Characterisation of early precipitation stages in 6xxx series aluminium alloys

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Abstract. Advanced microscopy techniques such as high angular annular dark field scanning transmission electron microscopy and energy filtered transmission electron microscopy are being explored to study early precipitation stages of 6XXX-series aluminium alloys. Observations are combined with those from 3 dimensional atom probe studies of the same materials. GP-zones are imaged by annular dark field scanning transmission electron microscopy and plasmon mapping. Developed clusters are investigated and quantified by atom probe, and a high number density of clusters with a Mg/Si-ratio close to the alloy composition are confirmed to be present in the alloy.

1. Introduction
The 6XXX age hardenable aluminium alloys have found industrial applications for several decades. Their main characteristic is the presence of small amounts of Mg and Si at levels of usually less than 1 at%. Addition of a small amount of Cu can further improve the mechanical properties. In recent years transmission electron microscopy (TEM), atomistic and quantum mechanical modelling and atom probe field ion microscopy have really started to elucidate the fundamental details of the precipitation sequences that control the mechanical properties [1]. There is a need to analyse segregation and precipitation processes down to the atomic scale, including the initial clustering stages, which are virtually invisible using conventional TEM imaging and analysis techniques.

3 dimensional atom probe (3DAP) is complementary to TEM. It is well suited to investigating local segregation at the sub nanometer scale, and is thereby a key technique for investigating the early stages of the precipitation sequence. Some early stage precipitation studies in 6XXX-alloys by 3DAP have been reported [2,3,4]. Clusters of either Mg, Si, or both, are seen in a high number density after a short heat treatment [2,3], although the Mg:Si ratio in clusters is generally reported to be close to the overall alloy composition [2]. Co-clusters of Mg and Si will coarsen upon heat treatment and it is suggested that they develop into GP-zones as the amount of solute in clusters increases. Cu additions are not believed to change the chemical nature of GP-zones in AlMgSi [5].
For energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS), analysis of Al, Mg and Si is limited due to overlapping of elemental peaks and the need to work in the high loss k-edges, respectively. In addition, for field emission gun (FEG)-TEM, secondary electrons from the source will overlap high energy loss signals [6]. However, segregation of Cu in particle interfaces can be studied by these methods, [7] and segregation of the relatively heavy Cu-atoms can be imaged by Z-contrast high angular annular dark field (HAADF) scanning transmission electron microscopy (STEM). For precipitates or clusters in the size range of nanometers, imaging is demanding. Al, as a light scattering element, gives low contrast in HAADF lattice resolution images. In principle, low energy filtered TEM (EFTEM) can distinguish different phases by mapping plasmon peak energies [8], with a high signal intensity, minimising beam damage, and a relatively high spatial resolution of 2-5 nm [8].

Earlier, we have compared 3DAP and TEM analyses for an alloy with well developed β’’-precipitates [9]. HAADF-STEM, EFTEM and 3DAP are now being applied to earlier stages of precipitation.

2. Experimental
Two AlMgSi alloys, labelled A and B were investigated. Composition and heat treatment are given in table 1. For comparison, details of the sample investigated earlier are included [9].

Material for 3DAP were first cut into the shape of 20 mm long match-sticks with a cross-section of 0.3 x 0.3 mm² and then necked by electropolishing in a 25% perchloric acid - 75% acetic acid solution at room temperature. Final polishing was performed with a 5% perchloric acid – 95% butoxyethanol solution, while back polishing was performed with a 2% perchloric acid – 98% butoxyethanol solution at room temperature. The 3DAP analysis was performed using an advanced delay line detector (ADLD) atom probe [10]. Samples were held at around 20K and a pulse fraction of 20%, under ultra high vacuum better than 2 x 10⁻⁸ Pa.

TEM foils were made by ion milling. Slices of heat treated material was first ground mechanically and then dimpled before being ion milled in a Gatan PIPS. Foils were examined at 200 kV in a JEOL 2010F TEM, equipped with a STEM unit and a post column energy filter (GIF) system.

Table 1. Composition (in at%), heat treatment and expected phase of samples investigated.

|           | Mg | Si | Cu | Heat treatment   | Expected phase |
|-----------|----|----|----|-----------------|----------------|
| Sample A  | 0.40 | 0.85 | 0  | 16h 100°C        | Clusters       |
| Sample B  | 0.58 | 0.72 | 0.3| 4h RT + 2.5h 175°C | GP-zones      |
| Sample β’’ [9] | 0.58 | 0.72 | 0  | 36h 175°C        | β’’            |

3. Results and discussion
For sample A, clusters did not show distinct contrast in high resolution TEM images. However, 3DAP analysis clearly revealed segregation of both Mg and Si into a high number density of small particles. The ADLD is valuable because it can tolerate the uneven evaporation of particles containing Si and Mg [9]. The formation of particles is obvious from frequency distributions of both elements. Clusters were isolated from the matrix by a cluster identification algorithm [11]. In figure 1, a limit has been set such that clusters should contain at least 10 atoms of both Mg and Si. Clustering is most easily seen in the distribution of Mg atoms. The clusters appear spherical and a particle number density of about 2*10⁷ particles/µm³ was calculated. The numbers of Mg and Si atoms in the identified clusters are presented in table 2. A Si/Mg-ratio of about 2 was found, quite similar to the alloy composition. Due to the difficulty in distinguishing the cluster matrix interface, it is hard to give definitive size and composition data. It might be difficult to distinguish between the particle and the matrix atoms inside and outside of the small clusters, especially for the Al-atoms. Furthermore, a small difference in the
evaporation field between atoms in the particles and the matrix may lead to defocusing effects which would lead to errors when measuring the particle size [12].

![Figure 1](image)

**Figure 1.** Clusters identified in 3DAP volume. Number corresponds to table 2.

**Table 2.** Mg and Si atoms found in clusters of figure 1.

| Cluster | 1  | 2  | 3  | 4  | 5  | 6  |
|---------|----|----|----|----|----|----|
| # Si    | 37 | 27 | 42 | 25 | 30 | 22 |
| # Mg    | 23 | 13 | 20 | 19 | 12 | 10 |

Sample B was investigated in order to image coherent GP-zones by HAADF STEM and EFTEM. The needle-like GP-zones, aligned in the Al \( <100> \)-directions, were easily seen by conventional TEM because of surrounding strain field in the matrix. HRTEM imaging showed a disordered structure for the GP-zones. HAADF-STEM was applied in order to investigate segregation of Cu in or around the precipitates. The ADF-image in figure 2a, taken in the Al \( [100] \)-zone axis at an inner detector angle of \( \sim 14 \) mrad, shows clearly the strain contrast around the GP-zones, both those aligned along \( [100] \) and \( [010] \). GP-zones were found to have cross-sections of \( 3-6 \) nm\(^2\) and a length of \( 15-20 \) nm. GP-zones were also investigated with atomic resolution ADF-STEM. The preliminary ADF-images showed no evidence of Cu-segregation, neither in the particles nor in the matrix.

The GP-zones in sample B were imaged by EFTEM in the plasmon energy loss region. The sample was tilted several degrees off the zone axis to minimise diffraction effects in the energy filtered images. Series were taken in an energy range from 10 to 20 eV with a minimum slit width of 1 eV, and with a step size of 0.5 eV. Particles showed bright contrast at 13 eV, while the same particles appeared dark in the 16 eV image, as seen in figure 2b and 2c. In metals, the plasmon energy shift depends primarily on the valence electron density. The plasmon peak of Al is 15.3 eV. Mg shifts the plasmon peak to lower energy [13], while Si would be expected to give an increase. The contrast observed as the plasmon peak shifts down in energy in the GP-zones may due to their being Mg-rich. For our system, containing Mg, Si and Cu, it is not possible to measure particle composition uniquely from the plasmon peak shift of particles although they can be imaged clearly. It remains to be seen if plasmon imaging will reveal the location of clusters, because of the smaller peak shift as the solute content is lowered and the small cluster size relative to the spatial resolution of the techniques.
Figure 2. a) ADF-STEM image of GP-zones; Plasmon maps of GP-zones at b) 13 eV, and c) 16 eV.

4. Conclusion

Preliminary analysis shows 3DAP to be a suitable technique for investigate clustering in AlMgSi-alloys. No Cu-enrichment of interfacial segregation is seen by Z-contrast HAADF STEM around GP-zones in an AlMgSiCu-alloy heat treated for 2.5 hours at 175°C. EFTEM plasmon energy mapping is demonstrated as a technique for imaging GP-zones when the sample is tilted off the [100]-zone axis orientation. Further work is underway to study the early stages of precipitate nucleation in these alloys using a combination of 3DAP and TEM techniques.

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