Precipitation in 6xxx Aluminum Alloys

Randi Holmestad¹, Calin D. Marioara², Flemming J. H. Ehlers¹, Malin Torsæter¹, Ruben Bjørge¹, Jostein Røyset³ and Sigmund J. Andersen²

¹Department of Physics, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway
²Department of Synthesis and Properties, SINTEF Materials and Chemistry, 7465 Trondheim, Norway
³Hydro Aluminium, Research and Technology Development, Romsdalsvegen 1, 6600 Sunndalsora, Norway

Norway produces over one million tons of aluminum alloys (roughly half of which is age hardenable Al-Mg-Si) per year. Our target is to understand more of the fundamental physics responsible for nucleation and precipitation in these alloys. The form, structure and strengthening properties of age-hardening precipitates depend on the alloy composition and the thermo-mechanical history of the material. Being able to understand the atomic structure of the precipitates, how they affect each other and the material’s physical properties, the right alloy for the right applications can be designed – and ‘alloy design’ can be used to tailor materials to the desired properties. This is the background for our group’s extensive studies of precipitate phases in ternary Al-Mg-Si alloys, which over many years have been a collaboration between SINTEF and NTNU, with Hydro Aluminium as the main industrial partner. We have mapped and determined most precipitate phases in Al-Mg-Si, including Cu and Ge additions. This has been possible by combining advanced transmission electron microscopy techniques with atom probe tomography and calculations based on density functional theory. This paper gives a review of the methods and show examples of recent and ongoing work in our group on precipitation in 6xxx alloys.

Keywords: Al-Mg-Si alloys, precipitation, transmission electron microscopy, electron diffraction, ab initio modeling

1. Introduction

The Al-Mg-Si(-Cu) alloys are an important group of age-hardening materials. Properties like high strength/weight ratio, good formability and weldability, combined with an excellent corrosion resistance, rank them among the most attractive alloys and have made them widely used by the industry. 6xxx alloys find applications in a wide range of areas, such as in building constructions, automobiles and marine applications. The significant increase in hardness during the ageing heat treatment is caused by the formation of a high density of metastable semi-coherent precipitates in the Al matrix. There is an increasing demand for improved control of properties, which requires knowledge and understanding of the finest details of the precipitation sequence. This includes diffusion and solute clustering, nucleation, growth and transformation of the precipitates. In this context, it is obvious that better knowledge and understanding of the atomic structures of the precipitates and their interfaces are particularly important. The quality of modern transmission electron microscopes (TEM), the use of recently developed quantitative analysis techniques and the availability of computer power and programs to perform first principles calculations have enabled the crystal structures of most precipitates in the ternary Al-Mg-Si alloys to be solved. For this system the following precipitation sequence has been found:

SSSS → Clusters → GP (pre-β”[1,2]) → β”[3] → β’[4], U1[5,6], U2[5,7], B’[8,9] → β, Si
with SSSS equal supersaturated solid solution. The U1, U2 and B’ phases are also called Type A, Type B and Type C, respectively [10].

Except the equilibrium phase $\beta$ with composition Mg$_2$Si and Si, all phases are metastable. Every stage of the sequence is complex and is a function of alloy composition, heat treatment (including cooling and heating rates) and storage time at room temperature prior to ageing. Cu additions to the ternary Al-Mg-Si system change the precipitation sequence and produce new phases [11-15]. The precipitation sequence for the Al-Mg-Si-Cu system becomes [15]:

SSSS $\rightarrow$ Clusters $\rightarrow$ GP $\rightarrow$ ($\beta''$), L[12,15], S (QC)[14,15], C[15] $\rightarrow$ Q’[9] $\rightarrow$ Q[16]

Except for the equilibrium Q phase [16], little has been known about the crystal structures of the other Cu-containing phases. However, in [15] it was demonstrated that at peak-hardness L, S and C precipitates are Q’-precursors, with L and S having partly disordered crystal structures.

This review paper will first (section 2) give an overview of the methodology used in the studies of precipitates in 6xxx alloys. We will then present some ‘showcases’ which illustrate how the different methods are used to acquire information on precipitate atomic structures at different stages, starting with the main hardening phase $\beta''$ (section 3). Section 4 describes the Cu-containing precipitates, while section 5 deals with the structural similarities in the precipitates, where a common network of Si atoms has been observed to connect all precipitates in the Al-Mg-Si(-Cu) system. This may stem from the earliest nucleation processes, namely the clustering, which is now extensively studied. Outlook and conclusions will be given in section 6.

2. Methodology

![Fig. 1. A collage illustrating the different techniques used at the different length scales. For determination of precipitate structures we work within the box to the right. Abbreviations are given in the text.](image)
Clustering, nucleation and precipitation happen at very small length scales, and to be able to study these processes in details, we need appropriate tools. Fig. 1 shows the length scales and the corresponding different techniques used at the given length scales. The different techniques used for the detailed study of precipitates in 6xxx alloys are placed in the blue box at the right and are described in the following. Often, before these detailed studies are done, other experiments are performed to correlate the information obtained at the smallest scale, like hardness and conductivity measurements, optical and scanning electron microscopy.

2.1 Experimental methods

As a consequence of the fact that all metastable precipitates in this system have needle/lath/rod/plate morphologies with longest directions parallel to <001>Al direction, the TEM specimens have to be oriented in this zone axis. Images recorded in Bright Field TEM (BFTEM) are used for finding precipitate number density and measuring the average precipitate length and cross-section that enables calculation of corresponding precipitate volume fractions. Our group has developed a methodology for accurate microstructure determination by taking into account errors originating from underestimation of average precipitate needle/lath/rod/plate length when some precipitates close to the specimen surface are cut during sample preparation [17]. Thicknesses of the samples are measured using Electron Energy Loss Spectroscopy (EELS) [18].

Atomic models of precipitate structures are constructed by analyzing High Resolution TEM (HRTEM) images that give input on atomic column positions and crystal symmetry. Unfortunately such images do not contain information about atomic column composition (type), or atomic heights. The heights can be inferred from projected inter-column distances, and approximate precipitate compositions can be obtained by Energy Dispersive X-ray Spectroscopy (EDS).

With heavier atoms like Cu, Ag or Ge present in the precipitates, Annular Dark-Field Scanning TEM (ADF-STEM) is used. ADF-STEM is an incoherent imaging technique based on Rutherford and thermal diffuse scattering of electrons to large angles as the incident probe propagates along atomic columns. Intensity peaks in the image correspond to atomic column positions and the intensity is strongly dependent on atomic number. Hence, ADF-STEM images are more directly interpretable than HRTEM images which rely on phase contrast [19]. The ADF-STEM technique has been greatly enhanced recently by the development of probe Cs-corrected STEM machines that are capable of achieving sub-Angström resolutions at superior signal to noise ratios [20]. Consequently, ADF-STEM is increasingly being used as the preferred high-resolution imaging technique. In the 6xxx system, it has already provided unique information that enabled solving disordered precipitate structures containing Cu, otherwise difficult to achieve with conventional techniques, as shown in section 4. One drawback of the ADF-STEM technique is the presence of distortions in the images due to specimen drift during the electron scan.

In the early stages of clustering, when clusters have small sizes and are highly coherent with the fcc Al matrix, TEM based techniques have proven difficult. Atom Probe Tomography (APT), which is performed using a three dimensional atom probe (3DAP) [21], is a unique method enabling real-space mapping of atoms with near-atomic resolution, and it is useful in the characterization of small clusters and precipitates in metallic alloys [21,22]. In addition to providing particle number density and morphology, APT gives information complementary to that of the TEM. For the case of well-developed precipitates APT can be used to accurately measure the particle composition [23,24]. It can also be used for investigating Room Temperature (RT) solute clusters, that are too small and highly coherent with the fcc aluminum for generating any contrast in TEM. By APT these can be observed at the atomic scale, and further characterized in terms of number density, morphology, compactness and composition [25,26].
2.2 Quantitative optimization

As a result of combining the above-mentioned experimental techniques, initial models of the precipitate atomic structures can be constructed. Verification of these models is achieved by using quantitative electron diffraction. For this purpose, relative intensities of diffraction spots in Nano Beam Diffraction (NBD) patterns recorded from individual particles are compared with the corresponding relative intensities generated from the proposed atomic model, taking into account dynamical diffraction. This is acquired by use of a Multi Slice Least Square (MSLS) method developed at TU Delft in the Netherlands [27,28]. After the experimental and theoretical intensities are compared, the atomic model is adjusted to optimize the fit with experimental data. For 3D refinement of atomic coordinates, the MSLS program is dependent on input from a collection of ED patterns originating from different zone axes and preferably from specimens with different thicknesses. All patterns applied should have a linear relation between intensities and the number of scattered electrons, and should be recorded using (near) parallel illumination and a small spot size (5-10 nm). In addition to atomic coordinate refinement, MSLS can also refine cell parameters, atomic occupancies and temperature factors. This has led to the crystal structure determination of several precipitates in the Al-Mg-Si(-Cu) systems [3-7,29-31]. However, since the MSLS program only optimizes a structure to fit experimental data, it needs to be verified whether the refined atomic structure is energetically favorable or not. Also, since the scattering cross sections of Al, Mg and Si are so similar, it is sometimes difficult for MSLS to distinguish between the different atomic species. This can be done by minimizing the structure bulk energy using first principles calculations.

First principles Density Functional Theory (DFT) [32-34] performing total energy calculations, therefore represents the selected complementary theoretical tool to MSLS for clarifying the structure and composition of the experimentally observed precipitates [3-7,24, 29-31]. The total energy investigations generally have employed the Vienna *ab initio* simulation package (VASP) [35,36], a plane wave based benchmark tool for condensed matter theoretical studies. A combined MSLS and VASP analysis is highly advantageous: MSLS makes direct reference to experimental observations, but rarely manages to determine the individual atom types unambiguously on its own (see e.g. [29]). DFT studies, on the other hand, involve well defined configurations, but within user defined restrictions (choice of unit cell size e.g.) of the analysis. When fed with input from a preliminary structural analysis, total energy calculations can provide a set of candidates for MSLS to analyze. In turn, the MSLS optimized structures may provide new information (such as the need of a larger unit cell) for VASP to address. In principle, this 'self-consistency loop' can fully clarify the precipitate structure. In practice, the level of success rests on the justification of any presumed basic knowledge introduced to simplify considerations, as emphasized for the case of the composition of the main hardening precipitate \( \beta'' \) in the Al-Mg-Si alloy, as discussed in next section. Inclusion of APT investigations in the above described loop promises increased reliability of the results.

When used for structural determination, theory conventionally ignores the precipitate interfaces with Al for reasons of computational efficiency. Evidently, a proper description of the precipitate interactions with Al requires interface studies [37-40], but bulk calculations also fail as a tool for predicting the existence of a given precipitate structure, being entirely dependent on experimental input. An example is the weak effects on the calculated precipitate binding energies of replacing Si with Ge [41], compared with the drastic experimentally observed changes to the precipitate sequence (section 5). It will require a precipitate generation algorithm or an atomistic understanding of the precipitate nucleation to achieve a truly independent theoretical precipitate structure analysis. This emphasizes the importance of experimental input for the theory.
3. β” – the main hardening phase in Al-Mg-Si

Knowing the exact composition of the main hardening phase β” in the Al-Mg-Si is important to produce materials of optimized strength. The Mg/Si ratio in the alloy should be adapted so as to match that of this phase. The story about the β” represents a good example of the use of the methodology presented in last section. Historically, all precipitates in these alloys were thought to have the same composition as the equilibrium phase Mg2Si[42]. In 1996, APT studies showed that the Mg/Si ratio in β” was close to 1 [43]. The year after, the structure was solved by MSLS and HREM, and the composition was found to be Mg5Si6[3, 44].

![Fig. 2. Overview of methods used when solving the β” structure and composition: a) Medium and high resolution (exit wave reconstructed) transmission electron microscopy and b) electron diffraction. c) An atom probe tomography volume revealing Al content in the phase. These methods were used to get an initial model of the phase, and the intensities in the electron diffraction were used for quantitative refinements in the MSLS program. d) Ab initio density functional theory calculations showing that Mg5Al2Si4 has the lowest energy. e) The structure model illustrates the Si1, Si2 and Si3 atom positions in the β” cell, where Si3 is the position which most likely is replaced with Al [24].](image)

A recent study including APT and VASP showed that the structure most likely also includes Al, and that a more accurate composition is Mg5Al2Si4 [24]. The difference from the Mg5Si6 structure is a replacement of Si with Al at one position in the unit cell. While this substitution was unexpected and therefore not considered earlier, the Mg5Al2Si4 structure has a better consistency with the structure of U2, one of the subsequent phases formed in the alloy precipitation sequence, and is also found to have the lowest formation energy of the configurations investigated. Fig. 2 illustrates the different methods used to solve the β” structure. The calculations support that Si atoms form a spacious network with strong bonds (Si1, Si2) where the penalty for substituting Si with Al is high, whereas smaller changes in the energy between Si and Al exist regarding the atom sites (Si3) in-between. MSLS also shows...
that the $\text{Mg}_5\text{Al}_2\text{Si}_4$ structure gives a better fit with the experimental data than $\text{Mg}_5\text{Si}_6$, due to lowering of temperature factors, although this method alone is not sensitive enough to clearly distinguish between the two structures.

4. Disordered (and ordered) precipitates in Al-Mg-Si-Cu

The advantage of the ADF-STEM technique when investigating metastable precipitates in the 6xxx system was first realized in the Al-Mg-Si-Cu system [15]. Here, we found disordered arrangements of Al, Mg and Cu atoms on a near-hexagonal network of Si atomic columns when viewed along the precipitates longest directions, which made HRTEM images and ED patterns difficult to interpret. This network has projected sub-cell dimensions $a = b \approx 0.4$ nm and its $c$-axis equal to $0.405$ nm or a multiple of it, corresponding to the highest precipitate coherency direction with the Al matrix. However, a direct confirmation of this could only be provided by ADF-STEM, which clearly shows a disordered distribution of Cu atomic columns and a lack of unit cell in these

![Fig. 3. Disordered precipitates in an Al-Mg-Si-Cu alloy with low Ag additions. a) HRTEM image. The spatial resolution is around 0.2 nm and all atomic columns are visible. However, there is no Z-contrast present in the image; b) ADF-STEM image. The positions of Cu and Ag atomic columns are clearly visible, although the spatial resolution and signal to noise ratio are lower than in the HRTEM image. The positions of Al, Mg and Si atomic columns are not clearly resolved. A few Cu columns in a local ordered area corresponding to the Q’ phase are connected by solid black lines. Two Ag-enriched areas are also shown; c) ADF-STEM image recorded with a probe Cs-corrected STEM instrument. The spatial resolution is higher than in the HRTEM image, approaching 0.1 nm, and the signal to noise ratio is high, making all atomic columns visible. In addition, the image contains Z-contrast. Some image distortions are caused by specimen drift during the electron scan; d) In order to reduce noise even further, an Inverse Fast Fourier Transform (IFFT) of image c) is presented, where all distances shorter than 0.14 nm have been filtered. A few Cu columns in a local ordered area corresponding to the Q’ phase are connected by solid white lines. Two Ag-containing columns are also shown. A few of the near-hexagonal sub-cells part of the Si-network are shown by white dotted lines. All images are taken in a <001>Al zone axis. The precipitates are viewed in cross-section.](image-url)
precipitates. The ADF-STEM images also show that many such particles contain local ordered areas corresponding to the hexagonal Q’ phase, and to the monoclinic C-plate phase. Recent investigations to the Al-Mg-Si-Cu system with low Ag additions confirm these findings and show that addition of Ag does not change precipitation sequence [45]. Fig. 3 shows an example from this work where it can be clearly seen that when compared to the conventional HRTEM technique, interpretation of probe Cs-corrected ADF-STEM images is much easier due to the superior spatial resolution and the presence of Z-contrast. Even uncorrected ADF-STEM images, when used in combination with HRTEM images, can provide the additional Z-contrast information that is of great importance in solving precipitate crystal structures. The importance of ADF-STEM is of equal importance when studying alloys where Si is replaced with Ge [46].

5. Structural similarities and common network

![Structural drawings](image)

Fig. 4. Schematic drawings with the same scale showing structures of a) β’, b) U2 and c) B’ viewed along their 0.405nm periodicity with the Al matrix. The similarity between these phases is obvious when their atomic structures are referred to the common near-hexagonal grid defined by the Si columns. Atomic heights are indicated by open (z = 0 nm) and solid (z = 0.2025 nm) circles. a) Solid lines: β’ unit cell (hexagonal, a = b = 0.715nm); the similarity with U2 is shown with dashed lines. b) Solid lines: U2 unit cell (orthorhombic, a = 0.67 nm, c = 0.79 nm); the similarity with the β’ phase is shown with dashed lines. c) Solid lines: B’ unit cell (hexagonal, a = b = 1.04nm); the similarity with the U2 phase is shown with dashed lines. All phases can be ‘decomposed’ into near-hexagonal 0.4 nm sub-cells (connected with pointed lines) defined by the Si columns. The phases are essentially different arrangements of Mg and Al atoms on this Si network.

Using the methodology presented in section 2, our group has solved the crystal structures of the most common ordered metastable precipitates in the Al-Mg-Si(-Cu) system [3-7, 33,34]. Also, the type of
disorder present in some precipitates of the Al-Mg-Si-Cu system has been resolved, as briefly explained in section 4. It has emerged that the near-hexagonal Si network having projected sub-cell dimensions \( a = b \approx 0.4 \) nm and its c-axis equal to 0.405 nm or a multiple of it, is always present in the precipitates crystal structures, and can be derived from diamond Si as viewed along \(<111>\)Si [15,32,38, 47-49]. To exemplify the importance of this network in explaining precipitate crystal structures, Fig. 4 shows as an example the structural similarities between the \( \beta' \), U2 and B' phases of the Al-Mg-Si system in connection to their common Si network. The network is most distorted from the hexagonal symmetry in \( \beta'' \) phase, probably due to the high coherency this phase has with the Al matrix. It is very interesting to observe that the Si3 sites in Fig. 2 e) are not a part of the network, and can be replaced by Al without energy penalties. Since the Si nano-pillars suggestion by Chen et al. would imply that this position is of equally importance as the other Si atoms for the stability, our model of \( \beta'' \) does not support the concept of nano-pillars [2]. The best and simplest description of the Si arrangements that ensures the stability of all the precipitates is the Si network.

To further explore the nature of the Si network, similar Al alloys with Si replaced by Ge have been examined. It would now be interesting to see if Ge goes into a similar Ge network and if the precipitates are of the same type. The interesting result here is that the \( \beta'' \) phase was not observed. Peak hardnesses similar to those achieved by \( \beta'' \) in Al-Mg-Si alloys were instead achieved by \( \beta' \)-like, U1-like and disordered phases, depending on the Ge/Mg ratios in the alloys composition [50]. The \( \beta' \)-like and U1-like precipitates were often disordered. In all cases, the precipitates had structures containing a near-hexagonal network of Ge atoms very similar to the Si network described above. Because of the relative high Z of Ge, this network could be directly visualized in ADF-STEM images [46]. Even more interesting is that the orientation of the precipitate unit cells and the Ge-network relative to the Al matrix differed from what has been observed for \( \beta' \) and U1 in the Al-Mg-Si system, which may indicate the importance of interface coherency and strain. VASP calculations are in progress, including theoretical studies of the interface, to get a better understanding of this.

The observations of the strong structural similarities in the precipitates may suggest that they are nucleated from similar clusters. Knowledge of the early stages of precipitation, before the more ordered precipitates form, can therefore give valuable information on the formation and growth of hardening precipitates. Due to its strong dependence on several parameters, e.g. total solute content, alloy Mg/Si ratio and heat-treatment history, the clustering process in these alloys is at present not sufficiently understood. Theoretical studies have investigated how solute atoms diffuse in the aluminum lattice [51], revealing what types of early-stage structures are most energetically favorable [52]. Experimental studies by TEM have investigated the effect of clustering during room temperature storage on subsequent precipitation during artificial ageing [53]. Recent advances in the cluster identification procedure applied to APT volumes have enabled the direct observation of clusters formed during direct pre-ageing and natural ageing in various alloys [26]. The difficulties of observing clusters make it interesting to calculate, by first principles, the interactions between solute atoms in the matrix. This can reveal the nature of the initial step of the clustering reaction, namely the solute pairing in the matrix.

6. Outlook and conclusions

Industrial research on precipitation hardened Al-Mg-Si alloys has been going on for 90 years and may be regarded as relatively mature. Further advances on optimizing alloy properties for specific purposes will rely on the fundamental understanding of precipitates as exemplified in this paper. We have developed a methodology combining several experimental techniques to study precipitate structures in Al-Mg-Si/Ge(-Cu) alloys, with the objective to design alloys for specific applications. This has revealed the existence of structural similarities between all metastable precipitates through a common Si network in all alloy systems investigated. The detailed structure of the precipitates can be used to compose alloys of Mg/Si ratios matching those of the main hardening phase(s), thus
optimising the alloy for strength applications. Our results seem to indicate that precipitate crystal structure does not have a direct effect on alloy strength. Instead, the size and the coherency of precipitate interfaces with the Al matrix are the most relevant parameters. The structural similarities of the precipitates make studies of early stage clustering more interesting, as these can be expected to discover if the Si network is a result of the initial nucleation process.

7. Acknowledgements

This work was financially supported by The Research Council of Norway via two projects: the FRINAT project (“Fundamental investigations of solute clustering and precipitation”) and the BIA programme “Kimdanningskontroll” (Nucleation Control), which is supported by Norwegian industry: Hydro Aluminium AS, Steertec Raufoss AS. Simulations are performed through access to the Notur (Norwegian High Performance Computing) facilities. Collaborations with Rouen University (Williams Lefebvre) within APT and recent collaborations with Monash University (Joanne Etheridge) and Denmark Technical University (Rafal Dunin-Borkowski) within aberration corrected ADF-STEM are highly acknowledged.

References

[41] R. Vissers (priv. commun.)