Disordered Precipitates in an Al-Mg-Si-Cu-Ag Alloy

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Precipitate types that form in an Mg-rich Al-Mg-Si-Cu alloy with 0.12 wt% Ag additions, during over-aging at 200°C, have been analysed by Annular Dark Field Scanning Transmission Electron Microscopy (ADF-STEM). It was found that most precipitates had lath morphology, with the long dimension along <001>Al and cross-sections along <100>Al. They have disordered crystal structures, with no unit cell present. The disorder can be explained as different arrangements of Al, Mg, Cu and Ag atoms on a common $a = b \approx 0.4$ nm hexagonal network defined by Si atomic columns as viewed along the laths longest directions. The base plane of the network is aligned along the <100>Al directions. Local ordered areas consistent with the hexagonal a = b = 1.04 nm, c = 0.405 nm Q'/Q phase and monoclinic a = 1.04 nm, b = 0.81 nm, c = 0.405 nm, $\gamma = 101^\circ$ C-plate phase exist on the Si network. The Ag additions therefore do not change the precipitation sequence in the analysed Al-Mg-Si-Cu alloy. The Cu atomic columns were found always to lie in-between the Si columns of the network, while Ag partly replaces Si. Both Cu and Ag atomic columns are centres of local symmetries in the crystal. The Ag atomic columns are preferentially found at the particle interfaces with the Al matrix, and do not seem to create any local periodic order.

Keywords: Annular Dark Field Scanning Transmission Electron Microscopy (ADF-STEM), Al-Mg-Si-Cu Alloys, Disordered Precipitates, Silicon Network.

1. Introduction

Al-Mg-Si alloys are a well-known group of age-hardening materials, with strength produced by the nucleation and growth in the Al matrix of a large number of nanometer-sized needle/lath/rod/plate -shaped metastable precipitates during aging. Factors like high strength to weight ratio, excellent formability, and a good corrosion resistance make these materials widely used as extruded goods, and are becoming increasingly attractive for the automotive industry.

Different heat treatments and alloy compositions produce different types of metastable precipitates, with different number densities, sizes and volume fractions. All these parameters have a direct influence on the mechanical properties. Therefore, for alloy development and industrial applications quantification of precipitates can be very important. Also, detailed atomic investigations of precipitate crystal structures give valuable fundamental information that may lead to developing tools for better alloy design.

It has been observed that when Cu is added to the Al-Mg-Si system the precipitation sequence changes from:

SSSS \rightarrow atomic clusters \rightarrow GP zones $\rightarrow \beta^{"} \rightarrow \beta^{"}, U1, U2, B' \rightarrow \beta/Si$, equilibrium (Al-Mg-Si system [1-5]) to:

SSSS \rightarrow atomic clusters \rightarrow GP zones $\rightarrow \beta$ ", L, S, QC $\rightarrow Q' \rightarrow Q$, equilibrium (Al-Mg-Si-Cu system [2, 6-9]).

SSSS stands for Super Saturated Solid Solution. The U1, U2 and B' phases are also known as Type A, Type B and Type C respectively [2]. By using a combination of experimental techniques such as High Resolution TEM (HRTEM), Nano-Beam Diffraction (NBD) together with the dedicated software MSLS (Multi Slice Least Square) [10] and first principles calculations by VASP [11], our group has solved the crystal structures of most metastable phases [9, 12-17]. It has emerged that although these phases have different symmetries, they are all based on a near-hexagonal network of Si atoms, with projected dimensions a = b \approx 0.4 nm in the precipitate cross-section plane [9, 15, 18]. The c axis of the network represents the main growth direction of all needle/lath/rod/plate -shaped metastable precipitates and is parallel and fully coherent with the <001>Al matrix directions. This means the network periodicity along c is an integer multiple of the Al lattice parameter, 0.405nm. The network is most distorted from the hexagonal symmetry in the case of β ", which is probably related to the high coherency this phase has with the Al matrix.

A particular type of precipitate (labelled L and S in the precipitation sequence) in quaternary Al-Mg-Si-Cu alloys was observed to consist of a disordered arrangement of Al, Mg and Cu atomic columns on the above-mentioned Si-network, as viewed along its c direction [9]. This conclusion was reached by analysing HRTEM images, NBD patterns and ADF-STEM images. However, although HRTEM images are capable of resolving smaller lattice spacings (smaller than 0.2 nm for a field emission TEM operated at 200kV without a Cs corrector), they do not provide good atomic number (Z) contrast and are less directly interpretable. The ADF-STEM technique offers better Z-contrast, but for a field emission TEM with no Cs corrector attaining a resolution better than 0.2 nm is difficult and the signal to noise ratio is low. With the development of Cs corrected TEM/STEM machines in the recent years, it has become possible to achieve spatial resolutions below 0.1 nm and Z-contrast with high signal to noise ratios in the ADF-STEM mode. One difficulty with the ADF-STEM technique is that image distortion can be introduced in the images if there is specimen drift during the acquisition.

The main goal of the present work is to investigate in detail the atomic structure of disordered precipitates in an Mg-rich Al-Mg-Si-Cu alloy with small Ag-additions. Images were acquired both with a conventional field emission instrument, and with a probe Cs-corrected TEM/STEM instrument. Studies have shown that Ag additions to the Al-Mg-Si system increase the overall hardness [19, 20], but little is yet known about the exact hardening mechanism and the location of Ag in the precipitate crystal structures.

2. Experimental

An Mg-rich Al-Mg-Si-Cu alloy with 0.12 wt% Ag additions was cast, homogenised 5 hours at 550°C and extruded into bars with 20 mm diameter round profile. The bars were cut into 120 mm long cylinders, given a solution heat treatment of 30 minutes at 530°C, water quenched, stored 4 hours at room temperature and aged 12 hours at 155°C. The resulting condition was further aged for 21 days at 200°C. All TEM analyses were performed in this final condition.

Specimens for TEM were prepared by electropolishing using a Tenupol 3 machine. The electrolyte consisted of 1/3 HNO₃ in methanol, used at temperatures between -20°C and -35°C.

ADF-STEM images were acquired with a JEOL 2010F TEM/STEM instrument (200 kV) using a 28 mrad inner collector angle and a 0.2 nm probe size. This collector angle is lower than for typical Z-contrast STEM imaging (> 50 mrad), but was proven to improve signal-to-noise ratio in precipitates [9]. ADF-STEM images were also acquired with a probe Cs-corrected FEI Titan 80-300ST TEM/STEM system operated at 300kV, with a 50 mrad collector angle and nominal 0.08 nm probe size.

Due to the typical morphologies and coherencies that the metastable precipitates have with the Al matrix, all micrographs presented in this work were acquired at the <001>Al zone axis.

3. Results and discussion

ADF-STEM images of representative precipitates found in the analysed condition, taken with the JEOL 2010F, are displayed in Fig. 1. The images show that although the atomic arrangement in these particles is complex, they can be classified as L precipitates [9, 17]: the Cu columns exhibit disorder, but regions with local order can be found, and correspond to the Cu-column positions of the hexagonal Q'-phase (a = b = 1.04 nm, c = 0.405nm), as shown in Fig. 1a, e, f, and to those of the monoclinic C-phase (a = 1.04 nm, b = 0.81 nm, c = 0.405 nm, $\gamma = 101^{\circ}$) as shown in Fig. 1c, d, f. It was demonstrated in [9] that the near-hexagonal Si-network of these precipitates, (with sub-cell a = b ≈ 0.4 nm, c = 0.405 nm), had one cell edge parallel to <100>Al. This also explains why the L-precipitate cross-section is elongated along <100>Al. Although the investigated alloy contains small amounts of Ag, this element seems to accumulate at particle interfaces, without any noticeable effect on precipitate type or crystal structure. The Ag enrichment is especially obvious at high strain locations, where the particles interface changes orientation with the Al matrix.



Fig. 1 Un-processed ADF-STEM images of precipitate cross-sections in the analysed condition, recorded with a JEOL 2010F. Only the Cu (Z = 29) and Ag (Z = 47) atomic columns can be resolved. All precipitates have various degrees of disorder. Local order that correspond to arrangements of Cu atomic columns in the hexagonal Q'-phase (a, e), monoclinic C-plate (c, d) and a combination of both (f), are observed. Some Cu columns are connected by overlaid dashed lines. Ag (with a stronger Z-contrast than Cu) seems to be present mainly at interfaces.

Although the strongest Z-contrast in Fig.1 is given by the Cu and Ag atomic columns, spots of lower intensity can also be observed, especially in Cu-free areas of the precipitates. To reduce noise, a Fourier filtered version of the image in Fig.1a is shown in Fig.2, obtained using a circular band pass mask that filtered out all spatial frequencies in the original image shorter than 0.3 nm. It can be observed that the weak intensities have near hexagonal $a = b \approx 0.4$ nm symmetry, which corresponds to the Si-network and shows that Si (Z = 14) atomic columns can be resolved in such images. The

Cu-columns appear with a triangular shape because the resolution in the image is too low to separate them from the three neighbouring Si columns. The Mg (Z = 12) and the Al (Z = 13) atomic columns are not visible in these Z-contrast images.



Fig. 2 The precipitate in Fig.1a after Fourier filtering to remove periods shorter than 0.3 nm. The Si-network with a near-hexagonal $a = b \approx 0.4$ nm sub-cell is observed to be present across the whole particle. Three such sub-cells are indicated (white diamonds). Arrows indicate one Cu atomic column (dotted), and one Ag atomic column (full) at the interface. The right-hand dotted lines connect a few Cu columns that are arranged in a Q' configuration.

Fig. 3 is an ADF-STEM image using a TITAN probe Cs-corrected microscope that shows a part of a similar precipitate to that in Fig. 2. The improved spatial resolution and signal-to-noise ratio with this microscope make all atomic columns of the precipitate and matrix visible. The Z-contrast information contained in the image facilitates the identification of Ag, Cu and Si atomic columns. Unfortunately, the difference in Z contrast between Al and Mg atomic columns is still not sufficient to discriminate between these elements. Analysis of several precipitates imaged in this way confirmed the previous interpretation of these structures; they all consist of a disordered arrangement of Al, Mg and Cu atomic columns on an ordered near-hexagonal Si-network with sub-cell dimensions $a = b \approx 0.4$ nm [9]. The network is clearly resolved in ADF-STEM images (see Fig. 3c, e as an example). Areas of local order, corresponding to the phases Q' and C [9, 17], can often be found in these precipitates. The present work also shows that low Ag additions to this system do not change the precipitate sequence. For the most part Ag accumulates preferentially at precipitate interfaces although some Ag atoms are clearly present in the interior of the precipitates. As a rule, here Ag replaces Si atoms in the network. This is opposed to Cu, which is always observed in-between the Si network columns (see Fig. 3c, d, e, f). Both Ag and Cu atomic columns clearly vary in intensities over the ADF-STEM images. This probably relates to varying occupancies of Ag and Cu in these columns. Moreover, there is a variation in the contrast (and position) of the columns around the Cu columns so they have a 'cluster-like' appearance with high (local) symmetry. The same applies around Ag on the Si-network, but the resulting 'cluster' differs from that of Cu (see Fig. 3f). Based on these considerations, the Q/Q' and C-plate phases can be described as different orderings of similar Cu 'clusters'. The Ag 'cluster' was not observed to create any local periodic order.

4. Conclusions

ADF-STEM is a very powerful imaging technique for studying precipitation in alloys. In the case of probe Cs-corrected machines, it provides both good spatial resolution and Z-contrast. After analysis, the Si-network, which previously has been demonstrated to be a common structural basis element in all precipitates of the Al-Mg-Si-(Cu) alloys, could be directly visualized. The disordered arrangements of Al, Mg, Cu atomic columns on this network, previously observed in precipitates formed in Al-Mg-Si-Cu alloys [9], was further confirmed. It was shown that small Ag additions did not change the precipitation sequence. Ag accumulates mainly at the precipitate/Al interfaces. A smaller fraction of Ag-atoms can enter into the precipitate replacing Si columns of the Si network. Ag appears to have varying occupancy in such columns. This is the only element so far observed to reside on Si-network positions. Cu is always observed in-between the Si columns. Both Ag and Cu columns create their own local symmetries in the precipitate structures.



Fig. 3 a) Unprocessed ADF-STEM image taken with a probe Cs-corrected Titan; b) As a) but Fourier filtered to reduce noise using a circular band pass mask that excluded all periods shorter than 0.17 nm; c) Simple manipulation of image in b), by increasing contrast and reducing brightness and gamma in order to better visualize atomic column Z-contrast; d) Full circles: Ag columns, dashed circles: Cu columns. Cu columns in local Q' atomic configuration are connected by continuous lines; e) Full circles: Si columns. One Si-network sub-cell is indicated with full lines; f) Specific local symmetries around Ag and Cu columns. The Si columns belonging to these symmetries are indicated by 'X', and the Al, Mg, or mixed Al-Mg columns are indicated by 'O'. The projected separation of the Si atomic columns is ~0.4 nm. In images d, e, f the different atomic columns are indicated as viewed in projection, disregarding the atomic heights.

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6. References

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