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SOLUTE-VACANCY CLUSTERING IN Al-Mg-Si ALLOYS STUDIED BY MUON SPIN RELAXATION TECHNIQUE

GRUPOWANIE WAKANCJI SUBSTANCJI ROZPUSZCZONEJ W STOPACH Al-Mg-Si ANALIZOWANYCH METODĄ RELAKSACJI SPINOWEJ MIONÓW

Zero-field muon spin relaxation experiments were carried out with Al-1.6%Mg₂Si, Al-0.5%Mg, and Al-0.5%Si alloys. Observed relaxation spectra were compared with the calculated relaxation functions based on the Monte Carlo simulation to extract the dipolar width (Δ), trapping (ν_t), and detrapping rates (ν_d), with the initially trapped muon fraction (P_0). The fitting analysis has elucidated that the muon trapping rates depended on the heat treatment and solute concentrations. The dissolved Mg in Al dominated the ν_t at lower temperatures below 120 K, therefore the similar temperature variations of ν_t were observed with the samples mixed with Mg. The ν_t around 200 K remarkably reflected the heat treatment effect on the samples, and the largest ν_t value was found with the sample annealed at 100°C among Al-1.6%Mg₂Si alloys. The as-quenched Al-0.5%Si sample showed significant ν_t values between 80 and 280 K relating with Si-vacancy clusters, but such clusters disappeared with the natural aged Al-0.5%Si sample.

Keywords: Al-Mg-Si alloys, muon spin relaxation, vacancy

Stopy Al-1,6%Mg₂Si, Al-0,5%Mg i Al-0,5%Si poddano badaniu relaksacji spinowej mionów w zerowym polu magnetycznym. Obserwowane widma relaksacyjne porównano z funkcjami relaksacji obliczonymi przy wykorzystaniu symulacji Monte Carlo w celu otrzymania informacji o szerokości dipolarnej Δ (ang. dipolar width) oraz szybkości uwięzienia ν_t (ang. trapping) i uwolnienia ν_d (ang. detrapping) z pierwotnie związaną frakcją mionów (P_0). Z przeprowadzonej analizy wynika, że szybkość uwięzienia mionów zależy od zastosowanej uprzednio obróbki cieplnej oraz stężenia pierwiastków domieszki. W przypadku Mg rozpuszczonego w osnowie Al dominowała szybkość ν_t w temperaturach poniżej 120 K, dlatego też w próbkach domieszkowanych Mg obserwowano podobne odchylenia temperaturowe szybkości ν_t . Szybkość ν_t w temperaturze około 200 K doskonale ukazuje wpływ zastosowanej obróbki cieplnej na omawiane próbki, z których najwyższą wartość ν_t wykazały te wyżarzane w 100°C spośród stopów Al-1,6%Mg₂Si. Próbką Al-0,5%Si wykazała znaczące wartości ν_t pomiędzy temperaturami 80 a 280 K wskazujące na aglomeracje wakancji Si, które jednak zanikają po naturalnym starzeniu stopu Al-0.5%Si.

1. Introduction

In many metallurgical studies, vacancy behavior quite often emerges as a key factor to understand observed phenomena. The positron annihilation spectroscopy (PAS) has been widely used for studies of defects, such vacancies, dislocations, voids, impurities, etc. [1, 2], in which relatively lower (negative against surroundings) electrical potential produced by defects attract positive charged positrons. The annihilation lifetime of positron depends on the defect concentrations and the trapping rate per defect. In applications of PAS technique, a main difficulty to estimate defect concentrations arises from a complicated temperature dependence of the trapping rate of positrons [3]. This difficulty limits an accessible temperature range of PAS technique.

There are also a plenty of investigations of defects in metals using positive muons since Seeger predicted the possibility in 1975 [4]. A positive muon has a spin of one half, half-life of 2.2 μ sec which is about four orders of magnitude longer than that of positrons in metals, and about 207 times mass of an electron (positron). This larger mass brings about an advantage of positive muons over positrons that muons are trapped by defects whose electrical potentials are too weak to trap positrons. The magnitudes of bound state energies of muons by defects are larger than those of positrons (the bound states of muons locate deeper in electrical potentials), so the temperature variation of thermally activated detrapping of muons can provide detailed information on the defect type. This feature has been demonstrated on the muon spin relaxation spectroscopy with aluminum [5-9]. Muons have been known to diffuse very fast

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in pure Al; hence quite dilute (several tens of ppm) impurities, such Mg, Mn, Cu, Ag, etc., produce significant influence on the muon trapping, and thus spin depolarization. The observed temperature variations of depolarization rates of muon spins in Al around 1~100 K were found to be quite sensitive to the concentrations and elements of impurities [10, 11].

We have commenced a muon spin relaxation spectroscopy (μ SR) 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 defects in Al alloys. Our recent work with Al-Mg-Si, Al-0.5%Mg, and Al-0.5%Si alloys has demonstrated that the muon trapping rates depended on the heat treatment and solute concentrations: 1) the concentration of dissolved Mg dominates the ν_i values at lower temperatures, 2) the ν_i values around 200 K reflect a number of clusters and vacancies, 3) a natural aging (alloys are stored at room temperature) effect is clearly observed with Al-0.5%Si [12-15]. This contribution will review recent experimental results of muon spin relaxation versus temperature.

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 25×25×1 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) μ SR measurement started immediately after the quenching (within approximately 15 min). The data set with this process is noted as *-AQ. 2) A sample was stored at room temperature for some days before measurement (noted as *-. . .d). 3) Soon after SHT, a sample was annealed again at a given temperature from 70 to 350°C for 1000 minutes (noted as *-. . .C). 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 μ SR spectra with the base Al to estimate a background from impurities. The sample compositions, the heat treatments and the corresponding label names for the acquired data are listed in Table 1.

The μ SR experiment was carried out at the RIKEN-RAL Muon Facility in Rutherford-Appleton laboratory [16]. The pulsed positive muon beams were produced via the decay of positive pions which were yielded from the nuclear reactions of high-energy protons with a carbon target in the ISIS synchrotron accelerator. The produced positive muons have the spins which polarize with 100 % along the opposite direction of their velocity. The positive muon decays into a positron and two neutrinos. The emission direction of positron via the decay is asymmetric with respect to the muon spin: $P(\theta) = 1 + A \cos(\theta)$, in which θ is the emission angle with respect to the muon spin. The asymmetric parameter A , reflecting the nuclear force, is approximately 0.3 in the present case. We used the ARGUS muon spectrometer, which detects positrons, 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.

TABLE 1

The sample composition (doped elements and concentrations in atomic percent), heat treatment after SHT and abbreviated label names for samples. RT means room temperature; AQ denotes “as quenched”

Composition	heat treatment		label name
1.07% Mg, 0.53% Si	~15 min	RT	1.6-AQ
	15~365 days	RT	1.6-15d, 1.6-163d, 1.6-1y
	1000 min	70~350°C	1.6-70C, 1.6-100C, 1.6-150C, 1.6-200C, 1.6-350C
0.5% Mg (0.5% Si)*	~10 min	RT	0.5Mg-AQ, (0.5Si-AQ)
	13 (12) days	RT	0.5Mg-13d, (0.5Si-12d)
	1000 min	200°C	0.5Mg-200C, (0.5Si-200C)
0.01% trace elements	66 days	RT	base

* parentheses denote the composition and conditions for binary Al-0.5%Si samples.

Muons would be thermalized in aluminum in a few psec. If muons are trapped at certain sites of Al, the magnetic dipole interaction between the muon magnetic moment and the nuclear magnetic moment of ^{27}Al ($I = 5/2$, $M_N = 1.84 \times 10^{-26}$ J/T) causes the depolarization of muon spins. The depolarization, therefore, gives information on the trapping site and the trapping-detrapping process.

3. Results and discussion

Figures 1(a)~1(d) show the zero-field relaxation spectra at selected temperatures with the samples of Al-1.6%Mg₂Si as quenched, base-Al, Al-0.5%Mg and Al-0.5%Si after natural aging. It is obvious that the muon spin depolarization rates depended on temperature. The spectra at 20 and 40 K with 1.6-AQ in Fig 1(a) appear a typical shape described by the Kubo-Toyabe function [17]:

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

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 nuclei are in a paramagnetic state, 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, which can be a measure of depolarization rate of muon spin. As the temperature was raised, the depolarization gradually slowed 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(a). In turn, the relaxation spectra with the base-Al sample in Fig. 1(b) indicate that muons were frequently trapped at 20 and 120 K in sites leading to fast depolarization, but at 40 K muons relatively freely moved causing slow depolarization. There certainly exist thermally equilibrium vacancies in the base-Al sample, of which the potentials seem not to be deep enough to trap muons at 300 K, clearly seen in Fig. 1(b).

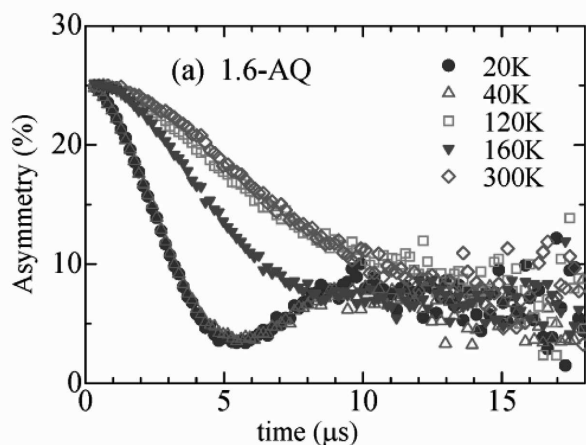


Fig. 1(a) Zero-field muon spin relaxation spectra with Al-1.6%Mg₂Si as-quenched sample observed at indicated constant temperatures

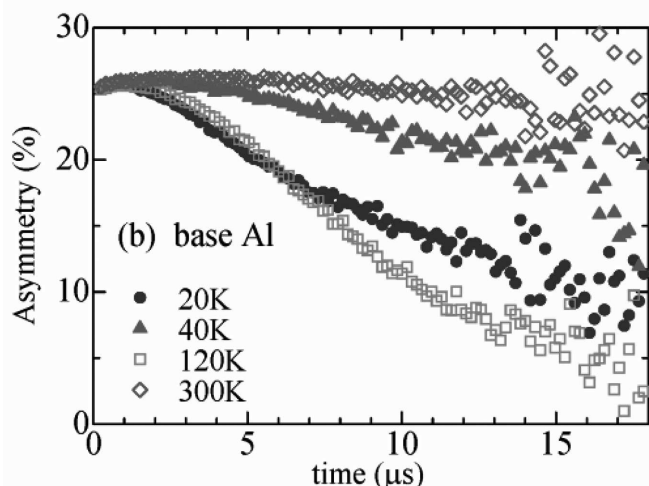


Fig. 1(b) Zero-field muon spin relaxation spectra with base-Al sample

The experimental results in Figs. 1(c) and 1(d) with the binary alloys stored at room temperature suggest rather interesting aspects of muon kinetics with Mg and Si elements: 1) from the spectra at 20 K it is clear that the dissolved Mg in Al well trapped muons, but Si did not. This result is consistent with the previous reports; low temperature depolarization rates depend on impurity elements [10, 11]. 2) From the spectra at 300 K there remained deep potentials in 0.5Mg-13d, probably associated with Mg-vacancy clusters trapping muons, but such potentials disappeared in the 0.5Si-12d sample; i.e. the natural aging effect underwent faster with the Al-0.5%Si sample.

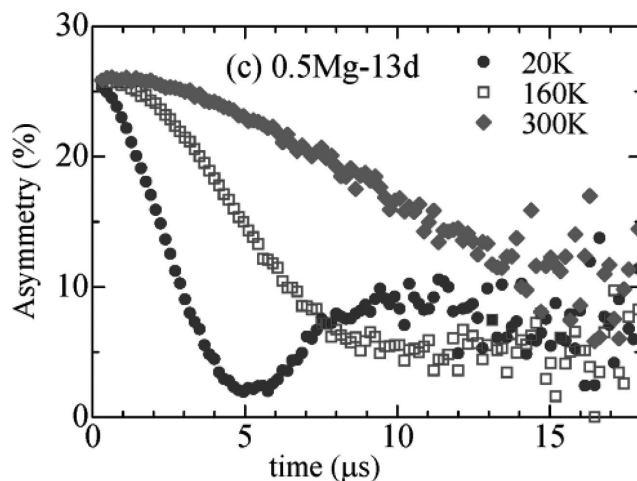


Fig. 1(c) Zero-field muon spin relaxation spectra with Al-0.5%Mg sample after natural aging for 13 days at room temperature

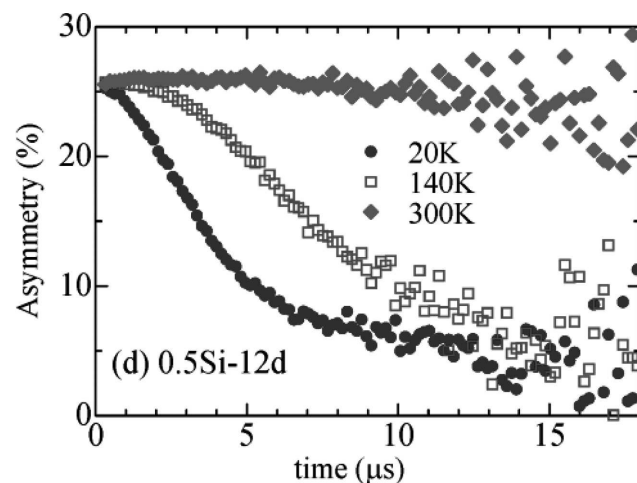


Fig. 1(d) Zero-field muon spin relaxation spectra with Al-0.5%Si sample after natural aging for 12 days at room temperature

Similar relaxation spectra were acquired with the samples listed in Table 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 [8, 9]. An ensemble of 60 million muons are simulated to produce a five dimensional relaxation function $f(\Delta, \nu_t, \nu_d, P_0, \text{time})$, 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 with the Al-1.6%Mg₂Si samples and the base Al sample are shown in Figs. 2(a) ~2(d). The deduced Δ values in Fig. 2(a) of the alloy samples are larger than that of base Al, which is most likely ascribed to the solute Mg and Si atoms 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. 2(b) is almost independent of temperature, and there is little variation among the present samples. The temperature variations of the trapping rates of the Al-1.6%Mg₂Si samples in Fig. 2(c) 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 all alloys which contained Mg elements, but not with Al+0.5%Si alloys. 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 electric potentials attracting positive muons. Oppositely the detrapping rates at low temperature in Fig. 2(d) gradually increase with increasing temperature, implying a thermal energy makes trapped muons to escape from the shallow potentials.

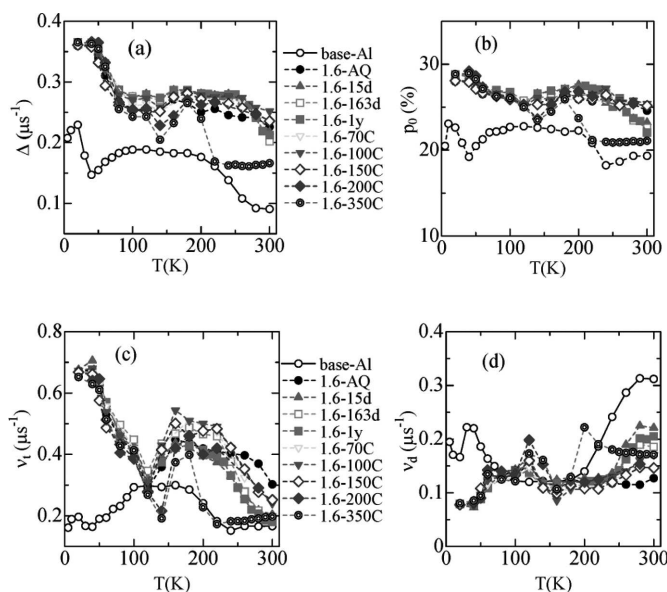


Fig. 2 Temperature variations of (a) dipolar width, (b) fraction of initially trapped muons, (c) trapping rates and (d) detrapping rates for Al-1.6%Mg₂Si samples with various heat treatment and the base-Al sample

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 trapping rates. 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 1.6-100C sample in Fig. 2(c); while the trapping rates near 300 K were relatively large like as the quenched 1.6-AQ sample. Similar phenomena have been found with the other quenched samples of Al-Mg-Si, Al-Mg, and Al-Si. It is therefore reasonable to consider that the high ν_t values around 300 K are associated with vacancies via muon-vacancy interactions.

It is apparent that the base Al sample has some impurities which trapped muons in the temperature range from 100 to 200 K. We made an attempt to estimate the trapping rates associated with the solute elements of Mg and Si by subtracting the ν_t values of base Al from those of the other samples at each temperature point. Figures 3(a) and 3(b) compare the subtracted ν_t values of the Al-Mg-Si and binary alloy samples, respectively. In Fig. 3(a), it is again evident that there is little noticeable difference among the ν_t values at low temperatures. Large ν_t values around 200 K were found with the samples

heat-treated at 100°C. This result suggests that the heat treatment of annealing at 100°C for 1000 min is a proper process to increase the density of Mg-Si-vacancy clusters and thus the mechanical hardness [18]. The result with the 1.6-350C sample indicates that there formed less clusters. This conclusion has been supported by the observed microstructure using a transmission electron microscope [14].

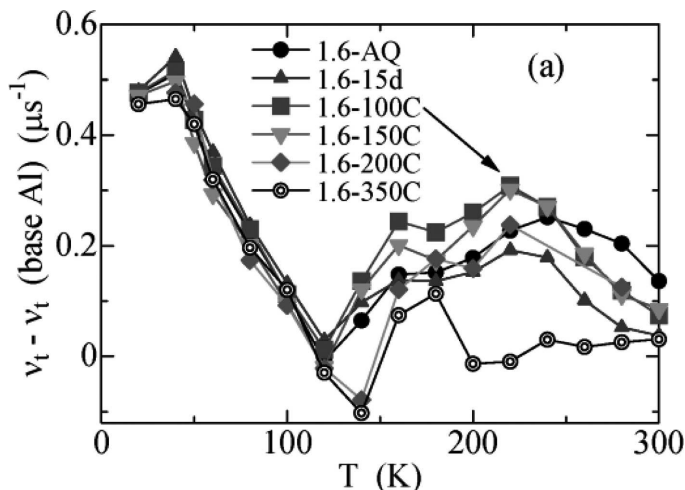


Fig. 3(a) Temperature variations of trapping rates caused by solute Mg and Si atoms for Al-1.6%Mg₂Si

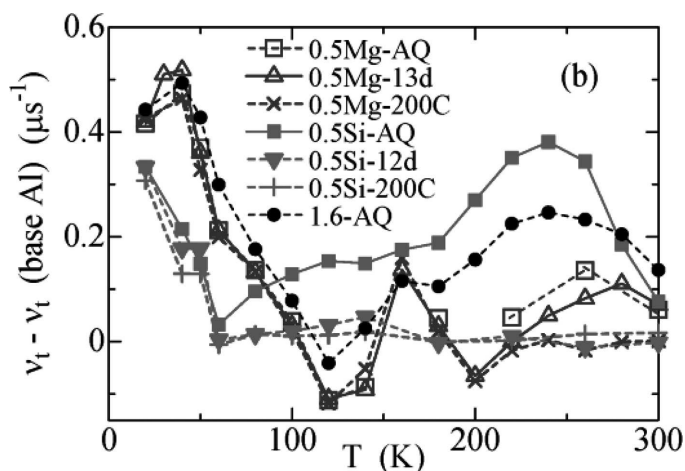


Fig. 3(b) Temperature variations of trapping rates caused by solute Mg or Si atoms for Al-0.5%Mg or Al-0.5%Si sample

There are drastic changes on the subtracted ν_t values with Al-0.5%Si samples depending on the heat treatment as seen in Fig. 3(b). There is a large peak around 240K with 0.5Si-AQ sample, implying that muon were trapped by dense Si-vacancy clusters. Those clusters seemed to disappear in the 0.5Si-12d and 0.5-200C samples; the trapping rates between 60 and 300 K of the samples are almost coincided with those of the base Al. The subtracted ν_t values of 0.5-AQ and 0.5Mg-13d samples around 260 K claim that there remain Mg-vacancy clusters. This result implies that Mg-vacancy has a larger binding energy than Si-vacancy. This conclusion, however, completely disagrees with the theoretical calculations for the solute-vacancy binding energy in aluminum [19]. The subtracted ν_t values of Al-0.5%Mg samples at low temperatures

confirm that muon were trapped in a shallow electrical potentials produced by dissolved Mg atoms.

In summary, 1) the temperature variations of the trapping rates below 120 K were found to resemble each other with the samples of Al-1.6%Mg₂Si and Al-0.5%Mg, in which the dissolved Mg atoms most likely produced electric potentials trapping muons. 2) The heat treatments on the Al-1.6%Mg₂Si samples made an effect on the trapping rates around 200 K. The largest trapping rate was found with the Al-1.6%Mg₂Si annealed 100°C for 1000 min, suggesting this treatment yielded the densest Mg-Si-vacancy clusters. 3) With the as quenched Al-0.5%Si sample, there formed dense Si-vacancy clusters, but these clusters easily disappeared after the sample was stored at room temperature for 12 days. A binding energy of Si-vacancy seems to be weaker than those of Mg-Si-vacancy and Mg-vacancy.

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