3DAP STUDY OF THE EFFECT OF Mg AND Ag ADDITIONS ON PRECIPITATION IN Al-Cu(-Li) ALLOYS

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ABSTRACT This paper reports three dimensional atom probe (3DAP) analysis results of solute clusters and precipitates in early stage precipitation in Al-Cu(-Li) alloys with minor additions of Ag and Mg atoms. In an as-quenched Al-1.9Cu-0.3Mg-0.2Ag (at.%) alloy, solute atoms are uniformly dissolved. After 15 s aging at 180°C, co-clusters of Ag and Mg atoms are present. Initially, these clusters do not have well-defined shape, but after aging for 120 s, they are aligned on the {111} planes. After 120 s aging at 180°C, plate-like precipitates on {111} are observed in addition to G.P. zones or θ″. Initially the {111} precipitates contain approximately 25 at.%Cu, 20 at.%Mg and 10 at.%Ag and do not have the distinct structure consistent with the Ω phase. In the well-defined Ω which appear after 2 and 10 h aging at 180°C, monoatomic layer segregation of Ag and Mg atoms at the Ω/α interfaces has been observed. In the T_1 phase, which appear in an Al-5Li-2.25Cu-0.4Mg-0.1Ag-0.04Zr (at.%) alloy, segregation of Ag and Mg atoms at the T_1/α interface has also been confirmed. Thus, trace additions of Ag and Mg atoms to both Al-Cu and Al-Cu-Li alloys appear to stimulate uniform dispersion of {111} plate-like precipitates with the same mechanism.

Keywords: *precipitation, age hardening, nucleation, clustering, Al-Cu alloy, Ω phase, T_1 phase*

1. INTRODUCTION

Trace additions of Ag and Mg in Al-Cu and Al-Li-Cu alloys drastically change the precipitation processes. In an Al-Cu-Mg-Ag alloy with a high Cu:Mg ratio, plate-like Ω phase precipitates on the {111} matrix planes, and this causes enhanced tensile strength and creep properties [1,2]. Similarly, trace additions of Ag and Mg to Al-Li-Cu alloy causes uniform dispersion of the T_1 phase on the {111} matrix planes, resulting in an ultrahigh tensile strength exceeding 700 MPa [3,4]. Ω and T_1 phases are structurally and morphologically similar [5], and it is anticipated that a similar mechanism works in both alloy systems to enhance uniform dispersion of the plate-like precipitates on the {111} planes.

The mechanism how precipitation of Ω and T_1 phases is enhanced by microalloying of Ag and Mg is still elusive. Abis et al. [6] proposed existence of a precursor phase to Ω, but the presence of the proposed Ω′ phase was not confirmed by more recent study by Ringer et al. [7]. Using a conventional atom probe (AP), Hono et al. [3] reported that Ag and Mg atoms form co-clusters in the early stage of aging and they proposed that these co-clusters provide heterogeneous nucleation sites for Ω. However, how these co-clusters actually serve as nucleation sites has not been directly observed, because conventional AP does not provide any information on the morphology of the clusters. More recently, based on careful transmission electron microscope (TEM) observations of Al-Cu-Mg-Ag alloys, Cui et al. [9] reported a new type of G.P. zones on {111} and they proposed that these {111}G.P. zones evolve to the Ω precipitates in the subsequent stage.

In a well-grown Ω phase, previous analytical TEM studies [10,11] suggested that Ag segregates to the α/Ω habit plane interface and some Mg is present within the precipitate. On the other hand, the previous atom probe study [12] found Ag and Mg atoms only at the α/Ω interface. In an Al-Li-Cu-Mg-Ag alloy, Ag and Mg atoms were found associated with the T_1 precipitates [13], but because of the thinness of the T_1 plates, exact location of these atoms has not been successfully determined by a conventional AP. Thus, understanding of the chemical nature of the Ω and T_1 precipitates in the Ag and Mg containing Al-Cu(-Li) alloys is still not complete.

A three dimensional atom probe (3DAP) is capable of mapping individual atoms in the real space with a near-atomic resolution [14,15], and thus it reveals information on the morphology of clusters and small precipitates. In addition, 3DAP has improved accuracy in determining concentration changes at the interface, and it is expected to reveal the location of Ag and Mg atoms in a ultrathin

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plate-like precipitate such as T_1 with great accuracy. This study aimed to characterize pre-precipitate solute clusters and various precipitation products in Al-1.9Cu-0.3Mg-0.2Ag and Al-5Li-2.25Cu-0.4Mg-0.1Ag-0.04Zr (all in at.%) alloys using a three dimensional atom probe (3DAP), in order to clarify the role of trace additions of Mg and Ag for uniform dispersion of plate-like {111} precipitates.

2. EXPERIMENTAL

Two types of alloys having chemical compositions of Al-1.9Cu-0.3Mg-0.2Ag (at.%) and Al-5.0Li-2.25Cu-0.4Mg-0.1Ag-0.04Zr (at.%) were used in this study. Alloy ingots were cut into square rods of approximately 0.2 x 0.2 x 10 mm or rolled to a sheet of 0.15 mm in thickness. These specimens were solution heat treated at 540°C for 15 min then quenched into water and immediately aged at 180 °C for various periods of time ranging form 5 s to 10 h. These pieces were electropolished to a sharp needle shape specimen for field ion microscope (FIM) observation or to a thin foil specimen for TEM observation. A three dimensional atom probe (3DAP) equipped with CAMECA's tomographic atom probe (TAP) detection system [15] was employed for this study. After obtaining He field ion images from a clean surface, atom probe analyses were carried out near the (111) pole at specimen temperature of about 25K, with a pulse fraction (the ratio of the pulse voltage to the dc standing voltage) of 20%, under a vacuum of ~1 x 10^{-10} Torr, using a pulse repetition rate of 600 Hz. The data visualization was made using KINDBRISK SDV 3DAP data analysis software under Advanced Visualization System (AVS). Conventional and high resolution TEM observations were performed by Philips CM200 and by JEOL JEM2000EX, respectively.

3. RESULTS AND DISCUSSION

Figures 1 (a) - (d) show a series of bright field (BF) TEM images and selected area diffraction patterns taken near the [011] zone axis. Presence of Ω phase is characterized based on diffraction spots at (1/3){022} and (2/3){022} as seen in Fig. 1 (d), where distinct Ω phase is clearly recognized in the BF image. Streaks along the <111> directions are from the plate-like precipitates on the {111} planes, and that along the [002] direction is from the G.P.zones or θ″. The selected area diffraction patterns (SADP) corresponding to the Ω phase can be seen from the specimens aged for longer than 120 s. Thus the fine contrast along the <111> observed in Fig. 1 (b) are believed to be due to the small Ω precipitate. However, some of the {111} platelets observed in this stage have not been

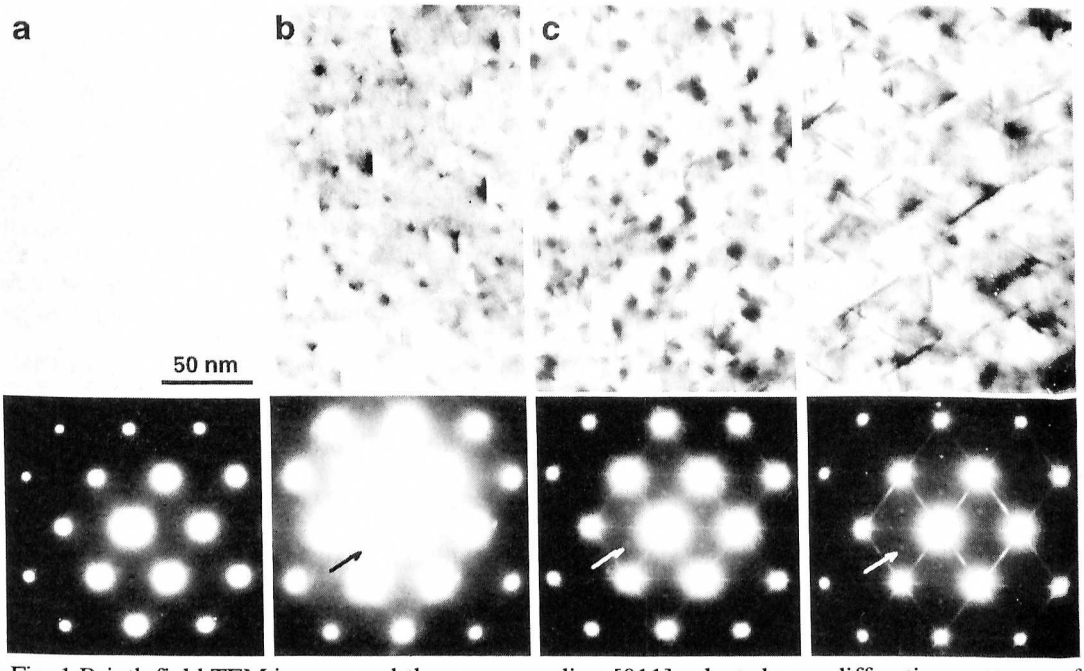

Fig. 1 Brigth field TEM images and the corresponding [011] selected area diffraction patterns of Al-1.9Cu-0.30.2Ag alloy aged at 180°C for (a) 15 s, (b) 120 s, (c) 300 s and (d) 2 h

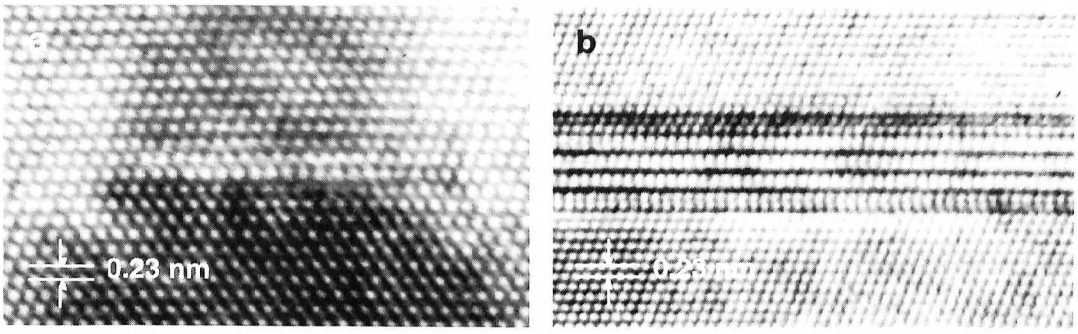

Fig. 2 <110> HREM images of {111} plate-like precipitates observed in Al-1.9Cu-0.3Mg-0.2Ag alloy aged for (a) 120 s and (b) 10 h

identified as Ω by microdiffraction patterns and high resolution electron microscope (HREM) observations as first reported by Cui et al. [9]. Figures 2 (a) an*d (b) show a typical <110> HREM images taken from (a) one of the {111} platelets in an Al-1.9Cu-0.3Mg-0.2Ag alloy aged for 120 s at 180°C and (b) a typical Ω plate with two unit cell thickness in the specimen aged for 10 h at 180°C. HREM image of the Ω phase is featured by thick bright layers and thin dark layers in the {111} stacking [16]. The HREM image obtained from a small platelet in the specimen aged for 120 s does not show such an image feature. Thus, some {111} platelets observed before 120 s do not have distinct structural feature as the Ω phase, although there is no doubt about the presence of Ω at this stage from the SADP shown in Fig. 2 (b).

Figure 3 shows 3DAP elemental mapping obtained from a selected region of an Al-1.9Cu-0.3Mg-0.2Ag alloy aged for 15 s. The data were obtained by locating the $(111)_\alpha$ pole facing the detector. In this figure, locations of individual Ag, Mg and Cu atoms are shown by spheres, and the distribution of Al atoms is shown by dots. The stacking of the $(111)_\alpha$ planes is resolved as seen from the layered pattern. This means that the 3DAP data have an atomic layer resolution in the [111] depth direction. It is seen that Mg and Ag atoms form co-clusters after 15 s annealing. The number of Ag and Mg atoms involved in the co-cluster ranges from 40 to 80 considering the detection efficiency of the microchannel plate (MCP) detector is less than 60%. The ratio of Mg to Ag atoms in these clusters is close to 1 and Cu atoms do not aggregate to this cluster yet. The shape of the clusters cannot be well defined at this stage. The presence of Ag and Mg co-clusters were previously reported by Hono et al. [8], but unlike the conventional AP studies, the present 3DAP result clarifies the morphology of the co-cluster in the earliest stage of formation.

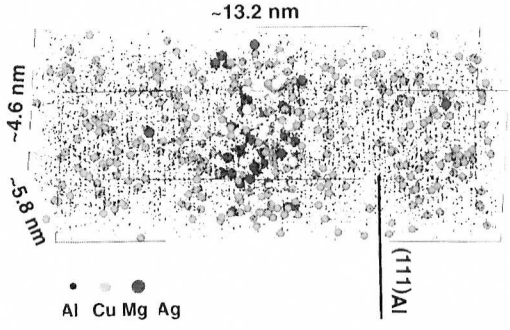

Fig. 3 3DAP elemental mapping of Al-1.9Cu-0.3Mg-0.2Ag alloy aged for 15 s at 180°C

Fig. 4 (a) - (c) shows 3DAP elemental mappings obtained from a selected region of Al-1.9Cu-0.3Mg-0.2Ag alloys aged for (a) 120 s, (b) 300 s, and (c) 10 h, and their corresponding depth profiles calculated normal to the platelets. After 120 s annealing, the co-cluster lie on the (111) plane as shown in Fig. 4 (a). Cu atoms aggregate to the Mg-Ag plate-like co-cluster, but they are not incorporated within the platelet. After 300 s aging, plate-like precipitates are observed with a better defined plate-like shape as shown in Fig. 4 (b). The thickness of the {111} platelets is estimated to be approximately four atomic layers, and Cu, Mg and Ag atoms are all within this precipitate. As shown in Fig. 1 (c), presence of the Ω phase has been confirmed by SADP at this stage, thus this {111} platelet probably corresponds to Ω. In a well-grown Ω plate formed after 10 h aging, Ag and Mg atoms are not incorporated within the precipitate, but they are strongly segregated to the broad Ω/α{111} interface. The segregation layer is restricted to a monoatomic layer, and no Mg atoms are detected within the precipitate unlike previous analytical TEM result by Howe [11]. Concentration of

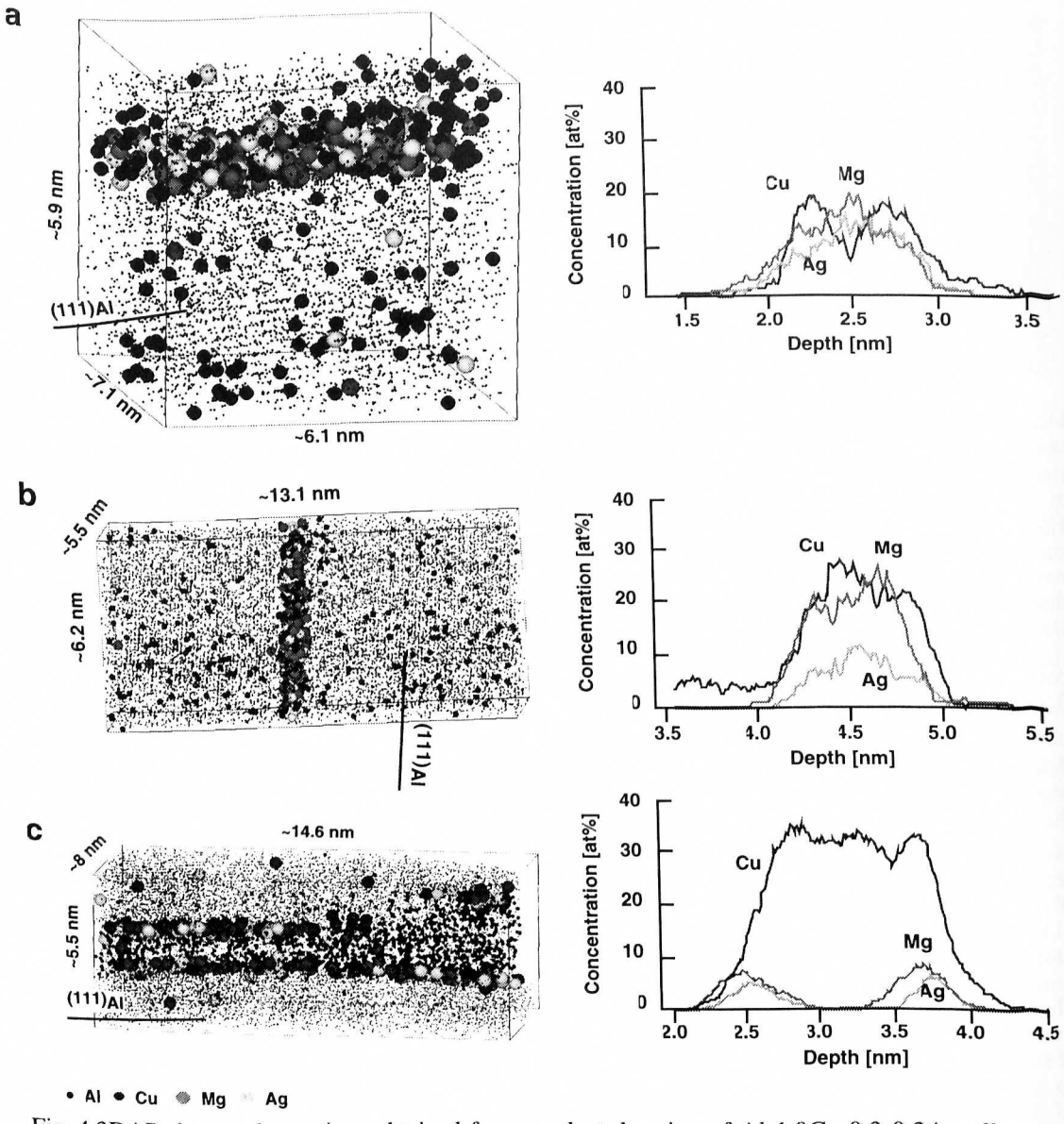

Fig. 4 3DAP elemental mappings obtained from a selected region of Al-1.9Cu-0.3-0.2Ag alloy aged for (a) 120 s, (b) 300 s and (c) 10 h at 180°C, and their corresponding depth profiles calculated normal to the platelets

the Ω is close to 33at.%Cu, which is consistent with the θ phase (Al_2Cu). This suggests that Ω is chemically equivalent to θ.

In this 3DAP elemental mapping (Fig. 4 (c)), a ledge is clearly observed on a habit plane interface of the Ω. At the ledge step of the Ω, Ag and Mg are not segregated, but they are segregated only to the habit plane interface of the Ω. Concentration of Cu atoms in the matrix phase in front of the ledge appears to be higher. This may indicate that this Ω is dissolving in the coarseing stage and the higher concentration of Cu near the ledge is probably due to diffusion flux from a dissolving precipitate to coarsening precipitates. To the author's knowledge, this is the first chemical mapping near a ledge of a plate-like precipitates. In order for the ledge to migrate to the lateral direction during dissolution of the precipitate, Mg and Ag atoms must migrate from the upper terrace to the lower terrace: thus if

diffusivity of Ag or Mg is lower than that of Cu, diffusion of these segregated atoms may control the dissolution or growth rate.

These 3DAP observation results indicate that rapid co-clustering of Mg and Ag atoms occurs first during the artificial aging and then these co-clusters lie on {111} as they grow. Then, Cu atoms aggregate at the sites of Mg-Ag co-clusters to form fine plate-like precipitates on $\{111\}_{\alpha}$. At this stage, these platelets do not have the distinct structure of Ω, but they are fully coherent with the matrix. Thus, these precipitates may be designated as {111}G.P. zones. These plate-like precipitates containing Ag, Mg and Cu atoms grow on {111} by subsequent aging and start to have structural feature as Ω. In the beginning (e.g. 300 s at 180°C), the fine Ω plates appear to contain Cu, Ag and Mg all within the precipitates. During the coarsening, Ag and Mg atoms migrate to the broad face of the Ω/matrix interface to minimize the strain due to the misfit at the {111} habit plane, thereby making the lateral growth easier. Muddle and Polmear [5] suggested that the segregation of Ag and Mg at the α/Ω interface may modify the lattice, thereby some orientation that satisfies the minimum misfit may cause the θ phase to grow in the {111} habit planes. Garg and Howe [6] suggested that the θ phase can match the {111} plane perfectly by expanding the lattice to the c-axis direction by 1.8% based on their convergent electron diffraction results. Since Mg has a larger atomic radius than Al, segregation of Mg leads to expansion of the lattice of the Ω phase at the interface. However, this is not sufficient to explain why Ag is also required for formation of Ω. Since the atomic radius of Ag is very close to that of Al, Ag segregation would not modify the lattice if it substitutes Al. However, since valence numbers of Ag and Cu are the same, Ag could substitute for Cu. If then, Mg substitutes for Al, and Ag for Cu in the θ phase near its interface with the matrix, the lattice of the θ phase would be elongated significantly. This may bring the modified θ phase, Ω, to match the $\{111\}_{Al}$ plane perfectly. Strong segregation of both Ag and Mg atoms to the habit plane interface of Ω within a monolayer thickness suggests that both Ag and Mg atoms are required for reduction of the interfacial strain, and thus the above mechanism is reasonable. Moreover, Ag addition is believed to be required for forming Ag-Mg co-clusters at the earliest stage of aging. As this work has convincingly shown that the Ag-Mg co-clusters evolve to the Ω precipiate as aging goes on, role of Ag to attract Mg atoms to form co-clusters in the early stage of aging is critical to enhance the density of {111} precipitates.

Figure 5 (a) shows 3DAP elemental mapping of a T_1 precipitate observed in an Al-5.0Li-2.25Cu-0.4Mg-0.1Ag-0.04Zr alloy aged for 10 h at 180°C. As in the case of the Ω phase in the Al-1.9Cu-0.3Mg-0.2Ag alloy, Ag and Mg atoms appear to be present at the T_1/α interfaces. As the thickness of this precipitate is only one unit cell of the T_1 (four $\{111\}_{\alpha}$ planes), the location of Ag and Mg atoms is

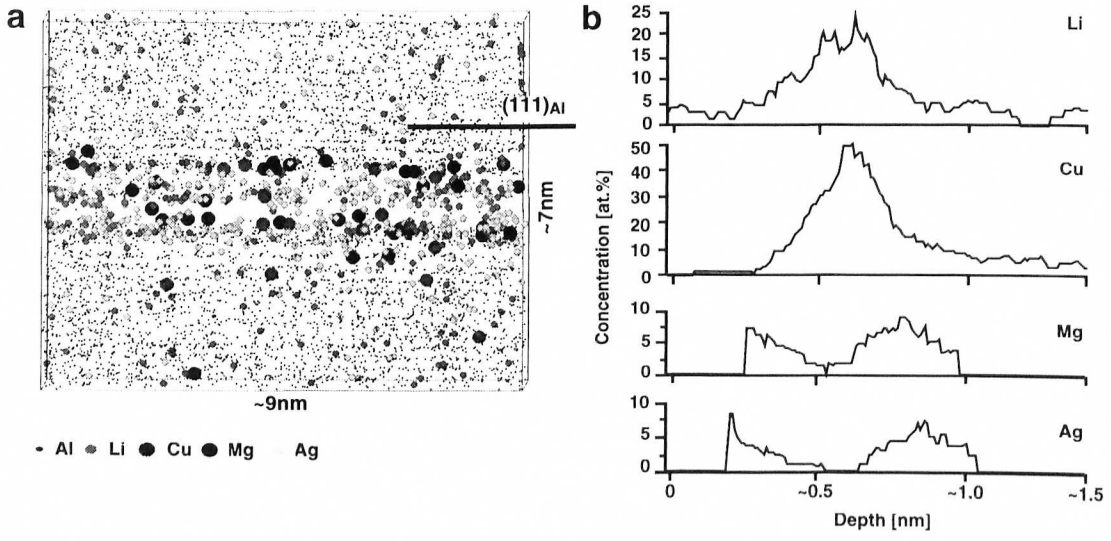

Fig. 5 3DAP elemental mapping obtained from a selected region of Al-5.0Li-2.25Cu-0.4Mg-0.1Ag-0.04Zr alloy aged for 10 h at 180°C and the corresponding depth profiles calculated normal to the platelet

visually not clear. However, the concentration depth profile obtained in the normal direction to the T_1 plate (Fig. 5 (b)) clearly demonstrates that Ag and Mg atoms are segregated at the T_1/α interface. This suggests that similar mechanism may work for stimulating pecipitation of T_1 phase by addition of Ag and Mg atoms to Al-Cu-Li alloys. In order to clarify the nucleation stage of the T_1, 3DAP analysis of earlier aging stages of the Al-Li-Cu-Mg-Ag alloy is in progress.

5. CONCLUSIONS

Three dimensional atom probe analyses of the pre-precipitation stage of Al-1.9Cu-0.3Mg-0.2Ag alloy have revealed that Mg-Ag co-clusters are present after 15 s aging at 180°C. Cu atoms are not incorporated in the Mg-Ag co-clusters at the initial stage and the shape of the cluster is not well defined. After aging for 120 s at 180 °C, the cluster shows more distinct feature as {111} platelet. Cu atoms aggregate to this cluster, and the concentration of Cu reaches approximately 33 at.%, which is consistent with that of Ω. After 300 s aging, Cu, Mg, and Ag atoms are all incorporated within the plate-like precipitate. After prolonged aging, Mg and Ag atoms are strongly segregated to the habit plane interfaces of well-grown Ω precipitates. No Mg atoms are incorporated within the precipitate. Ag and Mg atoms are also segregated at the T_1/α interfaces in Al-5.0Li-2.25Cu-0.4Mg-0.1Ag-0.04Zr alloy, and this indicates that precipitation of T_1 phase takes place with a very similar mechanism to that in Al-1.9Cu-0.3Mg-0.2Ag alloy. We have also demonstrated for the first time that the chemical distribution near a ledge can be observed by 3DAP.

[1] J. A. Taylor, B. A. Parker and I. J. Polmear, Metals. Sci. 12, 478 (1978).
[2] I. J. Polmear and M. Couper, Metall. Trans. 19A, 1027 (1988).
[3] J. R. Pickens, F. H. Heubaum, L. S. Kramer, Scripta Metall. Mater. 24, 457 (1990).
[4] F. W. Gayle, F. H. Heubaum and J. R. Pickens, Scripta Metall. Mater. 24, 79 (1990).
[5] R. A. Herring, F. W. Gayle, and J. R. Pickens, J. Mater. Sci. 28, 69 (1993).
[6] S. Abis, P. Mengucci and G. Riontino, Phil. mag. 67B (1993), 465.
[7] S. P. Ringer, K. Hono, I. J. Polmear and T. Sakurai, Acta mater. 44 (1996), 1883.
[8] K. Hono, I. J. Polmear and T. Sakurai, Scripta Metall. Mater., 30 (1994), 695.
[9] Q. Cui, G. Itoh and M. Kanno, J. Jpn. Inst. Met. 59 (1995), 492.
[10] B. C. Muddle, I. J. Polmear, Acta metall. 37 (1989), 207.
[11] J. M. Howe, Phil. Mag. Lett., 70 (1994), 111.
[12] K. Hono, N. Sano, S. S. Babu, R. Okano and T. Sakurai, Acta metall., 41 (1993), 829.
[13] S. P. Ringer, K. Hono, I. J. Polmear and T. Sakurai, Solid→Solid Phase Transformations. Eds by W. C. Johnson, J. M. Howe, D. E. Laughlin and W. A. Soffa, The Minerals, Metals & Materials Society, 1994, pp. 165.
[14] A. Cerezo, T. J. Godfrey and G. D. W. Smith, Rev. Sci. Instrum, 59, 862 (1988).
[15] D. Blavette, B. Deconihout, A. Bostel, J. M. Sarrau, M. Bouet and A. Menand, Rev. Sci. Instrum, 64 (1993), 2911.
[16] K. M. Knowles and W. M. Stobbs, Acta Cryst. B44 (1988), 207.