Muon spin relaxation study of solute-vacancy interactions during natural aging of Al–Mg–Si–Cu alloys†

K. Nishimura,[*1,*2] K. Matsuda,[*1,*2] S. Lee,[*1] I. Watanabe,[*2] T. Matsuzaki,[*2] S. Wenner,[*3] and R. Holmestad[*4]

Age-hardenable aluminum alloys are strengthened by nanometer-sized atomic clusters and precipitates that are coherent with the aluminum matrix. These are formed by the segregation of atoms (*e.g.*, Mg and Si) from a solid solution, where the solute atoms occupy substitutional sites in fcc-Al. Such a solid solution comprising a few at. % of alloying elements is achieved by solution heat treatment (SHT)—an annealing step at 770–870 K. The solid solution is highly unstable after quenching in ice water after SHT (SHTQ). During further heat treatments at a lower temperature (artificial aging) and even room-temperature storage (natural aging), vacancies and solute atoms co-diffuse and produce atomic clusters, with all atoms remaining at fcc-Al positions.[1,2] The most important techniques to detect and quantify precipitates in the Al-Mg-Si system have been transmission electron microscopy (TEM) and atom probe tomography (APT). However, small atomic clusters are difficult to detect in TEM, APT is unsuitable to investigate the crystallography of precipitates, and neither technique can map vacancies. Muon spin relaxation (μSR) is one technique that can map vacancies, and it investigates short-range magnetic fields and the presence of point defects in solids. This work builds upon earlier literature on aluminum with trace elements and Al–Mg–Si alloys,[3–7] and it extends the analysis to the same alloys with Cu additions.

Figure 1 shows the zero-field μSR spectra observed for Al-1.0%Mg_2Si-0.2%Cu-AQ (in the SHTQ condition) at measurement temperatures in the range of 20–280 K and for Al-1.0%Mg_2Si-0.2%Cu-350C (annealed at 623 K for 1000 min after SHTQ) at 280 K. The plot demonstrates that the muon spin depolarization rate depends heavily on temperature. Similar μSR spectra were acquired for all samples. We have interpreted the measured μSR spectra using a Monte Carlo simulation, in which four fitting parameters were employed: the dipolar width (Δ), trapping rate (ν_t), detrapping rate (ν_d), and fraction of initially trapped muons (P_0).[3,8]

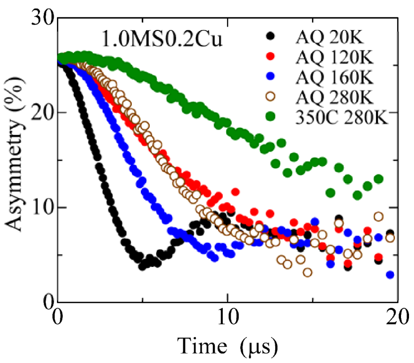

Fig. 1. Muon spin relaxation spectra for an as-quenched (AQ) Al-1.0%Mg_2Si-0.2%Cu sample at 20–280 K and a sample annealed at 623 K for 1000 min (350C) at 280 K.

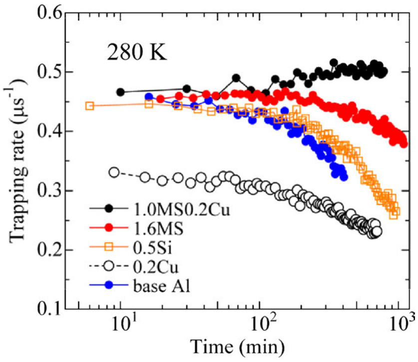

Fig. 2. Fitted trapping rates from isotheral relaxation spectra. Samples are quenched after SHT and kept at 280 K throughout the measurements. The trapping rates decrease with time for all alloys except the quaternary Al–Mg–Si–Cu alloy, the trapping rate for which increases with time.

From previous μSR studies, muons are considered to be trapped by single vacancies or vacancy-solute pairs near room temperature.[3–6] Therefore, in most cases, the ν_t values decrease with time during natural aging because excess vacancies are lost at imperfections, such as grain boundaries, voids, and surfaces. The change in trapping rate during storage at 280 K after SHTQ was measured for Al-1.0%Mg_2Si-0.2%Cu, Al-1.6%Mg_2Si, Al-0.5%Si, Al-0.2%Cu, and base Al, as shown in Fig. 2. The horizontal axis denotes the time from SHTQ on a logarithmic scale. The ν_t values for the Cu-free samples decrease with time. The speed of the decrease is inversely correlated with the solute concentration, which is expected because muons have more defects to be trapped in and more time to undergo spin relaxation. The reason why the ν_t values of Al-0.2%Cu start out lower than in the other alloys is unclear. A surprising result from the isothermal experiment is that the ν_t values (black circles) for the Cu-added sample increase with time. If muons are trapped only at vacancy-associated sites, the result indicates that the number density of vacancies increases with time after quenching when all the elements Mg, Si, and Cu are present in the alloy composition. This suggests that new vacancies are continuously diffusing into the material and binding to solute atoms, shifting the equilibrium concentration of vacancies to higher levels than in the alloys with fewer elements. Further investigation to clarify this phenomenon using positron annihilation spectroscopy is in progress.

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*1 Department of Materials Science and Engineering, U. Toyama
*2 RIKEN Nishina Center
*3 SINTEF Industry, Norway
*4 NTNU Norway

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