Characterization and structure of precipitates in 6xxx Aluminium Alloys

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Abstract. Solute atom nanoscale precipitates are responsible for the favourable mechanical properties of heat treatable aluminium alloys such as Al-Mg-Si (6xxx). The shape, structure and strengthening properties of age-hardening precipitates depend on alloy composition and thermo-mechanical history. We seek an improved understanding of the physics related to nucleation and precipitation on the atomistic level in these alloys. Once these mechanisms are sufficiently well described and understood, the hope is that 'alloy design' simulations can assist tailoring of materials with desired properties. In pure Al-Mg-Si we have determined the structure of nearly all the known metastable precipitate phases, by combining advanced TEM techniques (such as high resolution TEM and nano-beam diffraction) with atom probe tomography and density functional theory. We are now studying effects of additions /substitutions of Cu, Ag and/or Ge that promote formation of more disordered precipitates, employing aberration corrected high angle annular dark field scanning TEM. We find that all metastable precipitates contain variations of a widely spaced 'Si/Ge network'. In spite of disorder or defects, this network is surprisingly well ordered, with hexagonal projected sub-cell dimensions a = b ≈ 0.4 nm and c (along the fully coherent precipitate main growth direction) equal to 0.405 nm or a multiple of it.

1. Introduction

The Al-Mg-Si(-Cu) alloys are an important group of age-hardenable 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 ('alloy design'). This in turn requires knowledge of the finest details of the precipitation sequence, as some precipitates have considerably stronger hardening effect than others. The task is manifold, including diffusion and solute clustering, nucleation, growth and phase transformations of the precipitates. These topics are inherently atomistic, meaning that knowledge and understanding of the atomic structures of the precipitates and their interfaces with Al is paramount. 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. Disregarding the actual age temperature and time, for this system the following precipitation sequence can be given (with the structures largely determined within our group):

$$\text{SSSS} \rightarrow \text{Clusters} \rightarrow \text{GP (pre-}\beta\text{''[1,2])} \rightarrow \beta\text{''[3]} \rightarrow \beta\text{'[4], U1[5,6], U2[5,7], B'[8,9]} \rightarrow \beta, \text{Si}$$

Here, SSSS denotes the supersaturated solid solution. The U1, U2 and B' phases are also called Type A, Type B and Type C, respectively [10]. With exception of the equilibrium phase β (Mg_2Si) and Si, all phases are assumed 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 [11-14]:

$$\text{SSSS} \rightarrow \text{Clusters} \rightarrow \text{GP} \rightarrow \beta\text{''} + \text{L} + \text{S} + \text{QC} \rightarrow \beta\text{'} + \text{Q'} \rightarrow \text{Q}$$

This paper firstly reviews the methodology used in our studies [1,3-7,15] of precipitates in 6xxx alloys. We then show some examples of how advanced TEM methods are used to acquire information on precipitate atomic structures at different stages, including quantitative diffraction and probe corrected annular dark field scanning TEM (ADF-STEM).

2. Methodology

Figure 1 shows the length scales involved in aluminium alloy development. Clustering, nucleation and precipitation are phenomena that must be studied near and at the atomic scale, as demonstrated on the right hand side of the figure. Usually, before attempting such detailed studies, in order to correlate the information obtained at the smallest scale, it is normal to characterize the materials properties and investigate at lower magnifications using more conventional methods, like optical and scanning electron microscopy. The length scales are demonstrated on the images on the left hand side of Figure 1.

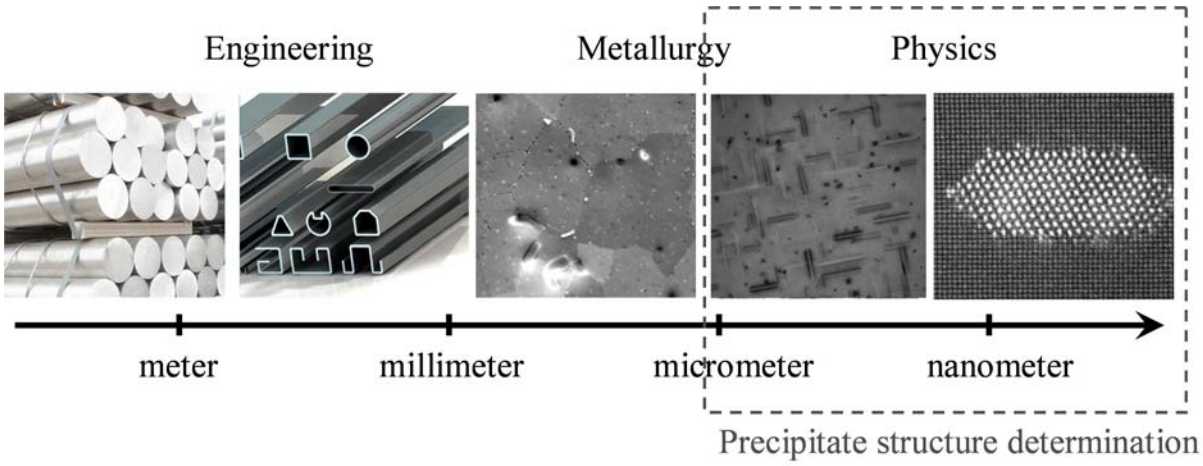

Figure 1. The different length scales investigated in aluminium alloys. Tools for studying the nano/micro-structure as shown in the stippled box would include high resolution TEM and annular dark field scanning TEM, nano-beam diffraction, atom probe tomography and density functional theory calculations.

2.1. Experimental methods

It is well established that age hardening strongly depends on the number density of precipitates as well as their type. Because all metastable precipitates in Al-Mg-Si(-Cu) have needle/lath/rod/plate morphologies with main growth direction along $<001>_{Al}$, for most purposes the TEM specimens should be oriented in this zone axis. Images recorded in bright field TEM are used for finding precipitate number density and measuring the average precipitate length and cross-section that enables calculation of corresponding precipitate volume fractions. Early on, our group 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 [16]. Thicknesses of the samples are needed here, and are measured using electron energy loss spectroscopy. Often, precipitates can be distinguished based on morphology and orientation, see e.g. [17].

Atomic models of precipitate structures are constructed by analyzing high resolution TEM (HRTEM) images that give input on atomic column positions and crystal symmetry. Since these images can only be acquired in main growth axis projection (with the precipitate occupying the entire region across the sample thickness direction), they do not contain full information about atomic heights or atomic column composition (type).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 a superior technique due to its Z-contrast information. In addition, ADF-STEM images are more directly interpretable than HRTEM images which rely on phase contrast [18]. The ADF-STEM technique has been greatly enhanced recently by the development of probe Cs-corrected STEM machines that are capable of achieving sub-Ångström resolutions at superior signal to noise ratios [19]. Consequently, ADF-STEM is increasingly replacing HRTEM. One drawback of the ADF-STEM technique is the presence of distortions in the images due to specimen drift during the electron scan.

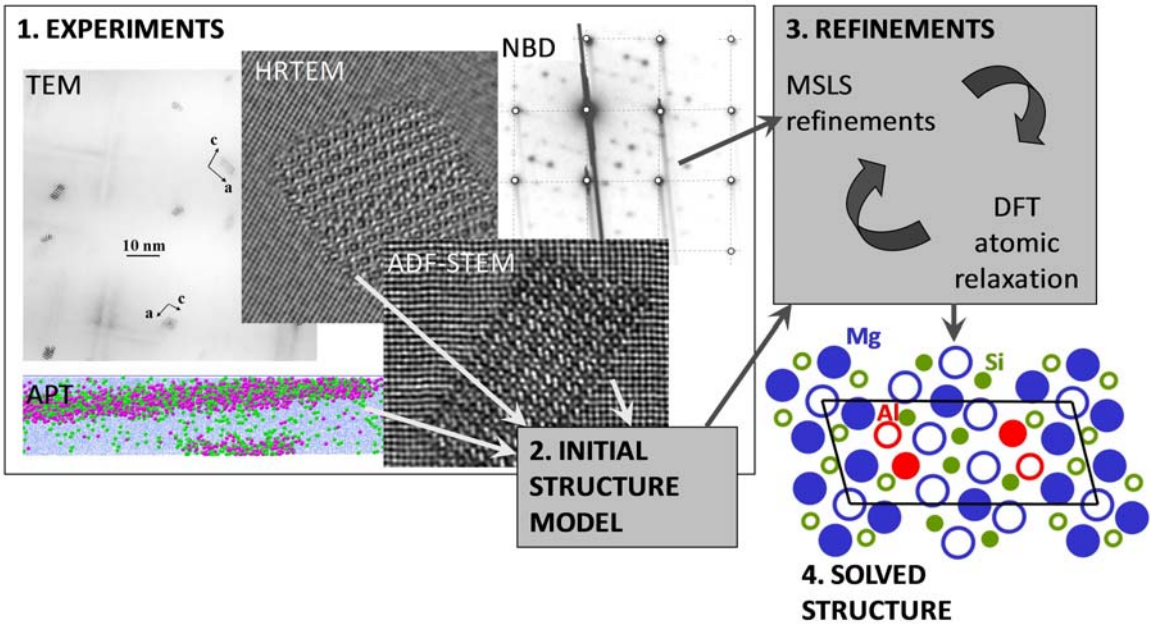

Figure 2. Overview of the methodology used to determine precipitate structures. Examples are shown for the main hardening phase β". Experiments (1) include medium magnification bright field TEM, HRTEM, APT, ADF-STEM and nano-beam diffraction (NBD). Theses are used to construct an initial structure model (2) as input to the quantitative refinements (3) where NBD intensities are used in a Multi Slice Lest Squares (MSLS) program and density functional theory (DFT) calculations are done in a self-consistent loop to solve the structure (4). Abbreviations not explained are given in the text.

In the early stages of clustering, when randomly distributed clusters have small sizes and are highly coherent with the face centred cubic (fcc) Al matrix, TEM based techniques have proven difficult. For Al-Mg-Si, even the exact pre-β" structure is still a matter of debate [1, 2]. Atom probe tomography (APT) [20], is a unique method enabling real-space mapping of atoms with near-atomic resolution, and it is superior in the characterization of small clusters and precipitates in metallic alloys [21]. 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. If precipitate compositional disorder is present, this will be most clearly revealed with APT [20]. Figure 2 shows an overview of the methodology.

2.2 Quantitative refinements

By combining some of the above-mentioned experimental techniques, good initial models of the precipitate atomic structures can be constructed. When possible, 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 squares (MSLS) method [22]. 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 electron diffraction patterns originating from different zone axes. In addition to atomic coordinate refinement, MSLS can also refine cell parameters, atomic occupancies and temperature factors. MSLS is presently an integrated part of our methodology [3-7,15]. However, since the MSLS program only optimizes a structure to fit experimental data, it needs to be verified whether or not the refined atomic structure has a favourable formation enthalpy. Also, precipitate compositional disorder can prove challenging, given the highly similar scattering cross sections of Al, Mg and Si.

First principles density functional theory (DFT) [23,24] based total energy calculations represent the selected complementary theoretical tool to MSLS for clarifying the structure and composition of the experimentally observed precipitates [3-7,15]. We generally employ the Vienna ab initio simulation package (VASP) [25], 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 can leave doubts with regards to the composition [15]. 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', as shown in figure 2, can fully clarify the precipitate structure. 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 [26-28].

As expected from the comparative dominance of bulk over interface energy contributions, bulk calculations do tend to get the relative stabilities of the phases qualitatively right [8]. However, we emphasize the crucial importance of experimental input for the theory: For Al-Mg-Ge, only some of the Al-Mg-Si precipitates remain stable according to experiment [29], whereas bulk calculations reveal no exclusion of any of these precipitates.

3. ADF-STEM on Cu-containing precipitates and the Si network

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 [14]. Here, the distribution of Cu-columns along

the needles' directions demonstrated that many of these precipitates had disordered structures. This, corroborated with the additional information provided by HRTEM images and NBD patterns enabled us to conclude that, as for the Al-Mg-Si system, the precipitates can be basically described as different arrangements of Al, Mg, Cu on a Si-network with projected hexagonal dimensions a = b ≈ 0.4 nm when viewed along the precipitates longest directions. A direct confirmation of this has been provided by aberration corrected ADF-STEM, where the Si atomic columns are clearly visible in Z-contrast. Figure 3 shows as example a partly disordered Q' precipitate image in aberration corrected ADF-STEM mode, with the Cu and Si atomic columns identified solely based on the Z-contrast information. The importance of ADF-STEM is of equal importance when studying alloys where Si is replaced with Ge [29].

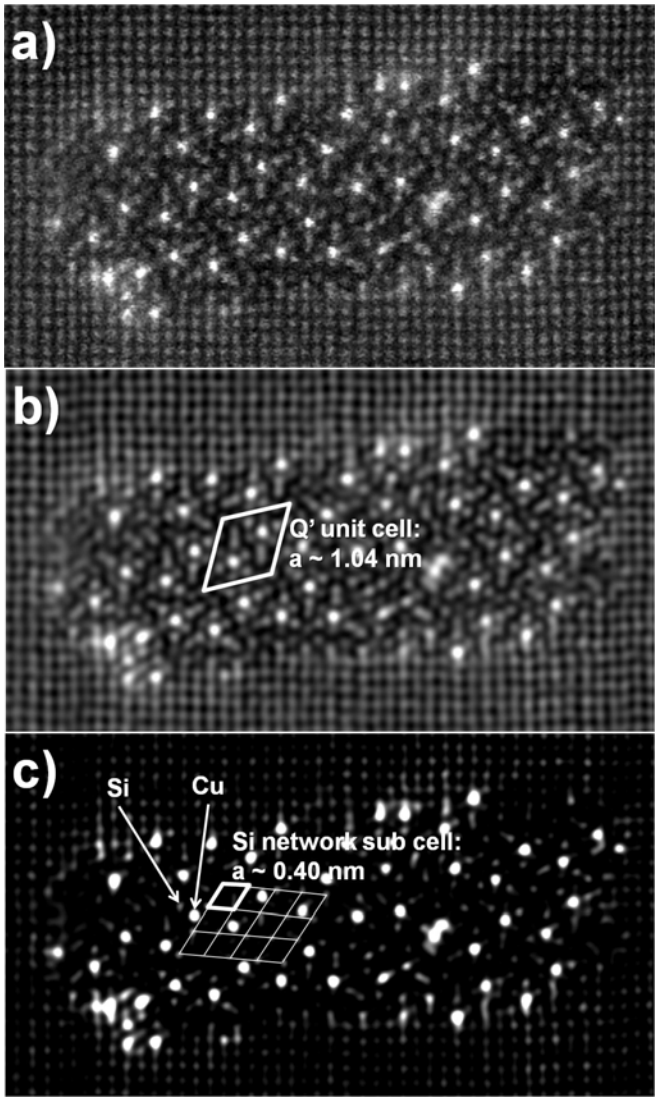

Figure 3. a) Unprocessed ADF-STEM image recorded along <001>Al of a partly disordered Q' precipitate viewed along its lath direction; b) Noise was removed by applying a band pass mask that removed all distances shorter than 0.17 nm. A Q' unit cell is marked; c) By enhancing contrast and reducing brightness of the image in b), the Cu and Si atomic columns inside the precipitate become visible, see arrows. The Si-network with projected hexagonal a = b ~ 0.4 nm is indicated.

4. Conclusions

Advances on optimizing alloy properties for specific purposes will increasingly be relying 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. This has revealed the existence of structural similarities between all metastable precipitates through a common Si network. ADF-STEM and NBD are central techniques in this

methodology, and probe Cs correction has proven extremely useful. Linking alloy composition and heat treatment with these results, 'alloy design' can be used to tailor materials with desired properties.

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