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Aberration-corrected scanning transmission electron microscopy 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 qualitative and quantitative aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM). The needle-shaped β′-Ge precipitates are coherent with the Al matrix along the needle direction which is parallel to a $\langle 0\,0\,1\rangle_{Al}$ direction, as well as one direction in the cross-section plane that is parallel to a $\langle 1\,0\,0\rangle_{Al}$ direction. This is linked to a smaller lattice parameter in the needle cross-section plane than that of coarser, less coherent β′ precipitates in Al–Mg–Si alloys, despite Ge having a larger atomic radius than Si. Quantitative HAADF STEM results show that the nominal Ge columns of the β′-Ge precipitates are not fully occupied by Ge, the intensity of these columns being consistent with an Al concentration of $30 \pm 10\%$, or a vacancy concentration of $20 \pm 10\%$. The coherent interface is atomically smooth, but with matrix columns containing Ge spaced periodically along the interface.

Keywords: Aluminium alloys; Precipitation; High angle annular dark field; Scanning transmission electron microscopy

1. Introduction

Al–Mg–Si alloys are an industrially important group of materials due to their high strength to weight ratios, formability, and resistance to corrosion. These alloys have found increased use as extruded profiles in construction and automotive applications. The alloys get their strength from the formation of nanometer-sized metastable precipitates during heat treatment. The precipitates most important at peak hardness are GP zones and β″ [1,2]. Upon overageing other metastable precipitates, known as β′, U1, U2, and B′, may form, depending on the alloy composition and heat treatment [3–6].

When Si is replaced by Ge in these alloys, no β″ phase is observed, perhaps due to the high degree of coherency this phase has with the matrix in Al–Mg–Si alloys [2]. Instead, phases similar to β′ and U1 appear close to peak hardness, as well as disordered precipitates [7,8]. The β′- and U1-like precipitates are finer and more coherent than their counterparts in the Al–Mg–Si alloy system, resulting in a similar hardness as in comparable Al–Mg–Si alloys [7].

To further investigate the β′-like precipitates (henceforth referred to as β′-Ge) that occur in the Mg–rich Al–Mg–Ge alloy of Bjørge et al. [7] these precipitates have in the present work been studied using aberration-corrected high angle annular dark field scanning transmission electron microscopy (HAADF STEM). The β′ structure, as determined in Al–Mg–Si alloys, is hexagonal with space group $P6_3/m$ and lattice parameters $a = 0.715$ nm,

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$c = 1.215$ nm, $\gamma = 120°$ [3]. The precipitate is needle-shaped with the c-axis parallel to the needle direction and a $\langle 0\,0\,1\rangle_{Al}$ direction. The precipitate is coherent with the matrix along this direction, with $c = 3a_{Al}$.

The β′-Ge precipitates are well suited to HAADF STEM because of the considerable atomic number difference between Ge ($Z = 32$) and Mg ($Z = 12$) and Al ($Z = 13$). Aberration-corrected HAADF STEM has enabled new insights into the nucleation, structure and growth kinetics of precipitates in light alloys [9–12]. In the present study we use quantitative HAADF STEM to estimate the composition of the Ge columns. Quantitative HAADF STEM relies on the incoherent nature of the HAADF STEM image, with intensity maxima corresponding to atomic column positions, as well as measurement of the HAADF detector response to allow quantitative comparisons between experimental and simulated images [13]. This technique has been applied to various materials such as $SrTiO_3$ [14], $PbWO_4$ [15], $Al_xGa_{1-x}N/GaN$ [16] and α-$Zn_7Sb_2O_{12}$ [17]. Recently it has also been used to determine the structure of the T_1 precipitate in Al–Li–Cu alloys [10].

2. Methods

An Al–0.87Mg–0.43Ge (at.%) alloy was cast and homogenized for 4 h at 550 °C before extrusion. The alloy was then solution heat treated for 2 h at 600 °C, water quenched to room temperature and held for 4 h at this temperature. The alloy was subsequently aged at 250 °C for 5 h before water quenching to room temperature, resulting in an overaged condition with large β′ precipitates. Transmission electron microscopy (TEM) samples were prepared by twin jet electropolishing with a 33% nitric acid/67% methanol solution at −25 °C and a voltage of 14 V. The STEM data was acquired over several days in an FEI Titan^3 80-300 FEG-TEM operating at 300 keV and equipped with aberration correctors (CEOS GmbH) for both the probe forming and image forming lenses. The STEM convergence semi-angle was 18.0 mrad.

In order to enable quantification of STEM images the response of the detector was characterised by scanning the focused STEM probe across the detector, forming an image of the detector. The brightness and contrast settings of the detector were then adjusted so that the minimum and maximum intensities were within the linear region of the detector. The acquired HAADF STEM images were normalized using the equation $I_{norm} = (I_{raw} - I_{vac})/(I_{det} - I_{vac})$, where I_{norm} is the normalized intensity, I_{raw} is the raw image intensity, I_{vac} is the intensity measured when the probe goes through the hole of the detector and I_{det} is the average intensity of the detector in the detector image. The HAADF detector inner angle of 59 mrad was determined from the detector image and not the shadow of the detector, thus ensuring that the inner angle corresponds to the edge of the scintillating material. The outer angle of the detector is determined by a fixed aperture, and not the detector itself. The outer angle was measured to be approximately 200 mrad.

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 on the top and the bottom of the TEM sample. These are included 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 [18]. 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 [19]. The accuracy of the method was estimated to be ±2 nm.

STEM images were simulated with the frozen phonon multislice program *Stemimg* [20], using a convergence semi-angle of 18 mrad and a HAADF detector from 59 to 200 mrad. The supercell used for aluminium was 3.24×3.24 nm^2, with a slice thickness of 0.2025 nm. The simulated β′-Ge structure was identical to the structure of β′ but with Ge replacing Si. The supercell used for β′-Ge was 2.86×2.48 nm^2, with a slice thickness of 0.2025 nm. A 1024×1024 pixel sampling mesh was used in both cases. A STEM image was calculated every two slices. Each simulation was averaged over eight frozen phonon configurations, which should be enough for the thicknesses considered here since a different phonon configuration is calculated for each slice. Partially occupied atomic sites were replaced by a fully occupied site or a vacancy when generating the projected potentials using a random number generator. Temperature factors for the elemental phases at 300 K were used. These were 0.0083, 0.0188 and 0.0063 nm^2 for Al, Mg and Ge, respectively [21].

The average intensity measured in the Al matrix was consistently higher than in simulations of the Al matrix for the thickness determined from CBED. As a reactive metal Al will always form a native oxide layer, and scattering from layers on the surfaces of the specimen were assumed to be responsible for this intensity increase. To reduce this effect the intensity difference was subtracted from each normalized experimental image [10].

The effective source size, which has a significant effect on peak intensities [22], 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 vary from 0.10 to 0.13 nm full-width at half maximum (FWHM).

Once the effective source size had been determined using the Al matrix experimental images could be compared with simulated images for different compositions using the thickness measured by CBED. This was done using line profiles and by measuring the column intensities. The column intensities were determined by measuring the average