (For interpretation of colour mentioned in this figure, the reader is referred to the web version of this article.).

[14,20–22], and that the Ω phase nucleates from co-clusters of Mg and Ag atoms [20,21], it seems likely that vacancies will also accompany these atoms as they segregate to the Ω /matrix interfaces.

Coincidence Doppler broadening (CDB) positron spectroscopy is particularly suited to the chemical analysis of vacancy–solute complexes [23]. In this work, CDB has been used in an attempt to determine how vacancies and different solute species interact during various stages in the ageing of the supersaturated solid solution (SSSS) obtained by cold water quenching from the solution treatment temperature. CDB results on primary ageing of a similar alloy were reported in Ref. [22].

The four sets of samples selected for this investigation were taken from the same alloy used in earlier studies [2,7,8,15]. The material was solution-treated at 523 °C for 2 h, cold-water-quenched, then artificially aged at 185 °C and held at 22 °C as specified in Table 1. The selection of the heat treatments was guided by the results of positron lifetime measurements [15]. In Figure 1b, the

circles with labels *A*, *B*, *C*, *D* represent the stage of evolution of the four sets of samples in a positron lifetime/ageing–time diagram. All CDB measurements were performed at liquid nitrogen temperature. The measurements and the analysis were carried out as described elsewhere [10]. The data analysis, based on the fitting of the CDB spectrum with a linear combination of reference CDB spectra $\rho_{\text{Al}}^{\text{bulk}}$, $\rho_{\text{Al}}^{\text{vac}}$, $\rho_{\text{Cu}}^{\text{vac}}$, $\rho_{\text{Mg}}^{\text{vac}}$, $\rho_{\text{Ag}}^{\text{vac}}$ measured, respectively, for annealed Al and for vacancy-like defects in pure elements [10,24]. The analysis did not include searching for Mn and Zr, since these metals form stable particles prior to solution treatment and ageing [25] that are not expected to contribute significantly to positron trapping. The fitting function therefore results:

$$\rho_{\text{fit}} = (1 - F_{\text{trap}}) \rho_{\text{Al}}^{\text{bulk}} + F_{\text{trap}} (C_{\text{Al}} \rho_{\text{Al}}^{\text{vac}} + C_{\text{Cu}} \rho_{\text{Cu}}^{\text{vac}} + C_{\text{Mg}} \rho_{\text{Mg}}^{\text{vac}} + C_{\text{Ag}} \rho_{\text{Ag}}^{\text{vac}}) \quad (1)$$

where the fitting parameters are F_{trap} (fraction of positrons that are annihilated after being trapped by vacancy-like defects) and the fractional concentrations C_{Al} , C_{Cu} , C_{Mg} , C_{Ag} of the elements in contact with vacant atomic sites [10,26].

The CDB spectra for samples *A* and *B* are shown in Figure 2 by means of the relative difference function

$$\Delta = \frac{\rho - \rho_{\text{Al}}^{\text{bulk}}}{\rho_{\text{Al}}^{\text{bulk}}} \quad (2)$$

where ρ is the CDB spectrum measured in as-quenched conditions (sample *A* in Table 1) and $\rho_{\text{Al}}^{\text{bulk}}$ is the reference spectrum measured for annealed aluminium. The solid line through the experimental points is the result of the fitting by the linear combination model (Eq. (1)). CDB data for samples *C* and *D* are shown in the inset of Figure 2 in the form of relative differences to the CDB spectrum for sample *B*.

Best-fit values of F_{trap} and of the fractional atomic concentrations are reported in Table 1 together with the corresponding positron lifetimes. The statistical reproducibility of these data is of the order of 1%. Systematic distortions are possible due to the imperfect model adopted for the analysis. For comparison, Table 1 also includes: (a) in the bottom row, the concentrations that would be expected if no vacancy–solute clustering occurred (the nominal atomic

Table 1. Thermal treatments and results of the CDB analysis

Sample	Sequence of thermal treatments			Positron mean lifetime (ps)	Positron trapping fraction (%)	(b) Fractional atomic concentrations at vacancies (at.%)				
	Solution treatment + quenching	Ageing time at 185 °C (h)	Dwell time at 22 °C (h)			Al	Cu	Mg	Ag	
<i>A</i>	yes	0	0	214	89	74	19	2	5	← Measured
						(74)	(21.0)	(4.2)	(0.8)	← Expected
<i>B</i>	yes	1	0	193	66	45	29	18	8	← Measured
						(45)	(44.3)	(8.9)	(1.8)	← Expected
<i>C</i>	yes	1	55	194	65	43	30	18	9	← Measured
						(43)	(46)	(9.2)	(1.8)	← Expected
<i>D</i>	yes	1	278	203	72	49	26	15	10	← Measured
						(49)	(41.1)	(8.2)	(1.7)	← Expected
(a) Nominal atomic concentrations (not including Mn and Zr)						96.9	2.5	0.5	0.1	

The corresponding positron lifetimes from Figure 1 are included.

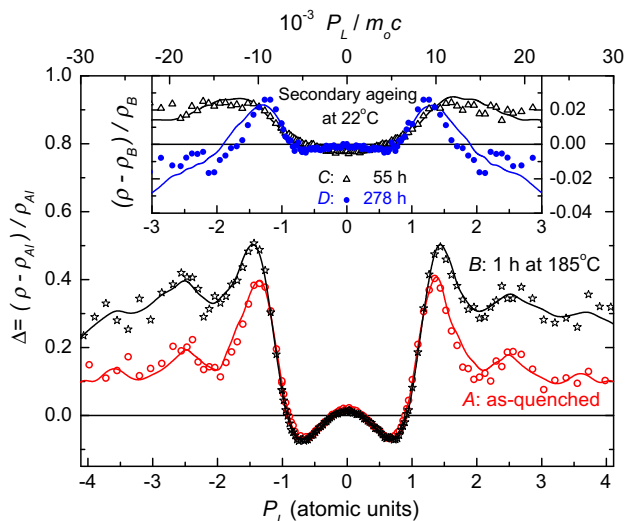


Figure 2. Momentum distribution of the positron–electron annihilation radiation of the samples in as-quenched condition (sample *A*) and after 1 h at 185 °C of artificial ageing (sample *B*). CDB data for samples *C* and *D* are shown in the inset in form of relative differences to the CDB spectrum for sample *B*. Solid lines: fit by a linear combination of reference spectra obtained for pure elements.

composition of the alloy, excluding Mn and Zr); (b) in parentheses, below the measured values, the concentrations expected if the tendency to form vacancy–solute clusters was identical for Cu, Mg and Ag atoms (as obtained by fixing the Al concentration at the experimental value and then dividing the remaining part in proportion to the average atomic concentrations of the different solute species).

A negative difference between the measured Al experimental concentration and the pure statistical prediction reported in the bottom row is indicative of the preferential localization of the vacancies in contact with solute aggregates. For example, in sample *A*, the tendency for vacancies to interact with solute atoms is revealed by the decrease of the Al concentration from the nominal values of 96.9 at.% to the measured value of 74 at.%. Positive or negative differences between the measured values and the calculated ones are indicators of the differing abilities of the solute species to bind vacancies. Taking again sample *A* as an example, the marked difference for Ag between measured (5 at.%) and calculated (0.8 at.%) concentrations, demonstrates the strong vacancy scavenging action of Ag.

Results shown in Table 1 may be analysed as follows.

Sample A. The highest value of the positron lifetime, observed in the as-quenched sample, also corresponds to the highest value of F_{trap} . On the assumption that the positron traps are uniformly distributed over distances of the order of the positron diffusion length L_+ (~ 100 nm), the measured trapping fraction (89%) is consistent with a vacancy concentration of about 10^{18} cm^{-3} , i.e. nearly 10% of the equilibrium concentration of vacancies C_v^{eq} at the temperature of the solution treatment [27]. These vacancies are strongly associated with solute atoms since, on average, more than 3 of the 12 nearest neighbours of the vacant atomic site are solute atoms.

The high concentration of solute in contact with vacancies is an indication that incipient decomposition

of the SSSS, involving the formation of solute clusters with Ag playing a leading role as a vacancy scavenger [14,20,21], takes place during or immediately after quenching. An alternative explanation, which does not imply incipient decomposition, is that the vacancies attach preferentially to solute clusters, which exist for statistical reasons even with a random distribution of solute. This possibility cannot be discarded a priori, because in a solid solution containing about 3 at.% solute, as in this case, the concentration of accidental clusters comprised of three or more atoms would be large enough to accommodate all existing vacancies. In fact, with a face-centred cubic (fcc) cell, the density of random solute clusters of at least three atoms is $3.5 \times 10^{20} \text{ cm}^{-3}$, i.e. more than one order of magnitude larger than C_v^{eq} . However, additional support for the conclusion that incipient decomposition of the SSSS is actually occurring comes from the comparison of the compositions derived from the CDB measurements with the compositions of purely accidental solute clusters (numbers in parentheses in Table 1). The Ag content is enhanced to above six times the random value (5 ± 1 at.% against 0.8 at.%). The opposite occurs with Mg, which is only about one half of the random value (2 ± 1 at.% against 4.2 at.%). Therefore, the hypothesis that the vacancies are bound to random clusters seems untenable.

Sample B. The CDB results demonstrate that the drop of the positron lifetime occurring after underageing for 1 h at 185 °C is concomitant with a marked reduction of F_{trap} . This means that the vacancy distribution is less dense, and/or less uniform at the scale of the positron diffusion length. As proposed earlier [15], a significant fraction of the vacancies is now likely to be sequestered to coherent Ω precipitates. At this early stage of ageing, additional open volume traps for positrons associated with the misfit surfaces of the θ' phase have not yet formed. Table 1 shows that the composition of the vacancy environment is significantly altered. This follows because the total amount of solute concentration in contact with vacancies is 55 at.% compared to 45 at.% for Al. It is also worth noting that the relative concentrations of the three solute elements again are not in proportion to the nominal composition of the alloy. This is illustrated by the higher measured than expected values for Mg (18 at.% against 8.9 at.%) and Ag (8 at.% against 1.8 at.%), and the lower measured than expected value for Cu (29 at.% against 44.3 at.%). It must be noted, however, that the ratio between the measured Ag concentration and the predicted random value is decreased from above 6 (5 at.%/0.8 at.%) to below 5 (8 at.%/1.8 at.%). This result is consistent with the hypothesis that vacancies sequester to the Mg/Ag rich layers at the surface of Ω precipitates rather than next to the almost pure Ag clusters present in the matrix.

Sample C. This sample has been underaged 1 h at 185 °C and held at 22 °C for 55 h. The duration still falls within the incubation period, when there is no evidence of secondary ageing in terms of changes in hardness or positron lifetime [7,15,16]. This behaviour is also reflected in the insert of Figure 2. However, the higher than expected concentrations of Mg and Ag indicate

that the vacancies are still predominantly sequestered by the Ω precipitates in an Mg/Ag rich environment.

Sample D. This sample has been given a similar ageing treatment as sample *C* except that the dwell time at 22 °C was extended to 278 h, which is longer than the incubation period for secondary ageing to proceed. Secondary ageing and hardening are observed [7,15,16] and the CDB results show that positron lifetime and F_{trap} are both increased. As this cannot be attributed to the formation of semicoherent θ' particles (which does not occur at 22 °C), the only possible explanation is that the vacancies previously sequestered by the Ω precipitates have been released to the surrounding matrix and are now associated with the finely dispersed solute clusters or Guinier–Preston (GP) zones. Comparison of sample *D* with samples *B* and *C* also indicates that, in these finely dispersed aggregates, the vacancies are more exposed to Al atoms and less to Cu and Mg atoms. They also have an even stronger attachment to Ag atoms, the local concentration of which returns to a value close to six times the random value predicted for sample *A*.

Previous examination of secondary precipitation through changes to electron diffraction patterns in the same alloy showed streaking around the $1/3\{220\}$ and $2/3\{220\}$ diffraction points (associated with Ω precipitates) [7,28]. Such streaking is characteristic of GP zones [9].

In accordance with the CDB results of Ref. [22], this experiment confirms that:

- (a) the vacancies are strongly attracted by Ag clusters formed during or immediately after cold water quenching from the solution treatment temperature;
- (b) when the Ω precipitates form, sequestered vacancies are located predominantly in Mg–Ag rich regions.

The additional information regarding the evolution at room temperature following underageing at 185 °C is that:

- (a) during the incubation period, the vacancies are still contained in a Mg and Ag rich environment, probably near the interfaces between the Ω plates and the matrix;
- (b) secondary ageing is promoted when these vacancies diffuse from the interfaces into the still supersaturated matrix and facilitate the formation of clusters and/or GP zones which appear to be precursors of the Ω phase.

In conclusion, these results confirm the earlier hypothesis [15], namely that the positron lifetime variations that occur during primary and secondary ageing of the Al–Cu–Mg–Ag alloy are related to the sequestration and release of vacancies in/from precipitates of the Ω phase.

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