Transmission Electron Microscopy Study of Precipitation Behaviors in Cu–15 mass% Sn Alloy Annealed at 593 K

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We have investigated precipitation behaviors of Cu–15 mass% Sn alloy annealed at 593 K by using transmission electron microscopy. Three kinds of precipitates with different morphologies have been observed. Inside grains, plate-like precipitates of approximately ten µm in length were found to display regular configuration. They are the equilibrium α phase, and the orientation relationship with the matrix α phase can be expressed as (001) // (111), [100] // [110], with (001), habit planes. At grain boundaries, Sn-rich precipitates of irregular shapes were found to precipitate. They are the δ phase, which is stable above 623 K. Some of them exhibit an incipient stage of growing cellular morphology brought about by induced grain boundary migration. In addition, there are intragranular particle-like grains of several µm or less, some of them are confirmed to be the δ phase. The observed precipitation behaviors are discussed from the viewpoints of crystallography of these phases. [doi:10.2320/matertrans.MAW201206]

1. Introduction

The Cu–Sn binary system provided the first major alloy for man, known as bronze, and has been utilized for a long time. Yet, their phase separation behaviors are often complex, and there remain several unanswered questions. For example, in a systematic study of discontinuous precipitation in Cu-based alloys, Kim et al. pointed out that the reaction rate of Cu–Sn alloys was the slowest among six alloy systems examined (Cu–Ag, Mg, Sb, In, Cd and Sn), and they discontinued the study on Cu–Sn alloys after annealing them at 723 K for 11 days.1,2 Aaronson and Pande also pointed out the necessity for the investigations on the phase separation behaviors of Cu-based systems, including Cu–Sn alloys, from the viewpoints of the formation of cellular morphology.3 In this regard, the present paper illustrates hitherto unknown precipitation behaviors found in a Cu-rich Cu–Sn alloy.

The phase diagram of the Cu–Sn system shows the solubility of Sn increases drastically from about 9 mass% at 593 K to the maximum value of 15.8 mass% at 793 K.3 In the past, this large increase in the solubility within a temperature span of 200 K led several researchers to explore possible age-hardening caused by precipitation of Sn-rich phase(s) from quenched Cu–Sn alloys supersaturated with Sn. According to an early report by Haase and Pawlek, who measured hardness changes of 90% cold-rolled alloy upon annealing, the increase in hardness was, however, insignificant in the temperature range of 473–623 K,5 despite the fact that their optical microscopy (OM) observation on the annealed specimen showed the existence of a number of intragranular precipitates. On the other hand, Böhm first reported the development of a cellular morphology around grain boundaries.5 This type of phase separation phenomena, which are initiated at heterogeneous sites, typically grain boundaries, are generally expressed as discontinuous precipitation, and known to occur in a number of alloy systems.6

Later, a metallographic study of Tsubakino revealed that discontinuous precipitation and intragranular precipitation, also known as continuous precipitation, in fact compete each other in such a way that the development of the latter impede the progress of the former.7,8 The sluggishness of the phase separation reaction in Cu–Sn alloys was noted by several other researchers using different techniques, such as OM and scanning electron microscopy (SEM),3 Mössbauer spectroscopy,3 OM and thermal analysis.9 In addition, in a detailed calorimetric study by Varscheavsky, no thermal events was detected during annealing of a quenched Cu–Sn alloy.10 Partly because of the slowness of the reaction, several researchers employed mechanical deformation, often cold-rolling, to accelerate phase separation processes. For example, kinetic evaluations of differential scanning calorimetry led researchers to speculate possible existence of a metastable phase.11

In fact, identification of the phases involved in the precipitation processes is not well documented. The Cu–Sn phase diagram shows that the α matrix phase is in equilibrium with the ε phase (Cu5Sn4, Cu3Ti type, Pmnm, a = 0.549 nm, b = 0.432 nm, c = 0.474 nm) below 623 K. In the literature,7,8 it is reported that the presence of the ε phase had been confirmed by using X-ray diffraction (XRD) technique. However, XRD detects only an average structure and not really suited for detecting local microstructural changes, such as those taking place at grain boundaries. In this respect, transmission electron microscopy (TEM) has advantage in finding both crystallographic and morphological transformations in a limited area of a specimen.

Therefore, the purpose of the present research was to elucidate the phase separation behaviors in the Cu–Sn alloy annealed at 593 K for 2.85 × 10⁵ s. This annealing condition was selected based on the onset temperatures of the reactions provided by Tsubakino.7,8 Namely, he reported, in the form of time-temperature diagram, that the initiation of hardening at grain boundary regions takes place after annealing at T = 593 K for approximately 1.1 × 10⁸ s, while the onset of hardening inside grains was observed after about 2 × 10⁹ s of
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A Cu–Sn alloy was prepared from high purity Cu and Sn (99.99%) by induction melting, followed by furnace cooling. Inductively-coupled plasma spectroscopy (ICP) showed that the composition of the alloy is Cu–15 mass%Sn, while OM observation indicated a dendrite structure. The ingot was cut into a 4 × 4 × 5 mm³ block and sealed in a silica tube under a vacuum better than 1.0 × 10⁻³ Pa. They were annealed at 1023 K for 120 h for initial homogenization, followed by annealing at 853 K, at which the solubility is the maximum, for 120 h to complete solution treatment, and finally quenched in iced water. Our OM observation on the quenched specimen showed a uniform microstructure with an average grain size of 100–150 μm. Subsequent annealing was then carried out at 593 K for 2.85 × 10⁶ s in the furnace under a vacuum better than 1.0 × 10⁻³ Pa.

We used electron probe micro analyzers (EPMA), JEOL JXA-8621MX and JXA-8530, to obtain SEM images with the acceleration voltage of 15–20 kV both in secondary electron (SE) and back-scattered electron (BSE) modes. Identification of elements in these EPMA has been done by using LIF and PET analyzer crystals for Cu Kα and Sn Lα lines, respectively. In order to prepare TEM specimens, we employed an FIB machine (FEI Quanta 3D) equipped with SEM and Omniprobe™ to identify and pick up the area of interest. A rectangular block with a size of 20 × 2 μm² was covered with carbon in order to prevent them from damage, and Ga ion at 30 kV was used to ‘dig’ the surrounding areas. After thinning of the block, we employed an ion-milling machine (Gentle Mill, Technoorg-Linda) to remove damaged surfaces. An image formed by SEs, which are generated by scanned Ga ions, is referred to as scanning ion microscopy (SIM) image in this report. TEM observation was carried out by using JEM-2000EX microscopes operating 200 kV. In the present paper, diffraction patterns are presented after proper rotation calibration.

3. Results

Figure 1 shows a BSE-SEM image of the specimen annealed at 593 K for 2.85 × 10⁶ s. In this mode, heavy elements show bright contrasts. Thus, it can be seen that Sn-rich phases are distributed at grain boundaries and inside grains, whose sizes are on the order of several ten μm. Careful observation on the contrast distribution inside the grains revealed that there are two kinds of intragranular precipitates. One is plate-like precipitates of about ten μm in length, displaying lucid arrangements of parallel line contrasts, while the other is particle-like precipitates of about several μm, randomly located inside grains. It can also be noticed that the morphology of the grain boundaries are often not straight, as judged by irregular white contrasts. This observation suggests that precipitation has taken place also discontinuously along grain boundaries, though it did not give rise to a clear cellular morphology, typically observed during discontinuous precipitation.⁶,⁷ We checked other areas of the specimen, and confirmed that no cellular morphology was visible at this magnification.

Figure 2 is a Sn elemental mapping image obtained from the same specimen. Inside grains, it can be seen that plate-like precipitates align themselves in parallel to each other, and that small particle-like precipitates also exist in a rather irregular manner. Deep blue contrasts surrounding these precipitates suggests that Sn is depleted in the α matrix in the vicinity of precipitates.
Figure 3(a) is a plan-view SIM image taken from an intragranular region, where plate-like precipitates dominate. The white rectangle indicates the area selected for FIB sampling. Note that this area covers two sets of plates, i.e., those which are almost vertical, and the others which are inclined, with respect to the bottom of the figure. The inscribed area was ‘dug’ about 10 µm in depth, picked up, and placed in a specimen holder, as shown in an SIM image, Fig. 3(b). The two sets of the plate-like precipitates are visible in this cross-sectional view.

Figure 4(a) is a bright field (BF) image of the above specimen. Contrasts due to bend contours, traversing from the top center to bottom left corner, suggest that the specimen is slightly curved. (As shown below, this bend contour is a part of the (110) zone axis pattern of the fcc structure of the α phase.) Figures 4(b) and 4(c) are selected area diffraction (SAD) patterns obtained from the circular areas indicated, respectively, by the circles b and c in Fig. 4(a). The SAD pattern in Fig. 4(b) is presented at a small camera length setting, in order to show both the pattern from the α matrix and that arising from the plate-like particle. The SAD pattern in Fig. 4(c), which is presented at a large camera length, is basically the same pattern as that in Fig. 4(b). These observations thus suggests that these plate-like particles possess the same orientation relationship (OR) with the matrix. Figure 4(d) is a dark field (DF) image taken with a spot from the precipitate, as indicated by the arrow in Fig. 4(b). Note that all the long precipitates perpendicular to the bottom of the figure give rise to strong contrasts, indicating that they all possess the same orientation.

The pattern due to the α matrix, though it is not along an exact zone axis, can be indexed as the (110) diffraction pattern of the fcc structure, while the pattern due to the precipitates as the [001], pattern of the ε phase, even though the zone axes of the two phases are not exactly parallel. We can roughly estimate the angular deviation between the [110]α and [001], axes by measuring the reciprocal distance between the poles in the superimposed diffraction pattern. This procedure yielded the angle between these two axes is about 1.2 degrees. In addition, in the SAD pattern in Figs. 4(b) and 4(c), it can be seen that the spots arising from the α matrix and that from the ε plate overlaps systematically. For example, the double arrow in Fig. 4(c) shows that 220, and 023, spots overlap. (d) DF image obtained with the spot indicated by the arrow in (b), showing that all the vertically oriented planar precipitates possess the same orientation.

Fig. 3 (a) Plan-view SIM image of the specimen. The dark line contrasts and particle-like contrasts arise from Cu-Sn precipitates. The white rectangle indicates the area, where FIB sampling was carried out. (b) SIM image of the sampled specimen attached to a TEM specimen grid. The white rectangle is the area, from which TEM observation was made, as shown in Fig. 5.

Fig. 4 (a) BF image of the FIB specimen. The bend contour at the center is a part of the (110) zone axis pattern of the α matrix. Circles b and c indicate the areas, where SAD aperture was set. (b) SAD pattern obtained from the area b indicated in (a), showing superposition of slightly off-axis [110] diffraction pattern of the α matrix and diffraction pattern from the precipitate, which can be assigned as the [100] diffraction pattern of the ε phase. (c) SAD pattern obtained from the area c in (a). The double arrows show that 220, and 023, spots overlap. (d) DF image obtained with the spot indicated by the arrow in (b), showing that all the vertically oriented planar precipitates possess the same orientation.
with the two orientations deviating each other by 1.2 degrees. In addition, it can also be seen from the BF and DF images that the (001) plane is parallel to the broad face of the precipitate, suggesting that this is the habit plane of the ε planar precipitates.

Figure 5(a) is a BF image taken from the area indicated by the rectangle shown in Fig. 3(b), with the specimen tilted approximately 60 degrees with respect to that shown in Fig. 4. Figures 5(b) and 5(c) are SAD patterns (with different camera length settings) taken from the circular area indicated in Fig. 5(a). It can be seen that the pattern in Fig. 5(b) is a superposition of two patterns, one from the matrix and the other from the precipitate. The pattern from the α matrix can be indexed as the [147] zone axis pattern, while that from the ε phase [102] zone axis pattern. Note that the [147] direction is about 60° away from [110] and so is [102] from [100]. This observation thus suggests that these inclined plate-like precipitates are another variant of the ε plates in the identical α matrix. Figure 5(d) is a DF image taken with the spot indicated by the arrow in Fig. 5(d), showing that these planar ε precipitates possess the same orientation.

Figure 6(a) is a plan-view SIM image of the specimen, where grain boundaries, plate-like precipitates, and particle-like precipitates appeared as black contrasts. Seen at the center of the figure is an rectangular area subject to FIB sampling, which included a grain boundary and particle-like precipitates. Figure 6(b) is a SIM image of the inscribed area by Ga ion. As shown, the area at the grain boundary is actually protruded toward the grain on the left, as indicated by the circle. In addition, there are a number of small intragranular particle-like precipitates. Figure 6(c) is a SIM image of the TEM specimen obtained after primary thinning. In the protruded region indicated by the rectangle A, it can be seen that two lamellar precipitates, as indicated by the arrows 1 and 2, are growing in parallel into the facing grain. This feature can be regarded as an incipient stage of the development of a cellular morphology. On the other hand, intragranular precipitates exhibit various shapes, even though they are bordered by clear straight edges. Careful comparison of the two SIM images, Figs. 6(b) and 6(c), before and after final thinning, reveals that the distribution of these small precipitates are slightly different because some of them are etched away during the milling process. This observation suggests that the size of individual precipitates are often smaller than 1 µm. Subsequent TEM observations have been made on the rectangular regions A and B, as we explain in detail below.

Figure 7(a) is a BF image corresponding to the area shown by the rectangle A in Fig. 6(c). This BF image exhibits a cellular morphology, where the lamellar precipitates seen in
the SIM image are indicated by the arrows 1 and 2. The circles d, e and f indicate areas, from which SAD patterns have been obtained, as shown, respectively, in Figs. 7(d), 7(e) and 7(f). These patterns can be indexed as the [001] and [125] patterns of the δ phase. Superimposed on (e) is a schematic illustration of the boundaries of these phases, where the original grain boundary is indicated by the letter GB, and the orientations of the α phase are indicated as α112 or α136. Note that the growing α lamella possess an identical orientation with straight sub-boundaries within the α lamella, as indicated by the arrows in (b), which suggest approximate growing direction of the cellular structure.

Fig. 7 (a) BF image of the rectangular area A in Fig. 6(c), showing discontinuously precipitated phases with a lamellar morphology. (b) and (c) DF images obtained with 311 and 111 spots of the α phase, respectively, while (d), (e) and (f) are [112], [112], [136] zone axis SAD patterns of the α phase taken from the areas indicated by the circles d, e and f, respectively. (SAD patterns from circles i and j are identical to e and f, and not shown.) (g) and (h) SAD patterns obtained from the areas indicated by the circles g and h. These patterns can be indexed as the [001] and [125] patterns of the δ phase. Superimposed on (c) is a schematic illustration of the boundaries of these phases, where the original grain boundary is indicated by the letter GB, and the orientations of the α phase are indicated as α112 or α136. Note that the growing α lamella possess an identical orientation with straight sub-boundaries within the α lamella, as indicated by the arrows in (b), which suggest approximate growing direction of the cellular structure.

The contrast distribution in these DF images suggests that (1) diffusion induced grain boundary migration (DIGM) has taken place, and (2) sub-boundaries in the α grains are initiated at the triple junction of the original grain boundaries, lamellar precipitate and the growing α phase, as indicated in the circles in Fig. 7(b). In fact, since these two sub-grains share the 311 axis, and since the angle between 112 and 136 axes is 52.3°, it can be shown that the sub-boundary is close to the Σ15 coincidence boundary.13 We summarized these observations in the form of schematic illustration, which is superimposed on the DF image (c). Here, the approximate original grain boundary position is indicated by the letter GB, while the orientations of the α grains are indicated as α112 or α136, respectively, for those exhibiting [112] or [136] diffraction patterns, as described above. Also indicated in the figure is the lamellar precipitates having the δ phase, which we will describe below.
for small particle-like precipitates. On the other hand, there are large plate-like precipitates inside grains. They are the equilibrium \(\varepsilon\) phase, and they display a well-defined OR with the \(\alpha\) matrix with (001), habit plane. In what follows, we discuss these observations from the viewpoints of discontinuous reaction of the \(\delta\) phase at grain boundaries, and coherent precipitation of the \(\varepsilon\) phase inside grains.

The morphology of the precipitates at grain boundaries indicated that they are not merely segregation of Sn atoms, but that nucleation and growth of the \(\delta\) phase have taken place heterogeneously at grain boundaries. However, the size of the precipitates does not exceed several \(\mu\)m. Indeed, in the past, a metallographic study on the discontinuous precipitation of a Cu–15 mass\%Sn alloy annealed at 593 K by Tsubakino reported that cellular morphology develops only slowly, and terminates as homogeneous, or continuous, precipitation of plate-like precipitates dominates inside grains.\(^7\) In the literature, it is also reported that the precipitating phase is the \(\varepsilon\) phase by using an X-ray diffraction technique.\(^7,9\) Our observation is, to some extent, in agreement with their reports. Namely, the cellular morphology extends only several \(\mu\)m, and ceases to develop at 593 K. However, the precipitating phase at grain boundaries in this case is not the \(\varepsilon\) phase, but the \(\delta\) phase. There, the growing \(\delta\) precipitates and the depleted \(\alpha\) matrix often display an embryonic cellular microstructure, which is protruding into one of the facing grains.

The origin of the protruded cellular region, as observed in Figs. 6 and 7, deserves some discussion. First, note that the orientation of the \(\alpha\) phase in the protruded region is the same as that of the grain, at which the reaction initiated. This indicates that grain boundary moved, as phase separation due to partitioning of Sn atoms proceeds. This is the phenomenon known as DIGM, as mentioned before.\(^15,16\) The resultant cellular morphology, albeit its small size, is the one typically observed in discontinuous precipitation.\(^6\) In the past, two mechanisms have been proposed to explicate the origin of the microstructure. Briefly, on one hand, Tu and Turnbull attributed the asymmetry of interfacial energies of opposing faces of a precipitating phase to the deriving force for the development of cellular morphology (TT mechanism).\(^17,19\) On the other hand, Fournelle and Clark discovered another mechanism, where a secondary phase periodically precipitates along a moving grain boundary, and the precipitates and depleted matrix grow simultaneously (FC mechanism).\(^20\) In the former, each lamella builds up one by one, while in the latter lamellae grow more or less in parallel. Our observation, for example, the presence of a sub-boundary within the growing \(\alpha\) matrix, which indicates the growing direction, suggests that each lamella grows one by one, signifying that TT mechanism is probably operating in the current discontinuous precipitation process.

The cellular morphology, however, never extends more than several \(\mu\)m. One of the reasons for the interruption of its growth is a diminishing driving force due to precipitation of Sn rich phases inside grains, as pointed out by Tsubakino.\(^7\) As mentioned earlier, the several literatures ascribe sluggishness of the discontinuous reaction in the Cu–Sn system to the formation of the equilibrium \(\varepsilon\) phase. Yet, the current study has disclosed that, in addition to the plate-like \(\varepsilon\) precipitates, the \(\delta\) phase is present both at grain boundaries and inside the

Fig. 8 (a) BF image of the rectangular area B in Fig. 6(a), showing several differently shaped particle-like precipitates. (b), (c) are SAD patterns from the circles indicated by the same letters. They are [115] and [001] zone axis patterns of the \(\delta\) phase.

Figures 7(g) and 7(h) are SAD patterns obtained from the lamellar precipitates 1 and 2 in this protruded region, as indicated by the arrows. These patterns can not be assigned as those that could arise from the equilibrium \(\varepsilon\) phase, but as those that arise from the \(\delta\) phase (Cu\(_4\)Sn\(_{11}\), \(\gamma\) brass structure, \(F\bar{4}3m, a = 0.1798\) nm\(^{14}\)), which is metastable at 593 K, the temperature of heat treatment. Namely, Figs. 7(g) and 7(h) can be assigned as [001] and [125] patterns of the cubic \(\delta\) phase, respectively. We obtained SAD patterns along other axes, such as [113] or [299]s, and confirmed that these lamellae are the \(\delta\) phase. It should be noted, however, that the crystallographic orientations of these two precipitates are different from each other, despite the microstructural similarity of their shapes.

Figure 8(a) is a BF image corresponding to the rectangular area B shown in Fig. 6(c), while Figs. 8(b) and 8(c) are SAD patterns from the precipitate indicated by the circle in Fig. 8(a). These patterns can not be assigned either as those expected from the \(\varepsilon\) phase, but from the \(\delta\) phase. Namely, Figs. 8(b) and 8(c) are the [115] and [001] patterns of the \(\delta\) phase.

4. Discussions

We have shown that quenched Cu–15 mass\%Sn alloy decomposes into Sn-rich phases and the \(\alpha\) matrix in three different ways. At the grain boundaries, elongated precipitates have been observed with an incomplete cellular morphology, which can be regarded as an incipient stage of discontinuous reaction. The precipitates here have been identified as the \(\delta\) phase, which is metastable at 593 K, the temperature of annealing. The \(\delta\) phase has also been found
grains in the alloy annealed at 593 K. Thus the intragranular precipitation of both the δ and ε phases results in the decrease of supersaturation of Sn, effectively reducing the driving force for the cellular growth.

We currently can not give a plausible explanation as to the emergence of the metastable δ phase along grain boundaries, but only offer the following hypothesis. First, we note that the annealing temperature in the present study is close to the eutectoid temperature of the δ phase. This suggests that the difference in the free energies of the δ and ε phases is relatively small at the annealing temperature, implying that these two phases can compete each other to nucleate and grow. Thus, the final selection of the phase depends not only on the thermodynamics, i.e., free energy including both chemical and interfacial, but also on the kinetics. The δ phase possesses a complex structure, having a super-structure of the γ brass, which itself is composed of 3 × 3 × 3 unit cells of the body-centered arrangement of the β phase \((a = 0.298 \text{ nm})\).\(^{13}\) Therefore, the δ phase is composed of 6 × 6 × 6 fundamental unit cells with overall 416 atoms. Presumably, such a complex phase would require a high activation energy for its nucleation. In contrast, the ε phase has 8 atoms in the unit cell, exhibiting a pseudo-hexagonal structure. As shown in the present study, the (001) plane has an excellent matching with the \{111\}_α planes and thus, the activation energy for the nucleation can be low. The fact that the ε phase preferably nucleates on the \{111\}_α planes, especially on twin boundaries, supports this view. This, in return, may favor the nucleation of the δ phase at grain boundaries, since heterogeneous sites, notably grain boundaries, are normally preferred by phases, which require high activation energy for nucleation.

The planar precipitates are the ε phase, which is the equilibrium phase at this temperature. This observation itself is not too surprising. However, the origin of the plate-like morphology and OR should be addressed.

First, TEM examination revealed that the large faces of the ε precipitates are (001), and this habit plane is parallel to a (111) plane of the α matrix. With this information, it is now explicable why these lamellae displayed geometrically distinct morphology, as found in the BSE picture (Fig. 1) and Sn elemental mapping (Fig. 2). That is, there are four equivalent \{111\} planes in the fcc structure, and since the δ phase precipitates along these planes, the position of bright planar contrasts in these images correspond also to the traces of these planes. In addition, since the ε phase belongs to the orthorhombic crystal class, there are three possibilities as to the way, in which (001) planes match one of the \{111\} planes. Thus, there are altogether twelve variants in single δ grain, even though we can only distinguish four basic sets of variants in plan-view images. In addition, it is known that the stacking fault energy of Cu is low,\(^{21,22}\) and thus twin can easily be formed on \{111\} planes. With this in mind, it is now possible to point out some of the ε precipitates exist along the traces of twins in the BSE image, for example, the one shown in Fig. 1. That is, when looked carefully, the contrasts of subgrains bordered by a twin boundary differs slightly, implying an orientation dependency of the back-scattered electron yield, and some of large planar ε precipitates can be confirmed to exist there.

In Fig. 9, we show an atomic model of the ε phase viewed in the [534] direction. Here, four unit cells are shown and some of the atoms are connected by bonds to emphasize a layered structure in this structure. The crystal structure of this phase can be interpreted in several ways. If the unit cell is viewed along [010], axis, they can be regarded as a pseudo-hexagonal net, as indicated at the top face, or the (010), plane, of the drawing. There are four distinct bonds in this hexagonal net, but their lengths are either 0.274 or 0.275 nm, based on the literature values of the unit cell constant of the ε phase. On the other hand, the unit cell constant of the depleted α phase can be estimated as follows. Namely, the unit cell constant of the pure Cu, \(a_0\), is 0.36078 nm.\(^23\) However, the unit cell constant of the α phase, \(a\), is known to follow the Vegard’s law,\(^23\) and assuming the maximum solubility of Sn at 593 K, which is about 9 mass%, we have \(a = 0.366 \text{ nm}\). This value yields 0.259 nm as the nearest neighbor distance in the fcc structure of the α phase. It can then be seen that this value is about 6% smaller than the aforementioned distance between the neighboring atoms in the hexagonal nets in the (010), plane of the ε phase. When this value is converted to areal mismatch, it amounts to about 10%.

On the other hand, the same structure can be viewed as a stacking of distorted hexagonal nets parallel to the (001), plane, as indicated by upright layers in Fig. 9. This distorted hexagonal nets match quite well with \{111\} planes of the α phase without changing atomic configuration, as described below. First, the bond lengths of Cu atoms in 4\{f\} positions and other atoms (Cu and Sn atoms at 2\{a\} and 2\{b\} positions, respectively) in this distorted layers are all 0.268 nm. Next, when this bond is projected onto the (010), plane, it yields 0.256 nm. This means that the configurational mismatch of the ε and α phases along the [010], and [112]_α, axes is about 1%. In addition, the area of the projected hexagonal net of the δ phase is 0.178 nm², which can be compared with 0.174 nm² of the corresponding net of the α phase, with the difference...
being less than 3%. Therefore, it can be understood that the interfacial energy becomes small when (001) planes of the $\varepsilon$ phase is in parallel to the (111) planes of the $\alpha$ phase. We can thus propose that this reduction of the interfacial energy leads to the planar morphology of the $\varepsilon$ precipitates with aforementioned OR and (001)$_\alpha$ habit plane.

5. Conclusions

We examined the microstructure of the Cu–15 mass%Sn alloy annealed at 593 K for $2.85 \times 10^6$ s by using TEM. The results can be summarized as follows.

1. At grain boundaries, the $\delta$ phase, which is metastable at this temperature, appears in the form of irregularly shaped precipitates. Development of incipient cellular morphology on the order of several $\mu$m, composed of the lamellar $\delta$ phase and depleted $\alpha$ phase is also confirmed.

2. The $\delta$ phase also appears inside grains in the form of particles of about 1 $\mu$m.

3. Inside grains, the $\varepsilon$ phase appears in the form of plates on the $\{111\}$ planes of the $\alpha$ matrix, with the habit plane of (001)$_\varepsilon$. The OR of these two phases can be expressed as:

\[(001)$_\varepsilon$ // (111)$_\alpha$, [100]$_\varepsilon$ // [110]$_\alpha\]

with two axes deviating by about 1.2 degrees.

4. The observed OR and habit plane can be explained by configurational matching of atoms projected on these planes, where the misfit along [010]$_\varepsilon$ and [112]$_\alpha$ was estimated to be about 1%.

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