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Abstract

A new type of precipitate has been found out in aged Al-Mg-Si alloys. The precipitate did not show characteristic diffraction spots in selected area diffraction patterns, nor diffraction contrast in bright field images. The sizes of these precipitates were about 0.02 to 0.2 μ m in diameter. In dark field images taken with a background portion in a selected area diffraction pattern, the precipitates were observed with bright contrast. Energy dispersive X-ray analyses showed that the precipitate was composed of Si, Al and O. The precipitate is an amorphous phase precipitate with Al-Si oxide.

1. Introduction

Many precipitate phases are reported to be formed during aging in aluminum alloys with Al-Mg-Si system as well as commercial A6061 aluminum alloys, that it, G. P. zone, β ", β ' and the stable precipitate β (Mg₂Si) in ternary Al-Mg-Si alloys [1, 2], and additionally several types of metastable phases in commercial alloys [3]. The stable and metastable phases have similar lattice constants each other, which confuses identification of precipitate phases by transmission electron microscopy (TEM). As a result, unclear diffraction patterns tend to be neglected. The present authors intentionally focused their interest on such precipitates which show unclear or indistinct diffraction patterns, because more precipitate phases seem to be necessary to interpret results of differential scanning calorimetric measurements or electric resistivity measurements [4].

2. Experimental Procedures

Chemical compositions of the alloys are listed in Table 1. The compositions of Mg and Si in the base alloy are 1.16 and 0.58 in at%, respectively, so the ratio of Mg/Si is just two. The ratios in other alloys are about the same except the Si-rich alloy. Specimens were solution heat treated at 813 K for 3.6 ks, quenched into iced water and then aged at 453 K. Foils for TEM observations were prepared by electropolishing using a perchloric acid :

Alloy	Mg	Si	Cr	Cu	Fe	AI
Base alloy	1.05	0.60	-	-	0.01	bal.
Si-rich alloy	0.79	1.03	-	-	0.01	bal.
+Cu	1.11	0.58	-	0.15	-	bal.
+Cr	1.08	0.59	0.11	-	0.1	bal.
+Cu+Cr	1.07	0.58	0.11	0.15	0.1	bal.

Table 1: Chemical compositions of alloys (mass%).

ethanol = 1 : 8 solution, and then finished by a twin-jet method using a nitric acid : methanol = 1 : 3 solution at about 240 K. Some foils were prepared by using a ultramicrotome or ion-thinning method. Transmission electron microscopic observations were carried out using JEM-200CX and JEM-2010 equipped with an energy dispersive X-ray (EDX) analyzer under an accelerating voltage of 200 kV.

3. Results and Discussion

Typical microstructures in the alloys after aging at 453 K for 1.8 Ms are shown in Figure. 1. Precipitates elongated along <100> α directions were observed in all the alloys. Although the sizes and densities are different each other, these precipitates are the same kind of precipitate phase, β ' or β . Detailed analysis on the well known precipitate phase is omitted from the present study. In grain interiors, precipitates formed by aging are not different from those reported by many other researchers [1, 2], new type of precipitate phase was not observed.



Figure 1: Precipitates in the specimens aged at 453 K for 1.8 Ms. (a) Base alloy, (b) +Cu alloy, (c) +Cr alloy, and (d) +Cu+Cr alloy.

On the other hand, curious precipitates were observed near grain boundaries in all the alloys used. Figure 2 shows grain boundary precipitates and also grain interior precipitates formed in the base alloy aged at 453 K for 260 ks. Images (a), (b) and (c) were taken at the same view filed with tilting the specimen at +8, 0 and -8 degree, respectively. Contrasts of all the precipitates formed in the grain interior were changed by tilting. When the changes in contrast on the precipitates indicated with A to E formed at grain boundary are noticed, it is observed that the contrast of only the precipitate A is not changed. In order to show that the image A is not an artificial product, such as corrosion products or surface dusts, the view field around A is enlarged and shown in Figure 3.

Thickness contours are shrunk and bent near the object A, especially at the portion indicated by the arrow, which shows that A is embedded in the foil.

Analyses of chemical compositions on the matrix near the grain boundary, the precipitate B and A in Figure 2 were carried out using EDX, and the resultant spectra are shown in Figure. 4 (a), (b) and (c), respectively.



Figure 2: Precipitates formed near a grain boundary in the base alloy aged at 453 K for 260 ks. Tilting angles in (a), (b) and (c) were +8, 0, -8 degree, respectively.

On the matrix (a), only aluminum was detected as an alloy composition, a small peak for carbon is due to occurrence of contamination. On the precipitate B, magnesium and silicon were additionally detected as shown in (b) and the ratio of intensity of Mg to that of S i implies that the precipitate B is β (Mg₂Si) or β '. On the precipitate A, intensity of Si is strong and that of Mg is very weak as shown in (c), compared with those on the precipitate B in (b), moreover, oxygen was detected.



Figure 3: Magnified image near the precipitate A in Figure 2.

Precipitation of crystalline Si in Al-Mg-Si ternary alloys or commercial alloys with 6000 series was reported in the literatures [5]. Tilting experiment shown in Figure 2 shows that the precipitate A is not a crystalline phase. There are no intermetallic compounds in the binary Al-Si system. An alternative interpretation is that the precipitate A is an amorphous phase with Al-Si-O or Si-O systems. Precipitate A is too small for selected area diffraction patterns to identify the crystal structure.

Specimen was prolonged aged at 453 K for 1.8 Ms expecting growth of precipitates, which results in formation of relatively large precipitates. Figure 5 (a) shows the grain boundary precipitates in the prolonged aged specimen. However, in the selected area diffraction pattern on the precipitate indicated by the arrow in (a), neither characteristic diffraction spots nor halo rings were observed as shown in (c). The diffraction spots in (c) are interpreted as those for the upper or lower grains, (b) and (d), respectively, or grain interior precipitates.

It is considered that the intensity of diffracted beam is localized at the diffraction spots and the background intensity is weak in the case of crystalline materials, as schematically illustrated in Figure 6 (a). On the other hand, in the case of amorphous materials, intensity of diffracted beam should gradually change from the incident beam to background through broad diffraction rings as shown in (b).

In Figure 5 (c), two types of diffraction patterns due to crystalline and amorphous phases are superimposed, and the distribution of each intensity of diffracted beam would be schematically illustrated as Figure 6 (c).



Figure 4: EDX spectra on the matrix, and the precipitates B and A in Figure 2, (a), (b) and (c), respectively.





Figure 5: Precipitates in the specimen aged at 453 k for 1.8 Ms (a). Selected area fraction patterns for the upper grain, precipitate and lower grain, (b), (c) and (d), respectively.

When the objective aperture is set at the positions indicated by the arrows in (c) and dark field images are taken, the amorphous phase could be observed as brighter contrast than that for the crystalline matrix. Therefore, this technique is useful to identify amorphous phase precipitates. Figure 6 shows the same view field as Figure 5 with tilting so as to weaken the intensities of diffraction spots due to aluminum matrix. The dark field image (b) was taken with background intensity by setting the objective aperture at the position indicated in the inserted diffraction pattern in (b). Weak contrasts due to crystalline precipitates and the grain boundary are remained, but the contrast of the precipitate is quite high compared with them.



Figure 6: Schematic illustration for diffraction patterns on crystalline and amorphous specimens, (a) and (b), respectively. (c) Effective positions of objective aperture for observing dark field images of an amorphous phase embedded in a crystal matrix.



Figure 7: Bright field image of precipitates shown in Figure 4 (a), and dark field image taken with a background portion in the diffraction pattern (b).

The precipitates are an amorphous phase composed of AI, Si and O. Such precipitates are frequently observed near grain boundaries as shown in Figure 7 and also on grain boundaries as shown in Figure 2.

In other alloys, the amorphous phase precipitates were observed. Figure 8 shows grain boundary precipitates in the Cu-added alloy aged at 453 K for 260 ks. Diffraction contrast for the precipitate A in (a) was not observed in tilting experiments, while the contrast of the precipitate B was sensitively changed by tilting. The precipitate A is composed of Al, Si and O as shown in the EDX spectrum (b), while B is composed of Al, Mg, Si and Cu. The latter is believed to be Q' or Q phase precipitate [6, 7].





Figure 8: Precipitates in the Cu-added alloy aged at 453 K for 260 ks (a). EDX spectra for the precipitate A and B in (a), (b) and (c), respectively.

4. Summary

Amorphous phase precipitates are formed in Al-Mg-Si alloys with or without Cu or Cr addition. The sizes are in the range of about few tens nm to 200 nm in diameter. They are composed of Si, Al and O, and characterized by no-diffraction contrast in TEM observations.

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