X-Ray Study of G.P. Zones in Ternary Al-Zn-Mg Alloys

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X-ray diffuse scatterings at both small and high angles (111 Bragg angle) were measured with powder samples of Al-6.8 at %Zn base alloys containing 0.06 to 2.0 at %Mg.

In the alloys with low Mg concentrations the diffuse scattering around the 111 Bragg peak shows a size-effect scattering; the intensity becomes weaker with increasing Mg concentration and is scarcely observed beyond a certain Mg concentration. Such changes of scattering profiles with Mg concentration arise from the changes in static distortion around and inside a zone. The G.P. zones of the ternary alloys are discussed in view of this static distortion.

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I. Introduction

In the previous work⁽¹⁾ it becomes apparent that a simultaneous measurement of X-ray diffuse scattering at both small and high angles gives information on the structure of G. P. zones. For an Al-10 at %Zn alloy in which the G. P. zones are suspended in the matrix, the diffuse scattering curve at high angles (i.e. around the Bragg peak) is strongly dependent on the zone radius, that is, it changes from symmetrical to asymmetrical around the Bragg angle with increasing zone radius. This asymmetry of the scattering curve is interpreted as the scattering due to the "size effect"⁽²⁾. The static distortion inside and around the zone, which arises from the difference in atomic size between the solute and solvent atoms, is the origin of this "size effect scattering." The static distortion associated with a zone will change with zone radius as well as with the solute concentration inside and outside a zone. Therefore, when the solute concentration inside and outside a zone does not change during the growth of the zone, the change of the static distortion with zone radius can be measured. For an Al-Zn binary alloy it is well known that the zone changes its shape from spherical to ellipsoidal at a critical zone radius of about 35 Å⁽³⁾⁽⁴⁾. This shape change results from the anisotropy of strain field of G.P. zones.

The addition of Mg to a binary Al-Zn alloy as the third element will induce changes in the static distortion associated with a zone. On the G.P. zones in a ternary Al-Zn-Mg alloy there have been many investigations. Graf⁽⁵⁾ and Gerold et al.⁽⁶⁾⁽⁷⁾ proposed a model of the ordered G.P. zones, that is, the zone of MgZn when the concentration ratio of Mg to Zn is more than unity and the zone of Mg₃Zn₅ when the ratio is less than unity. Suzuki et al.⁽⁸⁾ reported the possibility of the co-existence of two kinds of G.P. zones in the alloy with a certain alloy concentration.

In the present experiment, in view of the static distortion associated with G.P. zones in ternary Al-Zn-Mg alloys measurements of X-ray diffuse scattering were carried out. In order to examine the effect of the Mg addition on the behavior of G.P. zones, the measurements were done for several Al-6.8 at %Zn base alloys with various Mg concentrations. From the measurements it was confirmed that the scattering curves are strongly dependent on the Mg concentration and are related to the shape change of zones which occur in the alloys with dilute Mg concentrations. Moreover, the structure of G.P. zones is discussed.

II. Experimental Procedure

The materials used in the present experiment are given in Table 1. The ternary alloys were prepared from aluminum, zinc and magnesium, each having the purity higher than 99.99 %. In Fig. 1, the alloys used in the present investigation are indicated by the numbers in a ternary Al-Zn-Mg phase diagram reported by Fink and Willey⁽⁹⁾. Alloy No. 1 is in the

Table 1 Chemical compositions of the ternary alloys.

Alloy number	Zn (at %)	Mg (at %)
1	6.7	0.06
2	6.8	0.27
3	6.9	0.65
4	6.8	0.98
5	6.9	2.0

Fig. 1 Phase diagram of the ternary Al-Zn-Mg system. The numbers in the figure correspond to alloys shown in Table 1.

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region ($\alpha_{Al} + \kappa$), alloys No. 2 to No. 4 are in the region ($\alpha_{Al} + \kappa + \theta$) and alloy No. 5 is in the region ($\alpha_{Al} + \theta + \eta$), respectively.

The method of heat treatment is similar to that of the previous experiment in Al-10 at%Zn alloy⁽¹⁾. The powder with diameters of more than 53 μ , sealed under vacuum in a silica tube of 0.5 mm diameter, was heated at 450°C for 1 hr and rapidly quenched in iced water. Aging was performed at temperatures between 38 and 110°C. The measurements of X-ray small angle scattering and the scattering around the Bragg peak were carried out by the method similar to that in the previous experiment⁽¹⁾. To examine whether the α' intermediate phase is present, the rotation pattern of a single crystal of an Al-6.7 at%Zn-0.06 at%Mg alloy which was aged at 110°C for 10000 min was taken.

III. Results

1. Changes in zone radius during aging

In Fig. 2 the change of zone radius[†] with aging time is shown for three specimens of Al-Zn-0.06, -0.65 and -2.0 at%Mg alloys. Only the aging curve for Al-Zn-0.06 at%Mg alloy aged isothermally at 38 and 110°C shows a plateau for a certain period of aging time. It is very interesting that the zone radius for this plateau is about 30~35 Å, since this zone radius corresponds to a critical zone radius at which the shape of the zone in a binary Al-Zn alloy changes from spherical to ellipsoidal⁽³⁾⁽⁴⁾. On the other hand, the aging curves for Al-Zn-0.65 at%Mg and 2.0 at%Mg alloys do not show such a plateau and these two curves show a similar change in zone radius with aging time. Taking into consideration the fact that the compositions of these two specimens exist in the different regions in the phase diagram (Fig. 1), this similarity between the

Fig. 2 Change of zone radius with aging time at 38 and 110°C for various Al-Zn-Mg alloys.

[†] Zone radius was determined by using the Guinier approximation⁽¹⁰⁾ from the X-ray small angle scattering curve.

aging curves becomes very important. Whether a plateau is present or not may depend on the structure of the G.P. zone. Consequently, in order to examine this possibility, the scattering intensities around the 111 Bragg peak were measured.

2. Diffuse scattering around the Bragg peak

In Fig. 3 to Fig. 5, the X-ray profiles around the 111 Bragg peak and the diffuse scattering profiles in a high

Fig. 3 X-ray scattering profiles around the 111 Bragg angle for Al-Zn-0.06 at%Mg alloy aged at 110°C for various times.

Fig. 4 X-ray diffuse scattering curves in high angle regions of the 111 Bragg peak for Al-Zn-0.06 at%Mg alloy aged at 110°C for various times.

Fig. 5 X-ray diffuse scattering curves in high angle regions of the 111 Bragg peak for (a) Al-Zn-0.65 and (b) Al-Zn-2.0 at%Mg alloys aged at 110°C for various times.

angle region of the 111 Bragg peak, which were determined in the same way as that in the previous report⁽¹⁾ are given.

In Fig. 3 the broadening of the Bragg peak is observed in a curve of 10000-min aging, which may be due to the formation of the intermediate phase with a very small size. In fact, the existence of the α' intermediate phase was confirmed by the rotation pattern. By a small addition of Mg, the G.P. zones are shown to be very similar to those in a binary Al-Zn alloy. This is the case for an Al-Zn-0.06 at%Mg alloy. In Fig. 4 the scattering intensities increase with aging time until 1500 min and after this aging time the decrease of the scattering intensities was observed. The increase of intensities at the first stage is attributed to the increase of the static distortion inside and around G.P. zones. According to the curve of an Al-6.8 at%Zn-0.06 at%Mg alloy, as shown in Fig. 2, the zone might change its shape from spherical to ellipsoidal at about 34 Å, which is very similar to the case for the binary alloy. In fact, in Fig. 4 the diffuse scattering intensities of the 30-min aged specimen with a zone radius of 30 Å and of the 180-min aged specimen with a zone radius of 34 Å are not so remarkable in comparison with those of the specimens having the G.P. zones larger than 34 Å. The decrease of the intensities at the later stage may be interpreted as the transition stage from G.P. zones to the intermediate phase. The total size effect scattering decreases since the formation of the intermediate phase which is incoherent with the matrix yields the relaxation of lattice distortion. The same tendency was also observed in the scattering curves of the specimen aged at 38°C.

On the other hand, in the case of Al-Zn-0.65 at%Mg and Al-Zn-2.0 at%Mg alloys, the diffuse scattering around the 111 Bragg peak was scarcely observed, as shown in Fig. 5(a) and (b). The reason why the back ground in these figures was high is unknown. The difference between these scattering profiles and those of Al-Zn-0.06 at%Mg alloy must arise from the difference of the structure of G.P. zones in these alloys. It can be concluded that the static distortion inside and around a zone in an Al-Zn-0.06 at%Mg alloy is larger than that of other alloys having higher Mg concentrations. In consideration of the fact that the static distortion arises from the local arrangement of atoms with different atomic size, it seems reasonable to assume that the structure and/or the solute concentration of G.P. zones in an Al-Zn-0.06 at%Mg alloy are different from those of Al-Zn-Mg alloys containing 0.65 and 2.0 at%Mg. Since the diffuse scattering around the Bragg peak was observed in an Al-Zn-0.27 at%Mg alloy, a boundary at which the diffuse scattering around the Bragg peak appears may be put between 0.27 and 0.65 at%Mg.

It should be noticed that the diffuse scattering around the Bragg peak was scarcely observed in the alloys with higher Mg concentrations than 0.65 at%, while the small angle scattering was observed experimentally. From this fact, it can be concluded at least that the static distortion associated with a zone is very small in these Mg-rich alloys.

IV. Discussion

Figure 6 shows a comparison of the diffuse scattering curves for an Al-Zn-0.06 at% alloy when the aging temperatures are different such as 38 and 110°C for the same zone size such as 30 or 35 Å. The intensity of the diffuse scattering around the Bragg peak of the specimen aged at higher temperature is smaller than that aged at lower temperature, even when the size of the zones is the same. This indicates that the intensities of the diffuse scattering depend on the volume fraction of G.P. zones. Moreover, in order to make clear the effect of Mg concentration on the diffuse scattering around the Bragg peak, the scattering curves for the two specimens having Mg concentrations of 0.06 and 0.27 at% are compared under the same average zone radius such as 30 or 35 Å, as shown in Fig. 7. It is apparent that the diffuse scattering around the Bragg peak decreases with increasing Mg concentrations. Thus, the diffuse scattering around the Bragg peak, which reflects mainly the static distortion of the zone, decreases with the increase in Mg concentration and is scarcely observed at 0.65 at%Mg. This experimental result offers some important information in regard to the structure of G.P. zones in ternary systems. For several ternary aluminum alloys such as Al-Ag-Cu, Al-Ag-Zn⁽¹¹⁾ alloys, the co-existence of two kinds of G.P. zones was observed. Graf⁽⁵⁾ and Gerold et al.⁽⁶⁾⁽⁷⁾ suggested that there exist two kinds of zones which correspond to the compositions of either MgZn or Mg_3Zn_5 depending on the ratio of Mg and

Fig. 6 Comparison of the diffuse scattering curves of the Al-Zn-0.06 at%Mg alloy aged at two different temperatures. The zone size is the same.

Fig. 7 Comparison of the diffuse scattering curves of Al-Zn-0.06 at%Mg alloy with those of Al-Zn-0.27 at%Mg alloy under the same zone size.

Zn concentrations in Al-Zn-Mg alloys. It is well known that zinc causes the decrease in the inter-atomic spacing of the aluminum lattice, whereas magnesium has an opposite effect. Because of this, it might be expected that an overall decrease in the distortion

of the G.P. zone would occur if the zinc and magnesium atoms aggregated together. Thus, the present experimental result may be interpreted by the existence of different kinds of G.P. zones, and it seems reasonable to consider that the Mg concentration within the zone would increase with the Mg concentration in the alloy.

V. Conclusions

To examine the nature of G.P. zones in a ternary Al-Zn-Mg alloy in view of the static distortion around and inside a zone, X-ray diffuse scatterings at both small and high angles (around Bragg peak) were measured for Al-6.8 at%Zn base alloys containing 0.06, 0.27, 0.65, 0.98 and 2.0 at%Mg.

In an alloy with a low Mg concentration such as 0.06 at%, the diffuse scattering around the 111 Bragg peak was very similar to that in the binary Al-Zn alloy. With increasing Mg concentration, the intensity became weaker and was scarcely observed for the alloys having Mg concentrations more than 0.65 at%. This indicates that with increasing Mg concentration, the total size effect scattering decreases which arises from the static distortion associated with a zone. Namely, the static distortion of a zone decreases with increasing Mg concentrations in the zone. On the basis of these results, the structure of the G.P. zones formed in the Al-Zn-Mg alloys was discussed by comparing the structures of G.P. zones previously reported by other authors with the present ones.

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