



Early stages of solute clustering in an Al–Mg–Si alloy

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Received 11 November 2014; accepted 10 February 2015

Available online 7 April 2015

Abstract—The processes taking place during natural ageing (NA) of the aluminium alloy Al–0.4Mg–0.4Si (wt.%) are characterised by positron annihilation lifetime spectroscopy carried out both in situ during ageing and ex situ after cooling down samples to low temperatures (–180 °C to –60 °C) between NA steps. We find a pronounced dependence of positron lifetime on temperature, which is the signature of the presence of vacancy-free solute clusters in addition to vacancy-related defects. Such clusters are also found in as-quenched samples, indicating that clustering takes place already during quenching. The decomposition of positron lifetime spectra into various components allows us to apply the three-state trapping model and to determine the trapping rates into vacancy-related defects and solute clusters. By modelling the time dependence of positron data we are able to describe the natural ageing process as a gradual decrease of vacancy density associated with a pronounced increase of the density of solute clusters. © 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Aluminium alloys; Ageing; Kinetics; Positron annihilation lifetime spectroscopy

1. Introduction

Immediately after quenching aluminium alloys from the solutionising temperature to ‘room temperature’, normally 20 °C or below, vacancy migration and solute diffusion set in and give rise to the continuous formation and development of solute clusters. In alloys such as Al–Mg–Si, these changes lead to pronounced macroscopic effects such as a rise of electrical resistivity and hardness as well as of a decrease of positron lifetime [1–3]. Moreover the formation of such clusters influences the subsequent artificial ageing process, either positively [4] or negatively [5], which explains the interest in studies of ‘room temperature’ natural ageing (NA). Little is known about the phenomena during the early stages of NA.

The clusters formed at ‘room temperature’ have not been visualised in the transmission electron microscope. Only atom probe can make them visible, but at the earliest after ~1 h [6], which is the time the samples age during sample preparation. Therefore, atom probe can tell us only what happens after 1 h or later. In addition, the results of the various studies are partially contradictory. 70 d of NA produced co-clusters with Mg:Si ratios around 1 in one study [7,8], after 7 d of NA the Mg:Si ratio was 1.2 in another [9]. Some Mg clusters [7] or no clusters [10] were

found in the ‘as-quenched’ state, i.e. after short NA during sample preparation. In these studies, Cu-free alloys containing about 0.75% Mg and Si were used. In a Si-rich alloy after 1 week of NA, only Si clusters were found, no Mg–Si co-clusters [11]. In Mg-rich alloys, NA was found to increase the average Mg:Si ratio from 0.8 after 2.5 h of NA to 1.6 after 2.5 years of NA [12]. The Mg:Si ratio of individual clusters was found to vary from ~0.5 to >4 while the cluster size remained almost constant between 1 week and 2.5 years of NA with clusters containing mostly between 20 and 50 solute atoms [13]. Directly after quenching, no solute clusters were found at all [14]. Torsæter [15] confirmed the wide distributions of Mg:Si ratio for a similar alloy, but found a Mg:Si distribution centred around 1 for an alloy with low solute content. NMR spectroscopy has recently shown that an increasing amount of Mg can be detected in the clusters after 100 min of NA in Al–Mg–Si alloys [16]. In summary, it is known that clusters are formed and grow during NA, but the exact details especially for the very early stages (i.e. <1 h) remain unknown.

Positron lifetime spectroscopy has been used to study NA in a series of Al–Mg–Si alloys directly from the onset of NA after quenching with a repetition time of measurements around 2 min [3]. It was found that the (one-component) positron lifetime evolves in four typical stages. In Al–0.4Mg–0.4Si – the alloy investigated in this work – the initial positron lifetime 2 min after quenching is around 0.240 ns, slightly lower than in a single vacancy in aluminium (~0.250 ns). After a short transient stage I of slightly increasing lifetime (only measurable at NA

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temperatures of 0 °C or below [17]), the lifetimes drop by more than 0.03 ns in stage II, which lasts for about 84 ± 12 min. A possible explanation for this decrease would be a progressive loss of vacancies which causes the positrons to increasingly annihilate in the bulk matrix where they live for shorter periods. This, however, would give rise to a measurable and increasing second lifetime component, which was not found. In contrast, the measurements reported in Ref. [3] rather gave evidence for a second component right after quenching that vanished towards the end of stage II. However, due to limited resolution of the spectrometer used this result was not considered conclusive. A second lifetime component that vanished for longer NA has been reported in a similar alloy 5 min after quenching [18], but the measurements are not consistent with those of Ref. [3]. To explain these findings the idea was developed that a further kind of positron trap with a characteristic positron lifetime of ~ 0.200 ns is formed during NA and gains importance during NA. It was postulated that this component is caused by vacancy-free solute clusters of Mg and Si [3]. A reported temperature dependence of the measured positron lifetime [19] strengthened this viewpoint since only shallow positron traps such as solute clusters would show this temperature dependence but not vacancy-related traps or the bulk matrix [20]. In stage III, the positron lifetime increases again. This has been attributed to the influence of Mg that – once incorporated into the clusters – would increase the positron lifetime [3]. Stage IV is a final decrease of positron lifetime which continues for a few weeks.

The one-component positron lifetime evolution during NA at different temperatures has been successfully modelled based on the above-mentioned idea, namely that there are two types of traps, one vacancy-related trap with a typical lifetime $\tau = 0.244$ ns and another with τ ranging from 0.209 to 0.218 ns. No bulk annihilation component was assumed [16]. Although the success of this model makes the existence of two kinds of positron traps more likely, nothing is said about the nature of these traps and a direct experimental verification is still lacking.

One aim of this paper is to provide decompositions of the positron lifetime into various components to identify the various positron traps directly. For this we employ a high-resolution lifetime spectrometer. Another aim is to measure the temperature dependence of positron lifetime in various stages of natural ageing and to relate the dependence to the results of the lifetime compositions. The final result is the identification of the processes during natural ageing.

2. Experimental

2.1. Sample preparation

A ternary aluminium alloy containing 0.4 wt.% Mg and 0.4 wt.% Si (0.45 at.% Mg and 0.38 at.% Si) was used for this study. It is the same alloy investigated and described in previous studies [2,3]. For the positron annihilation experiments, 1-mm thick pieces of (10×10) mm² size were used. Pairs of samples were solutionised at 540 °C for 1 h in an Ar atmosphere. Mainly two quenching procedures were applied. (i) Water quenching (QW): the samples fall through a vertical glass tube from the heating zone into ice water.

While falling, the samples are kept inside a metal heat shield and reservoir out of which they are ejected just above the water level, thus avoiding premature cooling. (ii) Solid state quenching (QS): the samples are manually removed from a furnace and rapidly put onto a copper block precooled with liquid nitrogen. Then, a second precooled copper block is placed on top of the samples within less than 0.5 s, thus leading to a very good thermal contact. QW provides slightly higher quenching rates as seen from the initial positron lifetime value (see results and discussion part), but QS allows us to process the quenched samples at low temperatures, thus preventing ageing during mounting. After quenching, the samples were dried (only for QW) and mounted to a sandwich containing the positron emitter (²²Na₂CO₃ in a Kapton® envelope) in between. For QS, mounting was carried out in a glove box at a sufficiently low temperature to avoid the condensation of humidity on the sample, for QW mounting was done at ‘room temperature’.

2.2. Positron annihilation lifetime spectroscopy and data analysis

Two spectrometers were used. The one at the laboratory in Berlin (B) is an analogue fast–fast coincidence spectrometer with photomultiplier tubes H3378-50 from Hamamatsu and BaF₂ scintillators. Backscattering was suppressed by lead shields [21]. The count rate achieved was usually 700–800 s⁻¹. Spectra typically contained $\sim 10^5$ counts for spectra measured in situ in about 2 min, and $\sim 2 \times 10^6$ counts in spectra meant for lifetime component decompositions. The measured positron lifetime spectra contain contributions from the 20 μCi ²²Na₂CO₃ source itself. We used spectra measured on pure annealed Al and Si to determine the contributions of the positron source to the measured spectra. They contain a component of about 11% from the two 7.5-μm thick Kapton foils and the sodium salt (both ~ 0.400 ns) and less than 1% of a component with a long lifetime due to positronium formation at surfaces and pores (~ 3 ns). Determination of the source corrections of Kapton and salt was carried out for each of the different measurement temperatures independently to account for a possible temperature dependence, which, however, was found to be negligible in accordance to Ref. [22]. For the positronium component, we adopted the strategy outlined in Ref. [3] to treat the lifetime and intensity of that component as a variable at low temperatures and to check whether it takes reasonable values after fitting. The programme LT9 was used to subtract the source contributions as well as the background and to deconvolute the spectra from the spectrometer resolution function which we found to be well represented by one Gaussian with a FWHM of ~ 0.220 ns. The spectrometer is attached to a liquid-nitrogen cooled cryostat which allows for measurements at any temperature down to -180 °C.

The spectrometer in Prague (P) [23] is digital and optimised for high resolution (FWHM of resolution function is 0.145 ns) but has a lower count rate of 50 s⁻¹. The spectrometer is equipped with BaF₂ scintillators optically coupled to Hamamatsu H3378-50 photomultiplier tubes. Pulses from the detectors are sampled by a pair of Acqiris DC211 digitisers at a rate of 4 GHz. A 27 μCi ²²Na₂CO₃ positron source is sealed by a 2-μm thick titanium foil. Decomposition of positron lifetime spectra is

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