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MUON SPIN RELAXATION AND POSITRON ANNIHILATION SPECTROSCOPY STUDIES OF NATURAL AGING IN Al–Mg–Si ALLOYS

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Abstract

Muon spin relaxation (μSR) is sensitive to magnetic fields from atomic nuclei, making it suitable for studying vacancies and solute clustering inside aluminium alloys. Positron annihilation spectroscopy (PAS) gives complimentary information about the electron density. We have conducted μSR and PAS experiments on an Al alloy with 1.07 at.% Mg and 0.53 at.% Si during natural aging after solution heat treatment. Three stages of positron lifetime change are visible, while the muon depolarization shows a decrease through the first two of these. This is explained on the basis of vacancy migration, vacancy–solute binding and solute clustering.

Introduction

Aluminium alloys containing Mg and Si as main alloying elements (6xxx series alloys) are used extensively as structural materials due to their formability, mechanical strength and corrosion resistance. The alloys are heat-treatable, meaning that their thermomechanical history changes their microstructure, which significantly affects the mechanical properties. Typically, 6xxx alloys are given a solution heat treatment (SHT) before subsequent aging, to distribute the solute elements evenly in the Al matrix. At aging temperatures below ~ 100 °C, alloying elements in solid solution will tend to form solute clusters [1, 2]. When alloys are stored at room temperature, this effect is referred to as *natural aging* (NA). Upon aging above ~ 150 °C, metastable phases having well-defined crystal structures precipitate in the Al matrix [3]. NA is detrimental to this process, and thus to the mechanical strength, if the Mg+Si-content is above 1 at.% [4, 5]. The

processes of clustering and precipitation are very sensitive to parameters such as alloy composition, storage time, aging temperature and heating/cooling rates.

Muon spin methods have been used for probing the microscopic properties of a wide range of materials, including superconducting and magnetic materials [6–8], biological molecules [9] and semiconductors [10, 11]. Most of the research activity using muons on aluminium took place in the early 1980s [12, 13]. In a diamagnetic material, polarized positive muons (μ^+) act as probes for sub-nanometer-scale magnetic fields which cause spin precession during the μ^+ lifetime (on average 2.197 µs). By measuring the muon polarization in these fields, we are able to deduce how the muon is moving, and thus what kind of defects the material contains. The method has been proven to be very sensitive to point defects such as trace elements in metals [12, 14]. In this paper, the acronym µSR refers to muon spin relaxation, with which no external magnetic field is applied. The most significant fields in a diamagnetic material are dipole fields caused by nuclear spins, which are relatively easy to model. A muon decays asymmetrically, such that the main decay product, a positron, is more likely to be emitted in the direction of the muon spin. The detection of these positrons enables us to follow the evolution the of muon polarization.

Positron annihilation spectroscopy (PAS) is an older technique and has to a greater extent been applied to Al alloys [15]. A few variants of positron spectrometers exist, designed for different methods. Common to these is that positrons are generated by positive beta decay in a radioactive source and annihilate with electrons inside the material under study, after which the resulting annihilation photons are detected. The most commonly measured quantity is the positron lifetime, but estimation of electron velocities is also possible through Doppler broadening and photon angle correlation measurements. PALS, with the L meaning lifetime, has been shown to be sensitive to both vacancies and solute clusters in Al alloys [16, 17]. It uses the property that the average lifetime τ of a positron is inversely proportional to the electron density at its position (τ = 100–400 ps in metals) [18].

The µSR and PAS experiments were conducted at the Rutherford Appleton Laboratory (RAL), UK and Helmholtz-Zentrum Berlin, Germany, respectively. Both muons and positrons are trapped by nanometre-sized defects, enabling us to estimate properties of such defects as averaged over a macroscopic volume of the material under study. We have utilized the two methods on identical samples in order to investigate the behavior of vacancies and the diffusion-controlled reactions in Al–Mg–Si alloys during storage after SHT. The combination of these two techniques as well as *in situ* µSR as applied to Al alloys is novel work, and is expected to give new insights into the relevant kinetics.

Experiments and data analysis

The alloy used in this study is ultra-pure and has the composition Al–1.07at.%Mg–0.53at.%Si. Many industrial 6xxx alloys have comparable amounts of Mg and Si, but Fe, Mn, Cu and other elements are added in smaller amounts. Both µSR and PAS were done *in situ* during NA. Other techniques such as atom-probe tomography and hardness measurements have been used to study alloys with similar compositions during NA [19, 20].

The µSR experiment was conducted at the RIKEN-RAL Muon Facility [21]. Its pulsed muon beamline provides an intensity which gives about 1 million positron counts (events) per minute. All samples were given a SHT at 575 °C for 1 hour before being quenched in ice water. After quenching, they were inserted into the muon spectrometer and kept at room temperature (27 °C) during the measurements. One spectrum was measured every 6 minutes for a few hours. The same procedure was carried out with pure Al (99.99%) for comparison.

We fit the relaxation functions from µSR using a Gaussian with standard deviation $1/\sigma$, where σ is a measure of the *depolarization rate* of the muon spin. Muons jump between interstitial sites in a material, and this decreases the depolarization rate (*motional narrowing* [22]). A simple, yet successful model of the depolarization is the Kubo–Toyabe (KT) model [23]. It takes into account diffusion, but ignores trapping and detrapping processes, and will only give accurate results in the limits of high and low trapping rates. Generally, the relaxation will be a convolution of these two cases [14], which most often fit well to a Gaussian. To explain variations in the σ parameter in the experimental results, we simulate the diffusion, trapping, spin precession and decay of muons using a Monte Carlo algorithm. We obtain a relaxation function with $\sigma = 0.6084(13)$ µs^{-1} for stationary muons in tetrahedral sites (see [24]) in a perfect aluminium lattice. Considering the high muon diffusion rate at room temperature, we expect that σ is reduced to zero in a prefectly pure material. Even small concentrations of defects will cause trapping, leading to a higher depolarization rate.

We used a spectrometer with a ^{22}Na source for the PALS experiments. Two samples of the alloy were given SHT at about 550 °C for 1 hour before being quenched in ice water. Each spectrum consists of about 250 000 counts gathered over 4 minutes. This is sufficient to determine the average lifetime [17]. Previous experiments have shown that lifetime spectra in Al-Mg-Si alloys can be approximated by an exponential described by a single lifetime after the source corrections (components with known lifetimes) have been subtracted [17]. The temperature during the measurements was 21 °C, slightly lower than the temperature used with µSR.

Results

The variation in the obtained fitting parameters from the µSR and PAS *in situ* experiments are shown in Fig. 1. The average positron lifetime shows the typical behaviour observed before for similar alloys [17]: A slowly varying lifetime within the first 10 minutes (stage I), a pronounced decrease until about 40 minutes after quenching (stage II), a lifetime recovery until 300 minutes (stage III) and a subsequent slight decrease for the rest of the experiment (stage IV). The activation energy for stage II is about 85 kJ/mol [17], while that of stage III is slightly higher. From thermodynamical considerations we find that the observed processes would be about twice as fast at 27 °C when compared to 21 °C. This is taken into account by multiplying the time in the µSR data by 2 when comparing the kinetics. The depolarization rate σ in pure Al is seen to decrease slowly. It was measured to 0.0265(12) µs^{-1} after 25 hours and 0.0099(50) µs^{-1} after about 200 days. In the alloy, σ shows a single decrease, through stages II and III. This decrease is greater than that of pure Al during stage III.

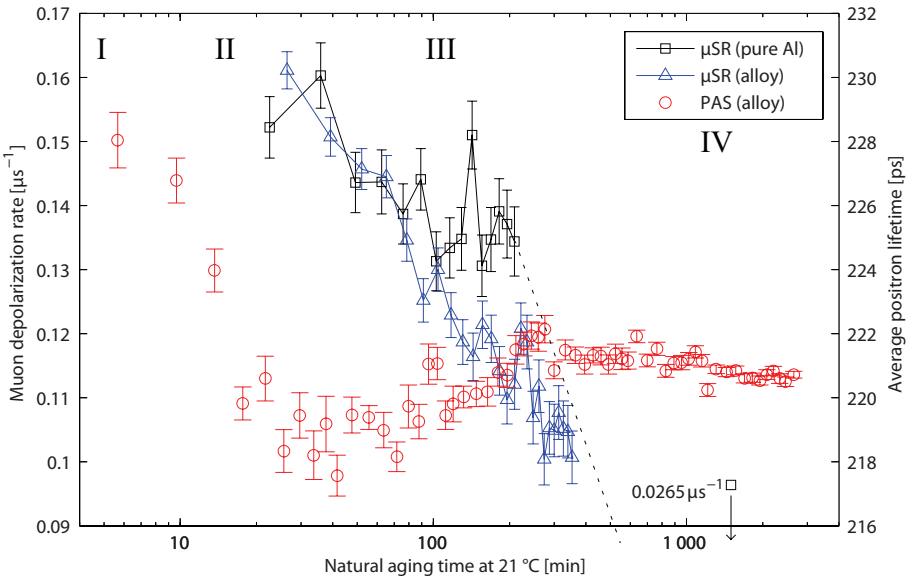

Figure 1: Muon depolarization rates σ (with lines) and average positron lifetime τ (no line) as a function of storage time at 21 °C. A temperature of 27 °C was used with μSR. This is corrected for by a shift in logarithmic time.

Discussion

Interpretation of the results is difficult for both techniques because the change in different variables may have similar effects on the measurements. These variables include the density and trapping potential of all defects, as well as the lifetime of positrons trapped by them. Using the techniques in parallel helps to resolve such potential ambiguities.

The *in situ* PAS procedure described in this paper has earlier been used to measure the positron lifetime τ in pure Al (99.999%) after quenching. It was found to decrease quickly and reach an equilibrium value ($\approx$ 165 ps) after about 100 minutes [25]. The muon depolarization rate in pure Al shows a slower change and stabilization, telling us that μSR is sensitive to lower concentrations of vacancies than PAS.

A complicated variation in microstructure of Al–Mg–Si alloys is known to occur in several steps during NA for days and weeks [20, 26]. The shape of the positron lifetime curve is characteristic for these alloys and will vary appreciably with solute content (especially Mg content) and temperature [17]. The measured positron lifetime is the result of positron annihilation at various locations: Trapping in the bulk will produce a lifetime component of up to 165 ps [16]. Trapping in vacancies, either free or bound to solute atoms, will lead to a positron lifetime around 250 ps [16]. Trapping in vacancy-free coherent solute clusters is expected to lead to a component around 200 ps [17]. Already during quenching some clusters are formed, which is why the initial lifetime is lower than the value for vacancies. At this stage we have concurrent annihilation in vacancies and clusters. After a time of 10 minutes the lifetime decreases as trapping in vacancies loses importance. In stage III, the trend reverses, which can be explained by two possible

scenarios. The existing clusters either change in composition when Mg diffuses into them or further Mg-rich clusters are formed [17].

We see a faster decrease of the muon depolarization rate in the alloy than in pure Al after about 60 minutes. As the depletion of vacancies is slower when a significant concentration of solute elements is present, something else must cause this fast decrease. Vacancy–solute pairs formed during NA are crucial to the nucleation and growth of solute clusters. Such pairs or larger complexes may have a lower trapping potential than monovacancies in Al, which would lead to faster muon diffusion and thus a lower depolarization rate. The apparent difference between the curves for pure Al and the alloy in stage III could be seen as a measure of the tendency of vacancies to bind to solute atoms.

At much lower temperatures, muons are trapped by other defects such as single solute elements in Al [12]. Low-temperature measurements of samples with different aging conditions are ongoing. Further experiments both at high and low temperatures are needed to see how trapping by solute clusters influence the μSR spectra.

Conclusion

We have applied two related techniques for investigating the kinetics of natural aging in Al–Mg–Si alloys. The effect of clustering on the positron lifetime has been investigated earlier, while attempts at quantifying clustering kinetics using μSR have been few. We observe from our *in situ* results that μSR is very sensitive to vacancies in pure Al at 27 °C, but this sensitivity is apparently reduced when probing an Al–1.07at.%Mg–0.53at.%Si alloy. A significant increase in the muon diffusivity inside the alloy is observed around 60 minutes. At this time we see clear indications of an ongoing solute clustering stage in the PAS measurements. The increase in muon diffusivity is most probably linked to vacancy–solute interactions during this clustering. With the aid of these and further experimental results, we hope to establish a new method for studying the kinetics of clustering in aluminium alloys in a flexible and efficient way.

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