Proceedings of the 9th International Conference on Aluminium Alloys (2004)
Edited by J.F. Nie, A.J. Morton and B.C. Muddle

Positron Studies of Precipitation in 6061 Aluminium Alloy

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Keywords: Positron annihilation spectroscopy, age hardening, secondary precipitation

Abstract

Positron annihilation lifetime spectroscopy (PALS) was used to study the precipitation reactions occurring during the age hardening of a 6061 Al alloy. Vacancy-solute interactions that take place during natural ageing at room temperature and artificial ageing at 177˚C were investigated. The phenomenon of secondary ageing at room temperature following short ageing periods at 177˚C was also studied. The value of mean lifetime generally decreases as the level or ordering of precipitates increases during the initial stage of ageing at 177˚C. A few minutes of ageing at 177˚C diminishes vacancy supersaturation and suppress the formation of fine clusters.

1. Introduction

6000 series aluminium alloys have a very wide range of applications and their age-hardening response has been extensively studied by many conventional techniques. The precipitation processes in these Al-Mg-Si type alloys are known to be complex and the following precipitation sequence has been proposed [1,2]:

Supersaturated solid solution → separate clusters of Mg and Si → co-clusters containing both Mg and Si → GP zones → β” → β’ → β (Mg_2Si)

The role of quenched-in vacancies in the precipitation processes in these alloys is not well understood. One of the techniques that is finding increasing application in the observation of vacancies in Al alloys is positron annihilation lifetime spectroscopy (PALS). This technique has been used in studies on precipitation reactions and the decomposition kinetics in both 2000 and 7000 series alloys [3-6]. Positrons probe open volume defects such as vacancies and dislocations. However, they may also be used to investigate different solute aggregates associated with vacancies, coherent zones and incoherent precipitates [3,4].

In the present work, PALS was applied to the study of the precipitation process in aluminium alloy 6061. The objective of the present work was to investigate the role of quenched-in vacancies in the precipitation sequence in this alloy, especially during the early stages of ageing. The complex vacancy-solute interactions that take place during natural ageing, as well as during the initial stage of artificial ageing at 177˚C were used for study. In addition, the process of secondary precipitation that takes place at room temperature following short artificial ageing at 177˚C (T6I4 temper) was investigated [7].

2. Experimental

The material used was a commercial Al–Mg–Si alloy 6061 supplied by Comalco in the form of extruded billet. The composition of the material was (in wt %): 0.99 Mg, 0.59 Si, 0.25 Cu, 0.16 Fe, 0.13 Mn, 0.112 Cr, 0.012 Ti, (bal. Al). The alloy was solution treated at 560˚C for 2 h in an air circulating furnace, followed by cold water quenching. After quenching, the alloy specimens used for examination were aged either at room temperature for up to 48h, or up to 15h at 177°C. For studies of secondary precipitation for the T6I4 temper, ageing was conducted at 177°C for up to 30 minutes, quenched into petroleum ether, then aged at room temperature.

Positron annihilation lifetime spectroscopy (PALS) measurements were made in air at room temperature using an automated EG&G Ortec fast-fast coincidence system where the timing resolution of the system was 240 ps. Polished samples with a thickness of 1.5 mm were placed on either side of the 30 μCi ^{22}Na-Ti foil source. Each spectrum took from 50 to 90 minutes to collect. The spectra were modelled as a single exponential decay using the computer program PFPOSFIT. Differential scanning calorimetry (DSC) was carried out in a TA Instruments 2010 cell with high purity aluminium used as a reference. The heating rate used was 10°C/min. Samples for transmission electron microscopy were prepared by standard techniques and examined using a Phillips CM200 TEM operated at 200 kV.

3. Results and Discussion

Figure 1 a) shows a plot of mean positron lifetime τ as a function of ageing time t at room temperature after solution treatment and quenching (T4). During this measurement, a lifetime spectrum (one data point) was collected every 50 minutes up to a time of 2880 minutes (48 hours). Since no change in the lifetime was observed at longer times of natural ageing, only data up to 1250 minutes are plotted in Figure 1. The initial value of mean lifetime measured during the first 50 minutes of the experiment was 231 ps. However, it must be considered that during the 50 minutes of natural ageing, a rapid change in the microstructure, and hence in the lifetime value takes place. A linear extrapolation (shown as a dashed line in Figure 1a) was performed from t<100 minutes to t=0 and a value of 238 ps was estimated as a lifetime that may correspond to the as–quenched condition. As this value is close to the characteristic lifetime in a mono-vacancy in Al of 240 ps, it is likely that mono-vacancies retained in supersaturation in the alloy immediately after quenching trap the majority of positrons.

As the natural aging continues to times over 150 minutes following quenching, the value of mean lifetime rapidly decreases to a nearly constant value of 221 ps. The majority of excess vacancies are expected to disappear shortly after quenching [8]. However, this would not affect the value of mean lifetime in the absence of other positron traps. Knowing that the diffusion range of positrons in Al is around 100 nm and the density of precipitates that form during ageing is very high, it is expected that the majority of positrons would be trapped by the precipitates and vacancies associated with them, not by the bulk Al, which is the case for saturated trapping. Therefore the decrease in the lifetime value indicates the formation of another type of defect with a shorter characteristic lifetime, which captures positrons concurrently with the mono-vacancies. As shown in Figure 1 b), this suggestion is confirmed by the DSC thermograms.

The thermogram of the as-quenched material shows four characteristics precipitation reactions reported elsewhere [3,4]. Peak A corresponds to the formation of clusters and co-clusters of solute Mg and Si atoms. Peak B indicates the formation of GP zones and appears as a shoulder of peak C, associated with the formation of β” precipitates. Peak D indicates the formation of β’ precipitates. The DSC trace for the sample naturally aged for 25 minutes prior to heating shows that a small amount of precipitation was induced under peak A, and the mean positron lifetime confirmed this. However, the value of mean lifetime, stabilizes after 150 minutes and remains close to 221 ps over the entire duration of the experiment (48 hours). Recent atom probe field ion microscopy (APFIM) findings in Al-Mg-Si alloys show that discrete clusters of solute atoms dominate the microstructure during natural ageing [9]. The increase in natural ageing time effects peak A through the formation of more clusters as natural ageing proceeds. However, these clusters completely dissolve upon heating to a temperature close to that of peak B, instead of transforming into GP zones within peak B. A high supersaturation of solute and vacancies released from the clusters may nucleate a small number of coarse GP zones, which rapidly consume remaining solute and grow into coarse β” precipitates, causing the increasing exothermic reaction under peak C. This explains the means by which natural ageing has a deleterious effect on subsequent artificial ageing [10-12].

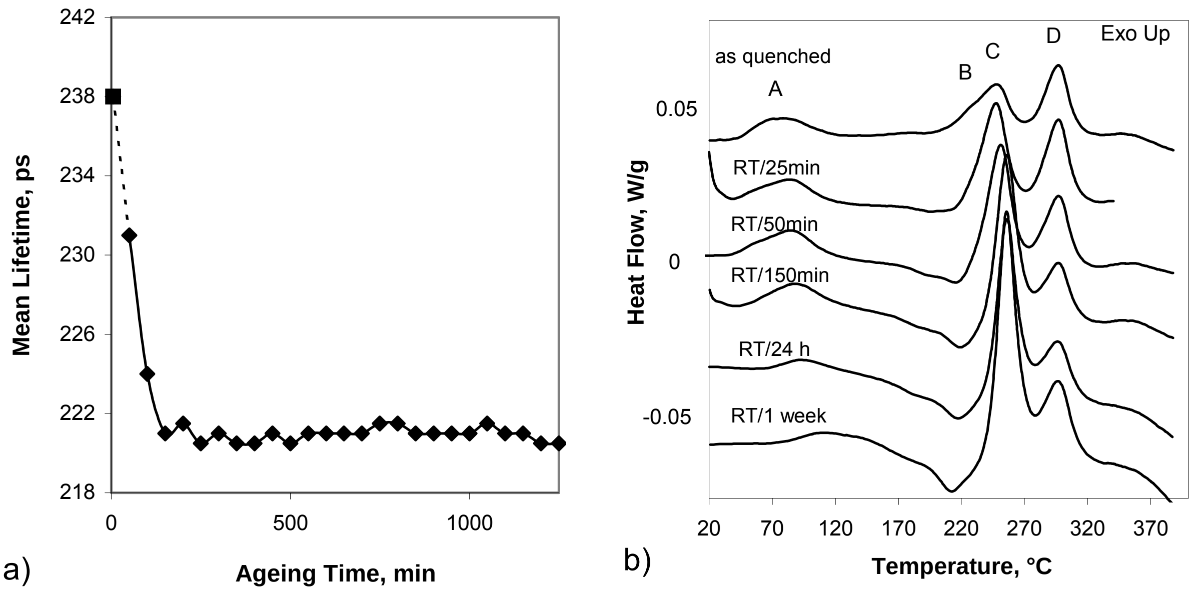

Figure 1: a) Mean positron lifetime during ageing at room temperature after solution treatment and quenching, b) Differential scanning calorimetry (DSC) thermograms after ageing at room temperature (RT) for the times indicated in the figure. The curves have been offset for clarity.

The observation that the value of mean lifetime stabilises after 150 minutes natural ageing, suggests that the majority of free mono-vacancies, with the characteristic long positron lifetime of 240 ps, are lost from the supersaturation after this time. These mono-vacancies may become incorporated into clusters of solute atoms that form at room temperature soon after quenching. The change in chemical environment of vacancies shortens the lifetime of positrons in them. Therefore, the measured mean lifetime of ~221 ps may correspond to the lifetime of positrons trapped by vacancies associated with discrete clusters of Mg and Si. These clusters are likely to remain the only trapping site for positrons after 150 minutes of natural ageing so that their further formation does not affect the value of mean lifetime.

Figure 2 a) shows the results of the lifetime measurements taken during natural ageing after the alloy samples had been aged at 177˚C for times ranging from 1 minute to 15 hours. The measurements made on the as-quenched sample are plotted for comparison. The results show that ageing at 177˚C for only 1 minute causes significant reduction of mean lifetime to a value of 214 ps.

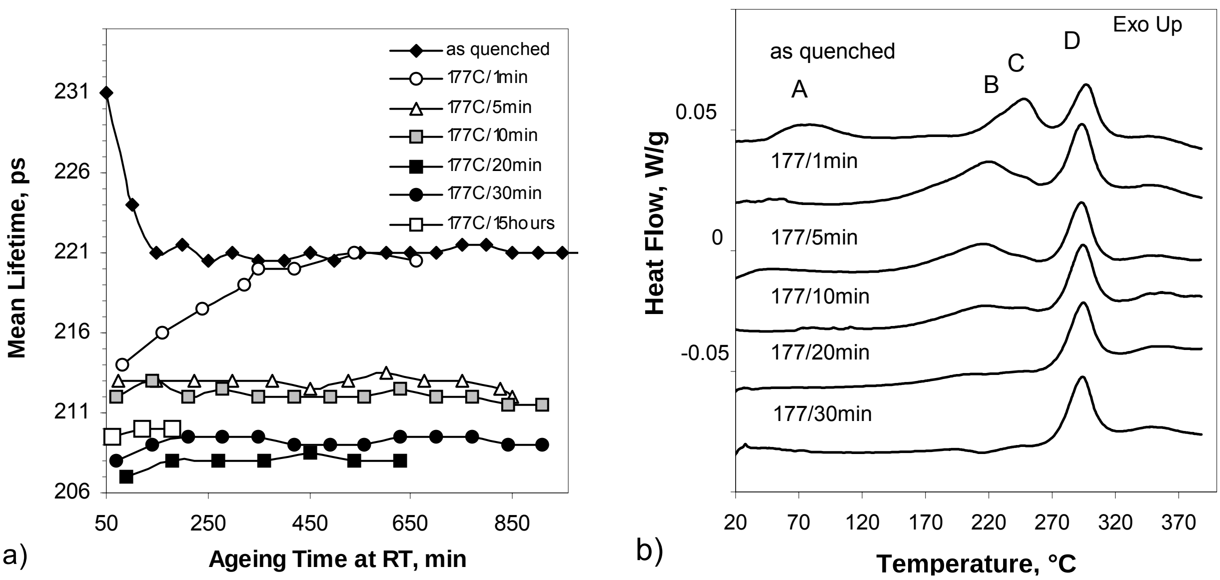

Figure 2: a) Evolution of mean positron lifetime during natural ageing after solution treatment and quenching or after artificial ageing at 177°C for different times (as indicated in the figure) b) Differential scanning calorimetry (DSC) thermograms after solution treatment and quenching and after ageing at 177 °C for different times (as indicated in the figure). The curves have been offset for clarity.

After 1 minute of ageing the mean lifetime increases over a period of 450 minutes at room temperature and reaches a plateau at around 220 ps, corresponding to secondary precipitation occurring during this period. The increase in the lifetime observed at room temperature is believed to be due to the contribution coming from the long characteristic lifetime of discrete clusters of solute atoms, as these may form by secondary precipitation at room temperature in the presence of both vacancy and solute supersaturation.

One minute of ageing at 177˚C appears to induce the precipitation of a phase that has a characteristic lifetime close to or shorter than 214 ps. The corresponding DSC trace, (Figure 2b), suggests that precipitation by clustering occurs due to the absence of peak A. These clusters transform into GP zones during the scan, causing broadening of peak B. The amount of vacancies and solute atoms in supersaturation decreases with the time of ageing at 177˚C, so that after 5 and 10 minutes no significant change in the lifetime at room temperature was observed. The thermograms in Figure 2 b) show that ageing at 177˚C for 5 minutes had almost completed precipitation by clustering within peak A, while 10 minutes of ageing had induced a considerable precipitation of GP zones within peak B. Figure 3 a) shows a TEM micrograph of the sample aged at 177˚C for 10 minutes, which reveals the first visible contrast arising from a few very fine precipitates, presumably GP zones. These results indicate that a lifetime value around 214 ps is likely to be the characteristic lifetime for the co-clusters of solute atoms. The results also indicate that ageing at 177˚C up to 5 to 10 minutes significantly reduces the high supersaturation of mono-vacancies in the alloy. This might explain why a short times of artificial ageing can inhibit the deleterious effects of room temperature ageing prior to final artificial ageing [10]. These co-clusters may also represent vacancy rich reservoirs. As ageing continues, these vacancies may be released and aid diffusion of residual solute, enabling the growth of the precipitates and increase their level of internal ordering.

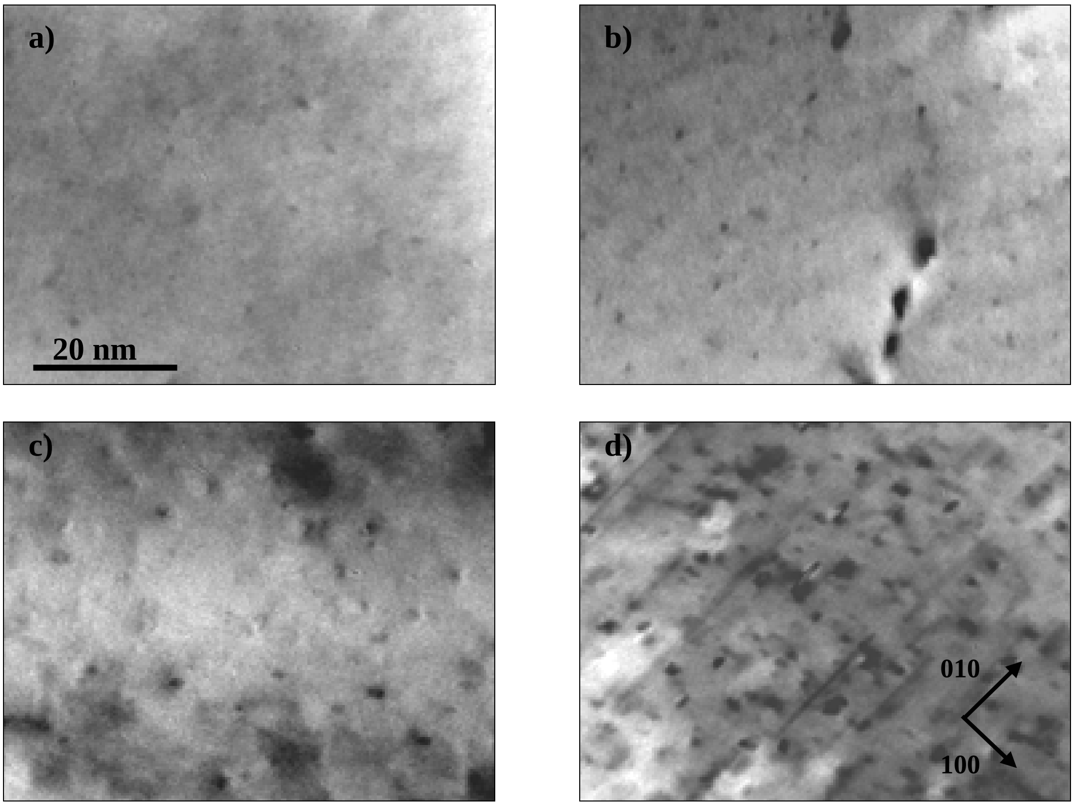

Figure 3: TEM bright field images obtained from the alloy samples a) immediately after ageing at 177˚C for 10 minutes, b) immediately after ageing at 177˚C for 20 minutes, c) immediately after ageing at 177˚C for 30 minutes and d) after ageing at 177˚C for 15 hours. All images were taken at the same magnification and with a $[001]_\alpha$ orientation.

Further ageing at 177˚C decreases mean lifetime and values of around 209 and 208 ps were measured at room temperature after ageing at 177˚C for 20 and 30 minutes respectively. These values are different from that believed to correspond to co-clusters (i.e. 214 ps), meaning the structure and/or density of the traps formed could also be different from that of the co-clusters. The corresponding DSC thermograms in Figure 2 b) show that 20 minutes of ageing finalized the clustering reaction under peak A, and almost completed the GP zone and β'' reactions within peaks B and C respectively. TEM observation confirmed the DSC results for 20 minutes ageing and showed contrast arising from spherical precipitates, identified as GP zones (Figure 3 b)). These precipitates are fully coherent with the matrix and may act as positron traps either as small bulk regions or because they contain vacancies within them. This suggests that GP zones in Al-Mg-Si alloys may also contain vacancies stabilized by the presence of Mg atoms.

The value of mean lifetime in the sample aged for 30 minutes at 177˚C also remained virtually unchanged at room temperature and slightly lower than in the sample aged for 20 minutes. The corresponding DSC thermogram in Figure 2 b) showed that 30 minutes ageing completed the formation of the GP zones (peak B), while some formation of β'' was still taking place under peak C. Subsequent TEM observation revealed a high density of GP zones for this condition (Figure 3 c)).

Prolonged ageing for 15h at 177˚C to the peak aged condition resulted in the formation of needle-like β" precipitates shown in Figure 3 d). The growth of these precipitates is associated with the formation of mismatch dislocations in the precipitate-matrix interfaces, which are effective positron traps. A lifetime value of around 210 ps was measured in this sample suggesting that the loss of coherency of β” precipitates, and positron trapping at incoherent interfaces causes the slight increase of mean lifetime, indicated by Figure 2a.

4. Conclusions

1. Quenching after solution treatment produces mono-vacancies that trap the majority of positrons. Many of these vacancies disappear within a few hours of natural ageing. This may occur by their being captured by discrete Mg or Si clusters of solute atoms that form after quenching at room temperature. These vacancy-solute clusters act as positron traps that have a mean positron lifetime of approximately 221 ps. These clusters completely dissolve at higher temperatures and suppress GP zone formation.

2. Artificial ageing at 177˚C rapidly reduces the value of mean lifetime below that measured during natural ageing. The formation of clusters is suppressed by the formation of a more stable phase, such as Mg-Si co-clusters. After ageing at 177˚C for more than 5 minutes, the majority of vacancies may be incorporated into the co-clusters, rather than left in solid solution. These co-clusters also act as effective positron traps, which have the lifetime of close to or shorter than 214 ps. Co-clusters may represent vacancy rich reservoirs. These vacancies may then be released during subsequent ageing, facilitating solute mobility.

3. A value of close to or shorter than 208 ps appears to correspond to the lifetime of positrons trapped by GP zones, while a slight increase of mean lifetime after 15 hours of ageing at 177˚C to a value of 210 ps is ascribed to the lifetime of positrons trapped at semi-coherent β” precipitates.

Acknowledgments

This work was supported by a CSIRO postgraduate scholarship.

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