*µ*SR study of Al-0.67%Mg-0.77%Si alloys

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µSR study of Al-0.67%Mg-0.77%Si alloys

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Abstract. Zero-field muon spin relaxation measurements were carried out with Al-0.67%Mg-0.77%Si alloys in the temperature range from 20 K to 300 K. Observed relaxation spectra were compared with the relaxation functions calculated by a Monte Carlo simulation with four fitting parameters: the dipolar width, trapping rate, detrapping rate and fraction of initially trapped muons. From the fitting, the temperature variations of the trapping rates reveal that there are three temperature regions concerning muon kinetics. In the low temperature region below 120 K, muons appeared to be trapped in a shallow potential yielded by dissolved Mg atoms, and thus little effect of heat treatment of the samples was observed, while in the mid and high temperature regions, the trapping rates clearly depended on the heat treatment of the samples suggesting muon-cluster and/or muon-vacancy interactions.

1. Introduction

High energy-efficiency is a common requirement in industries, along which Al-Mg-Si alloys, commercially known as 6xxx series aluminum alloys, are in high demand as a material for vehicles because of their low weight, excellent formability and age-hardenability. It is a peculiarly attractive feature of 6xxx aluminum alloys that only 1 % Mg + Si solute atoms increase the mechanical hardness by a factor of approximately 5 from the pure aluminum after a proper heat treatment[1, 2]. This motivates intensive studies of physical properties and microstructures to facilitate a practical use of the alloys. Previous investigations with electrical resistivity[3, 4], transmission electron microscope (TEM)[5, 6], atom probe tomography (APT)[7, 8, 9], differential scanning calorimetry (DSC) [10] etc., illustrate a broadly acceptable relationship that a large number of small size precipitations of solute elements result in a high strength, but a small number of large size precipitations lessen the strength. A key factor has been considered to be a vacancy behavior which stimulates diffusion of Mg and Si and nucleation of clusters. The Mg-Si-vacancy clusters could lead to initial precipitations of Mg and Si. The vacancies and clusters are important, but they are too small to be observed directly. The positron annihilation spectroscopy (PAS) has been sometime used to monitor a number of vacancies in materials[11, 12].

We have commenced a muon spin relaxation spectroscopy to study a behavior of vacancies in Al-Mg-Si alloys. The observed muon spin relaxation functions give us rich information on muon hopping between vacancies and defects in Al alloys. Our recent work with Al-1.6%Mg$_2$Si, Al-0.5%Mg, and Al-0.5%Si alloys has demonstrated that the muon trapping rates (ν_t) depended on the heat treatment and solute concentrations: 1) the concentration of dissolved Mg dominates the ν_t values at lower temperatures, 2) the ν_t values around 200 K reflect a number of clusters, 3) a natural aging (alloys are stored at room temperature) effect is clearly observed with Al-0.5%Si[12, 13, 14]. This contribution will report experimental results of muon spin relaxation versus temperature with Al-0.67%Mg-0.77%Si (balanced concentrations of Mg and Si, noted as 1.4B). Observed zero-field relaxation spectra were compared with the simulated functions by the Monte Carlo technique.

2. Experimental

Samples were prepared using pure elements of Al, Mg and Si, of which the purities are more than 99.99%. The materials were cast, rolled to 1 mm thickness sheets, and cut to dimensions of $25 \times 25 \times 1$ mm plates. All the samples underwent a heat treatment at 575 °C for 1 hour and subsequently quenching in ice water (usually called as solution heat treatment, SHT). After SHT, three kinds of processes were employed: 1) μSR measurement started immediately after the quenching (within approximately 15 min). The data set with this process is noted as 1.4B-AQ. 2) A sample was stored at room temperature for 163 days before measurement (noted as 1.4B-163d). 3) Soon after SHT, a sample was annealed again at 70 °C for 1000 minutes (noted as 1.4B-70C).

Muons have been known to diffuse very fast in Al; hence several tens of ppm of impurities, such Mg, Mn, Cu, Ag, etc., produce significant influence on the depolarization rate[15, 16]. Since the base aluminum used in this study carries a few ppm of Si, Fe, Cu, Mn and Mg, we measured a temperature dependence of μSR spectra with the base Al to estimate a background from impurities. The μSR experiment was carried out at the RIKEN-RAL Muon Facility in Rutherford-Appleton laboratory[17]. We used the ARGUS muon spectrometer with a helium flow cryostat to control the temperature of the samples. The 20 to 60 million positron counts (events) were recorded at a constant temperature in the range from 20 to 300 K, increasing the temperature.
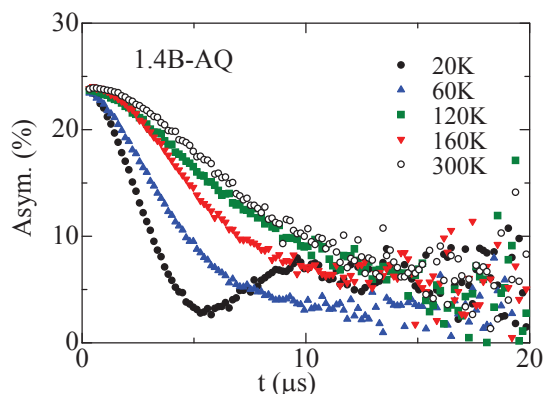

Figure 1. Zero-field muon spin relaxation spectra with the quenched Al-0.67%Mg-0.77%Si sample observed at selected temperatures from 20 to 300 K.

3. Results and discussions

Figure 1 shows the zero-field relaxation spectra at selected temperatures of the sample, 1.4B-AQ. It is obvious that the muon spin depolarization rate depended on temperature. The spectrum

at 20 K appears a typical shape described by the Kubo-Toyabe function [18]:

$$g(t) = \frac{1}{3} + \frac{2}{3}\left(1 - \Delta^2 t^2\right)\exp\left(-\frac{1}{2}\Delta^2 t^2\right).$$

In the present samples, Al nuclei dominantly generate dipole fields causing muon spin relaxation; contributions from Mg and Si nuclei are negligibly small. At the present experimental temperatures, the nuclear magnetic moments of Al are randomly oriented, and thus we assume that the resultant averaged field acting on trapped muons in a certain site has a Gaussian distribution, of which the field vector oriented randomly. The parameter Δ is the dipolar width of the Gaussian distributed field. As the temperature was raised, the depolarization rate was gradually decreased due to detrapping of muons by thermal agitation. The diffusion of muons effects not only on a correlation time between the trapped muons and the magnetic field, but also the dipolar width, which would decrease as motional narrowing; consequently data analysis by only the Kubo-Toyabe function is difficult. It is worth mentioning that the depolarization at 120 K is slower than that at 160 K as seen in the relaxation spectra in Fig. 1.

We have successfully interpreted the observed relaxation spectra using a Monte Carlo simulation, in which four variable parameters were employed: the dipolar width (Δ), trapping rate (ν_t), detrapping rate (ν_d), and fraction of initially trapped muons (p_0)[13, 14]. This method has been introduced in the literature[19, 20]. An ensemble of 60 million muons are simulated to produce a five dimensional relaxation function $f(\Delta, \nu_t, \nu_d, p_0, time)$, in which a muon spin is assumed to depolarize only when it is trapped, but no relaxation occurs during diffusion (two state model). Simulated relaxation functions are compared with the experimental ones to extract the best fit parameters.

The results of fitting are shown in Figs. 2 $\sim$ 5. The deduced Δ values in Fig. 2 of the alloy samples are larger than that of base Al, which is most likely ascribed to the solute Mg and Si elements since randomly substituting Mg and Si for Al sites lead to inhomogeneous magnetic fields at muon sites. The fraction of initially trapped muons in Fig. 3 is almost independent of temperature, and there is little variation among the present samples. The temperature variations of the trapping rates of the three 1.4B samples in Fig. 4 closely resemble each other in the low temperature region; the ν_t decreases as temperature increases. It means that the heat treatments of the samples made little influence on the trapping rates below 120 K. This property of ν_t at low temperatures has been also observed with the alloys of Al+1.6%Mg$_2$Si and Al+0.5%Mg, but
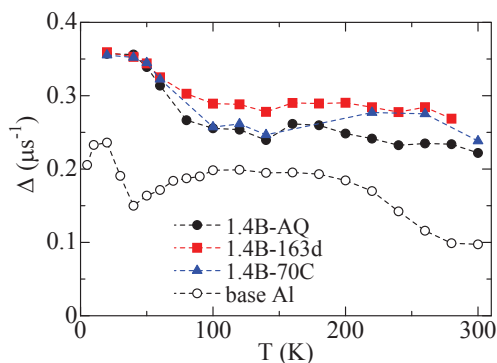

Figure 2. Temperature variations of dipolar width for Al-0.67%Mg-0.77%Si and base Al samples.
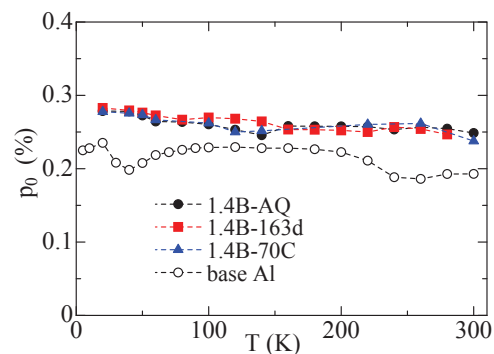
Figure 3. Temperature variations of fraction of initially trapped muons for Al-0.67%Mg-0.77%Si and base Al samples.

not with Al+0.5%Si alloys[14]. The ν_t variations below 120 K are, therefore, related with the dissolved Mg atoms via Mg-muon interactions. There are possibly a large number of dissolved Mg atoms which provide shallow potentials attracting positive muons. Oppositely the detrapping rates at low temperature in Fig. 5 gradually increase with increasing temperature, implying a thermal energy makes trapped muons to escape from the shallow potential.

According to our previous studies[13, 14], the trapping rates around 200 K were found to be dominated by the Mg-Si-vacancy clusters since the heat treatment of samples significantly affected the extracted ν_t values. The sample heat-treated at a proper temperature and a proper period of time would have a high density of small Mg-Si-vacancy clusters, resulting in a high ν_t value as seen with the 1.4B-70C sample in Fig. 4; while the trapping rates near 300 K were relatively large like as the quenched 1.4B-AQ sample. Similar phenomena have been found with the other quenched samples of Al-Mg-Si, Al-Mg, and Al-Si[13, 14]. It is therefore reasonable to consider that the high ν_t values around 300 K with the 1.4B-AQ are associated with vacancies via muon-vacancy interactions.

In order to make the above interpretations clearer, the trapping rates associated with solute elements of Mg and Si were estimated by subtracting the ν_t values of base Al from those of 1.4B
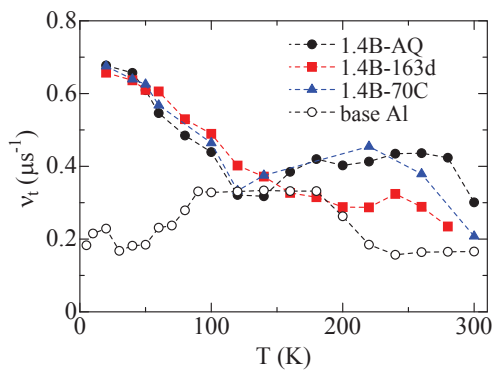
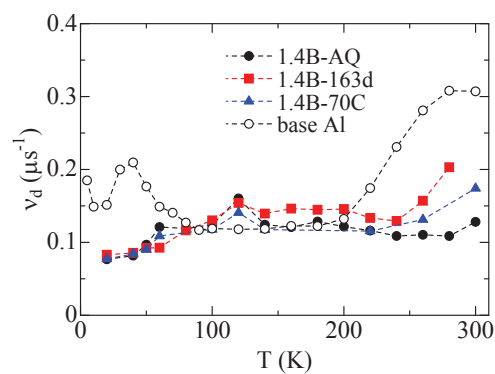**Figure 4.** Temperature variations of trapping rate for Al-0.67%Mg-0.77%Si and base Al samples.

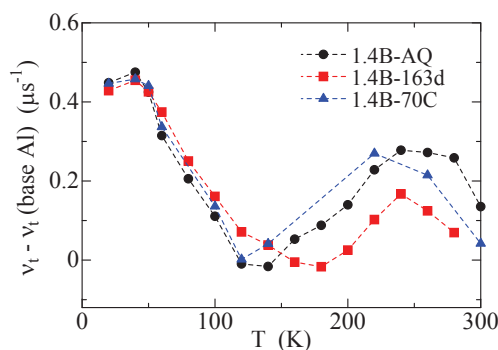**Figure 5.** Temperature variations of detrapping rate for Al-0.67%Mg-0.77%Si and base Al samples.

Figure 6. Temperature variations of trapping rate caused by solute Mg and Si atoms for Al-0.67%Mg-0.77%Si.
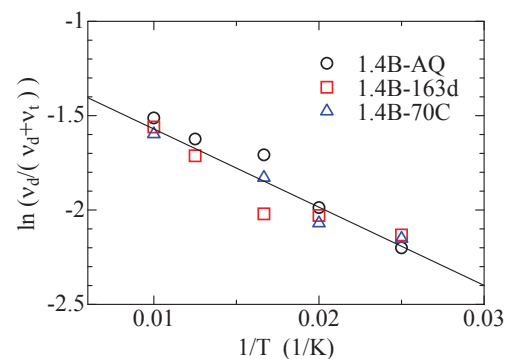
Figure 7. Arrhenius plot of the equilibrium fraction of free muons in the temperature range 40 - 100 K.

samples at each temperature point in Fig. 6. The trapping rates at low temperature appear overlapping considerably. A density of Mg-Si-vacancy clusters would reflect on the trapping rates at 220 K; that is, the largest with the heat treated sample, 1.4B-70C. The larger trapping rates with the 1.4B-AQ above 260 K most likely result from a larger number of vacancies. It is interesting that the 1.4B-163d alloy stored at room temperature forms a less number of the Mg-Si-vacancy clusters, as it is clear from the trapping rates around 200 K. This explanation would be supported by the study of atom probe tomography; an appropriately heat treated Al-Mg-Si alloy produced about five times more clusters than that stored at room temperature[9]. It should be noted that absolute values of density and size of clusters largely depends on the solute Mg and Si concentrations, as well as a heat treatment condition[10].

It is meaningful to investigate binding energies of muons in Al-Mg-Si alloys to clarify structure of Mg-Si-vacancy clusters. Although a typical Arrhenius plot is unlikely accessible in the mid and high temperature regions, the data points in Fig. 6 at low temperatures yield a reasonably linear Arrhenius plot, as shown in Fig. 7. Since little effect of the heat treatment on the trapping rates was noticeable in the low temperature region, we fit all the data from 40 K to 100 K to a straight line, which provides a activation energy of 3.6 ($\pm$0.4) meV. This value is comparable to 6.9 meV found with Al-1.6%Mg_2Si in the similar temperature region[14]. The activation energy with a dilute Mg and well annealed alloy (Al-250ppmMg) has been reported to be 11 meV[19]. The order-of-magnitude agreement between these energy values supports our interpretation that muons are trapped by a shallow potential by dissolved Mg atoms in the low temperature region.

The present results of trapping rates suggested that a storage at room temperature of Si rich 6xxx Al alloys would bring about a significant negative effect on the mechanical strength because the trapping rate with 1.4B-163d related with a number of clusters is rather smaller than those of Al-1.6%Mg_2Si and Al-1.0%Mg_2Si stored in the same condition[14]. If a long period of room temperature storage is inevitable after SHT, it is desirable to control the concentration ratio of Mg/Si to be around two.

Acknowledgments

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