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The Effect of Ag Addition on Transition of Crystal Structure for β'-phase in Al-Mg-Si Alloy

Junya Nakamura[1], Kenji Matsuda[2*], Tatsuo Sato[3], Calin.D. Marioara[4], Sigmund.J. Andersen[4], Randi. Holmestad[5] and Susumu Ikeno[2]

[1]Graduate School of Science and Engineering for Education, University of Toyama, Gofuku, Toyama, Japan

[2]Graduate School of Science and Engineering for Research, University of Toyama, Gofuku, Toyama, Japan

[3]Graduate School of Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552, Japan

[4]SINTEF Materials and Chemistry, Strindveien 4, 7465 Trondheim, Norway

[5]Department of Physics, Norwegian University of Science and Technology, Høgskoleringen 1, 7491 Trondheim, Norway

*corresponding author: matsuda@eng.u-toyama.ac.jp

In the present work, β' phase in alloys Al -1.0 mass% Mg_2Si -0.5 mass% Ag (Ag-addition) and Al -1.0 mass% Mg_2Si (base) were investigated by high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), in order to understand the effect of Ag. The β' phase is rod-shaped; with longest directions parallel to <001>Al. HRTEM images and SAED patterns recorded along these directions were similar for the β' phase in both alloys. The unit cell of β'-phase in Ag-addition alloy is hexagonal with the same c-axis dimension as the Ag-free β', but with shorter a-axis. Ag was found in the composition of the rod-shaped precipitates in Ag-addition alloy by energy dispersive X-ray spectroscopy (EDS). In addition, the distribution of Ag was investigated by energy filtered mapping and high annular angular dark field scanning transmission electron microscopy (HAADF-STEM). One Ag-containing atomic column was observed per β' unit cell, and the unit cell symmetry is slightly changed as compared with the Ag-free β'. The Ag-containing β' rods have complicated domain structures. The interfaces of these particles are enriched with Ag atoms that occupy lattice positions on the Al matrix. The occupancy of the Ag-containing atomic columns seem to vary both inside particles, as well as at the interfaces.

Keywords: *Aluminum-Magnesium-Silicon alloy, precipitate, Ag addition, β'-phase, crystal structure, High-Resolution Transmission Electron Microscope, High-Angle-Annular-Dark-Field Scanning Transmission Electron Microscope* .

1. Introduction

The modification of the uniform tensile elongation and the increase of the age-hardening rate in Ag-addition Al-Mg-Si alloys have been reported [1-3], although the crystal structure and the chemical composition of the metastable phase in these alloys are not yet understood clearly [4]. The β'-phase in the alloys Al -1.0 mass% Mg_2Si -0.5 mass% Ag (Ag-addition alloy) and Al -1.0 mass% Mg_2Si (base alloy) was observed by using HRTEM and electron diffraction technique in the present work to clarify the effect of Ag on its crystal structure. Rod-shaped precipitates in the Ag-addition alloy were observed along <100>Al directions, which was similar to the observation in previous work on the base alloy. HRTEM images and SAED patterns of the rod-shaped precipitates were similar to those taken from the β'-phase in the base alloy. Previously, we have reported the crystal structure of the β'-phase in the Ag-addition alloy as hexagonal, with unchanged c-axis but shorter a-axis as compared to the Ag-free alloy [5-7]. Ag was detected in the rod-shaped precipitates in Ag-addition

alloy by EDS analysis [5-7]. In addition, the distribution of Ag was observed by using energy filtered mapping and HAADF-STEM image. Ag was observed on the interface between the matrix and the precipitate, as well as inside precipitates. According to our analysis of HRTEM images, SAED patterns and HAADF-STEM images a more complicated crystal lattice made of distorted hexagons is proposed in this paper.

2. Experimental procedure

Al -1.0 mass% Mg_2Si -0.5 mass% Ag (Al- 0.63 at.%Mg – 0.37 at.% Si- 0.12 at.% Ag, (Ag-addition)) alloy was prepared using 99.99% purity Al, 99.9% purity Mg, Si and Ag metals. The ingot obtained was hot- and cold- rolled to 0.2 mm thick sheets, heat treated at 873 K for 3.6 ks, and then quenched into chilled water at 273 K. These sheets were overaged at 523 K for 120 ks in a salt bath or 423 K for 12 Ms in an oil bath. Thin foils for TEM observation were made by a conventional electrolytic polishing technique using a solution of ethanol (9 parts) and perchloric acid (1 part). HRTEM (Topcon EM-002B) with EDS was operated at 120 or 200 kV. Also, HRTEM was performed using a JEOL 4010T instrument operated at 400 kV, and chemical analysis of precipitates was performed by EDS. The HAADF images were obtained by using two Cs probe corrected field emission gun STEM (Jeol-ARM200F and Hitachi-HD-2700) with resolutions towards 0.1 nm.

3. Result and discussion

Figure 1 shows TEM bright field images taken in <001>Al zone axis of the Ag-addition alloy under two over aged conditions. It can be seen that the rod-shaped precipitates arrange along <100>Al directions of the matrix. The precipitates appearing as black spots in the figure are observed in cross-section, along their rod lengths. The microstructures of the precipitates formed in the two over-aged conditions appear similar, although the precipitates formed at 423K (Fig. 1(b)) are finer than those formed at 523 K (Fig. 1(a)).

Figure 2 shows typical cross-section HAADF-STEM images of the precipitates in the Ag-addition alloy aged at 523K for 120ks (Fig. 2(a)), and at 423K for 12Ms (Fig. 2(b)). The corresponding elements are attributed to Mg, Al, Si and Ag to understand these images, according to component of alloy. The images seem to indicate atomic columns consisting of Mg, Al, Si and Ag, with the atomic number of 12, 13, 14 and 47, respectively. It is assumed that the strongest contrast is caused by Ag because the intensities in HAADF-STEM images are related to the weight of atomic columns along the viewing direction. It can be seen that there are two different parts with and without periodic strong contrasts inside the precipitate. Ag is observed inside the precipitates with a complicated structure consisting of the domains. The periodicity of Ag-containing atomic columns in the domains is 0.7nm. The strong contrasts were also observed surrounding the precipitate on the Al matrix lattice at the interface between the matrix and the precipitate. Ag probably replaces Al on its face-centered cubic (FCC) positions adjacent to the precipitate interfaces. Some Ag-free areas are also observed inside the precipitates, examples being the upper left region in Fig. 2(a) and the lower right in Fig. 2(b).

Figure 3(a) shows the enlarged image of the Ag-free area in HAADF-STEM image of Fig. 2(a) indicated by the white square. One unit cell is shown in Fig. 3(a, b) with atomic positions indicated by circles on the filtered image in Fig. 3(b). This structure is in agreement with the crystal structure of the β'-phase reported by R. Vissers [8]. The strongest bright dots were observed at the corners of the unit cells, corresponding to the higher occupancy (1.33) Si columns in the β' model [8]. Weaker spots are observed in the centers of equilateral triangles corresponding to Si columns having occupancy 1.0. The weakest spots are hexagonally arranged around the corner atoms, and correspond to Mg columns with occupancy 1.0. Fig. 3(c) shows the schematic graph of the crystal structure of β'-phase. The white or black circles correspond to the $Z = \pm 0.5$ heights. The small circles with bold line at the corners of unit cells show the Si atoms with 1.33 occupancy. The circle size indicates the type of atom, large circle shows Mg, and small one is Si.

Figure 4(a) presents a HAADF-STEM image of a β'-phase aged at 523 K for 120 ks. Fig. 4(b) is the average image of the part inside the white-line rectangle in Fig. 4(a). It shows strong bright dots attributed to Ag columns inside a precipitate domain. In Fig. 4(b) a unit cell is indicated together with atomic overlay. The black and white circles show the Z = ±0.5 heights and the size of circle indicates the type of element as in Fig. 3, with the exception that Ag seems to replace Si in the corners of the unit cell. This replacement is slightly changing the positions of Mg atoms around the unit cell corners, from hexagonal in the Ag-free β' (Fig. 3), to triangular in the Ag-containing β' (Fig. 4). All Si atoms within one domain seem to have the same height in the Ag-containing β' (Fig. 4(c)). EDS measurements indicate that Mg may be partly replaced by Al in the Ag-containing β'.

4. Summary

It is proven that Ag enters the crystal structure of β' phase by replacing Si in the corners of the unit cells and thus changing the unit cell symmetry. The Ag-containing β' precipitates have a complicated structure containing domains. A strong Ag-enrichment is observed at the precipitates interface with the Al matrix. Most of this Ag is partly replacing Al on its FCC sites.

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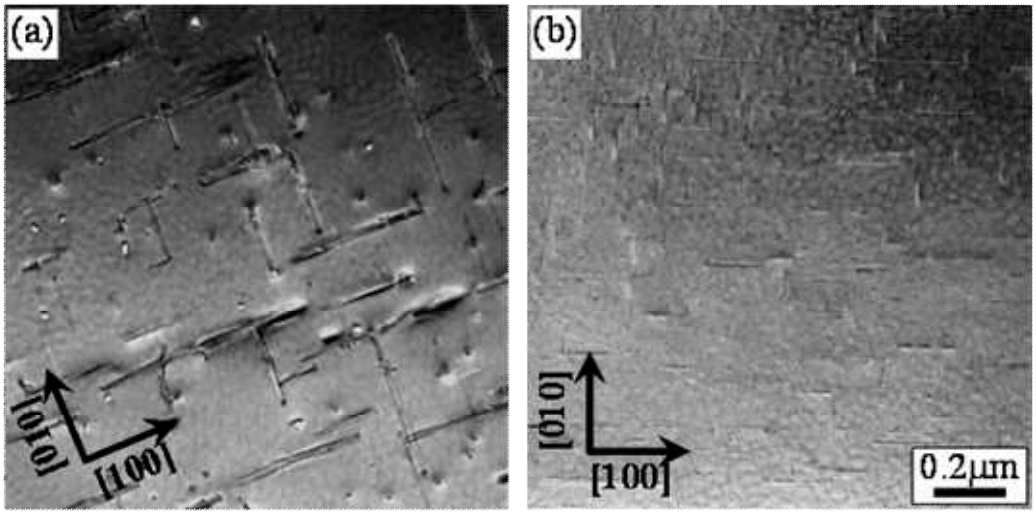

Fig. 1: TEM bright field image of the Al-1mass%Mg_2Si-0.5mass%Ag alloy
(a) aged at 523 K for 120 ks, (b)aged at 423 K for 12 Ms.

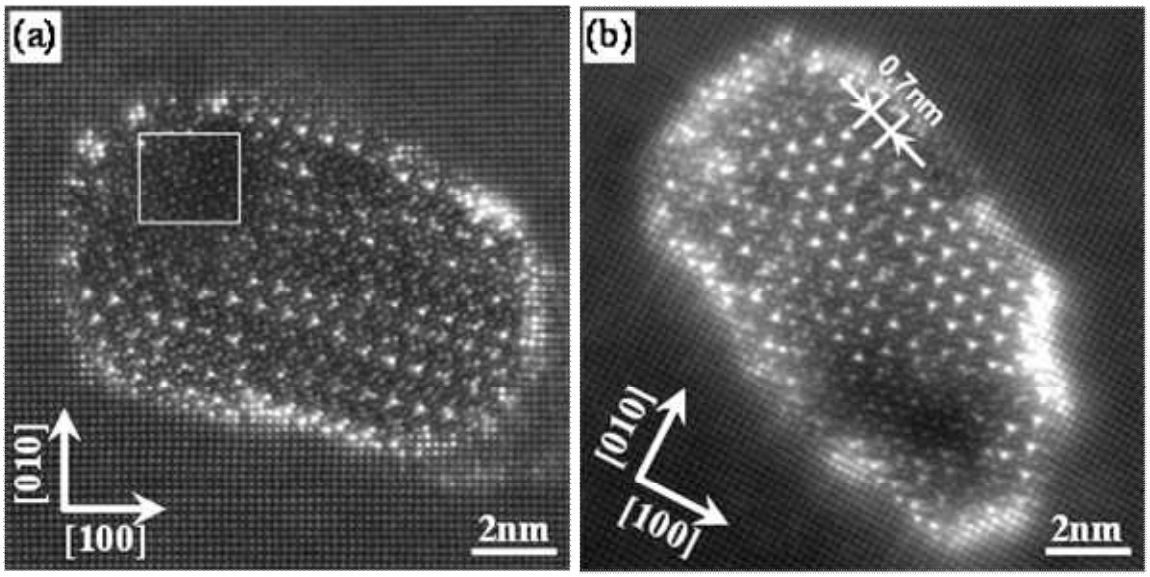

Fig. 2: HAADF-STEM image of a β'-phase were observed in the Al-1mass%Mg_2Si-0.5mass%Ag alloy aged at (a)523K, for 120ks (b)423K, for 12Ms.

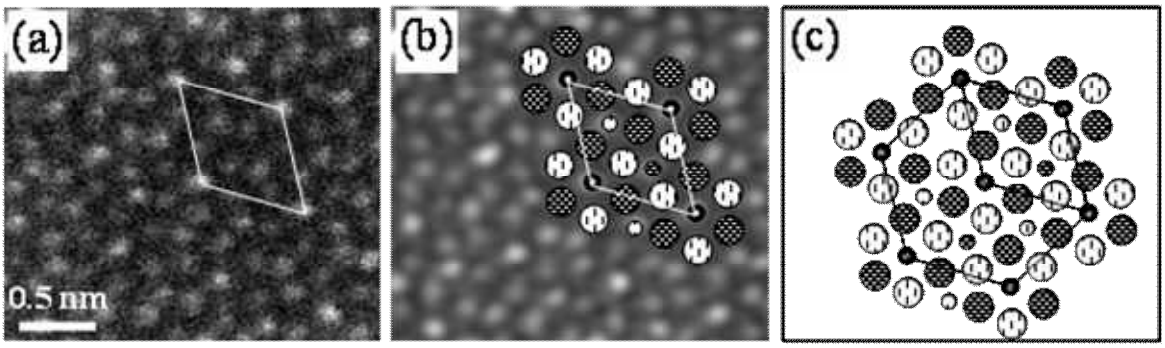

Fig. 3: A part of Ag free area in HAADF-STEM image of a β'-phase (a) part of Fig. 2(a), (b) filtered image used by FFT, (c) schematic image of β'-phase without Ag.

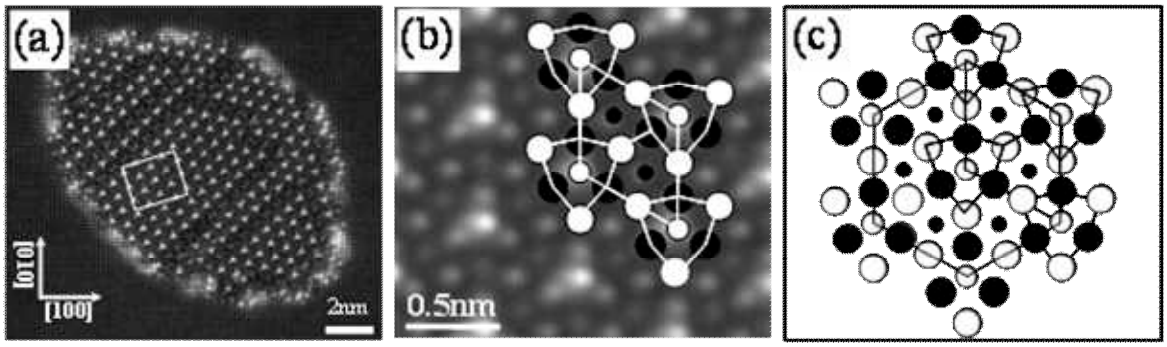

Fig. 4: The average image of the parts including Ag observed in a HAADF-STEM image. (a)HAADF-STEM image of the β'-phase, (b) the average image, (c) schematic image of β'-phase with Ag.