Development of Microstructures of Long-Period Stacking Ordered Structures in $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ Alloys Annealed at 673 K (400 °C) Examined by Small-Angle X-Ray Scattering

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Development of LPSO structure and in-plane ordering during annealing the $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ ternary alloy sample at 673 K (400 °C) was examined by synchrotron radiation small-angle scattering/diffraction measurements. By examining the first diffraction peaks for 18R, 10H, and in-plane order spot, the growth kinetics of in-plane order domain and the transition from 10H into 18R were discussed. The domain growth of in-plane order was characterized by small domain with little correlation between neighboring segregation layers.

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I. INTRODUCTION

LONG-PERIOD stacking ordered (LPSO) structures having periodic modulation in composition and stacking fault have drawn attention due to their mechanical performance as new light metal alloys^[1,2] and their unique structure and mechanical properties,^[3–5] in particular, their characteristic deformation mechanism.^[6,7] Although the details of LPSO structure having several periodicities, namely, 10H, 14H, 18R, and 24R, were examined by electron microscopy,^[1–7] there are many aspects yet to be examined from the viewpoints of formation kinetics and phase stability/phase diagram. Earlier phase diagram studies^[8] give LPSO structures as a phase with a limited composition range as a single-phase region. However, the works made with electron micrographic observations suggest a rather wider range for the 18R phase region,^[3,9,10] although it is not necessarily identified as a single-phase region under equilibrium state. Recent experimental phase diagram studies extended in a wider composition region^[11] do not yet explain the microstructural changes reported by these transmission electron microscopy (TEM) works. To discuss the microstructures in this viewpoint, it is important to know if the microstructures of the alloy we are examining are described by a simple two-phase or single-phase model that we usually adopt for the

precipitation case.^[12] Many electron microscopic results^[3,13,14] suggest fluctuations in periodicities of LPSO structures, degree of in-plane orders and segregation, leading to a conclusion that formation kinetics of LPSO microstructure is not as simple as described by a simple two-phase precipitation model.

To determine phase diagram and microstructural characteristics of LPSO in MgYZn alloys, therefore, we need to examine the more quantitative characteristics of the microstructure. In the present work, small-angle X-ray scattering (SAXS)/diffraction was used to examine the temporal evolution of the diffraction peaks corresponding to the first peaks of LPSO and in-plane ordering appearing in the SAXS region, as described in our previous work.^[15]

II. EXPERIMENTAL

Polycrystalline cast ingot and directionally solidified ingot were used in the present work. The composition of the samples is Mg-9 at. pct Y-6 at. pct Zn. The cast ingot (hereafter referred to as cast sample) exhibited polycrystalline microstructures. The directionally cast sample showed^[6,7] large and faceted grains with a thickness up to a hundred micrometers and length of a couple of millimeters with a preferred orientation of $\langle 1\ 1\ -2\ 0 \rangle$ in the growth direction (hereafter referred to as the DS sample). The volume fraction of the LPSO phase is reported to be 90 pct or more for the present composition. The sample was heat treated under vacuum in sealed Pyrex* tubes at temperatures between 673 K and

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*Pyrex is a trademark of Corning Incorporation, Corning, NY.

773 K (400 °C and 500 °C) and polished down to the thickness used for the measurements, and the samples annealed at 673 K (400 °C) were examined in detail.

Small-angle scattering measurements were made at BL6A of Photon Factory with a wavelength of 0.15 nm and at BL04B2 of SPring8 with a wavelength of 0.03 nm.

III. RESULTS AND DISCUSSION

Figure 1 gives the temporal evolution of small-angle scattering patterns obtained for the cast samples annealed at 673 K (400 °C) up to 2 weeks. The scattering patterns show sharp diffraction peaks in two Debye rings and outer diffuse spots. The magnitudes of the scattering vector, q , for the sharp diffraction spots are about 4.01 and 4.86 nm⁻¹, respectively. This spacing agrees with the distance between the stacking fault in 10H and 18R structures reported in the TEM works by Itoi *et al.*,^[5] $2\sqrt{3} \times 2\sqrt{3}$ Egusa *et al.*,^[3] and other researchers for MgYZn alloys and also close to that of the reported MgAlGd alloy.^[4] In the as-cast sample, the outer diffuse spot showed a well-defined sixfold pattern, showing that the diffraction comes from only one of the crystals in the sample. These spots agreed with the in-plane ordering of L1₂ clusters with structure formed in the segregation layer of the LPSO structure reported by Yokobayashi *et al.*,^[4] as shown in the previous work.^[15] As-cast samples used in the present work showed one or two sets of sixfold patterns. The present result, that the number of crystals that give a sixfold pattern is much smaller than that of crystals giving diffraction peaks of 10H and 18R as Debye rings, can be explained by two reasons. First, the in-plane ordering is much more sluggish than the formation of LPSO

stacking, so that not all the crystals giving LPSO diffraction peaks are necessarily fully ordered in the in-plane directions. This idea is supported by the fact that the full-width at half-maximum (FWHM) of the diffraction spot for the in-plane ordering is much larger than those for the LPSO peaks for 10H and 18R, whose FWHM values are already equal or close to the resolution limit of the present small-angle scattering setup, about 50 nm, even for the as-cast sample. The second point is that in-plane order spots appear only when the X-rays transmit in the direction close to the c -axis of the sample. In contrast, LPSO diffractions are observed when the c -axis lay parallel to the detector, *i.e.*, normal to the direction of X-rays. These points are discussed later. For longer annealing times, diffraction peaks from the 10H structure decreased and eventually disappeared after 1 week of annealing. The LPSO peaks are very sharp compared with the diffuse spot of in-plane ordering appearing around 6 nm⁻¹. Figure 2 gives the change of the integrated intensity of 10H relative to that of 18R for isothermal annealing at 673 K and 773 K (400 °C and 500 °C). For both annealing temperatures, the integrated intensities of 10H structure monotonically decreased with time. This finding suggests that the transition from 10H to 18R during heat treatment is gradual. A first-principles calculation by Iikubo *et al.*^[16] suggested that the stability of 18R and 10H at high temperatures is better than the 2H (hcp) structure when the effect of lattice vibration is taken into account for Mg. Although the calculation does not directly evaluate the stability of the present ternary alloys, this tendency is in good agreement with the present results that 10H did not show fast disordering or collapse to form hcp structure, but instead was slowly replaced by 18R structures. Therefore, the 10H structure is still more stable than hcp at the annealing temperatures in the present condition.

The in-plane order spots became sharper with annealing time, suggesting that the domain size of the ordered region within the segregated layer increased.^[15] Figure 3

Fig. 1—Two-dimensional SAXS patterns of Mg₈₅Y₉Zn₆ cast alloy: (a) as-cast and (b) annealed at 673 K (400 °C) for 48 h and (c) for 2 weeks. The 10H peaks decreased with annealing time, and only 18R peaks were observed after 2 weeks of annealing at 673 K (400 °C).

Fig. 2—Integrated intensity of the 10H peak relative to that of 18R for the sample annealed at 673 K and 773 K (400 °C and 500 °C). At 673 K, the 10H peak disappeared after 2 weeks of annealing.

shows the temporal change of the domain size of the in-plane ordered region at the annealing temperatures of 673 K and 773 K (400 °C and 500 °C) and the lattice constant of the order structure. The domain size, D , was calculated from the FWHM of the peak, Δq , by $D = 2\pi/\Delta q$. As shown in Figure 3, the average domain size of the as-cast sample was about 2.5 ± 0.5 nm. Since the lattice constant of the in-plane order structure is about 1 nm in the present data, an ordered region contains only 5 to 10 $L1_2$ clusters within a domain, suggesting that it is rather a two-dimensional medium-range ordered state. Considering that the domain thickness of the LPSO structure in the c direction evaluated from the diffraction peaks of 18R and 10H in the Debye ring is more than one order of magnitude larger, it is concluded that the in-plane ordering is not a necessary condition to form the LPSO structure, but the existence of SRO or even $L1_2$ clusters distributed randomly in the segregation plane should be enough to stabilize the stacking fault and, consequently, the stacking order. The domain size increased with annealing time and reached 7.1 nm after annealing at 673 K for 2 weeks, when the 18R structure was the only LPSO structure in the sample. Yet, it is worthwhile to note that the lattice constant for the in-plane ordering monotonically decreased during annealing, when the order domain size grew, suggesting that the long-range in-plane order has a locally strained structure.

As discussed previously, the lattice parameter for in-plane ordering monotonically decreased with annealing time, as shown in Figure 3, while that in the stacking direction did not change with time, as shown in Figure 4. When we look into the SAXS pattern around the first peaks of 18R and 10H in Figure 1, there are three important points to note. First, the peaks on a Debye ring are separated from each other, meaning that each peak represents different grains having different orientations. Second, there are many pairs of peaks of 18R and 10H, where a 18R peak and a 10H peak are on

Fig. 3—Change of in-plane order domain size and the lattice parameter of in-plane ordering during annealing at 673 K (400 °C). The domain size monotonically increased with time, and the peak position decreased as the order domain grew.

the common radial directions and connected to each other with a strong streak. This suggests that 18R and 10H structures coexist or are mixed in a coherent way in the same grain. Therefore, the development of such streaks represents the growth kinetics of 18R over 10H structures. It is also worth noting that the atomic layer distance in the c direction calculated from the coexisting 10H and 18R, 0.258 nm, agreed well. Third, the distribution in the peak position is observed on the same Debye ring. Such variation in the peak position, *i.e.*, the lattice constant for LPSO, should be sensitive to the statistical characteristics stemming from the heterogeneity of the sample, such as compositional fluctuation/heterogeneity among grains, kinetic partitioning effect between 18R and 10H, residual strain, and so on. To illustrate the third point, the distribution of the peak position of 18R peaks from individual grains is shown in Figure 4. Since we can distinguish the diffraction from the isolated 18R structure from that from the 18R that coexists with the 10H structure, they are plotted separately in the figure. The average peak positions for the two conditions agree each other, and also they do not change with annealing time. In both cases, the peak positions distributed around the average lattice constant with the standard deviation of 1 pct. As mentioned previously, the lattice parameter may scatter when the composition of the grains fluctuates. Another possibility is that the lattice parameter may vary if the lattice parameter of 18R depends on whether it is formed during casting or transformed from 10H during annealing, or whether the in-plane ordering occurs. Heterogeneous residual stress may also affect the distribution. However, if the lattice parameter of 18R depends on when and how it was formed, its distribution should differ in the as-cast state as opposed to after long annealing, where 10H structures are fully transformed to 18R. The lattice parameter should increase with time if it depends on the degree of in-plane order. The results shown in Figure 4 do not agree with these stories. Distribution cannot be easily explained by residual strain, since the internal strain of ± 1 pct, as an average,

Fig. 4—Temporal evolution of the distribution of the peak position of 18R peaks as a function of annealing time.

is quite large. Assuming the Young's modulus for the alloy, the calculated stress slightly exceeds the yield stress of the alloy, which is not feasible as existing in the samples annealed at 673 K (400 °C) for 2 weeks and polished down to a hundred micrometers for SAXS study. Therefore, we propose that the cast $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ polycrystalline sample has compositional heterogeneity, which is large enough to result in about 1 pct of differences in the lattice parameters of LPSO, but still small enough to keep the alloy within the 18R structure region. Considering the result that the lattice parameter of 18R is the same for the isolated one and the one coexisting with 10H, the preceding discussion also implies that the composition range where 18R is stable or metastable is relatively large, and 18R as well as 10H is not a stoichiometric phase. On the other hand, the structural model proposed by Yokobayashi *et al.*^[4] for MgAlGd alloy gives a stoichiometric picture when the degree of order is perfect. They found that the order domain in MgAlGd alloy developed in large scale compared with the MgYZn system, and the stacking sequence in the alloy resulted in order-disorder structure. However, the order structure between the neighboring segregation layers does not correlate well for MgYZn alloy systems, resulting not in order-disorder structure, but in LPSO structure. In contrast, Egusa and Abe discussed that long-range correlation of in-plane ordering in the c direction can be observed, via TEM observations, when the sample is annealed long enough.^[3] Then, the question is how to evaluate such a correlation in a quantitative way and how to relate the microstructures on the in-plane ordering domains and LPSO structures. Figure 5 shows SAXS patterns obtained for an as-cast $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ DS sample. Figure 5(a) shows a well-defined sixfold sharp diffraction peak showing in-plane ordering; in contrast to the SAXS pattern observed for the cast samples, only a couple of faint 18R LPSO peaks from misoriented small crystals are observed. This is because the typical thickness of the grain is close to that of the thickness of the sample; therefore, a DS sample prepared for SAXS contained

only a couple of large grains. Figure 5(b) shows another SAXS pattern of the same sample with incident X-ray perpendicular to Figure 5(a). The pattern has two important features: (1) the in-plane order spots show twofold symmetry, and the shape of the spot is strongly elongated in the tangential direction; and (2) strong 18R diffraction peaks appear in the direction perpendicular to the order spots. The relationship of the two figures is schematically shown in Figure 5(c). The FWHM of the spot in Figure 5(a) corresponds to the in-plane domain size, D , of 9.6 nm, and the size obtained in the elongated direction in Figure 5(b) using the same equation is 1.1 nm. If there is no relationship between the neighboring segregation layers, the spots become a rod corresponding to a two-dimensional reciprocal lattice. Figure 5(b) suggests that the correlation length in the direction perpendicular to the ordering plane does not go beyond a couple of layers in the as-grown DS sample examined here. Although the FWHM of the spot may depend also on the stacking sequence, as discussed for the MgAlGd case,^[4] it can be treated as a correlation length ξ that the stacking sequence is coherent in the present case. It is reasonable because the in-plane order domain size is

Fig. 6—Schematic illustration of the angle of acceptance of the diffraction condition for the 18R peak and the in-plane order spot.

Fig. 5—SAXS pattern of directionally solidified samples: (a) X-ray parallel to c -axis, (b) X-ray perpendicular to the c -axis, and (c) schematic illustration of the cuts.

still just 6.4 times larger than the distance between the segregation layers, *i.e.*, 2.1 times the lattice constant of 18R. This picture is also consistent with the result that the average LPSO distance did not change, although the in-plane distance changed with domain growth, considering that the in-plane strain is averaged over each layer and did not affect the lattice constant in the *c* direction due to the lack of correlation in that direction.

With the preceding discussion on the SAXS pattern of DS samples, let us return to the question of why only one or two sets of sixfold order spots appeared while more than 50 diffraction spots of 18R were observed in the as-cast polycrystalline samples. The number of observed 18R LPSO peaks for an exposure with a two-dimensional detector was between 50 and 120, and that for a sixfold pattern was one or two. The FWHM of the measured order spot was 2.5 nm^{-1} and that calculated for the 18R LPSO diffraction spot corresponding to a domain thickness of 50 nm was 0.1 nm^{-1} , which is close to the present SAXS resolution and of the same order of magnitude as the measured data. When only the solid angle of acceptance defined by the FWHM of the spots determines the number of allowed diffraction, as schematically shown in Figure 6, the solid angle for the 18R peak, $1.5 \times 10^{-1} \text{ sr}$, is about 5 times larger than the solid angle for the sixfold order spot. Therefore, there is still a gap of a factor of 10 between the ratio of the number of 18R diffraction peaks to the number of order spots and the expected ratio. Some of the discrepancy may be explained by an effect of warpage or mosaicity of the 18R grains. Figure 1 shows that the shape of some of the LPSO peaks elongated along the ring about a couple of times, keeping the FWHM in the radial direction small. As schematically shown in Figure 6, this warpage increases the acceptance angle to satisfy the Bragg condition for 18R diffraction by several times for some of the diffraction spots when $\Delta q < \delta'$. On the other hand, as shown in Figure 5(c), the number of in-plane ordering should increase with overlapping twofold order spot conditions. Therefore, the number of order spot sets that in-plane ordering appears is still less than expected. This result implies that not all the LPSO grains giving well-defined 18R diffraction are ordered in the in-plane direction, and it agrees with the SAXS pattern that for 2 weeks of annealing, the number of sets of order spot increased while the FWHM of the spot decreased.

IV. CONCLUSIONS

Small-angle scattering/diffraction measurements were applied to examine the microstructures and their evolution of $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ polycrystalline cast alloys during annealing at 673 K (400 °C) and compared with as-cast directionally solidified alloys. The temporal change of the cast sample showed that development of in-plane order is far slower than that of LPSO order, and the correlation of the order structures between the neighboring segregation layers is still slower. Although the

18R and 10H LPSO structures developed in plates whose thickness was larger than the resolution limit of present SAXS measurements, even in the as-cast state, the in-plane ordering was much slower with a domain size of typically 2.5 nm and grew to 7.2 nm after annealing for 2 weeks when all the 10H structures were transformed into 18R structure. A 90-degree rotation of sixfold pattern for the directionally cast sample gave twofold elongated order spots and 18R LPSO diffraction perpendicular to the order spot, suggesting that there was little coherent interference between neighboring order domains. A temporal change of statistical nature of the 18R diffraction spot suggests that the lattice constant in the stacking direction has distribution stable during transformation from 10H to 18R, keeping the average atomic layer distance in the *c* direction constant.

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