Evaluation of active slip systems during deformation by In-situ XRD in precipitation hardening Mg Alloys

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Abstract. The effect of precipitates on active slip systems was evaluated in precipitation-hardening Mg Alloys. In a Mg-5% Y-4% Nd (WE54) alloy, the radius and thickness of disc-shaped $\beta''$ precipitates were measured by small angle X-ray scattering measurements. The active slip system was then measured during tensile deformation by in situ X-ray diffraction measurements. The average radius and thickness of the precipitates increased with aging time, and approached 19.4 and 3.85 nm, respectively, at a peak aging time of 2160 ks. The uniform elongations of the as-quenched, 1.08 ks aged and 360 ks aged alloys were determined to be approximately 9.7, 5.5 and 2.3%, respectively. Various slip systems were active in the as-quenched alloy. On the other hand, in the alloy aged for 360 ks, non-basal $<a>$ slip was found to be dominant.

1. Introduction
Lightweight, high-specific-strength magnesium has gained attention for use in the transport industry. However, magnesium shows low ductility at room temperature due to the anisotropy of plastic deformation because of its crystal structure. There are multiple deformation mechanisms involving dislocation slip in the hexagonal close packed (HCP) structure of magnesium, such as basal $<a>$ slip, prism $<a>$ slip and pyramidal $<c+a>$ slip. At room temperature, the critical resolved shear stress (CRSS) for basal $<a>$ slip in pure magnesium is reported to be about 0.5 MPa [1]. On the other hand, the CRSS for prism $<a>$ slip and pyramidal $<c+a>$ slip is reported to be more than 10 times higher than that for basal $<a>$ slip [2]. Therefore, basal $<a>$ slip occurs preferentially in magnesium, and the number of independent slip systems is small, so that the von-Mises criterion cannot be satisfied [3]. For this reason, non-basal slip mechanisms such as prism $<a>$ slip and pyramidal $<c+a>$ slip are necessary to improve the ductility of magnesium.

It has been reported that the addition of yttrium enhances non-basal slip [4,5]. Mg-Y alloys are well-known precipitation hardened alloys; therefore, it is important to investigate the effect of the precipitates on the active slip systems in order to control the mechanical properties. Transmission electron microscopy (TEM) observations of dislocations are generally used to identify active slip systems in HCP metals. However, in TEM observations, although the Burgers vectors of dislocations can be identified easily, much effort is required to identify the slip planes, and it is difficult to obtain statistical data from many grains. On the other hand, methods such as X-ray diffraction (XRD) can obtain statistical information from many grains during tensile deformation using synchrotron radiation [6,7]. The purpose of this study is to evaluate the effect of the precipitate size on active slip systems during tensile deformation by in situ XRD measurements of Mg-Y-Nd alloys.
2. Experimental Procedures

Mg-5 wt% Y-4 wt% Nd (WE54) extruded alloys were solution treated at 823 K for 9 ks, subsequently quenched in water, and aged at 473 K to cause precipitation of the β′ phase. Samples with different precipitate sizes were prepared by varying the aging time between 1.08 and 2160 ks. For the samples for the tensile tests, in order to refine the crystal grains, high-pressure torsion (HPT) was performed after a 9 ks solution treatment at 823 K and water quenching. The samples were disks with a thickness of 0.9 mm and produced at a pressure of 2 GPa, and 7 rotations were performed at a rotation speed of 0.2 rpm. The tensile-test specimens had a length of 10 mm, a width of 3 mm, and a thickness of 0.6 mm. For comparison, pure Mg was prepared. The specimens were subjected to electron beam backscatter diffraction (EBSD) measurements at an acceleration voltage of 15 kV, in an oriented imaging microscopy (OIM) system provided by TSL, and equipped on a JSM-6500F scanning electron microscope provided by JEOL Ltd.

To measure the change in the precipitate size with aging time, small angle X-ray scattering (SAXS) measurements were performed at the BL19B2 beamline of the SPring-8 synchrotron radiation facility. The X-ray energy was 25 keV, the exposure time was 60 s, the camera length was 3046 mm, and the scattering intensity for each sample was measured using a two-dimensional pixel detector (PILATUS-2M, DECTRIS). The scattering profile of the as-quenched (A.Q.) alloy was subtracted so that only the scattering profile of the precipitate was obtained. The precipitates in the Mg-Y-Nd alloys were disk-shaped and lay on (110) prism plane in the matrix, as determined by TEM observations [8]. The data are presented as scattering intensity I(k) vs. scattering vector k (=4πsinθ/λ). The Guinier approximation was used to measure the precipitate size [9]. In the low-k region of the scattering curve, the relationship between ln(I(k)) and k is expressed as \( \ln(I(k)) \propto k^2 \), and its slope is \((-1/3)R_g^2\) using the Guinier radius, \( R_g \). Therefore, \( R_g \) was calculated by finding the slope of the \( \ln(I(k)) \) vs. \( k^2 \) plot (Guinier plot). \( R_g \) is a size parameter that is not dependent on the shape of the precipitates. Assuming that the actual radius and the thickness of the cross section of the disk-shaped precipitate are \( r \) [nm] and \( t \) [nm], respectively, the relationship between \( R_g \), \( r \), and \( t \) is expressed as \( R_g^2 = r^2/2 + t^2/12 \). In addition, in the medium-k region where \( k \) is approximately \( 1/R_g \) or more, the relationship between \( I(k) \) and \( k \) is expressed as \( \ln(I(k)) \propto k^2 \), and its slope is \(-1/12r^2\) [10]. In the same way as when the Guinier radius was calculated, the thickness of the cross section of the disk-shaped precipitates was calculated by finding the slope of the \( \ln(I(k))k^2 \) vs. \( k^2 \) plot (thickness plot). By substituting the obtained \( t \) and \( R_g \) values into the relational expression of \( R_g \), \( t \), and \( r \), the radius \( r \) of the disk-shaped precipitates was obtained.

To evaluate active slip systems during tensile deformation, in situ XRD measurements were performed at the BL46XU beam line of SPring-8 using the measurement system shown schematically in Fig. 1. The X-ray energy was 30 keV, and the incident beam was 0.5 and 0.2 mm in the horizontal and vertical directions. The detector system was an array of six MYTHEN detectors (DECTRIS) and was positioned about 22° from the transmission direction with a 721.24 mm distance between the specimen and the MYTHEN detectors. The tensile test was performed with an initial strain rate of 1.6 \( \times 10^{-4} \) s\(^{-1}\), while oscillating the tensile test at a rate of 1 mm/s and a width of 3 mm. Oscillation was performed to increase the number of grains in the irradiated volume and to obtain XRD peaks of sufficient intensity [11]. The time resolution in this experiment was 4 s. Profile fitting of the obtained diffraction peaks was performed using the Voigt function, and the diffraction angle and full width at half maximum (FWHM) were obtained. The Williamson-Hall equation [12] is often used to separate the FWHM into the effect of crystallite size and the effect of nonuniform strain introduced by dislocations. However, this equation does not consider elastic anisotropy and is not appropriate for application to HCP metals with large elastic anisotropy. Therefore, a modified Williamson-Hall equation that takes elastic anisotropy into account was used in this study [13]:

\[
\Delta K_{hkl} = \frac{49}{D} + \left( \frac{\pi b^2}{2} \right) \frac{1}{\rho^2} \frac{1}{C_{hkl}} \frac{1}{K_{hkl}} + O(K^2 C_{hkl}),
\]

where \( K \) is the diffraction vector (=\(2\sin\theta/\lambda\)), \( \Delta K = \Delta(2\theta\cos\theta/\lambda) \), \( \theta \) is the diffraction angle, \( \Delta2\theta \) is the FWHM, \( \lambda \) is the wavelength of the incident X-rays, and \( D \) is the crystallite size, \( b \) is the magnitude of the Burgers vector, \( \rho \) is the dislocation density, \( M \) is a constant that depends on the effective outer cut-
off radius of dislocations, and \( \bar{C}_{hk.l} \) is the average dislocation contrast factor that depends on the diffraction plane. \( O(K^2\bar{C}_{hk.l}) \) is a higher-order term and is typically ignored. The first-order coefficient of \( K \) represents the nonuniform strain \( \varepsilon_{hk.l} \). The transformation of Eq. (1) is as follows:

\[
\varepsilon_{hk.l} = \sqrt{\frac{(\Delta K_{hk.l} - \alpha K_{hk.l})}{K_{hk.l}}}.
\]  

The subscript \( hk.l \) in Eq. (2) corresponds to the XRD peak data obtained from the diffraction plane \( (hk.l) \), i.e., \( \varepsilon_{hk.l} \) represents the nonuniform strain in the direction normal to \( (hk.l) \) planes. The nonuniform strain in the direction normal to each set of diffraction planes was obtained using Eq. (2). To express the anisotropy of the nonuniform strain, polar coordinates were created with the nonuniform strain for each set of diffraction planes as the radial diameter and the angle between the direction normal to each set of diffraction planes and the basal planes as the declination. An approximate curve was then created in the polar coordinates, and this is referred to as the nonuniform strain distribution in this study.

For comparison with the experimental values, Fig. 2 shows the nonuniform strain distribution reported by Dragomir and Ungár that was calculated assuming that only one type of slip system is active and dislocation densities for each slip system is \( 10^{14} \) m\(^{-2} \) [14]. From Fig. 2, when basal \(<a> \) slip is active, the nonuniform strain distribution becomes relatively isotropic. When prism \(<a> \) slip is active, nonuniform strain is generated in the in-plane direction of basal plane, and when pyramidal \(<c+a> \) slip is active, the nonuniform strain is approximately twice as large in the \( c \)-axis direction as in the in-plane direction of basal plane. The active slip systems were evaluated by comparing the nonuniform strain distributions shown in Fig. 2 with those obtained experimentally.

3. Results

Fig. 3 shows the radius and thickness of the disk-shaped precipitates as a function of the aging time. When the aging time was 1.08 ks, the radius and thickness were 0.98 and 0.61 nm, respectively, and after increasing gradually up to 36 ks, they increased rapidly up to 180 ks. The radius then continued to
increase rapidly, while the increase in thickness slowed down. Finally, the radius and thickness at an aging time of 2160 ks were 19.4 and 3.85 nm, respectively. The EBSD measurements results for the A.Q. WE54 alloy and pure Mg, indicated that the grains in both alloys were both coarse with a size of about 10 μm. The change in grain size with aging time was not so large. Fig. 4 shows tensile test results for WE54 at each aging time and those for pure Mg. The uniform elongation for pure Mg was about 2.6%, while that for the A.Q. WE54 alloy indicated a high ductility of about 9.7%. In addition, as the aging time increased, the strength tended to increase while the ductility decreased. The tensile strength and uniform elongation of the alloy aged for 2160 ks were 280 MPa and 2.9%, respectively. In addition, EBSD measurements of the gauge section after fracture of pure Mg and the WE54 alloy indicated no twinning in any of the samples, and the main cause of deformation was dislocation slip.

Fig. 5 shows XRD results for the A.Q. WE54 alloy before tensile testing, during elastic deformation, and during plastic deformation. Compared to that before tensile deformation, the peak angle during elastic deformation shifted downward. This represents an increase in the diffraction plane spacing in the tensile direction as a result of elastic deformation. The increase in peak width during plastic deformation is due to an increase in the dislocation density and the amount of nonuniform strain. Nineteen peaks from the low angle side were used for the analysis.

Fig. 6 shows the nonuniform strain distribution for each nominal strain of the A.Q. alloy and each aging time of the WE54 alloys. As shown in Figs. 6(a) and 6(b), the nonuniform strain at a nominal strain of 1%, which is the elastic deformation region, was small in the sample where aging was not so advanced. On the other hand, as shown in Figs. 6(c) and 6(d), nonuniform strain was present in the elastic deformation region in the sample with advanced aging. For all samples, the graph expanded due to the increase in nonuniform strain as the deformation progressed. In the A.Q. alloy, the nonuniform strain in the c-axis direction and the in-plane direction of basal plane was about 1.2 times larger than that in the 45° direction, as shown in Fig. 6(a). Compared to Fig. 2, not only basal <a> slip where the nonuniform strain is relatively isotropic, but also prism <c+a> slip where a large strain is generated in the in-plane direction of basal plane and pyramidal <c+a> slip, where a large strain is generated in the c-axis direction, were active. Therefore, the high ductility of the A.Q. WE54 alloy is due to activation of non-basal slip. Figure 6(b) shows that in the alloy aged for 1.08 ks, the nonuniform strain distribution changed at the deformation stage. Up to a nominal strain of 4%, the nonuniform strain in the c-axis direction was about 1.5 times larger than that in the in-plane direction of basal plane, compared to Fig. 2, which suggests that pyramidal <c+a> slip was active. When the nominal strain was 5.5%, both the nonuniform strain in the c-axis direction and that in the in-plane direction of the basal plane were about 0.0033. Therefore, it is inferred that prism <a> slip is active in the latter stage of plastic deformation. As shown in Fig. 6(c), the nonuniform strain in the in-plane direction of basal plane in the alloy aged for 360 ks was approximately twice as large as that in the c-axis direction at any stage during plastic deformation. Compared to Fig. 2, it can be seen that prism <a> slip was active. Figure 6(d) shows that the amount of nonuniform strain in the alloy aged for 2160 ks increased again in the c-axis direction and in the in-plane direction of basal plane. Compared to Fig. 2, not only basal <a> slip, but also prism <a> slip and pyramidal <c+a> slip were active. In addition, the nonuniform strain in the 45° direction was smaller than that for the A.Q. WE54 alloy shown in Fig. 6(a). Therefore, the alloy aged for 2160 ks had
less activity for basal \(<a>\) slip than the A.Q. alloy.

4. Discussions

To investigate the effect of the precipitates generated by aging on each slip system, the increase in CRSS for each slip system was calculated. The Orowan mechanism and shearing mechanism are well-known precipitation hardening mechanisms [15]. In the Orowan mechanism, dislocations move around the precipitates and leave an Orowan loop, where the amount of strengthening is given by [16]:

\[
\Delta \tau_{\text{Orowan}} = \frac{G b}{2\pi \lambda \sqrt{1-\nu}} \ln \frac{d_p}{r_0},
\]

where \(d_p\) is the mean planar diameter of the point obstacles, \(r_0\) is the core radius of dislocations, \(\lambda\) is the effective planar interparticle spacing on the slip plane, \(G\) and \(\nu\) are the shear modulus and Poisson’s ratio of the matrix phase (17.3 GPa and 0.291 for Mg). In the shearing mechanism, dislocations move while shearing precipitates, and the amount of strengthening is given by [8]:

\[
\Delta \tau_{\text{Shear}} = \frac{y_{\text{APB}}}{2b} \left( \frac{d_p}{\lambda} - \frac{d_p}{L_p} \right),
\]

where \(L_p\) is the mean planar center-to-center interparticle spacing on the slip plane, and \(y_{\text{APB}}\) is the anti-phase boundary (APB) energy for basal \(<a>\) dislocation shearing of the precipitates (210 mJ m\(^{-2}\)) [8]. In past reports, TEM observations of Mg-4 wt% Y-3 wt% Nd (WE43) alloys confirmed that basal \(<a>\) slip occurs via the shearing mechanism, and non-basal slip occurs via the Orowan mechanism with respect to the precipitates [8]. Therefore, the increase in the CRSS for each slip system was calculated geometrically using Eq. (4) for basal \(<a>\) slip and Eq. (3) for non-basal slip, based on the SAXS results assuming that the precipitates are rationally oriented. The calculation results are shown in Fig. 7. The increase in the CRSS for prism \(<a>\) slip shown in Fig. 7 is large, and that of basal \(<a>\) slip is small during the initial stage of aging. The increase in CRSS for prism \(<a>\) slip decreases significantly with aging time, and becomes smaller than that for pyramidal \(<c+a>\) slip and basal \(<a>\) slip after aging for 108 ks. In addition, the increase in CRSS for basal \(<a>\) slip increases monotonically with aging time.

The calculation results in Fig. 7 were used to consider the results for the nonuniform strain distribution shown in Figs. 6(b)-(d). As shown in Fig. 6(b), for the alloy aged for 1.08 ks, the increase in CRSS for prism \(<a>\) slip is large; therefore, the amount of prism \(<a>\) slip is small during the initial stage of deformation. Prism \(<a>\) slip was active in the alloy aged for 360 ks, as shown in Fig. 6(c). This is because the increase in CRSS for prism \(<a>\) slip is smaller than that for the other slip systems, so that it is more easily activated. In the alloy aged for 2160 ks, the activity of basal \(<a>\)
slip is small, while the activities of pyramidal <c+a> slip and prism <a> slip are large, as shown in Fig. 6(d). This is because the increase in CRSS for basal <a> slip became large and the difference from the CRSS for pyramidal <c+a> slip narrowed; therefore, the activity of pyramidal <c+a> slip became relatively large.

5. Conclusions
SAXS and in situ XRD measurements were performed on WE54 alloys to evaluate the precipitate size and the active slip system for different aging times.
1. In the A.Q. alloy, the nonuniform strain distribution indicated that not only basal <a> slip, which is the main slip system, but also non-basal slip, were active.
2. In the 360 ks aged alloy, pyramidal <c+a> slip activity decreased and prism <a> slip activity increased, which is in agreement with the calculated results that indicated that the amount of precipitation hardening due to prism <a> slip decreases as aging progresses.
3. Pyramidal <c+a> slip was also active in the alloy aged for 2160 ks because the difference in CRSS between basal <a> slip and pyramidal <c+a> slip narrowed.

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Fig. 7 Increase in ΔCRSS for basal slip, prism slip and pyramidal slip as function of aging time.