Quantitative HAADF STEM study of β’-like precipitates in an Al-Mg-Ge alloy

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Abstract. Precipitates in an Al-Mg-Ge alloy similar to the β’ phase in Al-Mg-Si alloys were investigated using quantitative aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM). Quantitative investigation into the Ge-rich columns of the precipitates found the intensity of these columns to be consistent with an Al concentration of 30±10 %, or a vacancy concentration of 20±10 %. Possible errors involved in the determination of the column composition are discussed.

1. Introduction

Al-Mg-Si alloys are an industrially important group of materials due to their high strength-to-weight ratio, formability, and resistance to corrosion. These alloys get their strength from the formation of nanometre-sized, metastable precipitates during heat treatment. One of the precipitate phases that form is known as β’ [1]. A phase similar to β’ also forms in Al-Mg-Ge alloys [2-3].

In the present study, the β’-like precipitates (henceforth referred to as β’-Ge) that occur in the Mg-rich Al-Mg-Ge alloy in [2], have been investigated using quantitative high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM). The hexagonal β’-Ge phase precipitates as needles with the hexagonal axis parallel to the needle direction and a <001>Al direction. The precipitate is fully coherent with the matrix along this direction.

β’-Ge precipitates are well-suited for HAADF STEM because of the considerable atomic number difference between Ge (Z=32), and Mg (Z=12) and Al (Z=13). Here, we use quantitative HAADF STEM to estimate the composition of Ge-rich columns. This technique has recently been used to determine the structure of the T1 precipitate phase in Al-Li-Cu alloys [4].

2. Methods

An Al-0.87Mg-0.43Ge (at. %) alloy was cast and homogenized for 4 hours at 550 °C, before extrusion. The alloy was then solution heat treated for 2 hours at 600 °C, water quenched to room temperature and held for 4 hours at this temperature. The alloy was subsequently aged at 250 °C for 5
hours before water quenching to room temperature. TEM samples were prepared by twin-jet electropolishing with a 33% nitric acid / 67% methanol solution at -25°C with a voltage of 14 V. The data was acquired on a double aberration-corrected FEI Titan™ 80-300 FEG-TEM operating at 300 kV.

The response of the detector was measured by scanning the focused STEM probe across the detector. The acquired HAADF STEM images were normalized to obtain the intensity $I_{\text{norm}}$ from the raw intensity, $I_{\text{raw}}$, using the equation $I_{\text{norm}} = (I_{\text{raw}} - I_{\text{vac}})/(I_{\text{det}} - I_{\text{vac}})$, where $I_{\text{vac}}$ is the intensity measured when there is no scattering to the detector, and $I_{\text{det}}$ is the average intensity when the probe is placed on the detector. The thickness of the specimen in the vicinity of each precipitate was determined using convergent-beam electron diffraction (CBED) patterns of the Al matrix. Using CBED means that the determined thickness does not include the thickness of any amorphous layers, unlike when using electron energy-loss spectroscopy. The probe was scanned over an area corresponding to several unit cells in order to remove coherent effects, resulting in a position-averaged CBED pattern [5]. A smaller condenser aperture was used for CBED in order to reduce the amount of overlap between discs. The thickness was determined by comparing the acquired CBED pattern with CBED patterns simulated using JEMS [6]. The accuracy of the method was estimated to be ±2 nm.

STEM images were simulated using the multislice program stemimg [7], using the following parameters: convergence semi-angle: 18 mrad, HAADF detector: 59-200 mrad. The supercell used for aluminium was 3.24 x 3.24 nm², with a slice thickness of 0.2025 nm. The supercell used for β’-Ge was 2.86 x 2.48 nm², with the same slice thickness. A STEM image was calculated every two slices. 8 frozen phonon configurations were averaged over for each simulation, which should be more than enough for the thicknesses considered here since a different phonon configuration is calculated for each slice. Partial occupancy was implemented by using a random-number generator when creating each slice so that each atomic site was either fully occupied or empty. Temperature factors for the elemental phases at 300 K were used [8].

Due to amorphous layers on the surface of the specimen, the average intensity measured in the Al matrix was consistently greater than in simulations of the Al matrix for the thickness determined from CBED. To reduce the effect of the amorphous layers, this intensity difference was subtracted from the normalized experimental image [4].

The effective source size, which can have a significant effect on peak intensities, was determined for each image by matching simulated images of aluminium for different Gaussian source sizes to the acquired images. Line profiles were used in order to fit both the peaks and the background. The effective source size was found to lie between 0.10 nm and 0.13 nm full-width at half maximum (FWHM).

Once the effective source size had been determined using the Al matrix, the intensities of many Ge-rich columns and Al matrix columns in each acquired image were determined by measuring the average intensity within a circle of radius 76 pm, 68 pm, and 59 pm, for corner Ge-rich columns, interior Ge-rich columns, and Al matrix columns, respectively. The circle was shifted around in order to find the maximum average intensity for each column. The radius of the circle was chosen large enough to reduce the effect of a finite source size, but small enough to limit the intensity contribution from neighbouring columns. Columns close to the precipitate/matrix interface were not used. The same method was applied to simulated images of β’-Ge for different compositions of the Ge-rich columns and of Al.

3. Results

A HAADF STEM image of a β’-Ge precipitate viewed in a <001>Al zone axis is shown in figure 1. The structural similarity with the model of β’-Si shown in the figure is clear. In the c-direction, the repeat distance is 1.215 nm. In the corner Si column in β’-Si, there are 4 Si sites per repeat distance, while in the interior Si columns, there are only 3. This difference in occupancy between the corner and the interior columns is clear in the β’-Ge precipitate as well.

A position-averaged CBED pattern was acquired near the precipitate in figure 1. Comparison with simulated CBED patterns for aluminium gave a thickness of 50±2 nm. A line profile through a part of
the Al matrix was used to determine the effective source size. The best match was found to be a source size of 0.11 nm FWHM.

Measurement of the column intensities of corner and interior Ge-rich columns in this precipitate as well as 20 other precipitates showed that these were considerably lower than the expected intensity if the Ge-rich columns were fully occupied. Two types of modification of the Ge sites were therefore considered in order to get a match between simulation and experiment. The first kind consisted of replacing some of the Ge with Al. In the second kind, Ge was replaced by vacancies. These replacements were done by making all the Ge sites partially occupied, that is, the Al atoms or vacancies were distributed randomly on Ge sites throughout the crystal.

In order to reduce the effect of the source size, we plot the ratio of the Ge-column to matrix-column intensities as a function of thickness for the 21 precipitates considered (figure 2). Comparing the experimental data points with simulations, it can be seen that for both corner and interior Ge columns, the experimental data corresponds to an Al concentration of roughly 30±10 %. Simulations where Ge was replaced by vacancies (not shown), gave a vacancy concentration of 20±10 %.

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**Figure 1.** Quantitative HAADF STEM image of a β'-Ge precipitate. The hexagonal unit cell is indicated with white lines. The dimmer Mg atoms are arranged hexagonally around the corner Ge-rich columns, and triangularly around the interior Ge-rich columns, just as in the model of β'-Si shown in the lower left corner. The Si atoms are black and the Mg atoms are white in the model.

**Figure 2.** Plot of Ge peak/Al peak ratio as a function of thickness, \( t \), for the corner Ge-rich columns (left) and interior Ge-rich columns (right). Each experimental data point corresponds to one image. The simulated peak ratios are for a source size of 0.10 nm FWHM.
4. Discussion
The measured Ge composition of the Ge-rich columns in $\beta'$-Ge is significantly lower than the Si composition of corresponding Si columns of $\beta'$ in Al-Mg-Si alloys. It was not possible in this work to distinguish between a replacement of Ge atoms with Al, or a smaller amount of vacancies. It is possible that the Ge columns contain both Al and vacancies.

The fact that the precipitates are embedded in the matrix presents a challenge as it is crucial that the precipitates and the surrounding matrix are equally thick. It is simple to check that the precipitate and matrix are at the same height at the entrance surface, but this is not possible at the exit surface. The composition for several precipitates and for different specimen thicknesses was therefore determined in order to verify the results. The results show a fair amount of variation in the composition. This is probably due to measurement errors, but it could also be partly due to compositional variations among the precipitates.

Other possible sources of error include errors in the determination of the CBED thickness and the detector inner angle, non-uniformities in the detector response, and also the presence of an oxide layer and contamination on the entrance surface of the specimen. Simulations of the first two errors suggest that their effect would be small. Non-uniformities in the detector response could affect the results. However, the uniformity as determined from the detector image was very good except for a dip at one side for low angles. The non-uniformity should therefore only have a small effect on the result, also because ratios of column intensities were considered. An amorphous layer on the specimen surface might modify the column intensity, but the effect of this is partly taken into account by determining the effective source size from the matrix surrounding the precipitate.

The precision of this result was estimated by investigating the sensitivity of the composition to errors in thickness measurement in the following two ways. The effect of an error in the thickness measurement of the matrix, with the precipitate having the same thickness, can be assessed from the column intensity ratio plot in figure 2: Because the slope of the curves is not very steep, an error in the thickness measurement of a few nanometres would have only a small effect. A precipitate that is shorter than the matrix thickness would have a more serious effect on the calculated composition. This could happen if the specimen preparation preferentially attacked the precipitates. This was rarely observed at the entrance surface since the precipitate and surrounding matrix could in most cases be focused at the same time, and such an effect is therefore unlikely to have caused a systematic error.

5. Conclusions
$\beta'$-Ge precipitates in an Al-Mg-Ge alloy were investigated using aberration-corrected HAADF STEM. The composition of columns in $\beta'$-Ge precipitates thought to consist of Ge was investigated using quantitative aberration-corrected HAADF STEM. The intensity of the Ge columns was found to be consistent with an Al content of 30±10 %, or a vacancy concentration of 20±10 %.

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References
[1] Vissers R et al. 2007 Acta Mater. 55 3815–23
[2] Bjørge R et al. 2010 Metall. Mater. Trans. A 41 1907–16
[3] Bjørge R et al. 2011 Acta Mater. 59 6103
[4] Dwyer C, Weyland M, Chang L Y and Muddle B C 2011 Appl. Phys. Lett. 98 201909
[5] LeBeau J M, Findlay S D, Allen L J and Stemmer S 2010 Ultramicroscopy 110 118–25
[6] Stadelmann P A 1987 Ultramicroscopy 21 131–45
[7] Dwyer C 2010 Ultramicroscopy 110 195–8
[8] Gao H X and Peng L M 1999 Acta Cryst. A 55 926–32