High-Resolution Electron Microscopy on the Structure of Guinier–Preston Zones in an Al-1.6 Mass Pct Mg_2Si Alloy

K. MATSUDA, H. GAMADA, K. FUJII, Y. UETANI, T. SATO, A. KAMIO, and S. IKENO

The structure of the Guinier–Preston (GP) zone in an Al-1.6 mass pct Mg_2Si alloy aged at 343 and 423 K was investigated by high-resolution transmission electron microscopy (HRTEM). The morphology of the GP zone is that of a fine plate having the dimensions of a monolayer in thickness, 2.5 nm in width, and less than 30 nm in length. Its elongated direction is parallel to the $\langle 100 \rangle_m$ direction. The chemical composition of the GP zone in an Al-Mg_2Si alloy indicated a ratio of Mg/Si = 1.0. The zones aggregate with increasing aging time and exhibit a more complicated morphology because of the transformation to the metastable phase that takes place inside the GP zones.

I. INTRODUCTION

IT has been well known that the nuclei of metastable phases and composition fluctuation are found in an Al-Mg_2Si alloy during the early stage of aging.[1,2,3] In Table I, previous studies on the aging sequence of this alloy system before the equilibrium phase appears are summarized. The specific heat and the electrical resistivity measurements have been performed over the entire range of aging temperatures, and the existence of clusters and Guinier–Preston (GP) zones have been proposed.[1–5] However, the structures of the zones formed during aging were identified only in a limited range of aging temperatures higher than 423 K using X-ray and electron diffraction techniques.[2,6–11]

In our recent systematic work, new types of metastable phases were found in this alloy system. The morphologies, crystal structures, and crystallographic orientation relationship with the matrix of the metastable phases in this alloy system have been clarified using high-resolution transmission electron microscopy (HRTEM), a microbeam electron diffraction technique, and energy-dispersive X-ray spectroscopy (EDXS).[12,13,14] The changes in the number of each metastable phase have also been reported.[15] However, we have not yet clarified the structure and chemistry of clusters or GP zones during the early stage of aging.

The aim of this study is to clarify the structure and chemical composition of the GP zones in an Al-1.6 mass pct Mg_2Si alloy aged at temperatures lower than 423 K using HRTEM.

K. MATSUDA, Research Associate, and S. IKENO, Professor, are with the Department of Materials Science and Engineering, Toyama University, Toyama 930, Japan. H. GAMADA, formerly Graduate Student, Department of Materials Science and Engineering, Toyama University, is with the Department of Research and Development, Hokuriku Fabrication Center, Shin-Nikkei Co. Ltd., Toyama 933, Japan. K. FUJII, formerly Graduate Student, Department of Materials Science and Engineering, Toyama University, is Researcher, Industrial Research Institute of Ishikawa, Ishikawa 920-02, Japan. Y. UETANI, Associate Professor, is with the Research Institute for Technology, Toyama Prefectural University, Toyama 939-03, Japan. T. SATO, Associate Professor, and A. KAMIO, Professor, are with the Department of Metallurgical Engineering, Tokyo Institute of Technology, Tokyo 152, Japan.

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II. EXPERIMENTAL

An Al-1.6 mass pct Mg_2Si alloy was prepared using 99.99 pct pure aluminum, 99.9 pct pure magnesium, and 99.9 pct pure silicon. The ingot obtained was formed into 0.2-mm thick sheets by hot and cold rolling. A solution heat treatment was performed at 848 K for 3.6 ks and was followed by quenching in chilled water (273 K). The aging treatment was performed at 343 and 423 K. Thin specimens for HRTEM were prepared by ordinary electrolytic polishing and were observed using the EM-002B (Topcon Co., Ltd., Tokyo, Japan) operated at 100 kV. Electrical resistivities of the specimens were measured using the direct-current, four-terminal method in liquid nitrogen at 77 K. The HRTEM images were calculated using the multislice method to identify the experimentally observed images.

III. RESULTS

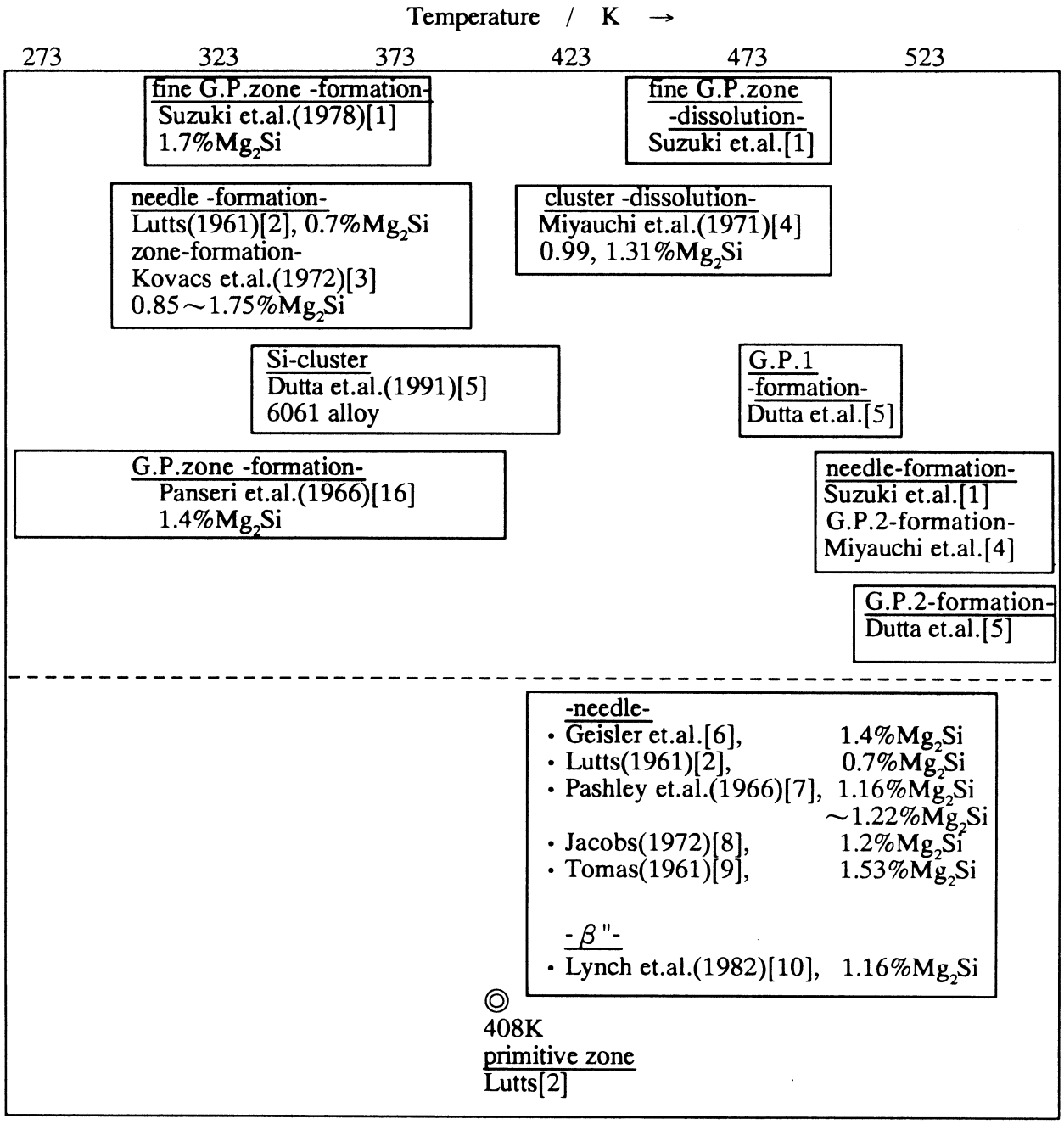
A. *GP Zones*

Figure 1 shows changes in the electrical resistivity (ρ) with aging time at 343 and 473 K. The values of ρ during the early stage at each aging temperature are higher than those of the quenched ones. The electrical resistivity in the specimen aged at 343 K slightly increases with increasing aging time in the range examined in this work. However, the values of ρ at 423 K decrease with increasing aging time after showing a constant value slightly higher than the as-quenched value during the early stage of aging. These are the same tendencies as the results of electrical resistivity reported by Panseri and Federish.[16]

Figures 2(a) through (d) show the bright-field images of the specimen aged at 343 K for 1200 to 6000 ks. Extremely fine dark contrasts are observed under all conditions, and the number of dark contrasts increases and the contrasts become sharpened with increasing aging time. Figures 2(e) through (h) show the selected-area diffraction patterns (SADPs) corresponding to Figures 2(a) through (d). Streaks along the [100] and [010] directions are observed between diffraction spots of the matrix in each SADP, and the intensity of the streaks increases with increased aging time. However, no clear precipitates with a needle shape are observed at a magnification of 200,000 times.

Figure 3(a) shows an HRTEM image of the specimen aged at 343 K for 1200 ks. Figures 3(b) and (c) are enlarged

Table I. Summary of the Aging Sequence in Al-Mg_2Si Alloys Prior to the Formation of the Metastable Phase (Upper Column: Results of the Specific Heat or the Electrical Resistivity Measurement; Lower Column: Results of the X-Ray or Electron Diffraction Technique)



photographs of the circled regions A and B in Figure 3(a), respectively. Bright lattice points, having a spacing of 0.405 nm, are arrayed in a row only along the (200) lattice plane of the matrix, as shown by the arrows in region A of Figure 3(a). Two rows of bright lattice points indicated by the arrows are arrayed parallel to each other in Figure 3(c). Figure 3(d) shows an SADP corresponding to Figure 3(a). Streaks were observed toward the [100] and [010] matrix directions on the center points of the 000 and 110 reciprocal lattice points. Figure 3(e) shows a schematic illustration of Figure 3(d). The morphology of the zones in this alloy is assumed to be that of a fine plate.

Figure 4 shows an HRTEM image of the needle elongated along the [100] direction of the matrix circled on the left. Such an HRTEM image was not frequently found. This fact suggests that the GP zone in this alloy is the fine plate along the $\langle 100 \rangle_m$ direction, based on the results of Figures 3 and 4, because the matrix existing at the top and bottom of the fine-plate GP zone significantly affects the formation of the HRTEM image when the longitudinal direction of the GP zone is perpendicular to the direction of observation.

Figure 5 shows HRTEM images of GP zones which were obtained from different directions of the matrix, [011] and [031], to confirm their shape. As shown by the arrows in

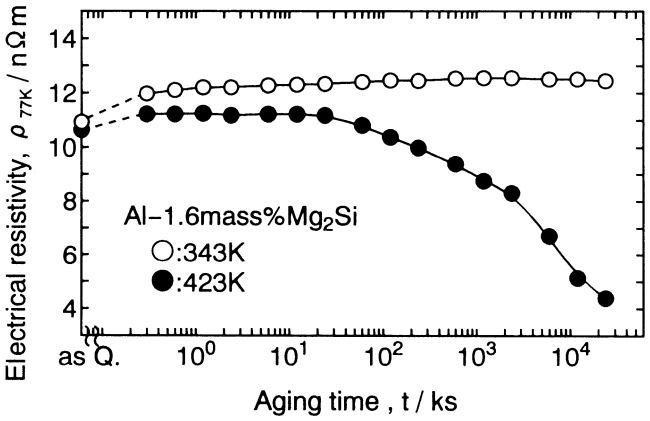


Fig. 1—Changes in electrical resistivity of the specimens aged at 343 K (○) and 423 K (●) *vs* aging time.

Figure 5, only brighter contrasts along the (200) plane of the matrix were observed in each direction of the matrix. No GP zones were observed as a particle or as other polygonal shapes. According to the results of Figures 3 through 5, the shape of these zones in the Al-Mg-Si alloys is that of a fine plate, like the GP zone in Al-Cu alloys along the $\langle 100 \rangle_m$ direction.

B. *Growth of GP Zones*

Figure 6 shows an HRTEM image of the specimen aged at 343 K for 6000 ks. There were observed many regions which consist of an aggregation of a few zones, as are marked by the arrows, instead of zones of a monolayer with a size of 1 nm along the (200) lattice plane of the matrix, as shown in Figure 3(b).

Figure 7 shows TEM images of the specimen aged at 423 K. The contrasts of precipitates were clearly observed at this magnification of less than 200,000 times. The morphology of the needle-shaped precipitates in the specimen aged for 600 ks (Figure 7(b)) is sharper than that of the specimen aged for 60 ks (Figure 7(a)). The SADPs of Figures 7(c) and (d) correspond to Figures 7(a) and (b), respectively. The streaks became sharp and strong in the specimen in which needle-shaped precipitates were visible, as shown in Figure 7(b), in contrast to those of Figure 7(c), in which only diffused streaks were observed. It is concluded that the clear streaks observed in this alloy aged at 423 K are caused by the crystal structure and orientation relationship of a metastable phase such as the β'' phase, rather than by the GP zone, although the streaks in the Al-Cu alloys are caused by a monolayer or by a few layers of GP zones.[17] In fact, a streaklike diffraction pattern is also taken from the specimen in which the metastable β' phase is predominant,[9] because the β' phase has crystallographic orientation relationships with the matrix.[12,18] Figure 8 shows an HRTEM image of the cross section of the needle-shaped precipitates (hereafter termed the needle section), as shown in Figure 7(b). The arrangement of the bright dots in this needle section was at random, and the ordering of atoms corresponding to its crystal structure was not observed. No periodic arrangement of the bright dots in the needle sections was similar to that of the β' phase.

IV. DISCUSSION

A. *Structure of GP Zone*

The zones in the alloy mentioned previously have a clear contrast along the {200} lattice planes of the Al matrix. The aging temperatures of 343 and 423 K used in the present study are the temperatures at which the GP zones are formed in the Al-Mg-Si alloys, as has already been reported by many workers. No reports, however, have clarified the structure of the GP zones based on the observed results. We propose the GP zone structure to be as shown in Figure

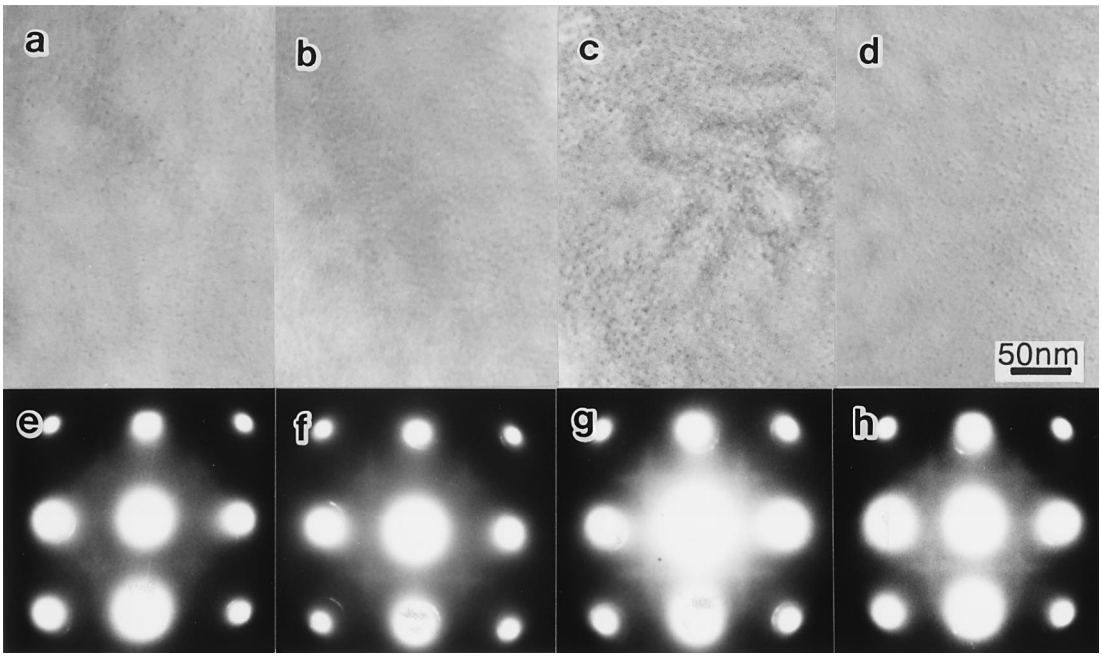


Fig. 2—Transmission electron micrographs of the specimens aged at 343 K for each time. (*a*) through (*d*) Bright-field images aged for 1200, 2400, 3600, and 6000 ks, respectively. (*e*) through (*h*) Selected area diffraction patterns corresponding to (a) through (d), respectively.

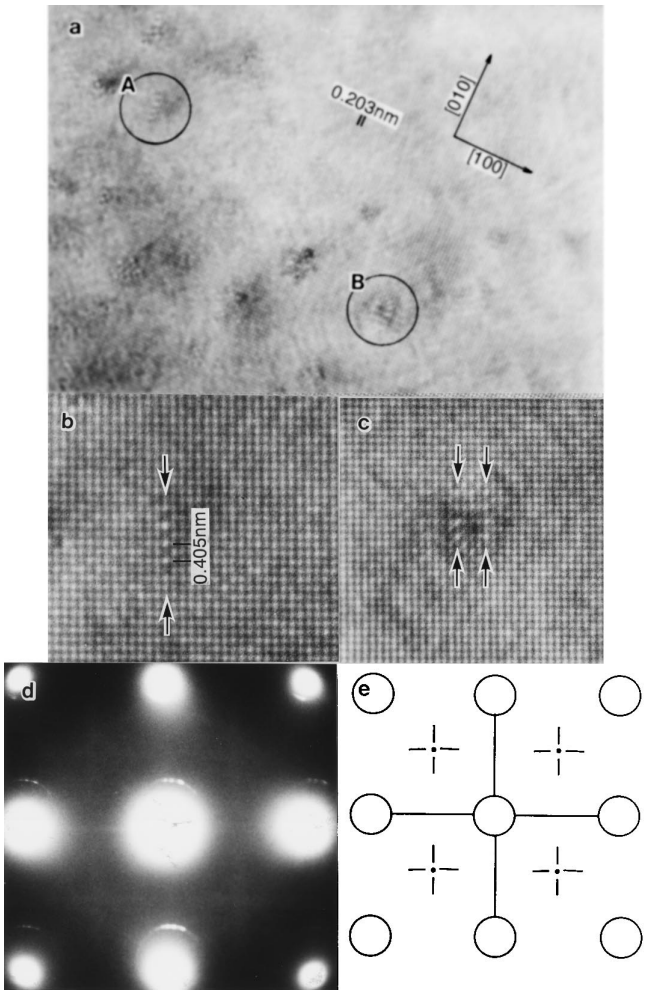


Fig. 3—Transmission electron micrographs of the specimens aged at 343 K for 1200 ks. (*a*) An HRTEM image. (*b*) and (*c*) Enlarged photographs of regions marked by circles A and B in (a), respectively. (*d*) Selected area diffraction pattern taken from (a). (*e*) Schematic illustration of (d).

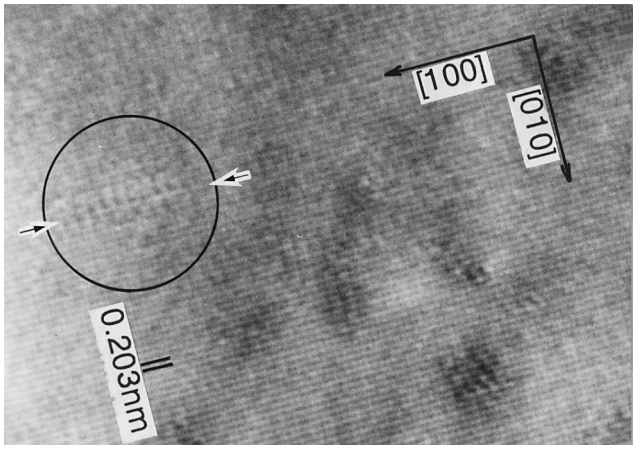
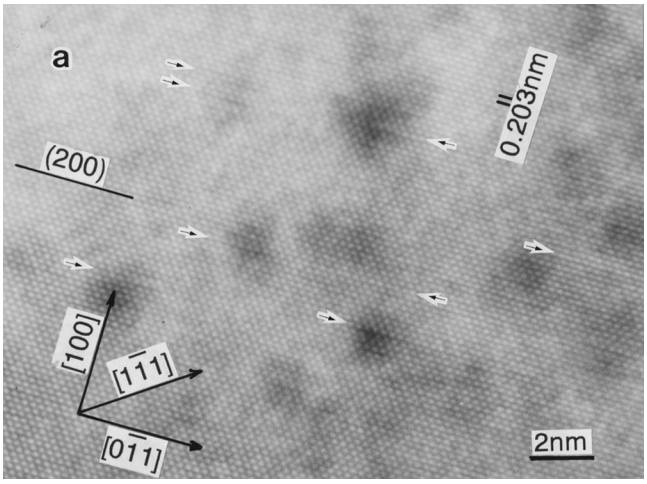


Fig. 4—An HRTEM image of the specimen aged at 343 K for 1200 ks. The longitudinal direction of the zone parallel to the $[100]_m$ direction can be seen in the circle.

3 for the Al-Mg-Si alloys. There are several structural models of the GP zones in this alloy.[6,7,10] The classical models are proposed by Geisler and Hill[6] and Guinier.[7] Geisler and Hill proposed that the shape of the zone was a fine



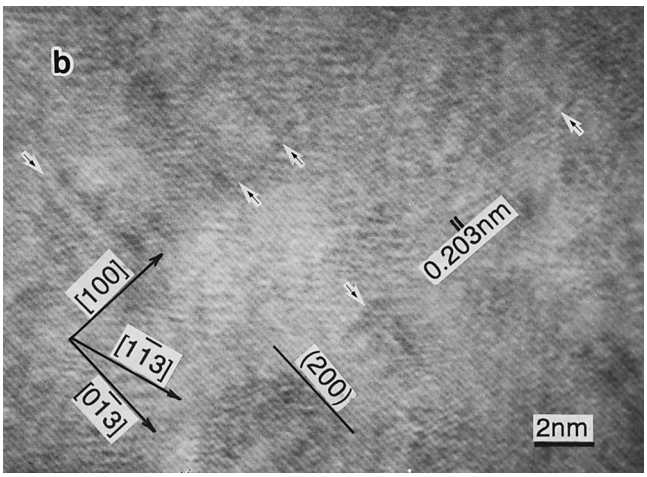


Fig. 5—HRTEM images of the matrix taken from other directions. (*a*) The incident beam direction parallels $[011]_m$. (*b*) The incident beam direction parallels $[031]_m$.

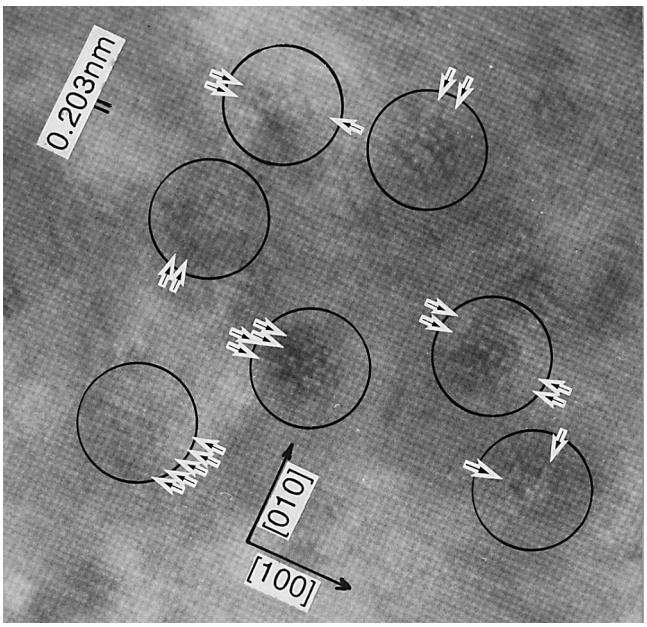


Fig. 6—An HRTEM image of the aggregation of the zones in the specimen aged at 343 K for 6000 ks.

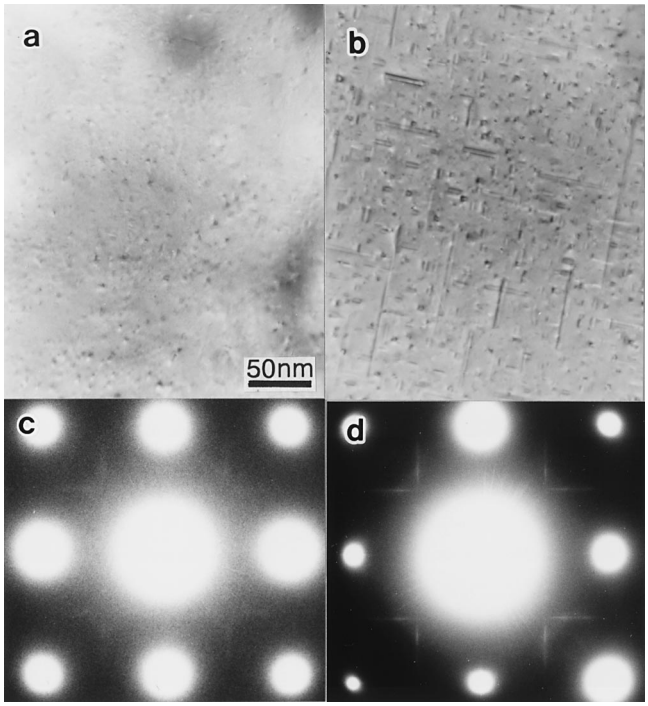


Fig. 7—Transmision electron micrographs of the specimens aged at 423 K for each time. (*a*) and (*b*) Bright-field images aged for 60 and 600 ks, respectively. (*c*) and (*d*) Selected area diffraction patterns corresponding to (a) and (b), respectively.

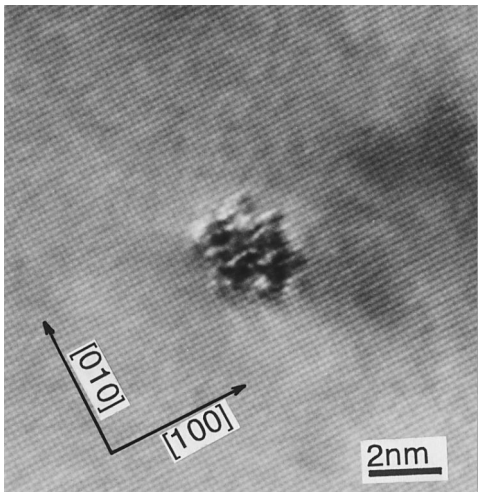


Fig. 8—An HRTEM image of the cross section of the coarse zone in the specimen aged at 423 K for 600 ks.

plate having dimensions of 2 nm in width and 1 nm in thickness. However, they did not describe the structure and the chemical composition of the zone. Guinier also proposed that the zone in this alloy had a chemical composition nearly equal to Mg_2Si stoichiometry and a part of the crystal structure of the anti-CaF_2 type, and that its shape was a needle. On the other hand, Thomas[10] proposed that zones were made by alternately stacking two Mg layers and one Si layer on the basis of the (011) lattice plane of the matrix, and that the zones grew along the [100] direction of the matrix. Recently, Huppert and Hornbogen[19] proposed the formation mechanism of the GP zone in this alloy as follows. First, the clusters composed of Al, Mg, Si, and vacancies were produced during the early stage of aging. Second, Al atoms diffused from the clusters to the matrix, and then GP zones comprised of Mg and Si atoms were

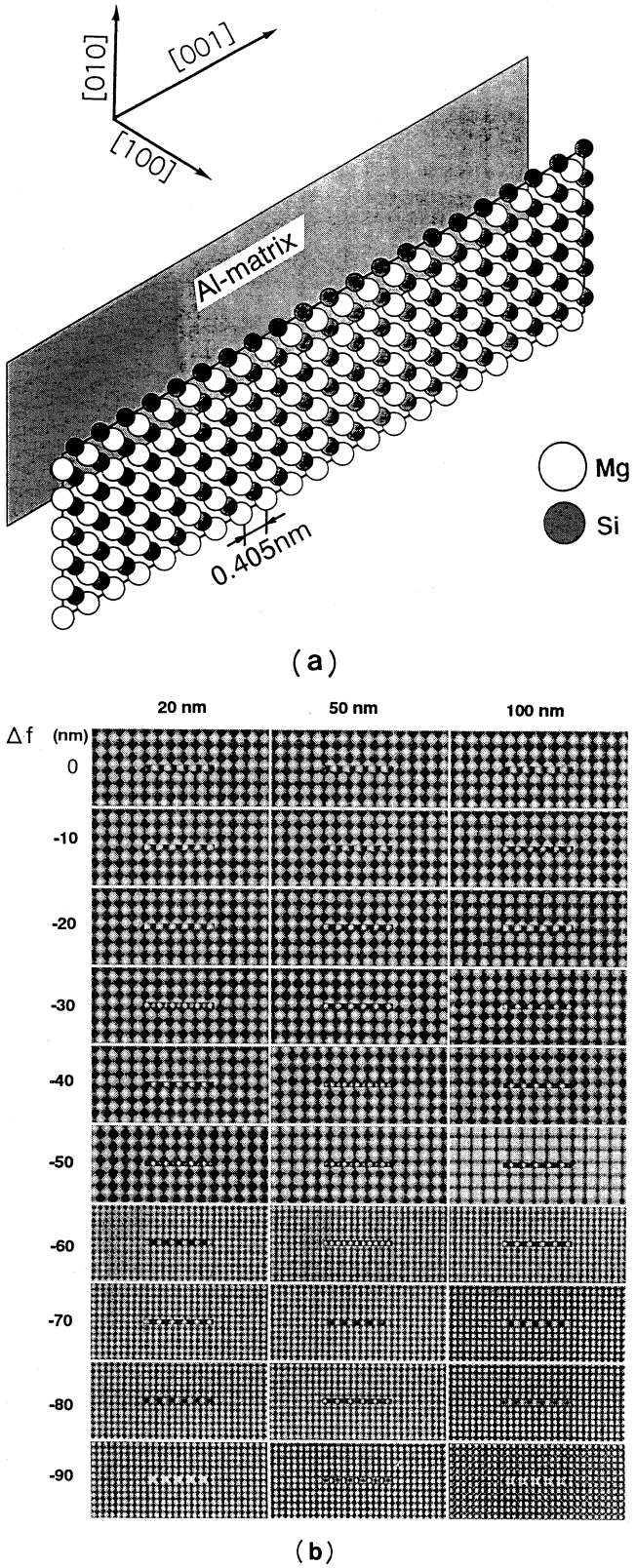


Fig. 9—The structure of the fine-plate GP zone in an Al-Mg_2Si alloy proposed in this work. (*a*) A schematic illustration. (*b*) Changes in computer-simulated HRTEM images with defocusing and thickness of the specimen.

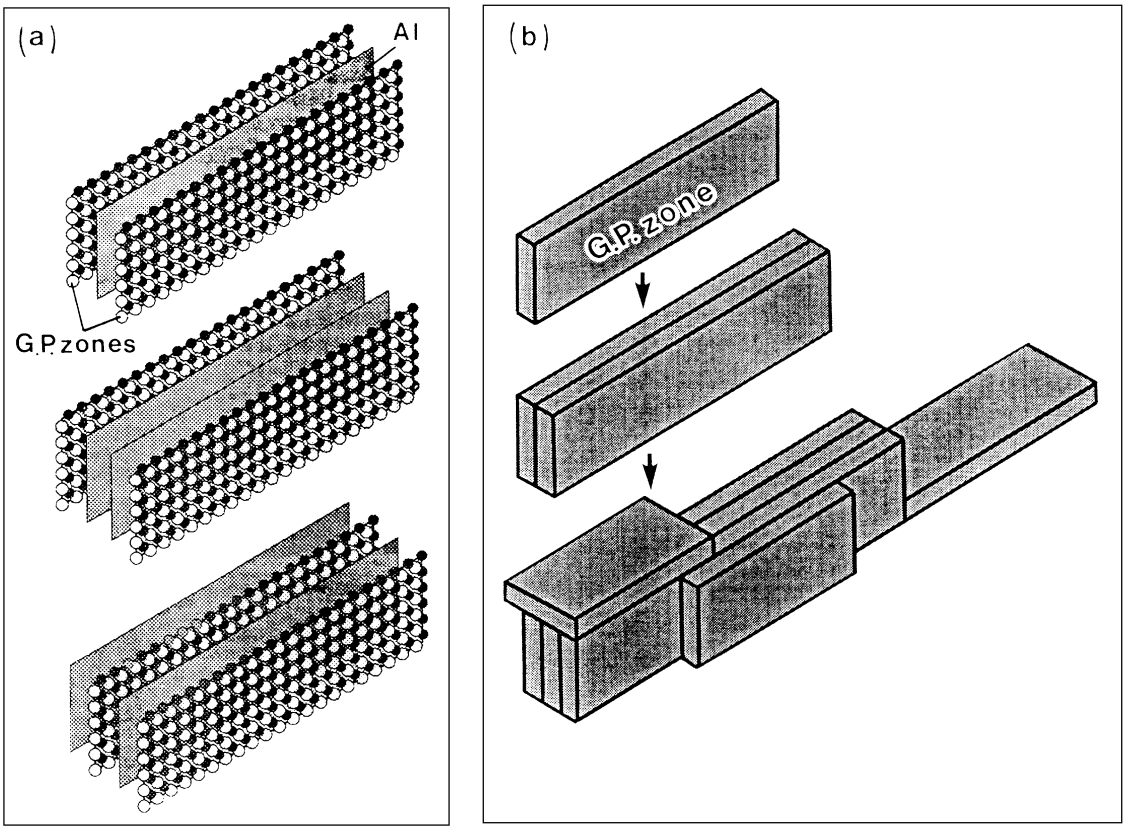


Fig. 10—Schematic illustration of the growth process of the GP zone. (*a*) Three patterns of aggregation of two GP zones. (*b*) Aggregation process of a number of GP zones.

finally formed. However, they had no direct evidence and did not describe the structure of the GP zones.

Based on our results, we propose that the GP zone is a fine plate that is one atomic layer in thickness, 2.5 nm in width, and less than 30 nm in length. It is considered that there is a periodic arrangement of Mg atoms or Si atoms, having a spacing of 0.405 nm, along the $[100]_m$ or $[010]_m$ directions, because strong bright dots are aligned, having a spacing of 0.405 nm, along the $[100]_m$ or $[010]_m$ directions. Simulated images of the HRTEM about the GP zone were suggested to provide one idea of its chemical composition, although the chemical composition of this zone has not been obtained by EDXs analysis in the present work because this zone is very fine. Figure 9(a) shows a schematic illustration of the GP zone that we propose. When a column of Mg atoms and a column of Si atoms along the $[001]_m$ direction are alternately arranged on the $(200)_m$ direction, the 0.405 nm spacing of bright dots was obtained, as shown in Figure 9(b). Namely, the GP zone in Al-Mg_2Si alloys is made by the alternating arrangement of the columns of Mg and Si atoms along the ⟨100⟩ direction having a spacing of 0.405 nm. The chemical composition of this GP zone is Mg:Si = 1.0. This model is similar to that proposed by Guinier, inadvertently, except for its chemical composition. We do not consider the existence of vacancies in this zone in our present work.

B. *Growth of GP Zone*

This fine-plate GP zone grows with increasing aging time by aggregating into several zones, as shown in Figure 6. Figure 10(a) shows a schematic illustration of the growth patterns of the GP zone. As aging time proceeds, the size of the aggregation of the GP zone becomes large. The GP zones also appear on equivalent $\{200\}_m$ directions, as shown in Figure 10(b). It is expected that the aggregation of GP zones produces strain that originates from the lattice misfit, which we do not take into account in our present work. In fact, a dark contrast due to a lattice strain is observed in the matrix surrounding the aggregation of the GP zones. Consequently, it is considered that periodic arrangement of bright dots cannot be observed in this region, as shown in Figure 8, when observed along the $[001]_m$ direction. This assumption is also supported by the fact that the width of the GP zone is 2 to 3 nm, and this value is equal to the mean diameter of the region having a nonperiodic arrangement of bright dots. It is considered that the aggregation of GP zones begins to grow as a metastable phase when the structure of the GP zones is lost by reconstruction of atoms in the coarse aggregation of the GP zones. The needle section shown in Figure 8 corresponds to the primitive zone proposed by Lutts based on an X-ray diffraction study.[2] The aging condition and chemical composition of Lutts' work are similar to the present work. He explained that the diffuse streaks of the X-ray pattern in the Al-0.7 pct Mg_2Si alloy aged at 423 K for 3.6 ks are due to the primitive zone with no internal order or periodic structure. In the HRTEM image, the needle sections exhibit no clear periodic atomic arrangement inside of them. These characteristically unclear images of atomic arrangements inside the needle section are well explained based on the elastic strain which is introduced by a number of vacancies inside of them.

Mingler and Karnthler[20] indicated the HRTEM image of GP zones in an Al_2O_3/6061 composite material, although they did not analyze its structure. In their HRTEM image, the GP zone was not parallel to the {200} lattice plane of the matrix, but revealed a zigzag morphology. Their result is similar to our result in Figure 10(b). Their result is not for a typical GP zone but for a coarse GP zone, because their specimen is a composite material and the aging temperature is high.

V. CONCLUSIONS

The structure of the GP zone in an Al-1.6 mass pct Mg_2Si alloy aged at 343 and 423 K was investigated by HRTEM. The obtained results are as follows.

1. The morphology of the GP zone is that of a fine plate having dimensions of a monolayer in thickness, 2.5 nm in width, and less than 30 nm in length. Its elongated direction is parallel to the $\langle 100 \rangle_m$ direction.
2. The assumption that the chemical composition of the GP zone is Mg:Si = 1.0 was in good agreement with the simulated HRTEM images and those actually obtained. The structure of the GP zone proposed in our present study was as follows: a column of Mg atoms and a column of Si atoms, having a spacing of 0.405 nm along the $[001]_m$ direction, alternately arranged on the $(200)_m$ lattice plane.
3. The zones become aggregated with increasing aging time and exhibit a complicated morphology.

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