Atom Probe Tomography Study of As-Quenched Al–Mg–Si Alloys**

By Phillip Dumitraschkewitz,* Stephan S. A. Gerstl,* Peter J. Uggowitzer, Jörg F. Löfler and Stefan Pogatscher*

This study deploys a new method to gain insight into the as-quenched microstructure of Al–Mg–Si alloys using atom probe tomography (APT) as an imaging method. Here, diffusion of solutes during sample preparation and handling is suppressed via application of cryogenic temperatures beginning from quenching in liquid nitrogen (LN2) through to APT experiments at 33 K. The solute distribution is studied via customized nearest-neighbor distribution and radial distribution function analysis. The influence of energy input on the solute distribution via cryogenic focused ion beam (FIB) preparation is also shown.

Al–Mg–Si–(Cu) alloys are a widely used material in various products, which are manufactured in rolling, extrusion, forging, and drawing processes.[1] The main strengthening mechanism used to enhance the mechanical properties in this alloy class is precipitation strengthening. The heat-treatment pathway is crucial for the in-application properties of these alloys.[2] The amount of time, the material is held or stored at room temperature (RT) after solution heat-treatment and quenching can have a negative influence on its mechanical properties if the material is artificially aged (AA) afterward at temperatures of typically 453 K. This “negative effect” due to natural aging (NA) lowers the hardness and yield stress of the material and reduces artificial aging kinetics. Nowadays, it is generally accepted that the “negative effect” is linked to solute clusters formed at room temperature.[3] It has also been deduced that quenched-in vacancies play an important role in nucleation of the clustering process during NA. However, targeted alloying and processing can be deployed to delay NA response and to improve the AA response.[3–6]

Indirect methods, such as positron annihilation spectroscopy (PAS), differential scanning calorimetry (DSC),[7] electrical resistivity measurements,[8] and hardness measurements are frequently applied to gain insight into clustering kinetics.[1] For NA, different stages have been determined, ranging from I to IV, where different mechanisms are assumed to predominate.[9] The kinetic details depend on the exact alloy composition and not all stages can be observed clearly in every alloy experimentally. In the first stage vacancy annihilation, vacancy-solute pair formation, vacancy-cluster formation, and build-up of Frank loops are thought to be the dominating processes. Stage II may be dominated by Si cluster formation. It has been proposed that Mg starts to contribute to NA during stage III. In stage IV, cluster growth takes place.[5,10] The latest results on time-dependent magnetization also indicate Si clustering in early stage II due to the Si-dependent activation energy of the stage II/III transition.[11]
Nevertheless, the role of Si before Mg gets involved is still under debate, because this stage is difficult to access experimentally in Al–Mg–Si–(Cu) alloys.
Interaction with blender[28] and VisPy.[29] In
4. Experimental Section
APT samples were prepared from alloy AA6016. The
composition of the material was measured with a spark optical
emission spectrometer and determined to be (in at%): 1.0% Si,
0.4% Mg, 0.03% Cu, and 0.005% Ga. Typical APT sample blanks
of 1 x 1 mm alloy were electropolished to a pre-tip radius of
approximately 20 µm. The large radius of the pre-tip was
designed taking into account Einstein’s diffusion distance for
Mg at 803 K to hinder preferential loss of Mg in our final APT tip,
which was then prepared via FIB in the center of the needle.

The pre-tips and Mg, which served as getter material, were
placed in capsuled quartz tubes (≈150 mm in length and
≈10 mm in diameter), which had been repeatedly evacuated
and purged with high-purity argon (5N) to a pressure of
≈300 mbar. The encapsulated pre-tips were solution heat-
treated at 803 K for 5 min in a furnace, and quenched to the
temperature of LN2 by plunging the capsules into LN2. The
plunged quartz capsules were cracked and opened under LN2 to access the
samples. The samples stored at LN2 were then dipped into ethanol at RT for handling
purposes and to remove moisture contamination, before inserting them into a Leica vacuum
cryo specimen transfer shuttle, which was rapidly pumped down to 10−5 mbar using a
Bal-Tec BAF060 freeze-etching chamber. The sample was subsequently vacuum-cryo-
transferred to a pre-cooled FEI FIB-SEM Helios 600i stage at 123 K. Note that the handling
procedure involved approximately 1 min at RT. Even this short time at RT may be omitted
in the near future via total handling under LN2. Final cryo-FIB sample preparation involved
cutting back the pre-tip by approximately 20 µm (to reach a region, where no Mg is
lost due to solution annealing). The APT tip was produced via standard initial 30 kV annular milling and a
final 5 kV cleaning. A schematic overview of the whole
procedure is illustrated in Figure 1. The APT tip was then
vacuum-cryo-transferred via the VCT shuttle to a modified
LEAP™400X-HR atom probe system; the VCT shuttle enables
cryogenic sample transfers into the atom probe analysis
chamber,[17,18] where the specimen then resides at 33 K.

The samples were analyzed in voltage pulse mode with a pulse fraction of 0.2, a pulse frequency of 200 kHz and a
detection rate of 0.5% at a specimen temperature of 33 K.

The reconstruction of APT datasets was performed using IVAS™3.6.10. To calibrate the reconstruction an advanced
method was used, which is briefly explained as follows:[19]
During an APT experiment, faceting of the tip can occur for stable
planes of the crystal, which can be observed as low relative hit
density regions on the detector hit map. These are called
crystallographic poles, because the specific planes are normal to
this direction. Here, spatial distribution maps (SDMs)[20] are used
to quantify the atomic plane distance for different orientations to
optimize input parameters, i.e., the field factor (k) and the image
compression factor (ICF), to ultimately calibrate the reconstruction.
The (200), (220), and (311) poles were used to calibrate the
reconstruction to their respective interplanar spacings, according
to the fcc lattice parameter of Al (unit cell, 0.405 nm).

Further, data treatment was realized using customized
scripts within python,[21] numpy,[22] the python binding to the
FLANN library,[23] matplotlib,[24] MATLAB,[25] and scripts from[26] and[27] in interaction with blender[28] and VisPy.[29]
In the vicinity of poles, artifacts are known to occur.[30,31] This is especially critical in the case of Al–Mg–Si alloys, where Si has
been shown to migrate toward or away from specific poles
during APT measurements.[32] To account for this in a
reproducible manner, a customized pole and surface identi-
cation routine was applied.[33] Based on the respective
100th nearest-neighbor distance, a local density value was
computed for all given atoms.[33] A density of 14 atoms nm−3
was applied as a threshold value, and the low density artifacts (indicating crystallographic poles) were, thereby, removed. Atoms located within a distance of 2 nm from such identified atoms were also removed.

2. Results

To characterize the solute distributions, we used the 10th nearest-neighbor distance distributions and a measure as defined in Equation 1 and 2, where $\mathbf{R}_i$ is the position vector of a specified solute atom. This defined measure is comparable to a radial distribution function or pair correlation function (Eq. 1) as used in refs. [13, 34]. Random comparator curves are generated through random labeling of the existing atom positions. The random samplings of the specified number of atoms are drawn 40 times from the set and the nearest-neighbor distribution and the so defined “RDF” are calculated and averaged. The standard deviation is calculated from the various random distributions drawn.

$$\text{RDF} = \text{Hist}(|\mathbf{R}_i - \mathbf{R}_j|) \leftrightarrow i \neq j$$ (1)

$$\text{ratio}(r) = \frac{\sum_0 \text{RDF}}{\sum_0 \text{RDF}_{\text{rand}}}$$ (2)

In the following, we discuss two different cases, a successfully measured as-quenched (AQ) condition and an as-quenched specimen, which was prepared under FIB conditions, resulting in Ga implantation (0.6% Ga on average) denoted here as “Ga implanted”. All runs showed a yield of around $3 \times 10^6$ collected ions.

For the AQ sample, the Si–Si spatial distribution shows no significant difference from a random solid-solution case, as can be seen in Figure 2a and b. A slight trend toward Si–Si aggregation may be deduced from Figure 2b, but the error bars partially overlap unity. Note that a value $>1$ indicates a non-random solute distribution and that the position of the drop-off to unity is always larger than the expected cluster radius, if we assume that clusters are surrounded by regions of lower solute concentration, which is inherent in the definition of clustering. For the Mg–Mg spatial distribution in Figure 2c and d, clearly no significant difference from a random solid solution is observed. Finally, a cross Si–Mg spatial distribution as presented in Figure 2e and f also shows no significant aggregation of Mg to Si atoms. For this case, the comparator was built by fixing the Si atom positions and randomly labeling the Mg positions on the remaining non-Si positions. Note that qualitatively the results are the same if the Mg atoms are fixed.

Figure 3a shows the results for the distribution of the solute Si in a freshly quenched state in the “Ga implanted” sample. Obviously, the distribution of Si atoms is now discernibly different from that in the random sampling. Even better visibility is provided by the ratio plot in Figure 3b. The Mg–Mg spatial distribution as shown in Figure 3c and d, however, shows no significant differences from a random solid-solution distribution. In addition, no cross Si–Mg aggregation was obtained; see Figure 3e and f. Note that the Ga concentration was, as expected for FIB-prepared APT samples, not uniform over the specimen and more Ga atoms are located near the surface of the specimen. Excluding this region near the surface from APT data would, however, not influence the analysis in Figure 3 in a relevant manner.

Fig. 2. As-quenched sample: (a), (c), (e) 10th nearest-neighbor distance distribution of Si–Si, Mg–Mg, and Si–Mg. Results for the nearest-neighbor distribution are normalized. (b), (d), (f) The ratio as defined in Equation 1 and 2. Error bars show the standard deviation of the random labeling results. To calculate the “ratio” error bars the limiting curves from the standard deviation of RDF$_{\text{rand}}$ were used and processed as in Equation 2. Si–Mg spatial distributions are calculated for fixed Si positions. The dashed blue line indicates the reference for a random distribution. No significant Si–Mg or Mg–Mg aggregation was determined.
Applying a cluster search algorithm similar to that described in ref.\[33,27\] showed that the Si clusters identified are located within the bulk of the sample. Here, the results for the “Core-Linkage” algorithm for Si, Mg, and Cu as possible core atoms with the parameters $d_{\text{max}} = 0.74 = d_{\text{link}} = d_{\text{reader}}$, and $K = 5$ are discussed. If we only consider the Si, Mg, and Cu atom coordinates, we calculate a mean Guinier radius\[35\] of $0.7 \pm 0.1$ nm. The inter-cluster distance is $6.8 \pm 1.9$ nm. It is important to note that Ga-free APT tips can certainly be produced via FIB. However, one needs to be careful and take into account the energy transfer into the system, when early clustering is studied in as-quenched alloys.

3. Discussion and Conclusions

The as-quenched state of Al–Mg–Si–(Cu) alloys shows no clustering of Si–Si, Mg–Mg, and Si–Mg solutes, even though Si–Si clustering is at the significance level (Figure 2). Unfortunately, only a low number of atoms could be obtained during these proof-of-principle experiments, and this number is reduced further due to the removal of artifact-filled data in the vicinity of poles. This and low solute concentrations generate large error bars in the resulting solute characterization measures, which we will try to improve in future measurements. However, the Ga-implanted sample clearly shows Si aggregation (Figure 3). In this sample, the energy input due to Ga-implantation is expected to induce clustering, even at 123 K. As a rule of thumb, ref.\[36\] states that for 0.1% Ga in a Fe sample, 0.75 displacements per atom are calculated using ref.\[37\]. Due to the fact that we have a higher Ga-implantation in Al, with a lower molar mass and Young’s modulus compared to Fe, we expect a much greater number of displacements per atom and many non-equilibrium vacancies\[38\] which accelerate diffusion.\[3\]

Currently no APT measurements for the as-quenched state are available in the literature due to the experimental limitations described in the introduction. Nevertheless, samples naturally aged for a short time (due to sample preparation and handling limitations) are sometimes inaccurately termed “as-quenched”. The earliest of such measurements, after approximately 1 h of natural aging, reveal Mg–Mg and Si–Si, but no Si–Mg correlations.\[13\] Comparing our results of the freshly quenched specimens to the indirect measurements via positron annihilation lifetime spectroscopy in ref.,\[39\] we are investigating samples at stage II of natural aging. Stage II is characterized by a drop in the average positron lifetime over natural aging time, which is attributed to vacancy annihilation and the commencement of Si cluster formation.\[5,10,39\]

For the as-quenched state, this study found no significant Mg–Mg, Si–Si or Si–Mg aggregation. However, Si–Si clustering is at the significance level, which fits stage II of RT clustering in Al–Mg–Si alloys. Further, insight into the early stage of low-temperature clustering is possible from our results on the significant Si–Si aggregation in Ga-implanted samples. We propose the clustering of Si to be caused by the vacancies introduced during FIB preparation. Because the vacancy concentration directly effects clustering kinetics,\[3\] high mobility is possible even at 123 K. The fact that only Si starts to form clusters and Mg is not involved in this process is a first direct evidence that Si, as long suggested, is the most mobile species during the early-stage decomposition of quenched Al–Mg–Si–(Cu) alloys.
In summary, we show here that it is possible to study the as-quenched supersaturated solid-solution state in Al–Mg–Si–(Cu) alloys via cryo-transfer enabled atom probe tomography, and that Si is likely to be the first solute involved in low-temperature clustering.

Article first published online: December 23, 2016
Manuscript Revised: November 30, 2016
Manuscript Received: September 23, 2016