Structural investigation of precipitates with Cu and Zn atomic columns in Al-Mg-Si alloys by aberration-corrected HAADF-STEM

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Takeshi Saito[1], Calin D. Marioara[2], Sigmund J. Andersen[2], Williams Lefebvre[3] and Randi Holmestad[1]

[1]Department of Physics, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway
[2]SINTEF Materials and Chemistry, 7465 Trondheim, Norway
[3]GPM, Université de Rouen, 76801 Saint Etienne du Rouvray, France

Email: takeshi.saito@ntnu.no

Abstract. Precipitates in Al-Mg-Si alloys with Cu addition (~0.1 wt%) and Zn addition (~1 wt%) were investigated by aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Most precipitates had no overall unit cell but contained ordered network of Si atomic columns for both the Cu and the Zn containing precipitates. It was found that both Cu and Zn atomic columns are located at specific sites and producing characteristic local configurations on the Si atomic columns.

1. Introduction

Al-Mg-Si alloys (i.e. 6xxx series) are important structural materials characterized by formation of high number density of nano-sized metastable precipitates. The strength in these alloys is achieved by precipitates setting up a surrounding strain fields, which prevent dislocation movements. There are several types of metastable precipitates in the alloy depending on the composition and thermo-mechanical processing. In the Al-Mg-Si alloy system, all precipitates are needle/rod/lath-like with main growth direction along <100> Al. In recent years, their crystal structures have been investigated in details by transmission electron microscopy (TEM) [1-8]. All metastable precipitates in Al-Mg-Si alloys are structurally connected via a network of Si atomic columns (Si-network) with hexagonal projected symmetry along needle growth direction [7, 9].

Influences of additional alloying elements on the Al-Mg-Si alloys are of interest as they affect the precipitate structure and consequently the mechanical properties. For instance, an addition of ~0.4 wt% Cu drastically alters the precipitation sequence [9-12]. Although Cu often makes the precipitates disordered, it does not break up the Si-network. The Cu atomic columns resides in specific local atomic configurations connected with the Si-network [13]. Zn is one of the main alloying elements in a different family of aluminum alloy (i.e. 7xxx series) and forms different types of metastable precipitates together with Mg. Our interest here concerns how Cu and Zn atoms interact with Mg and/or Si in forming precipitates, especially what atomic sites they take in the Al-Mg-Si alloys. In order to investigate the atomic structure of the precipitates, aberration corrected TEM plays an important role. High angle annular dark field scanning TEM (HAADF-STEM) has distinctive advantages since it provides atomic number (Z) contrast intensity, namely it is possible to distinguish

Cu (Z_{Cu} = 29) and Zn (Z_{Zn} = 30) atomic columns from Al (Z_{Al} = 13), Mg (Z_{Mg} = 12) and Si (Z_{Si} = 14) columns in the precipitates. In the present study, the structures of Cu and Zn atomic columns in precipitates in the Al-Mg-Si alloy system have been investigated by aberration-corrected HAADF-STEM.

2. Experimental procedure

Two Al-0.47Mg-0.42Si (wt%) alloys were prepared by extrusion from cast billets; one added 0.1 wt% Cu and the other added 1 wt% Zn. The Cu-added alloy was solution heat treated at 545°C for 5 minutes, kept 30 minutes at room temperature and isothermally heat treated at 190°C for 300 minutes. The Zn-added alloy was solution heat treated at 540°C for 60 minutes, kept 240 minutes at room temperature and isothermally heat treated at 185°C for 720 minutes. The final microstructures correspond to peak hardness condition. STEM specimens were prepared by electro polishing using a Tenupol 5 machine (Struers) on transversal slices along the extrusion direction. The electrolyte consisted of 1/3 vol% HNO_3 in methanol, and the solution was kept at a temperature between -20°C and -35°C.

The HAADF-STEM images were taken by a spherical aberration probe corrected JEOL ARM200F equipped with a Schottky field emitter operated at 200kV. The probe diameter was 0.1 nm and the collection angle of the HAADF detector was in the range of 45-150 mrad. All specimens were ion-milled by precision ion polishing system (PIPS Gatan) and plasma cleaned by plasma cleaner (SOLARUS Gatan) before the HAADF-STEM observation in order to minimise contamination on the specimens during the observation.

3. Results and discussion

All presented HAADF-STEM images have <001>Al orientation, namely along the precipitates needle growing direction, thus corresponding to the cross section of the precipitates. Projected positions of all atomic columns could be resolved in the structure owing to the high resolution of aberration-corrected HAADF-STEM. Based on Z contrast, Cu and Zn atomic columns could be identified even in the unprocessed HAADF-STEM images. Fast Fourier transform (FFT) filtering was applied to reduce noise using a circular band pass mask that removed all period shorter than 0.15 nm. After filtering the images, low contrast Si atomic columns could also be identified, as distinguished from those Al and Mg columns. Local symmetries with known structures have also been employed to identify the different atomic columns. The atomic overlays presented in figure 1 were readily determined by the method described. Figure 1 shows one of the Cu-containing precipitates consisting of perfect β" and a disordered part in the same precipitate needle (β"/disordered precipitate in [13]). In this image, the periodicity of the perfect β" part is easily identified (left side of the precipitate) while there is no clear periodicity in the disordered part. Bright spots, representing Cu atomic columns, are distinguished only in the disordered part and interface, but not in perfect β" part. However, the disordered part consists of ordered Si-network [13]. Although Cu atomic columns at the interface appear in a less systematic manner (as some take Al fcc positions), in the bulk structure they are consistently were identified with two specific configurations on the Si-network; these are *replacing the Si-network columns* and *in-between the Si-network columns*, see figure 1 (b) and (c). Note that the first case resembled the local configuration of the Cu atomic columns in β'_{Ag} phase [14] and the second case in the Q' phase [15]. In the first case Cu atomic columns are located precisely in Ag positions. Apart from this the local surrounding column symmetry is similar. It is worth mentioning that both atomic configurations have a 3-fold rotational symmetry around the Cu atomic column in this projection. In the Zn-containing precipitates, shown in figure 2, Zn atomic columns appear evenly in the bulk structure and interface. It is interesting to note that the two specific configurations as observed in Cu-containing precipitates, were also observed in a Zn-containing precipitate, see figure 2. In addition, the Zn atomic columns reside also in a disordered part. This indicates that Zn may also have an effect on nucleation and precipitation in the Al-Mg-Si alloys in a similar manner as Cu. Further analysis and investigations will be published elsewhere.

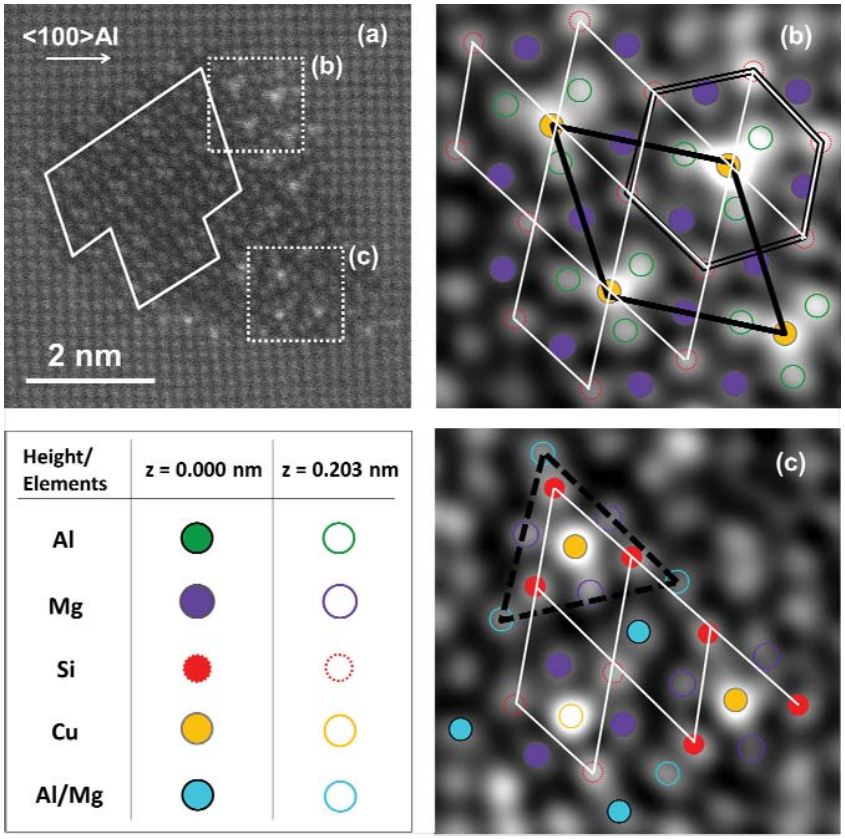

Figure 1. HAADF-STEM image of cross-section of one of Cu-containing precipitates (β"/disordered precipitate) taken along <001>Al. (a) unprocessed image with ordered β" part (white solid line) and two disordered part (b, c) (dotted line squares). (b, c) magnified and inverse FFT filtered disordered parts with hexagonal Si-network indicated (thin white lines). Legend is shown on lower left side. Different Cu atomic columns are shown with Si-network columns; these are (b) *replacing the Si-network columns* marked with black double lines and (c) *in-between the Si-network columns* marked with black thick dashed line. In (b), one unit cell of β'_{Ag} phase having Cu in the Ag site, is indicated with black solid line.

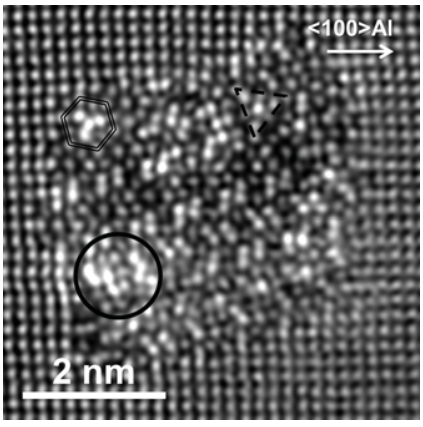

Figure 2. Inverse FFT filtered HAADF-STEM image of a Zn-containing precipitate cross-section taken along <001>Al. Local atomic configurations as in (b) and (c) in figure 1, but with Zn instead of Cu are indicated (hexagon and triangle). An area with disordered Zn distribution is marked by black solid line circle.

4. Conclusions

The Cu and Zn atomic columns in Al-Mg-Si alloys with respective Cu and Zn additions were investigated by aberration corrected HAADF-STEM. Results revealed that although most precipitates lack an overall periodicity, Cu and Zn columns form similar and specific local symmetries connected with the Si-network. Cu and Zn atomic columns were observed also on Al fcc positions in the precipitate/matrix interface. The results suggest that Cu and Zn atoms can have a considerable influence on precipitation in Al-Mg-Si alloys.

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