Metastable Phases in an Al-Mg-Si Alloy Containing Copper

KENJI MATSUDA, YASUHIRO UETANI, TATSUO SATO, and SUSUMU IKENO

The Q′ phase in an Al-1.0 mass pct Mg_2Si-0.5 mass pct Cu alloy at a peak-aged condition of 523 K was observed by a high-resolution transmission electron microscope (HRTEM), in order to identify its structure and chemical composition, and was compared with the type-C precipitate in an Al-1.0 mass pct Mg_2Si-0.4 mass pct Si alloy (the excess-Si alloy). The Q′ phase has similar features to the type-C precipitate, according to results of electron diffraction patterns and images taken by the HRTEM, that is, they have similar hexagonal crystal lattices (a = 1.04 nm and c = 0.405 nm) to each other. The type-C precipitate in the excess-Si alloy was the ternary Al-Mg-Si phase, and the Q′ phase was the quaternary Al-Mg-Si-Cu phase in the Al-Mg-Si-Cu alloy, as determined by energy-dispersive X-ray spectroscopic (EDS) analysis.

I. INTRODUCTION

IT is well known that the addition of copper to Al-Mg-Si alloys improves their mechanical properties, especially their ductility.[1] The metastable phase, however, has not yet been clarified in Al-Mg-Si-Cu alloys. Recently, the metastable phase containing copper has become known as the B′ phase, which Edwards et al.[2] have reported as behaving like the β′ phase in Al-Mg-Si alloys. Arnberg and Aurivillius[3] proposed a crystal structure for h-AlCuMgSi and determined its chemical composition to be $Al_4Cu_2Mg_8Si_7$. They also reported that the B′ phase formed in this alloy is the same as the β′ phase in a Cu-free Al-Mg-Si alloy. Dumolt et al.[4] reported that the crystal structure of B′ phase in the 6061 aluminum alloy has an orthorhombic structure or hexagonal one. These two types of precipitates have also been identified as being the type-B and type-C precipitates in our recent report,[5] which used high-purity Al-Mg-Si alloys without copper. Especially, it should be noticed that both precipitates appear in the high-purity Al-Mg-Si alloy without copper and contain no copper themselves. Laughlin and Miao[6] concluded, in their report on automotive 6000-series alloys, that all the Al-Mg-Si-Cu family alloys normally contain the quaternary phase Q. The Q′ phase is a metastable version of the Q phase and has the same crystal structure as the equilibrium Q phase. The Q′ phase has a lath morphology and a hexagonal structure, with the orientation of the long axis being parallel to the $\langle 100 \rangle_{Al}$ directions and $\{150\}_{Al}$ habit planes of the matrix.[6] Suzuki et al.[7] also reported that the Q′ phase existed in Al-Mg-Si alloys containing copper but did not determine its crystal structure. Perovic et al.[8] concluded that the AA6111 aluminum alloy has the β″ and Q phases in the peak-aged condition, although the AA6016 aluminum alloy contains only one precipitate phase, identified as β″. The AA6111 aluminum alloy used by them contains copper at about 0.75 mass pct; therefore, copper is an important element for precipitation of the quaternary Al-Mg-Si-Cu phase.

Recently, Caylon et al. have reported an interesting model for the Q, QC, and QP phases in the Al-Cu-Mg-Ag alloy and its composite materials.[9] They also extended their model to the metastable phases in Al-Mg-Si alloys. According to their report, metastable phases in Al-Mg-Si alloys can contain ternary elements, namely, Al, Mg, and Si, in the same way as the formation of the quaternary Q phase in Al-Cu-Mg-Si alloys.

We have already reported on the precipitation sequence of Al-Mg-Si alloys containing excess silicon, where we found three new types of precipitates: type A, type B, and type C.[5] The three types of precipitates differ both in chemical composition and size of crystal lattice from the β′ phase, which is a typical metastable phase in Al-Mg-Si alloys.[10] The type-C precipitate has a similar size of crystal lattice to the Q′ and B′ phases, but contains no copper. The type-C precipitate also has a tendency to nucleate on or near matrix dislocations in specimens deformed before aging.[11]

In this study, the metastable phases in an Al-1.0 mass pct Mg_2Si alloy containing 0.5 mass pct Cu were directly investigated using a high-resolution transmission electron microscope (HRTEM), since the precipitation sequence of this alloy is known and has a clear difference in the metastable phase from both the Al-Mg-Si alloy and the alloy containing 0.5 mass pct copper.

II. EXPERIMENTAL PROCEDURE

An Al-1.0 mass pct Mg_2Si-0.5 mass pct Cu alloy (the "0.5Cu alloy") was prepared using 99.99 pct pure aluminum and 99.9 pct pure magnesium, silicon, and copper ingots. An Al-1.0 mass pct Mg_2Si alloy (the "balanced alloy") and an Al-1.0 mass pct Mg_2Si-0.4 mass pct Si alloy (the "excess-Si alloy") were also prepared. The alloys obtained were hot and cold rolled to form 1.0-mm-thick sheets. The thickness of sheets used for TEM samples was 0.2 mm. The 0.5Cu alloy was homogenized at 803 K for a time of 604.8 ks prior to rolling. Sheets were solution heat-treated at 848 K for 3.6 ks and quenched in chilled water at ~277 K. An aging treatment was performed at 523 K, and the aging time was chosen to obtain the peak-aged condition at 523 K for each alloy. The TEM samples were made by a twin-jet electrical polishing technique using a nitric acid–methanol solution. The micro Vickers hardness of each alloy was also measured, with a load of 0.987 N and a holding time of 15 seconds. The

KENJI MATSUDA, Associate Professor, and SUSUMU IKENO, Professor, are with the Faculty of Engineering, Toyama University, Toyama, 930-8555 Japan. YASUHIRO UETANI, Associate Professor, is with the Research Institute of Technology, Toyama Prefectural University, Toyama, 939-0398 Japan. TATSUO SATO, Professor, is with the Faculty of Engineering, Tokyo Institute of Technology, Tokyo, 152-8552, Japan.
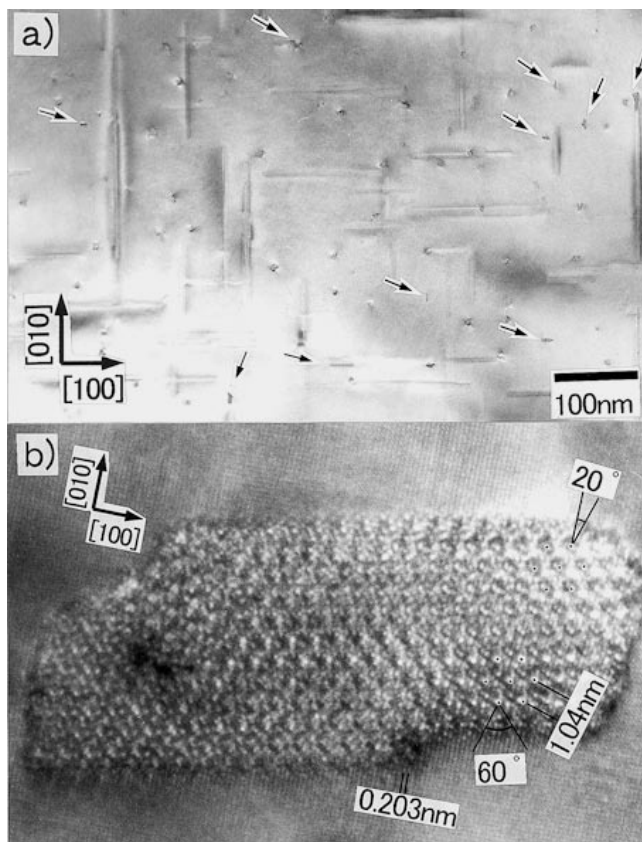Manuscript submitted December 27, 2000.

Fig. 1—(*a*) TEM images for 0.5Cu alloy aged at 523 K for 3.84 ks, giving peak hardness; and (*b*) a typical HRTEM image of the rod section of a lath-shaped precipitate in (*a*).

Fig. 2—Relative frequency plotted against the angular distribution between the $\langle 1\bar{1}00 \rangle$ direction of the Q' phase and $\langle 100 \rangle$ direction of the matrix.

Fig. 3—HRTEM images of rod sections Al-Mg-Si alloys: (*a*) the β' phase in the balanced alloy aged at 523 K for 12 ks; and (*b*) the type-C precipitate in the excess Si alloy aged at 523 K for 60 ks.

HRTEM images were taken by a Topcon EM-002B–type HRTEM operated at 200 kV, and its point resolution was 0.18 nm. A JEOL 2010F field emission–type TEM (FETEM) with a Be sample holder was also used to examine examine, energy-dispersive X-ray spectroscopic (EDS) data from fine precipitates obtained using an electron probe of 0.7 nm in diameter.

III. RESULTS

Figure 1(a) shows TEM images for the 0.5Cu alloy aged at 523 K for 3.84 ks, which is the aging time that gives a peak hardness at this aging temperature. Generally, rod-shaped precipitates are three-dimensionally aligned along the $\langle 100 \rangle$ directions of the matrix. The micrograph of Figure 1(a) shows a two-dimensional arrangement on the {001} plane of the matrix. Particle-like precipitates are also observed in this micrograph, as marked by arrows. They are rod-shaped precipitates aligning along the [001] direction of the matrix, that is, the cross section of the rod-shaped precipitates. It is called the rod section hereafter. Their rod sections are elongated and of a lath shape. Figure 1(b) shows a typical HRTEM image of the rod section in the 0.5Cu alloy overaged at 523 K for 2400 ks, and this HRTEM image exhibits similar properties to the Q' phase, as reported previously,[2–4,6–8] leading us to regard the precipitate as being in the Q' phase. The bright dots in this rod section form a hexagonal network with a spacing of 1.04 nm at an angle of 10 deg to the [010] direction of the matrix. The
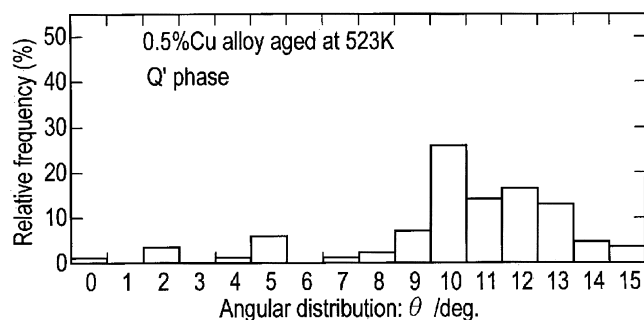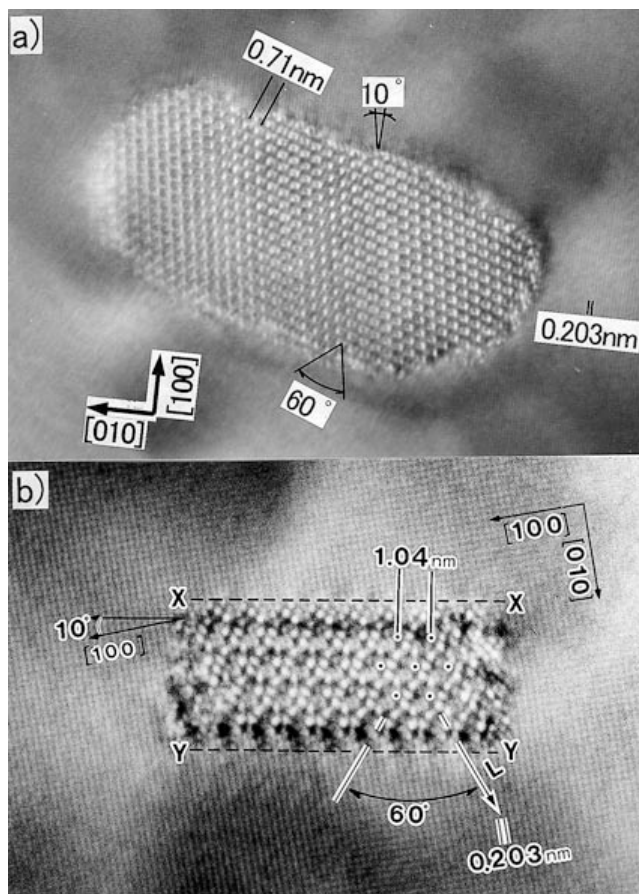
measured angle between the $\langle 1\bar{1}00 \rangle$ direction of the Q' phase and the $\langle 100 \rangle$ direction of the matrix ranges from 0 to 20 deg, as shown in Figure 2. The β' phase was observed in the balanced alloy aged at 523 K for 12 ks.[10] Although the β' phase shows an elongated rod section and a hexagonal network similar to the Q' phase, the spacing of the hexagonal network is typically about 0.71 nm, as shown in Figure 3(a). Figure 3(b) shows the type-C precipitate, which is observed in the excess-Si alloy overaged at 523 K[5] as well as in the same alloy aged after deformation.[11] This precipitate also exhibits the same hexagonal arrangement of bright dots inside the rod section, with a spacing equal to the 1.04 nm
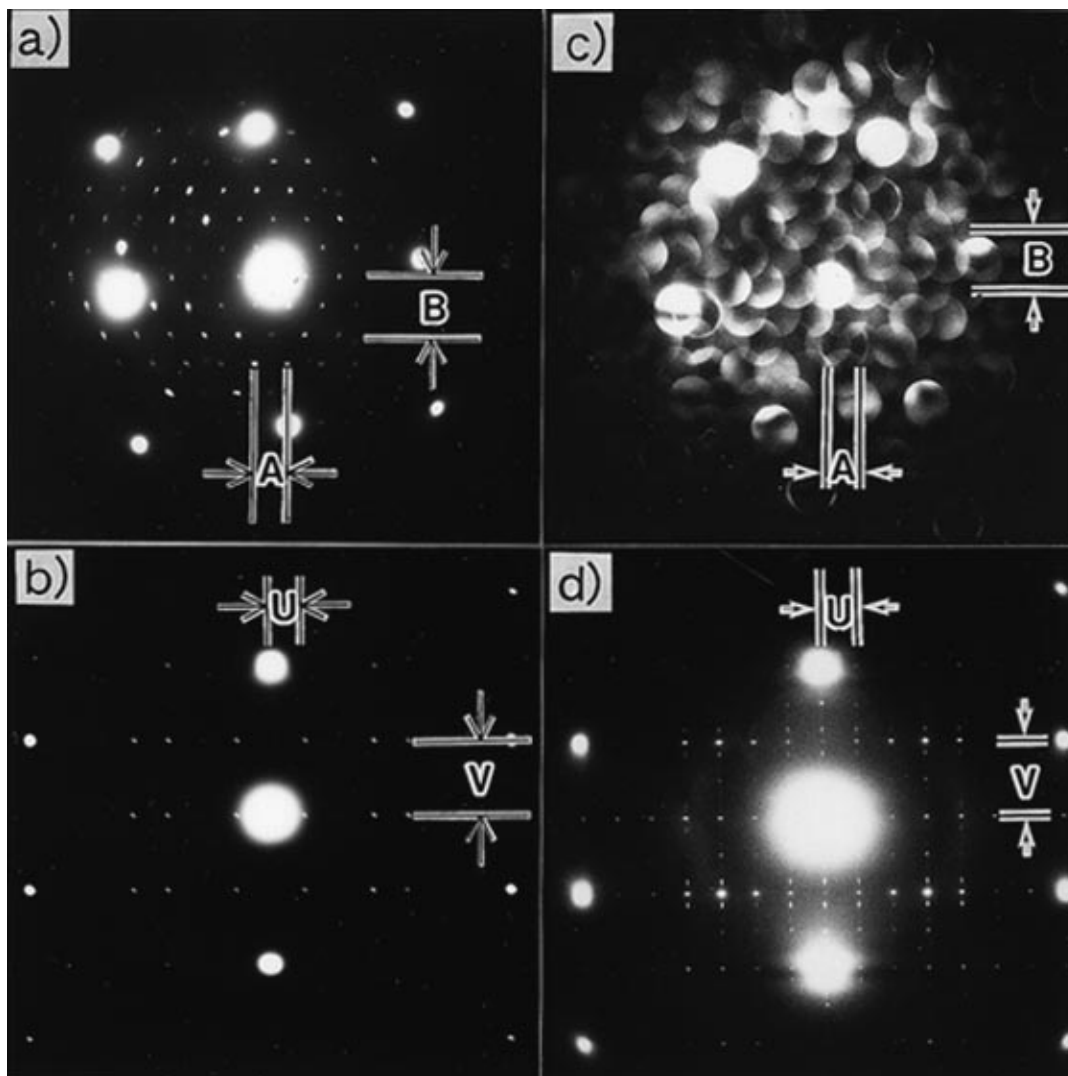
Fig. 4—Electron diffraction patterns taken from rod sections. (*a*) Selected area diffraction pattern (SADP) taken from the rod section of a precipitate and (*b*) SADP taken from a direction perpendicular to the longitudinal direction of the rod-shaped precipitate in the 0.5Cu alloy. (*c*) and (*d*) The microbeam electron diffraction pattern and SADP of the type-C precipitate in the excess Si alloy taken from the [0001] and [1$\bar{2}$10] directions.

spacing of the Q′ phase in Figure 1(b). The rod section is also elongated in shape.

Figure 4(c) and (d) show electron diffraction patterns (EDPs) of a type-C precipitate taken from the [0001] and [$\bar{1}$210] directions. These are compared with those of the Q′ phase in the 0.5Cu alloy shown in Figures 4(a) and (b). The spacings marked by the letters A, B, U, and V in Figures 4(a) and (b) were in good agreement with those in Figures 4(c) and (d). Spacing U is in good agreement with spacing A, and the lattice spacings derived from spacings U and V are 0.901 and 0.405 nm, respectively. These values are equal to the lattice spacings of the {1$\bar{1}$00} and {0001} planes of the type-C precipitate, respectively. The lattice spacing derived from spacing B is 0.52 nm and is equal to the spacing of the {1$\bar{2}$10} plane of the type-C precipitate. Thus, the EDPs of the Q′ phase are in good agreement with those of the type-C precipitate. The orientation relationship with the matrix is as follows: [001]$_{Q′}$//[001]$_m$ and [1$\bar{2}$10]$_{Q′}$//[130]$_m$.

Figure 5 shows EDS profiles taken from both precipitates by the FETEM, clearly showing the differences between them. The Q′ phase in Figure 5(a) produces a copper peak,
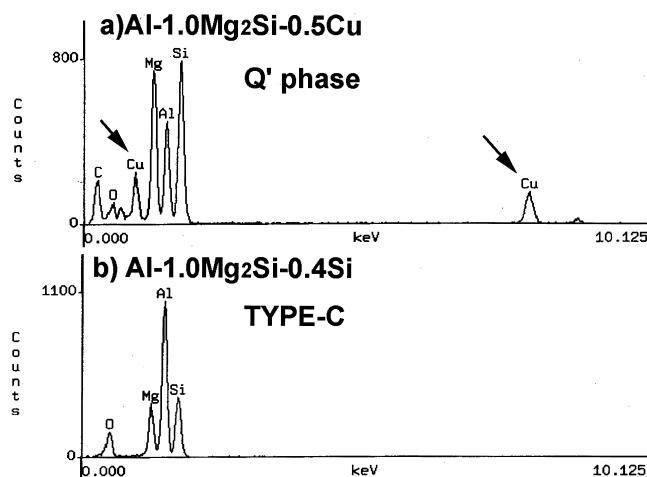

Fig. 5—EDS profiles for each precipitate taken by FETEM with a Be sample holder. (*a*) The Q′ phase in the 0.5 Cu alloy and (*b*) the type-C precipitate in the excess Si alloy. Clear Cu peaks can be seen in the Q′ phase. The type-C precipitate in the excess Si alloy produces no Cu peak.

while the type-C precipitate in the excess Si alloy produces no copper peak, as shown in Figure 5(b). The aging conditions needed to obtain the EDS profile of the type-C precipitate shown in Figure 5(b) were determined using Figure 8(c), which is referred to later in the text. Only magnesium, aluminum, and silicon peaks can be seen. The high-aluminum peak in Figure 5(b) is affected by the matrix, because the mean short radius of the type-C precipitate was about 1.0 nm and smaller than that of the Q' phase in this study. The chemical composition of the β' phase in the balanced alloy was about [Mg]/[Si] = 2.0.[10] The mean chemical composition of the Q' phase in the present study was Mg:Al:Si:Cu = 6:4:6:1 and is similar to that of the Q phase, where Mg:Al:Si:Cu = 8:4:7:2[3] or 8:5:6:2.[9] This result directly supports the hypothesis that the Q' phase consists of quaternary elements (aluminum, magnesium, silicon, and copper) similar to the Q phase. Although the Q' phase in the 0.5Cu alloy and the type-C precipitate in the excess-Si alloy have a similar crystal structure, their chemical compositions are different from each other. An EDS analysis and some other analytical techniques were performed in order to identify the chemical compositions of precipitates. For example, Cayron et al.[9] reported the chemical compositions of the Q, QC, and QP phases in T6-tempered Al-Cu-Mg-Si composites. Their ratios of [Mg]/[Cu] and [Si]/[Cu] were 4 and 3, respectively, for the Q phase; 7 and 3.5, respectively, for the QC phase; and 3.7 and 2.6, respectively, for the QP phase. The [Mg]/[Cu] and [Si]/[Cu] ratios obtained in the present study were higher than those reported by Cayron et al., because an Al-Mg-Si-Cu alloy was used in this study, and, therefore, the copper content of the metastable phase may be lower than that in an Al-Cu-Mg-Si alloy.[9]

IV. DISCUSSION

Figure 6 show schematic illustrations demonstrating the relationship between the crystal lattices of the β' and Q phases. There is a possibility that the crystal lattice of the β' phase changes to that of the Q phase by a 10-deg rotation of the β' phase around its [0001] direction. This may occur when the β' phase is of the 0-deg type with the following crystallographic orientation relationship with the matrix:[10] $\langle 1\bar{2}10 \rangle_{\beta'}//\langle 100 \rangle_m$ and $\langle 0001 \rangle_{\beta'}//\langle 001 \rangle_m$. Cayron et al.[9] also performed this operation on the crystal lattice and obtained the same result. This model has been confirmed in the actual relationship between the precipitate and the matrix as follows. Figure 7(a) shows the relative frequency plotted against an angular distribution between the $\langle 1100 \rangle$ direction of the β' phase and the $\langle 100 \rangle$ direction of the matrix reported previously.[12] Figure 7(a) can be redrawn as Figure 7(b), if the β' phase is rotated by 10 deg around its $\langle 0001 \rangle$ direction. The distribution is almost the same as that of the Q' phase shown in Figure 2. This also supports our concept of the transformation from the β' phase to the Q' phase, or the formation of the Q' phase instead of the β' phase.

Figure 8(a) shows the changes in the relative frequencies with aging time for all metastable phases. The relative frequency was calculated as the ratio of one metastable phase, i.e., the random-type and parallelogram-type precipitates, Q' or β' phase, to the total number of metastable phases in observed HRTEM images. The predominant precipitates are random and parallelogram types, which are the transition phases, as we reported recently.[13,14] The transition phases
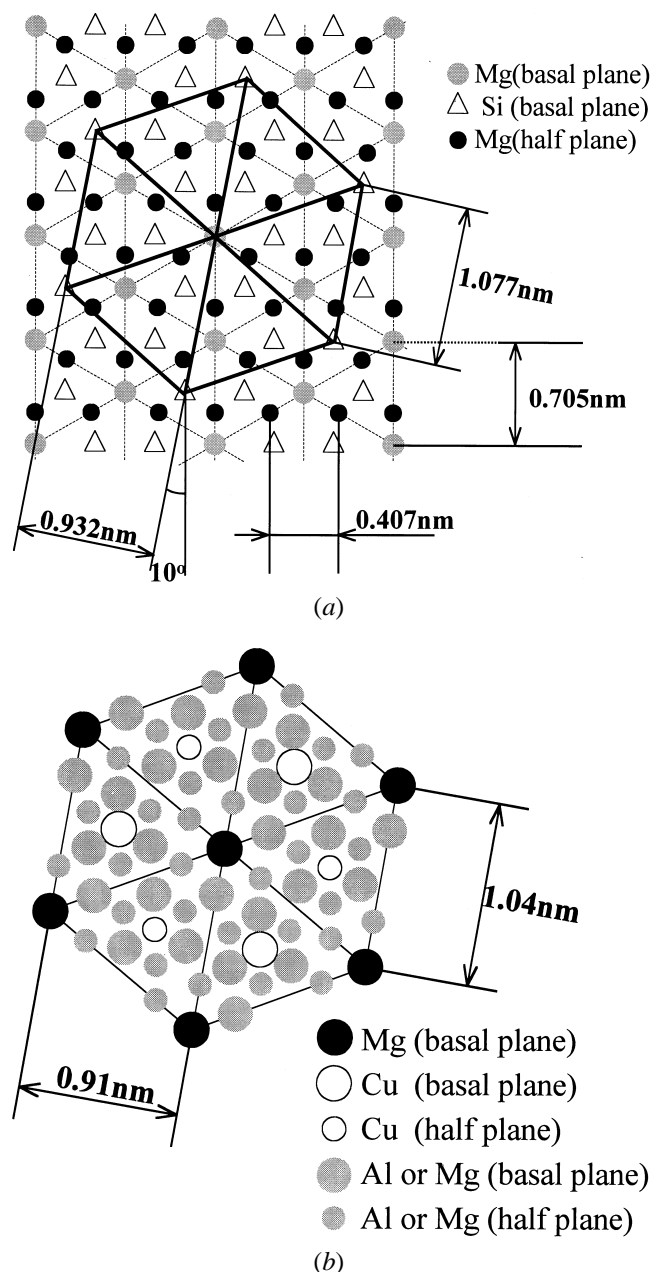

(a)

(b)

Fig. 6—Schematic illustrations demonstrating the relationship between the crystal lattices of the β' phase and Q' phase. (a) β' phase and (b) Q phase.

are products existing in the stage of aging between Guinier–Preston (GP) zones and metastable phases. The transition phases have no unique crystal structure and a fixed chemical composition. There is also the β' phase in Figure 8, but this is not a main phase. The Q' phase dramatically increases with increasing aging time after these transition and β' phases. Figures 8(b) and (c) are for the balanced and the excess-Si alloys. The β' phase becomes a major phase in an early stage of aging in the balanced alloy, and no Q' phase is observed, while in the excess-Si alloy, the type-C precipitate appears in the later stage of aging. Table I shows a summary of the several transition and metastable phases we reported.[5,13–15] These data also demonstrate that copper changes the precipitation sequence of this alloy, especially the stage of metastable phases.
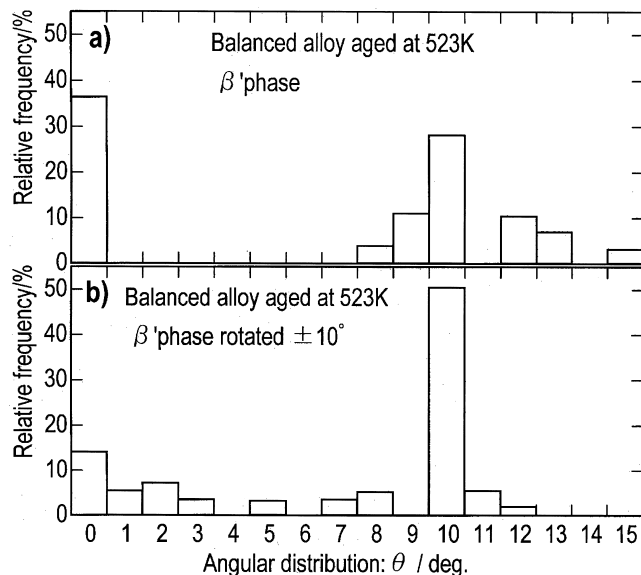
Fig. 7—(a) The relative frequency plotted against the angular distribution between the $\langle 1\bar{1}00 \rangle$ direction of the β' phase and $\langle 100 \rangle$ direction of the matrix, as reported previously.[12] (b) The modified relative frequency associated with a rotation of 10 deg around the $\langle 0001 \rangle$ direction of the β' phase. This distribution is almost equivalent to that of the β' phase shown in Fig. 2.
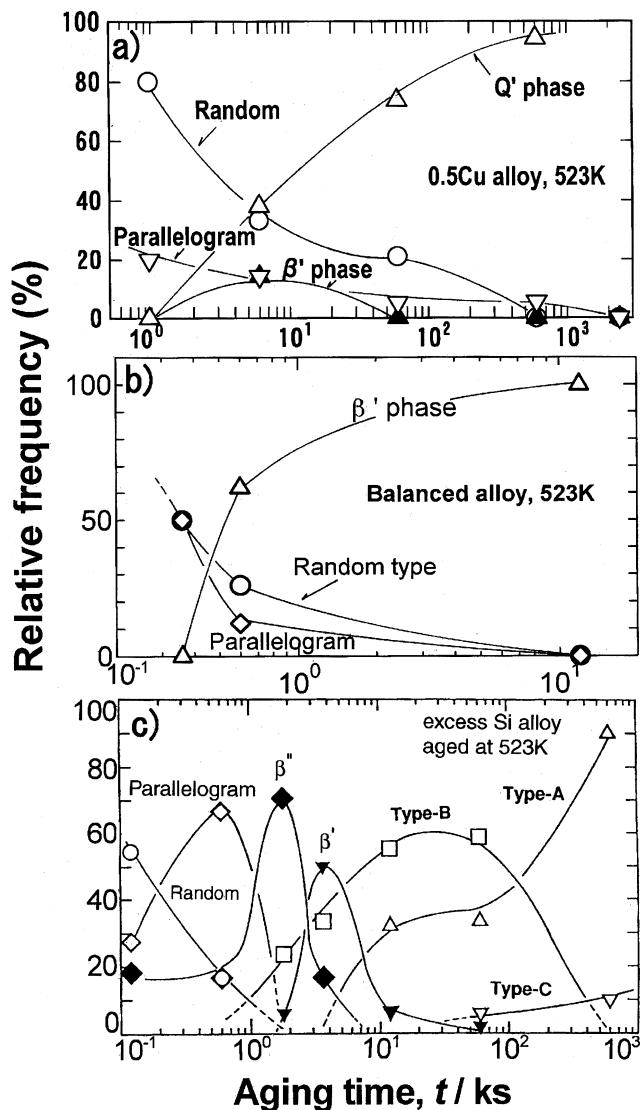

Fig. 8—Changes in the relative frequencies of metastable phases with aging time in each alloy aged at 523 K: (a) the 0.5 Cu alloy, (b) the balanced alloy, and (c) the excess Si alloy.

Figure 9 shows an HRTEM image of a complicated rod section, in which both the β' and Q$'$ parts are recognizable. Namely, it is suggested that the β' phase nucleates before the Q$'$ phase appears, and then the Q$'$ phase transforms from the β' phase or nucleates on the interface between the β' phase and the matrix, rather than direct nucleation of the Q$'$ phase in the matrix occurring. The structure of the Q phase is close to the Th_7S_{12} structure. The positions of the Si atoms are almost the same as those of the Th atoms, and the positions of the (Al, Mg) atoms are almost the same as those of the Si atom.[3] The only difference is the positions of the Cu atoms in the Q phase. The positions occupied by the Cu atoms are empty in the Th_7S_{12} structure, so the existence of a Q phase without Cu seems to be possible.[9] According to a model reported by Cayron et al.,[9] metastable phases in Al-Mg-Si alloys can include ternary or quaternary elements. If the Al-Mg-Si alloy contains the excess Si, the β' phase can contain much more Si than the β' phase in the balanced alloy and becomes a ternary metastable phase such as the type-C precipitate. In the same way, the β' phase becomes the Q$'$ phase in the same manner as the formation of the quaternary Q phase in Al-Cu-Mg alloys containing Si, when the Al-Mg-Si alloy contains Cu. Miao and Laughlin have recently reported this phase transformation using a calculation by Thermo-Calc.[21] They suggested the following precipitation sequence for the 6022 aluminum alloy:

For a small amount of Cu (0.07 wt pct), s.s.s.s.
$$- \text{GP zones} - \beta'' - [\beta' + Q'] - [\beta + Si]$$

Increase of Cu (0.9 wt pct), s.s.s.s. $-$ GP zones
$$- \beta' - Q' - [Q + Si]$$

where s.s.s.s. means the super saturated solid solution.

This result also supports the possibility that the Q$'$ phase is the major metastable phase in the present study, because 0.5 mass pct Cu is included in the 0.5Cu alloy. Si-rich

or Al-Mg-Si ternary phases have been reported by other researchers recently,[2,16,17] and, therefore, it is possible that they exist in Al-Mg-Si alloys, as we have already reported their existence.[15,18–20] Thus, the type-C precipitate can precipitate without Cu in the Al-Mg-Si alloy, although it has the same hexagonal parameter as the Q$'$ phase.

This result gives us one more important suggestion about this alloy. More careful observation should be done to identify the metastable phase in this alloy system, because there are many kinds of metastable phases in this alloy, especially in the case containing different chemical compositions of Mg, Si, or Cu and in the case performed under different aging conditions.

V.   CONCLUSIONS

The metastable phases existing in an Al-1.0 mass pct Mg_2Si-0.5 mass pct Cu alloy aged at 523 K were observed

Table I. Types of Transition Phases and Metastable Phases in Al-Mg-Si Alloys[5,12–14]

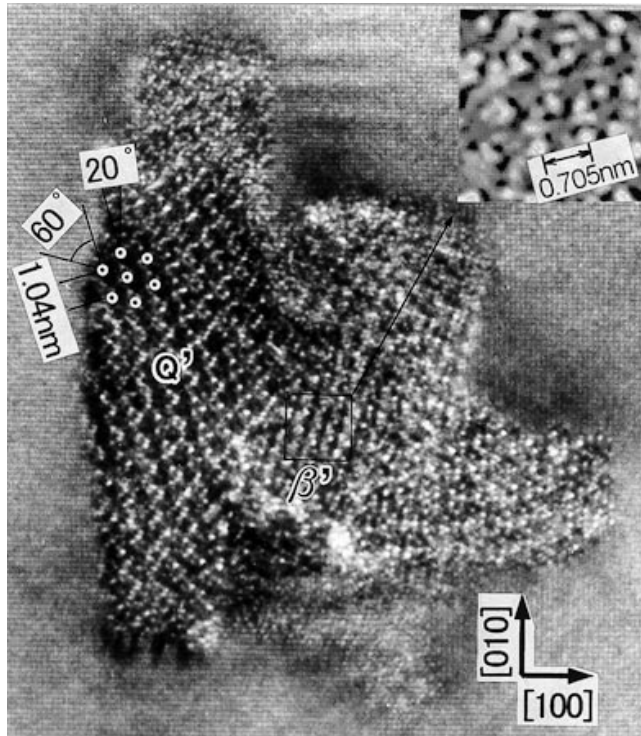| Phase	Balanced Alloy	Excess Si Alloy	Balanced Alloy with Copper
Transition	random type parallelogram type	random type parallelogram type* β'' phase	random type parallelogram type β'' phase*
Metastable	β' phase	type-A type-B type-C*	β' phase* type-C with Cu (Q')

*A minor phase.

Fig. 9—HRTEM image of a complicated rod section. Both the β' and Q' parts can be seen. The insert shows an inverse FFT image of a square area of the β' part.

by an HRTEM and an analytical TEM in order to investigate their precipitation sequence.

1. The Q' phase exists in the 0.5Cu alloy aged at 523 K. The rod section of the Q' phase has an elongated shape, and its crystal lattice is a hexagonal of a = 1.04 nm and c = 0.405 nm. The orientation relationship between the Q' phase and the matrix is $[0001]_{Q'}//[001]_m$ and $[1\bar{2}10]_{Q'}//[130]_m$. These characteristics are the same as those of the type-C precipitate, which is a special precipitate in the excess-Si alloy reported previously.[5]

2. According to results of EDS analysis by the FETEM, the Q' phase included Cu and contained Mg, Si, and Al, although the type-C precipitate consisted of Si, Al, and Mg. Namely, it has been clarified that the type-C precipitate in the excess-Si alloy was the ternary Al-Mg-Si phase, while the Q' phase was the quaternary Al-Mg-Si-Cu phase in the Al-Mg-Si-Cu alloy.

3. At the early stage of aging in the 0.5Cu alloy, the predominant precipitates are in the transition phases; *i.e.*, random and parallelogram types. There is also the β' phase, but this is not a main metastable phase. The Q' phase dramatically increases with increasing aging time after these transition and β' phases, while the β' phase becomes a major phase in an early stage of aging in the balanced alloy.

4. It is possible to explain the formation of ternary or quaternary metastable phases in Al-Mg-Si alloys in the same way as the formation of quaternary phases in the Al-Cu-Mg-Si alloys, according to a model proposed by Cayron *et al.*[9] Namely, the β' phase can contain much more Si than the β' phase in the balanced alloy or can contain Cu, when the Al-Mg-Si alloy contains excess Si or Cu.

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