Determination of interfacial atomic structure, misfits and energetics of Omega phase in Al–Cu–Mg–Ag alloy

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Abstract

The interfacial atomic structure and misfits of Ω precipitates formed in the FCC Al in the Al–Cu–Mg–Ag alloy have been determined by combining scanning transmission electron microscopy (STEM) Z-contrast imaging with chemical analysis and *ab initio* density functional theory (DFT) calculations. Precipitates of several thicknesses formed after heat treatment at 250 °C, starting from 0 to 2 unit cells of Ω phase, were examined by STEM in 4 different projections. Results show that a remarkably stable, double-layered, interface is formed at all observed thicknesses, which separates the Ω phase from the Al matrix. The outermost interfacial layer next to Al is composed of Ag atoms in a hexagonal structure and Mg or Cu atoms below the center of the hexagon. Structural models constructed based on the experimental data were relaxed using the DFT based molecular dynamics calculations. Results show that interfacial Mg atoms, together with Ag atoms, greatly stabilize the interface structure and consequently the Ω phase on the Al {111} habit planes. Comparison

between the measured and calculated precipitate misfit along the thickness direction suggests that atomic substitutions of light atoms, Al and Mg, at the interface mediate the misfit strain and free energy, which is further supported by experimental evidence obtained from STEM. Thus, we have identified here: 1) the driving force for the Ag and Mg segregation in the formation of the Ω phase, 2) the precipitation sequence characterized by a stable interfacial double-layer and 3) an interfacial substitution mechanism for misfit accommodation.

Keywords: Aluminum alloys, Interface, Z-contrast microscopy, Density functional theory, Structure determination.

1. Introduction

The Al–Cu–Mg–Ag alloy belongs to the Al alloy 2000 series. Minor addition of Ag (~0.1 at.%) into the Al–Cu–Mg system with a high Cu/Mg ratio (10 to 1) drastically enhances the formation of uniformly-dispersed Ω phase with a large width-thickness aspect ratio ($\sim 10^2$) on the $\{111\}$ planes of the Al matrix (FCC, α phase) [1–4]. The presence of the Ω phase leads to enhanced thermal stability, increased yield strength, and coarsening resistance, which has attracted considerable interests for aerospace and defense applications [5–7] as well as fundamental studies on the structure and stability of the Ω phase [8–11].

The Ω phase has a nominal composition of Al_2Cu . While several structure models have been proposed [3, 4, 12, 13], the difference between these structural models is small except the model proposed by Kerry and Scott [12]. The commonly accepted structure of the Ω phase has an orthorhombic unit cell with $a_\Omega=4.96$, $b_\Omega=8.56$, $c_\Omega=8.48$ Å [4]. It can be regarded as a distorted form of the structure of tetragonal θ - Al_2Cu precipitates found in the over-aged Al–Cu alloys. The Auld’s original model is monoclinic [3]. The Ω phase is oriented according to epitaxial relationships of $[211]_{\text{Al}}\parallel[100]_\Omega$, $[110]_{\text{Al}}\parallel[010]_\Omega$ and $(111)_{\text{Al}}\parallel(001)_\Omega$. Along two of these three direction, the a_Ω and b_Ω are 3 times the d -spacing of (211) and (110) of Al ($a_\alpha=4.05$ Å), respectively, with the lattice misfit at less than 0.015%. Along the c -axis of the Ω phase, the misfit based on the closest match of multiples of the $(111)_{\text{Al}}$ d -spacing is large at -9.3% for half Ω unit cell. This misfit fluctuates as precipitate thickness increases, contributing to either a tensile or compressive strain in the Al matrix depending on the misfit [11]. Because of the misfits in $[211]_{\text{Al}}\parallel[100]_\Omega$, $[110]_{\text{Al}}\parallel[010]_\Omega$ directions are small, the large misfit in the $(111)_{\text{Al}}\parallel(001)_\Omega$ direction, if it is unrelaxed, will dominate the precipitate strain energy. This energy will vary widely with the precipitate

thickness. However, the misfit between the precipitate and the matrix has an interfacial component. Because of the lack of knowledge about the interfacial structure for the reasons listed below, the exact misfit of the Ω precipitates is unknown.

Several research groups have examined the interfacial structure of Ω precipitates and its composition using high resolution electron microscopy [3, 4, 13, 14], X-ray energy dispersive spectroscopy (EDS) [15, 16], energy filtered electron imaging [17], scanning transmission electron microscope (STEM) imaging [11] and atom probe tomography [9, 10, 18, 19]. Composition analysis using EDS revealed strong segregation of Ag and Mg at the interface [16]. Atom probe tomography (APT) by Reich et al. [19] suggested that Ag is segregated in a single atomic layer. From the Z-contrast images obtained in a STEM using the annular dark field (ADF) detector, Hutchinson et al. concluded that Ag-Mg forms an interfacial double-layer [11]. The segregation of Ag-Mg has been observed at all precipitate thicknesses. It has been suggested that the Ag-Mg segregation is driven by the misfit strain energy because Ag and Mg atoms at the Ω - α interface modifies the lattice, which could satisfy the minimum misfit condition at the Al{111} planes [14]. However, so far there is no direct experimental or theoretical evidence to support this hypothesis.

More recently, Sun et al. reported an *ab-initio* calculation study of the structure of the Ω - α interface using the density functional theory (DFT) [20]. Their work suggested a bilayer of closely packed Ag and Mg at the interface. Inside this bilayer, Ag atoms are adjacent to the Al matrix, while Mg atoms are next to the Ω phase. This model, which was constructed based on the bilayer structure reported by Hutchinson et al. [11], provides a plausible model for the Ω precipitate interface; but, the referred experimental results were limited to a single

projection (along $[010]_{\Omega}$), and the resolution was not sufficient to resolve the atomic structure of the interface. Consequently, the results were inconclusive.

To gain insights about the Ω - α interface, we have made new observations by examining the precipitates along four different orientations based on the epitaxial relationships of $[100]_{\Omega} \parallel [2-1-1]_{\text{Al}}$, $[110]_{\Omega} \parallel [11-2]_{\text{Al}}$, $[010]_{\Omega} \parallel [01-1]_{\text{Al}}$, and $[310]_{\Omega} \parallel [1-10]_{\text{Al}}$. The image resolution is significantly improved by Cs correction [21, 22], which has only recently been applied to interfacial study in metals [23-25]. Using the obtained three-dimensional (3D) experimental data and additional information obtained from chemical analysis, we constructed 3D structural models of the Ω . Refinement of models using first-principle calculations allows an identification of the most stable interfacial structure and its relationship with precipitate misfits, as well as the effect of atomic substitutions. Specifically, DFT calculations of the heat of formation and the precipitate misfit were carried out. Together, they contribute to a free energy model based on the substitution of Mg, Al and Cu at selected interfacial sites. By comparing the calculated precipitate misfits with the experimentally measured misfit, we show that atomic substitutions at the Ω - α interface play an important role in minimizing the free energy. Overall, our work demonstrates the deterministic roles of Mg and Ag atoms in the formation of Ω precipitates in the Al-Cu-Mg-Ag alloy.

2. Materials preparation and methods

The alloy with the composition of Al-4%Cu-0.3%Mg-0.4%Ag by weight percentage was prepared from high purity materials by vacuum RF melting. The alloy was solution treated at 510°C for 1 h, and then water quenched. Immediately after water quenching, the

alloy was aged at 250°C for 24 hours. The composition and aging time were similar to one of the conditions reported by Hutchinson et al. in their study [11]. Specimens for transmission electron microscopy were prepared by mechanical polishing, followed by ion-milling.

Atomic resolution Z-contrast images were recorded using a JEOL 2200FS STEM equipped with a CEOS third-order probe-forming aberration corrector [26]. The Z-contrast was formed by detecting scattered electrons using a high-angle ADF (HAADF) detector. The inner and outer semi-angles for the HAADF detector were 100 and 250 mrad, respectively.

For composition analysis, electron energy loss spectroscopy (EELS) spectra were obtained using an in-column Ω -energy filter for energy dispersion. This setup allows a simultaneous acquisition of HAADF-STEM images and the EELS spectra, which were used for interfacial atomic identification. For the EELS recording, we used the probe convergence angle at 26 mrad and the EELS collection angle at 41 mrad. The EELS spectra were further processed using the principal component analysis (PCA) to reduce the noise in the acquired spectra.

Electron diffraction of precipitates was simulated using the computer program of Zmult, developed at University of Illinois based on the published multi-slice method [27]. In the simulation, electron scattering into the ADF detector was approximated using the absorptive potential method proposed by Ishizuka [28]. We used the Debye–Waller factors of $0.5 \text{ \AA}^{-2}$, which provided a good match with the experimental data. In our simulations, the sample thickness was varied incrementally from 5 to 30 nm, in a 5 nm step, and the best-matched simulation image was chosen. The electron probe was simulated using the aberration corrector (CEOS) parameters obtained by calibration and further adjusted to match the experimental image by slightly changing the aberration coefficient value of C_3 .

The ab-initio calculations were carried out using the Vienna *ab-initio* simulation package (VASP) code [29]. We used a pseudopotential based on the generalized gradient approximation (GGA) method [30] with Perdew–Wang exchange and correlation functional (PW91) [31] for all of the elements to solve the Kohn–Sham equations. The plane wave expansion for the valence electrons used an Energy cutoff value of 300 eV. A $2 \times 2 \times 1$ mesh was used for the K-point grid. Testing runs showed that the total energy converged to 1 meV atom⁻¹. Electron density relaxation stopped when the energy difference was less than 10^{-5} eV between the iterative steps. For structure relaxation, we used the conjugated gradient and residual minimization scheme–direct inversion in the iterative subspace (RMM–DIIS) algorithms [32]. The volume, atomic position, and unit cell shape were allowed to relax freely.

3. Results and Discussions

The results and discussions below are organized in 3 sections. The first section concerns with the determination of the precipitate atomic structure focusing on the Ω - α interface. This is followed by an examination of the synergistic roles of Ag and Mg at the interface and the effect of interfacial substitution on the precipitate misfit. The last section is a discussion on interfacial structure, energy and the impact of precipitate misfit on coarsening resistance.

3.1 Atomic structure determination and interfacial Ag

3.1.1 HAADF-STEM analysis

Fig. 1 shows the Ω precipitates formed on the $\{111\}$ planes of the α Al matrix. At a medium magnification, the platelet shaped precipitates appear as long bright needles in the

recorded Z-contrast images when it is viewed along the $[211]_{\text{Al}}$ direction. The precipitates have different sizes in the range from 0.85 to 9 nm in thickness. For atomic resolution study, we focused on these precipitates at the initial stages of growth. Fig. 2 shows the atomic resolution Z-contrast images of three Ω precipitates of 0.85, 1.21 and 2.64 nm in thickness, respectively. In all three cases, a double-layer atomic structure is seen on both sides of the precipitates. The precipitate shown in Fig. 2c has 2 unit cells of the Ω phase, in addition to the double-layered interfaces. In comparison, the thinnest precipitate seen in Fig. 2a is consisted of two double-layered interfaces with zero unit cell of the Ω phase. Thus, the double-layer interface appears to be the most significant structural feature of Ω precipitates, which is almost like a membrane separating the Ω phase from the Al matrix.

We investigated the atomic structure of the interfacial double-layer by examining the precipitates along four different sample orientations based on the epitaxial relationships of $[100]_{\Omega} \parallel [2-1-1]_{\text{Al}}$, $[110]_{\Omega} \parallel [11-2]_{\text{Al}}$, $[010]_{\Omega} \parallel [01-1]_{\text{Al}}$, and $[310]_{\Omega} \parallel [1-10]_{\text{Al}}$. Examples of the obtained precipitate images are shown in Fig. 3a-d. In all four sample orientations, the Z-contrast image resolution was sufficient to separate the projected atomic columns. For example, in the $[310]_{\Omega}$ orientation, the Cu atomic columns are separated by 1.24 Å inside the precipitate according to the structural model proposed by Auld [3]. They are clearly resolved in Fig. 3d.

Inside the precipitate, the observed atomic column arrangements agree with the orthorhombic structure proposed by Knowles and Stobbs [4]. The insets in Fig. 3a-d show the Z-contrast image simulation results based on this model together with the interface model we propose below. Good agreement with the experimental images can be seen in all simulated images. The support for Auld's structure model here with atomic resolution data is consistent

with the conclusions of previous experimental reports [3, 4, 11]. It should be noted that there are other studies that have suggested a tetragonal cell [13, 33], however, the Z-contrast images here are not sensitive enough to differentiate the small difference between these structure models.

At the double-layer interface, strong contrast is seen in the recorded Z-contrast images. The layer adjacent to the Al matrix has an atomic arrangement that is very different from that of Al_2Cu . The strong contrast can be attributed to Ag, which has the highest atomic number (Z) in this alloy and its ubiquitous presence at the interface has been detected by several experimental techniques [11, 16, 19].

3.1.2 EELS/EDX analysis at the interface

Elemental analysis of the precipitates was performed using EELS at high spatial resolution to help atomic identification inside the interfacial layer. The Ag $M_{4,5}$ (367 eV) and Cu $L_{2,3}$ (931 eV) edges were measured by EELS. EELS spectra were recorded in the STEM mode along lines across the precipitate and matrix interface. An example of EELS study is shown in Fig. 4a. The EELS spectra are displayed as spectrum image, in which the energy loss is along the horizontal direction and the probe position is along the vertical direction. Two spectrum images are shown, one without and one with background subtraction. The background subtracted spectrum image at the right in Fig. 4a show the Cu $L_{2,3}$, while the spectrum image without background subtraction show the tail of Ag $M_{4,5}$. Comparison of the two spectrum images shows that in the interfacial double-layer, a single atomic layer of Ag is clearly segregated adjacent to the Al matrix and Cu is detected next to the Ag layer.

Comparison of the EELS line scan and the HAADF-STEM signal shows that the spectrum signal from Ag matches the strong Z-contrast signal detected at the first interfacial atomic

layer, while the spectrum signal from Cu, immediately below the Ag spectrum signal matches with the Z-contrast signal from the second atomic layer of the interface. Thus, the EELS data here, together with previous reports [11, 19], supports the interpretation of the HAADF-STEM images and the identification of a single atomic layer of Ag.

Additionally, EDX signal is mapped simultaneously with HAADF-STEM image as displayed on Fig. 4b. Mapped EDX data shows very similar result to the EELS spectrum results for Ag and Cu.

Accordingly, the comparison between the EELS/EDX spectra and the HAADF-STEM images revealed a single layer of Ag atoms, as well as Cu atoms next to the Ag layer at the interface. While interfacial Ag atoms had been suggested in previous reports [11, 19], the detection of Cu atoms by EELS immediately adjacent to the Ag atoms is a surprising result.

3.1.3 Determination of interfacial atomic structure: hexagonal Ag layer

The atomic-resolution images of Fig. 3 and chemical information obtained from EELS/EDX (Fig. 4) provided important clues about the atomic structure at the interface. The image contrast observed contradicts the proposed double-layer structure made of one closed packed Ag layer and one with Mg [20]. First, in the projection along $\langle 110 \rangle_{\text{Al}}$ zone axes, Ag atomic columns seen in the recorded Z-contrast images have the same arrangement as the close-packed plane of Al. However, along the $\langle 112 \rangle_{\text{Al}}$ zone axes shown in Fig. 3(a) and (b), the Ag atomic columns of strong Z-contrast are arranged in pairs (dumbbells). Between the dumbbells, there is an atomic column showing a lower Z-contrast, but higher than that of Al. This atomic column is located slightly below Ag towards the precipitate. The two atomic columns inside a dumbbell are separated by a distance of 1.4 Å in projection, while the distance between two dumbbells is 2.9 Å. We note that the angle between the zone axes of

$\langle 110 \rangle$ Al and $\langle 211 \rangle$ Al is either 30° or 90° . These numbers together suggest a hexagonal arrangement for the Ag atoms like the structure of graphene, as the dumbbells are observed in projections perpendicular to the hexagonal edges, while projections along the vertices of the hexagon show equally spaced Ag atoms. The atomic column seen in between dumbbells (Fig. 3) is located slightly below the center of the hexagons. Furthermore, the atomic arrangement right below the interfacial layer is similar to the Ω precipitate, except that the contrast at the Al column positions near interface is higher than the contrast expected from Al and that these higher contrast Al columns are located in the same plane as the Cu layers.

3.1.4 Ab-initio DFT calculations: construction of the interface structure model, relaxed structure and energetics with Ag and Cu at interface

Based on above observations, we propose here an interface structure model as illustrated in Fig. 5. The starting crystal structure of the Ω phase has an orthorhombic unit cell as described in Introduction. The atomic positions inside the unit cell are: Al(1) at $(0, 1/3, 0)$, Al(2) at $(0, 0, 1/6)$, and Cu at $(1/4, 1/4, 1/4)$ with the $Fmmm$ space group [4].

The interface is made up of a layer of hexagonally arranged Ag in a graphene-like structure with atomic sized pores. In addition, three interfacial atomic sites next to Ag are identified, A(I) A(II) and A(III) as marked in Fig. 5. The A(I) site sits below the center of the Ag hexagon on the precipitate side. Next, an separate atomic layer that resembles the structure of the Ω precipitate provides two atomic sites, A(II) and A(III) respectively. Together, the hexagonal Ag and the identified three atomic sites make up the double-layer seen in the experimental Z-contrast images. In our starting model, all three sites of A(I), A(II) and A(III) are occupied by Cu in order to account for the high Z-contrast seen at these sites in the experimental images of Fig. 3.

All together, the supercell model has 208 atoms with a starting volume of $9.92 \times 8.59 \times 38 \text{ \AA}^3$. This model includes four Cu atomic layers (2 unit cells) of the Ω phase, two interfaces on each side and four layers of Al atoms representing the matrix. A separate calculation was also carried using a precipitate model with 0 cells of the Ω phase.

To examine the stability of our precipitate models, we conducted structural relaxation using the *ab-initio* DFT molecular dynamics calculations using the above constructed supercells. Fig. 5 plots the precipitate structure with 2 unit cells of the Ω phase after structure relaxation (for a better view, the supercell is doubled along the $[010]\Omega$ direction). During structure relaxation, the A(I) site occupied by Cu atom, initially placed in middle of Ag hexagon, moved down slightly towards the precipitate. This feature successfully reproduces the experimental observations. Immediately below, on the A(II) atomic site, Cu atom moved so that after structure relaxation it is positioned almost in the same plane as the A(III) atom site. Z-contrast image simulations using this relaxed structure are shown in Fig. 3; they are in good agreement with the experimental images. The match at the interface is especially remarkable.

The relaxed supercell of 2 unit cell Ω phase is monoclinic, with a distortion angle of 1.6° for the supercell. Since the Al matrix has a cubic symmetry, for a coherent precipitate, the monoclinic distortion contributes to an unrelaxed shear strain between the precipitate and the matrix (Table 2). The shear distortion seems not sensitive to the atomic substitutions at the interfacial sites (A(I), for example). Interestingly, the predicted monoclinic symmetry agrees with the X-ray study of Auld on thin Ω precipitates formed by aging at 200°C [3]. With Al_2Cu alone, the same calculations predicted a nearly tetragonal cell with $a=4.89 \text{ \AA}$, $b=8.56 \text{ \AA}$ and $c=8.57 \text{ \AA}$. This symmetry was seen by Garg and Howe using CBED on thicker Ω precipitates [13].

To gain an insight about the interfacial stability, we calculated heat of formation using $\Delta H = E_t - \sum N_i E_i$, where the E_t is the total energy obtained from the ab initio calculations for the relaxed structural model and the sum is over atomic energy E_i with N_i for number of same atoms inside the supercell. The calculated heat of formation is -19.83 eV/supercell for the 2 Ω unit-cells model shown in Fig. 5. The same calculations gave $\Delta H = -18.98$ eV/supercell for the interface model proposed by Sun et al. [20]. The formation energy is lowered by 0.85 eV per supercell with our new model.

For the precipitate model with 0 unit-cell of the Ω , the calculated heat of formation is -4.48 eV/supercell, presenting a stable formation energy even without Al_2Cu inside the precipitate. This calculation result further verifies the stability of our interface structure model.

3.2 The role of Mg at the Ω - α interface

3.2.1 Evidence of Mg at the interface

Experimentally, it has been observed that the addition of Ag greatly enhances the formation of the Ω precipitates in the Al-Cu-Mg alloys, but Ag alone in the absence of Mg has no effect on the precipitation. While the above proposed structure model successfully matches the experimental image contrast, further investigation is needed to understand the decisive roles of Mg atoms in the formation of Ω precipitates. To this end, we first examine the distribution of Mg. Our own EDX mapping using the Mg $K_{1,2}$ X-rays indicated that the Mg atoms are broadly distributed within the precipitate with an elevated Mg concentration at the interface (Fig. 6c). This is in agreement with the previous EDX analysis results [11, 16]. The elevated Mg concentration at the interface suggests a significant amount of Mg

substitution at the interfacial atomic sites. An elevated Mg concentration at the interface is also strongly supported by the 3D atom probe (3DAP) tomographic data of Reich et al [19]. Fig. 6a-b show a Z-contrast image of the interface observed along the $[100]\Omega/[211]\text{Al}$ direction; the arrows in Fig. 6b point to the A(I) sites in bright contrast, while other A(I) sites clearly show darker contrast, suggesting these are likely occupied by light atoms of Al or Mg. The Z contrast difference between Al and Mg is too small to differentiate these two. Identification of Mg/Al atomic sites using EELS was also difficult. To investigate the energetics of atomic substitution, we examined the stability of interface with Al and/or Mg atoms in the determined atomic sites by using DFT calculations.

3.2.2 Effects of interfacial substitution of light atoms

To investigate the effect of interfacial atomic substitutions, first we constructed atomic models with the A(I) and A(II) sites substituted by Al or Mg. The model with the A(I) and A(II) sites occupied by Cu serves as a reference. Fig. 7a and Table 3 show the effect of light atoms substitution. Substitution of Cu by Mg at A(I) leads to the largest reduction in the total energy, while Mg at the A(II) site leads to an increase in the formation energy. Mg atoms reduces the precipitate formation energy by 1.88 to 7.65 eV/supercell on the A(I) site as the percentage of substitution increases from 25% to 100%, while the reduction is smaller at 0.86 to 2.75 eV/supercell for Al substitution on the same site. The energy reduction amounts to ~ 0.96 eV/atom for Mg at A(I) and $0.34\sim 0.43$ eV/atom for Al at A(II). The reduction by Mg at A(I) site is especially large. Based on these numbers, we expect significant Mg accumulation on the A(I) sites inside the interfacial layer. In comparison, Ag and Cu tend to phase separate in the FCC lattice. Considering these factors, the observation

of Cu atoms at the A(I) sites in the Z-contrast images as well as in the EELS data is surprising and deserves further examination.

We first evaluate the effect of interface on precipitate lattice misfit by only considering Cu atoms at the three interfacial atomic sites. Before the misfit evaluation, it is necessary to define the thickness of the precipitates. The thickness value could be simply defined as Ag-Ag distance between the precipitate. However, because the spacing of Al layers next to the precipitate could be affected by the Ag-Al interaction, it is better to define the thickness and misfit of the precipitate along the direction of $[111]_{\text{Al}}$ based on the distances between Al layers on both sides of the precipitate. For this purpose, we used the simple formula below to define the precipitate misfit:

$$\varepsilon = \{(t_{\text{Al}(1)} + t_{\text{Al}(2)})/2 - t_{\text{Al}}\} / N t_{\text{Al}} \quad (1)$$

Here, $t_{\text{Al}(1,2)}$ is the precipitate thickness obtained by the thickness between the first or second Al layer adjacent to the Ag layer, subtracted by the appropriate number of bulk $[111]_{\text{Al}}$ d -spacing. N is the number of $[111]_{\text{Al}}$ layers, whose thickness closely matches the precipitate thickness. This formula treats the additional strain on interfacial Al layers by subtracting off the bulk $[111]_{\text{Al}}$ d -spacing from it and extract only the difference compared to the $[111]_{\text{Al}}$ d -spacing. The misfit was averaged by the value obtained from the first and second Al layers. The evaluated misfit value was -0.19% for the 2 unit-cell precipitate with 12 matching $[111]_{\text{Al}}$ d -spacing. Without the interface, the misfit caused by the presence of the Ω phase is -9.3%. Thus, the interface contributes to a significant relief of misfit associated with the 2 unit-cell Ω precipitate.

The substitution of light atoms further changes the precipitate thickness since the atomic radius of Mg (0.1602 nm) or Al (0.1432 nm) is larger than Cu (0.1278 nm). Figure 7b plots the calculated thickness of the interface, the thickness of the Al and Al_2Cu layers (See

Figure 5 for their definitions). The changes in the thickness of the Al and Al₂Cu are small in these calculations. Large changes are observed in the thickness of interface. With 100% Mg at A(I), the interfacial thickness increases by 0.26 Å from the interfacial thickness with 100% Cu at A(I). Similarly, with 100% Al at A(II), the thickness increases by 0.17 Å.

3.2.3 Interfacial intermixing and its effect on precipitate misfit

Figure 8 plots the obtained misfit from the measured precipitate thicknesses. We have measured the average precipitate thickness from the atomic resolution images using the distances between Al (111) planes above and below the precipitate. The Al (111) *d*-spacing recorded in the experimental image, which is subtracted off from the measured distances, was measured away from the precipitate and used for calibration. For the precipitate with 2 unit cells of Al₂Cu, the measured value was $\varepsilon(c) = 0.35\% \pm 0.29\%$. The precipitate has a calculated misfit of -0.19% with 100% Cu at A(I), while 100% Mg at A(I) gives 1.25% misfit. Thus, together with the observation of substantial amount of Cu at the A(I) sites, the result here suggest that interfacial substitution operates as the strain accommodation and free energy minimization mechanism, which will be discussed below.

For the precipitate with 0 unit cells of Al₂Cu, the calculated misfit is substantially larger and negative for 100% Cu at the A(I) site. Substitution of Mg reduces the negative misfit. Further substitution of Al at the A(II) site will bring the calculated misfit close to the experimental value (Fig. 8).

Together with Al at A(II) and Mg at A(I), the interfacial thickness increases by ~0.4 Å. This amounts to a change 2.6% and 1.6% in misfit for the precipitate with 0.5 and 1.5 unit

cells of Al_2Cu respectively. The measured strain at approximately $\pm 5\%$ for these two types of precipitate is thus beyond the interfacial strain accommodation range.

3.3 Discussions

3.3.1 Formation of stable interfacial phase

Several studies have focused on the nucleation and growth that lead to the formation of Ω precipitates [9, 10, 16, 18]. Using atom probe field ion microscopy, Murayama and Hono found evidences of Mg-Ag co-clusters after 5s aging at 180 °C and no evidence of Cu atoms being incorporated in the Mg-Ag co-clusters. Their study also shows that initially, the clusters are not well defined in term of their morphology, which evolves into more distinct $\{111\}$ platelets only after further aging. Furthermore, Cu atoms aggregate to the clusters, and the concentration of Cu reaches approximately 30 at%. It has been suggested that the formation of Mg-rich clusters along the $\{111\}$ habit plane of the Al matrix is driven by the volume strain energy [16, 34, 35]. Howe pointed out that because of the larger size Mg atom in solution, clustering of Mg atoms on a $\{111\}$ matrix plane during the nucleation process would tend to expand the Al lattice and to accommodate a portion of the misfit strain, thereby reducing the volume strain energy associated with nucleation of the Ω -phase on the $\{111\}$ matrix planes [16]. From a calculation of the orientation and shape dependence of the minimum strain energy for Cu, Cu-Al, Mg and Mg-Cu clusters in the Al matrix, Suh and Park [34] concluded that the presence of Mg gives rise to the minimum strain energy condition for the formation of thin disc-shaped Mg or Mg-Cu along $\{111\}$ of the Al matrix. They also suggested that the presence of Ag accelerates the nucleation kinetics by further reducing the elastic strain energy. Zhu et al. [35] analyzed clustering or co-clustering in the

Al-Cu-Mg-Ag alloy using a quasi-chemical model and strain energy associated with the formation of clusters. Based on these analyses, they concluded that Ag has an overwhelming tendency to form co-clusters with Mg and this leads to Ag-Mg-Cu co-clusters. They also suggested that Ag-Mg-Cu most likely, rather than Mg-Ag, co-clusters are the precursors for Ω precipitates.

The thinnest precipitate we observed is the precipitate with zero unit-cell of the Ω phase. This precipitate contains two interfacial double-layers. A comparison between the experimental and calculated misfit suggested that the first layer next to the Al matrix has the composition of Ag_2Mg with Mg occupying the A(I) site below the hexagonally arranged Ag. In the second layer, Al occupies the identified A(II) site with Cu at the A(III). Together, Cu and Al form a structure with the composition of Cu_2Al . As the precipitate thickens, experimental and theoretical evidences here show that there are substantial amount of Cu atoms at the A(I) and A(II) sites.

The formation of Ag-Mg co-clusters is driven by the Gibbs free energy of Ag and Mg intermixing. The bulk phase diagram of Ag-Mg contains several intermetallic phases, suggesting a strong cohesive energy between Ag and Mg. In contrast, Ag and Cu tend to phase separate and the Gibbs free energy of mixing Ag and Cu for the FCC phase is positive. Our DFT calculations show a large gain in the heat of formation energy with Mg at A(I) site next to Ag, compared to Cu at the same site. This large energy gain explains the synergistic role of Ag and Mg in the formation of Ω precipitates along the Al $\{111\}$ habit planes. Experimentally, studies have shown, without exception, that Ag and Mg segregates to the broad faces of the plates at all temperatures and the interfacial Ag/Mg layer extends to the entire width of Ω precipitates independent of the precipitate plate aspect ratios.

The two characteristics of the interface, e.g., its stability during coarsening and its distinct structure of the interface, make this interface very unique and distinct from the more commonly known precipitates, such as the θ phase in Al-Cu. The precipitation sequence of Al-Cu involves the formation of several meta-stable phases and different interfaces.

Ag atoms arranged in the unusual hexagonal network at the interface of Ω phase we identified appears to be an important feature in some of other Al alloy precipitates as well. Recent reports on Al-Cu-Li and Al-Mg-Zn-Cu alloys [25, 36] suggested hexagonal atomic arrangement at the interface with Cu and Zn atoms instead of Ag atoms. In the middle of these Cu and Zn hexagons, Li and Mg atoms are observed. Thus, a distinction can be made that the formation of a separate, stable, structure at the interface gives rise to interfacial phase.

3.3.2 Interfacial formation energy

In all cases shown in Figure 7(a), the calculated heat of formation is substantially negative, indicating that the Ω precipitate is highly stable. To examine the interfacial contribution to the heat of formation, we calculated the interfacial formation energy E_f , using the equation of

$$E_f = E_T - N_{Al_2Cu} E_{Al_2Cu} - \sum_i N_i E_i \quad (2)$$

Here, E_T is the calculated supercell total energy, N_{Al_2Cu} the number of unit cells of the Ω phase included in the supercell, and E_{Al_2Cu} the cohesive energy of Al_2Cu (θ'). E_i is cohesive energy and N_i is the number of each elements included in the supercell (excluding atoms in side Al_2Cu). The cohesive energy of Ag and Mg atoms were obtained from the metallic Ag and Mg, while that of interfacial Cu is obtained from the Al_2Cu structure. The choice of

Al_2Cu for Cu is for the reason to obtain energy difference compared to the stable Al_2Cu structure. E_f values are normalized to the unit of eV/nm^2 .

Using values listed in Table 1, we calculated that $E_f = -0.25 \text{ eV/nm}^2$ with 100%Mg and $E_f = +4.15 \text{ eV/nm}^2$ with 100%Cu at the A(I) site. In comparison, the interfacial formation energy of the Ω precipitate on $\{111\}_{\text{Al}}$ plane without the observed interface structure is positive with $E_f = +2.12 \text{ eV/nm}^2$. To put this in perspective, we also calculated $E_f = +1.55 \text{ eV/nm}^2$ for θ' precipitate on $\{100\}$ Al planes using the same methods described above. Thus, energetically on the heat of formation alone, the bilayer formation is favored and stable with 100% Mg at A(I) site.

3.3.3 Interfacial free energy model

The above results show that both the precipitate heat of formation and thickness are affected by atomic substitutions at the interfacial atomic sites. To examine their relative contributions to the precipitate free energy, we construct a model by considering the strain energy associated with the precipitate misfit. For this purpose, we used the formulation of Lee, Barnett and Aaronson for a coherent ellipsoidal precipitate [37]. The assumption could be applied to the plate-like precipitate since the precipitate has extremely large aspect ratio ($\sim 1/100$). The model gives the strain energy per precipitate volume as:

$$E_s = 2\mu_\alpha \varepsilon(c)^2 \frac{1+\nu_\alpha}{1-\nu_\alpha} f(\beta, \mu_\Omega / \mu_\alpha) \quad (3)$$

where c stands for interfacial composition, ε the misfit, μ_α and ν_α are the shear modulus and Poisson ratio of the Al matrix. According to Lee, Barnett and Aaronson [37], the value of the factor f depends on the aspect ratio (β) and the shear modulus ratio (μ_Ω / μ_α) and

anisotropic elastic constants of the precipitate, which is largely unknown here. Consequently, we will treat f as a parameter here. Using the above strain energy model, we then obtain

$$\Delta G / A = E_s t + \Delta H(c) - T \Delta S(c) \quad (4)$$

Where ΔG is the change in free energy with Mg or Al substitution at A(I) or A(II) sites, t the precipitate thickness and A for the surface area. The first term is the strain energy. For simplicity, we will consider substitution at A(I) site by Mg alone in what follows. There are ~ 11 A(I) sites on a 1 nm^2 precipitate interfacial area and the largest $T \Delta S$ contribution at 473.15K is $\sim 0.3 \text{ eV/nm}^2$, which is small and will be neglected here. The $\varepsilon(c)$ and $\Delta H(c)$ are linearized using the data in Fig. 7.

Figure 9 plots the change in free energy per nm^2 as function of Mg occupation on A(I) for a precipitate with 2 unit cells of Al_2Cu and $f = 1$ to 6. The precipitate has a calculated misfit of -0.19% with 100% Cu at A(I), while 100% Mg at A(I) gives 1.25% misfit. Mg atom at A(I) gives rise to $\Delta H = -0.96 \text{ eV/atom}$ or $\Delta H = -10.56 \text{ eV/nm}^2$. The thermodynamic model predicts a minimum in the free energy at intermediate Mg substitution when the strain energy contribution is large with $f \approx 2$ or above. The minimum shifts to lower Mg content as f increases.

3.3.4 Precipitate misfit and coarsening resistance

The plate-like Ω precipitates have high thermal stability and coarsening resistance compared to the more common Al alloy precipitates, such as the θ' phase. Experimental study has concluded a ledge mechanism for the Ω precipitate plate thickening kinetics and the overall thickening kinetics are restricted by a limited supply of ledges [11]. The reason for the limited supply of ledges could be found from the stable Ω precipitate interface, which is

difficult to nucleate ledges. In fact, we rarely observed ledges on thin precipitates.

Interestingly, the most frequently observed precipitate was 2 unit cell (Table 4), which we found to have most favorable strain accommodation capability. In most of the observed cases of 2 unit cell precipitates, there were no ledges on the entire precipitate. This is consistent with the stability predicted based on the above free energy model. Consequently, thickening of an integer unit cell precipitate is expected to have a large free energy barrier because of the large misfit associated with a half unit cell of the Ω phase, in addition to the energy barrier associated with the interfacial ledge.

The statistics of the number of Ω precipitates with integer unit-cells of Al_2Cu is larger than the ones with half unit-cell Al_2Cu (Table 4). However, the number of observed half unit-cell Ω precipitate is significant and cannot be neglected despite of their unfavorable free energy. We suspect that other mechanisms, for example, atomic substitutions inside the first or second Al layers above or below the precipitate, might mediate the strain energy of the half unit-cell Ω precipitates. The strain energy relief and ledge formation are closely related, and conclusively contribute to the coarsening resistance.

4. Conclusions

Our combined experimental and theoretical study shows that a highly stable double-layer interfacial structure separates the Ω phase from Al in the Al–Cu–Mg–Ag alloy. The outermost layer next to Al is composed of Ag atoms in graphene-like hexagonal sites and Mg or Cu atoms below the center of the hexagon. The interfacial Mg atoms greatly stabilize the interface structure and consequently the Ω phase on the Al {111} habit as well. Furthermore, atomic substitutions of light atoms, Al and Mg, at the interface mediate the misfit strain and

minimize free energy. Overall, atomic resolution microscopy played a critical role in the elucidation of interfacial atomic structure, while theory enables a construction of thermodynamic model based on calculated formation energy, precipitate strain and dependence on atomic substitutions.

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References

- [1] Auld JH, Vietz JT. The Mechanism of Phase Transformations in Crystalline Solids. Institute of Metals Special Report vol. No. 33. London: Institute of Metals, 1969 p.77.
- [2] Auld J, Vietz J, Polmear I. Nature 1966;209:703.
- [3] Auld J. Materials science and technology 1986;2:784.
- [4] Knowles K, Stobbs W. Acta Crystallographica Section B: Structural Science 1988;44:207.
- [5] Polmear I. JIM, Materials Transactions 1996;37:12.
- [6] Polmear IJ, Pons G, Barbaux Y, Octor H, Sanchez C, Morton AJ, Borbidge WE, Rogers S. Materials science and technology 1999;15:861.
- [7] Lumley RN, Polmear IJ. Scripta Materialia 2004;50:1227.
- [8] Garg A, Chang YC, Howe JM. Acta metallurgica et materialia 1993;41:235.
- [9] Hono K, Sakurai T, Polmear IJ. Scr. Metall. Materialia 1994;30:695.
- [10] Ringer SP, Hono K, Polmear IJ, Sakurai T. Acta Materialia 1996;44:1883.
- [11] Hutchinson C, Fan X, Pennycook S, Shiflet G. Acta Materialia 2001;49:2827.
- [12] Kerry S, Scott V. Metal science 1984;18:289.
- [13] Garg A, Howe J. Acta metallurgica et materialia 1991;39:1939.
- [14] Muddle BC, Polmear I. Acta Metallurgica 1989;37:777.
- [15] Chang YC, Howe JM. Metallurgical Transactions a-Physical Metallurgy and Materials Science 1993;24:1461.
- [16] Howe JM. Philosophical magazine letters 1994;70:111.
- [17] Moore KT, Howe JM, Veblen DR. Philosophical Magazine B 2002;82 13.
- [18] Hono K, Sano N, Babu SS, Okano R, Sakurai T. Acta metallurgica et materialia 1993;41:829.
- [19] Reich L, Murayama M, Hono K. Acta Materialia 1998;46:6053.
- [20] Sun L, Irving DL, Zikry MA, Brenner D. Acta Materialia 2009;57:3522.
- [21] Batson PE, Dellby N, Krivanek OL. Nature 2002;418:617.
- [22] Pennycook SJ, Varela M, Hetherington CJD, Kirkland AI. Mrs Bulletin 2006;31:36.
- [23] Bjorge R, Dwyer C, Weyland M, Nakashima PNH, Marioara CD, Andersen SJ, Etheridge J, Holmestad R. Acta Materialia 2012;60:3239.
- [24] Bourgeois L, Medhekar NV, Smith AE, Weyland M, Nie JF, Dwyer C. Phys. Rev. Lett. 2013;111:046102.
- [25] Marioara CD, Lefebvre W, Andersen SJ, Friis J. Journal of Materials Science 2013;48:3638.
- [26] Wen J, Mabon J, Lei C, Burdin S, Sammann E, Petrov I, Shah AB, Chobpattana V, Zhang J, Ran K. Microscopy and Microanalysis 2010;16:183.
- [27] Spence JCH, Zuo JM. Electron Microdiffraction. New York: Plenum, 1992.
- [28] Ishizuka K. Ultramicroscopy 2002;90:71.
- [29] Kresse G, Furthmüller J. Physical Review B 1996;54:11169.
- [30] Perdew JP, Burke K, Ernzerhof M. Phys. Rev. Lett. 1996;77:3865.
- [31] Perdew JP, Burke K, Wang Y. Physical Review B 1996;54:16533.
- [32] Pulay P. Chemical Physics Letters 1980;73:393.
- [33] Fonda R, Cassada W, Shiflet G. Acta metallurgica et materialia 1992;40:2539.
- [34] Suh IS, Park JK. Scr. Metall. Materialia 1995;33:205.
- [35] Zhu AW, Starke EA, Shiflet GJ. Scripta Materialia 2005;53:35.
- [36] Dwyer C, Weyland M, Chang LY, Muddle BC. Appl. Phys. Lett. 2011;98:201909.

- [37] Lee JK, Barnett DM, Aaronson HI. Metallurgical Transactions a-Physical Metallurgy and Materials Science 1977;8:963.
- [38] Gale WF, Totemeier TC. Smithells metals reference book: Butterworth-Heinemann, 2003.
- [39] Murray JL, Int Met Rev 1985;30:211.
- [40] Wang S, Starink M. International Materials Reviews 2005;50:193.
- [41] Wolverson C. Acta Materialia 2001;49:3129.

Figure Captions:

Figure 1 A HAADF image of the sample recorded at a medium magnification. The sample was viewed along the $[211]_{\text{Al}}$ direction.

Figure 2 Selected HAADF images showing the precipitates of different thicknesses and their structure models. The thinnest precipitate observed has 0 unit cell of the Ω phase between the observed interfaces. The structural models at the right constructed based on the results of this paper show that the precipitates retain its characteristic interfacial structure.

Figure 3 Experimental and simulated atomic-resolution HAADF images viewed from the $[100]_{\Omega}$ (a), $[110]_{\Omega}$ (b), $[010]_{\Omega}$ (c), $[310]_{\Omega}$ (d) of Ω precipitate. The experimental images are periodically averaged parallel to the precipitate. The averaging improves the visibility of light Al atoms. Simulated images based the structural model proposed here are displayed inside the white box for the comparison.

Figure 4 Interfacial composition analysis using EELS and EDX. (a) EELS spectra recorded using a line scan across the precipitate whose Z-contrast image viewed from $[110]_{\Omega}$ orientation is shown at left. The spectra are plot with the scan coordinate along the vertical axis and energy loss for the horizontal axis. The as-recorded spectra contain the Ag $M_{4,5}$ (tail of the edge) and Cu $L_{2,3}$ (middle). Background subtracted core loss spectra (right) is shown to remove the strong tail of the Ag $M_{4,5}$ signal in the spectrum at the precipitate interface. (b) Mapped EDX signals of Ag, Cu and Mg. Averaged signal of Ag is displayed on the right side of Ag signal. HAADF-STEM image obtained before the EDX mapping is shown on the left for the comparison.

Figure 5 At left, a 3D rendering of the atomic structure of Ω precipitate inferred from Fig. 3 and DFT calculations. The atoms are colored in white (Ag), red (Cu), blue (Al). Interfacial sites, A(I), A(II) and A(III) are labeled and colored separately.

Figure 6 (a) A Z-contrast image of a Ω precipitate viewed long $[100]\Omega$. The boxed section is magnified and shown in (b). The magnified image show strong Z contrast on some of A(I) sites that are marked by arrows. Dark contrast are seen at other A(I) sites. (c) Experimental recorded EDS ($\text{MgK}\alpha_{1,2}$) signal profile across the precipitate. The EDS signal was obtained from a region shown in the recorded Z-contrast HAADF image next to the profile.

Figure 7 Calculated layer thickness ($\text{\AA}$) (a) and formation energy (eV) (b) as a function of Mg and Al substitution at A(I) and A(II) sites. Exact values for the formation energies are listed on Table 3.

Figure 8 A comparison between the measured and calculated lattice misfits. The measurements are for precipitates with 0 to 2 unit cells of Ω phase. The calculated misfits are for the 0 and 2 unit cells cases with A(I)/A(II) sites occupied by Cu/Cu, Mg/Cu and Mg/Al respectively.

Figure 9 Calculated free energy curves as function of Mg on A(I) sites for selected f values for the 2 unit cell Ω precipitate. The box marks the measured misfit. For details, see text.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

<i>Element(Structure)</i>	<i>Lattice constant(Å)</i>		<i>ΔH(eV/atom)</i>	
	<i>Exp.^a</i>	<i>Calc.</i>	<i>Exp.^a</i>	<i>Calc.</i>
Al (FCC)	4.05	4.05	-3.35	-3.70
Cu (FCC)	3.62	3.64	-3.54	-3.73
Mg (HCP)	a=3.21 c=5.21	a=3.21 c=5.18	-1.67	-1.53
Ag (FCC)	4.09	4.14	-2.95	-2.73
Ω (Al ₂ Cu) Knowles'	a=4.96 b=8.59 c=8.48	a=4.89 b=8.56 c=8.57	-0.167 ^b -0.162 ($E_{\text{Al}_2\text{Cu}} = -92.92 \text{ eV/cell}$)	
θ' (Al ₂ Cu)	a=4.05 c=5.81	a=4.08 c=5.78	-0.209 ^c -0.200 ($E_{\text{Al}_2\text{Cu}} = -23.45 \text{ eV/cell}$)	
$E_{\text{Al}_2\text{Cu}(\Omega) \rightarrow \text{Cu}}$			-4.21	
Ω (Supercell) $N_{\text{Al}_2\text{Cu}} = 2, N_{\text{Al}} = 56$		a=9.58 b=8.61	$E_T = -389.55 \text{ eV/cell}$	
θ' (Supercell) $N_{\text{Al}} = 8$ $N_{\text{Al}_2\text{Cu}} = 1$		a=4.06 b=4.06	$E_T = -52.54 \text{ eV/cell}$	
Ω (Ag-Mg) $N_{\text{Al}_2\text{Cu}(\Omega) \rightarrow \text{Cu}} = 24, N_{\text{Mg}} = 8,$ $N_{\text{Ag}} = 16, N_{\text{Al}_2\text{Cu}} = 4, N_{\text{Al}} = 64$		a=9.89 b=8.78	$E_T = -765.87 \text{ eV/cell}$	
Ω (Ag-Cu) $N_{\text{Al}_2\text{Cu}(\Omega) \rightarrow \text{Cu}} = 24, N_{\text{Cu}} = 8,$ $N_{\text{Ag}} = 16, N_{\text{Al}_2\text{Cu}} = 4, N_{\text{Al}} = 64$		a=9.89 b=8.78	$E_T = -775.83 \text{ eV/cell}$	

Table 1. Calculated physical parameters used for formation energy calculations.

^a Experimental lattice constants (298 K) for Al, Cu, Mg, Ag are from [38], Ω from [4] and θ' from [39]

^b From [40]

^c From [41]

$E_{\text{Al}_2\text{Cu}(\Omega) \rightarrow \text{Cu}}$ is a chemical potential of a Cu atom obtained from Al₂Cu and $N_{\text{Al}_2\text{Cu}(\Omega) \rightarrow \text{Cu}}$ is a number of interfacial Cu atoms.

A(I)=100%Cu A(II)=100%Cu	A(I)=100%Mg A(II)=100%Cu
$a_1 = (9.85 \ 0.00 \ -0.08)$	$a_1 = (9.89 \ 0.00 \ -0.08)$
$a_2 = (0.00 \ 8.61 \ 0.00)$	$a_2 = (0.00 \ 8.61 \ 0.00)$
$a_3 = (-0.79 \ 0.00 \ 37.32)$	$a_3 = (-0.78 \ 0.00 \ 37.67)$

Table 2. Supercell dimensions obtained from DFT calculations.

Site	$\Delta H(eV)$	Occupation(%)	Site	$\Delta H(eV)$	Occupation(%)
	-21.71	25		-20.69	25
A(I)=Cu→Mg	-23.63	50	A(I)=Cu→Al	-21.09	50
A(II)=Cu	-25.57	75	A(II)=Cu	-21.36	75
	-27.48	100		-22.58	100
	-19.37	25		-20.57	25
A(I)=Cu	-18.81	50	A(I)=Cu	-21.09	50
A(II)=Cu→Mg	-18.11	75	A(II)=Cu→Al	-21.36	75
	-17.55	100		-21.79	100

Table 3. Formation energy as a function of occupation by Cu, Al and Mg at the interfacial sites, A(I) and A(II).

Precipitate thickness (unitcell)	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5
Observed number of precipitates	3	7	4	3	15	3	1	0	1	2

Table 4. Number of observed Ω precipitates and frequency.