Key Factor for the Transformation from hcp to 18R-Type Long-Period Stacking Ordered Structure in Mg Alloys

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Cast Mg85Y9Zn6 has an 18R-type LPSO structure. However, Mg85Y9Zn6 recovered after being subjected to a loading pressure of 7 GPa at 973 K shows a fine dual-phase structure composed of a face-centered cubic (fcc) structure superlattice (D03), as well as a hexagonal close-packed structure (hcp:2H). The D03/hcp structure transformed to 18R-type LPSO during heating at ambient pressure. In this research, the transformation process from the D03/hcp structure to 18R-type LPSO structure was discussed by means of in situ XRD and first-principles calculation. At first, lattice volume of 2H increased with an increase in the temperature, because of the Zn and Y emitted from the D03 phase into the 2H lattice. After the volume expansion of 2H lattice, the structure collapsed due to insert of random stacking faults (SFs). Then, a formation of 18R-type LPSO structure occurred. Based on a first-principles calculation for pure Mg, volume expansion of the 2H lattice causes the transformation to an 18R-type LPSO structure. Furthermore, the results of free energy calculations for the hcp and fcc structures in the Mg–Y–Zn ternary system show that the segregation of Y and Zn atoms on SFs occurs by the Suzuki effect. These segregated Y and Zn atoms in SF layers, which have a local fcc structure, create a synergy between the stacking and chemical modulations. Present result insists that the volume increase of 2H lattice takes place first, and then the transformation from the hcp structure to 18R stacking occurs. [doi:10.2320/matertrans.M2018213]

Keywords: magnesium alloy, long-period stacking ordered structure, X-ray diffraction, first-principles calculation, high pressure

1. Introduction

The development of lightweight structural materials has received much attention, motivated by the need for energy conservation and compliance with exhaust-gas regulations for vehicles. Mg–Y–Zn ternary alloys are potential lightweight structural materials because the 0.2% proof stress (σ0.2) of rapidly solidified powder metallurgy Mg85Y9Zn6 alloys exceeds 600 MPa.1) The σ0.2 values of Mg85Y9Zn6 alloys produced by conventional casting and extrusion exceed 320 MPa.2) Mg85Y9Zn6 alloys include a series of novel long-period stacking ordered (LPSO) structures synchronized with the chemical concentration, which can be classified into the 10H-, 18R-, 14H-, and 24R-types.3) The high strength of Mg85Y9Zn6 is ascribed to a kink deformation of the LPSO structure. This novel structure consists of periodically arranged stacking faults (SFs) with a local face-centered cubic (fcc) lattice structure in a hexagonal close-packed (hcp) matrix.4) The creation of the stacks in the LPSO structure will be called the “stacking modulation.” The atoms of the alloying elements Y and Zn strongly segregate on the SFs, which results in the modulation of the concentration of Y and Zn. This will be called the “chemical modulation,” to distinguish it from the stacking modulation. Furthermore, the segregated atoms follow an in-plane ordering in the SF layers and form L12-type clusters.4) First-principles total energy calculations within the framework of density functional theory (DFT) have revealed that the energy difference between the 2H and 18R structures in pure Mg decreases with increasing lattice volume.5) This result suggests that the 2H form of pure Mg has latent structural instability. In addition, a recent theoretical study reported that the 18R-type LPSO structure in the Mg–Y–Zn ternary system is energetically more stable than some other structures.6)

The formation process of the LPSO structure has been investigated experimentally. The Mg85Y9Zn6 alloy has the stoichiometric composition of 18R-type LPSO and consists of a large fraction of the 18R-type LPSO structure and a small fraction of the 10H-type LPSO structure.7,8) According to X-ray diffraction (XRD) and multicolor small-angle X-ray scattering (SAXS), during the solidification process of the alloy at ambient pressure, a peak corresponding to periodic distance of stacking fault, i.e. six-periodic chemical modulation and peaks corresponding to the 18R structure emerge from the molten state at the same temperature.7,8) In contrast, a supersaturated amorphous structure forms upon rapid quenching of the melt of the alloy. The formation process of the LPSO structure in this amorphous alloy has been studied by SAXS and wide-angle X-ray scattering measurements with heating at a rate of 10 K/min.9,10) These reports showed that the aggregation of very small Y–Zn clusters in the amorphous region was followed by the formation of a hcp lattice having high supersaturation. With an increase in temperature up to 550 K, the Y–Zn clusters grew to the approximate size of the fcc Y–Zn clusters in the 18R-type LPSO model.11) The clusters were distributed uniformly in the supersaturated hcp lattice. With a further
increase in temperature above 550 K, the distance between clusters started to divide into two groups: one was assigned to the periodic distance between the SF layers in the 18R-type LPSO structure, and the other corresponded to the inter-cluster distance within the SF layers in the LPSO structure. Based on these results, the transformation in the quenched Mg$_{85}$Y$_9$Zn$_6$ alloy was thought to have occurred through the following two steps. First, the cluster size increased to that of clusters in the 18R-type LPSO. Second, spatial rearrangement of the clusters was accompanied by a structural transformation from hcp to the 18R-type LPSO structure. However, in practice, in Mg$_{97}$Y$_2$Zn$_1$ alloys the alloying elements segregate to the last region to solidify, which is mostly at triple junctions of grain boundaries, and consequently the matrix hcp phase is almost pure Mg. These solute-enriched regions will act as a supply source of elements for the hcp-Mg matrix phase to form the LPSO structure. From this viewpoint, it is difficult to say whether the experiments described above that successfully observed the formation of an LPSO structure from a supersaturated amorphous structure can explain LPSO formation from practical dilute Mg alloys. Thus, the key step in the formation mechanism remains unknown at present.

In contrast with these previous studies, a Mg$_{85}$Y$_9$Zn$_6$ specimen recovered after being subjected to a loading pressure of 7 GPa at 973 K has been found to have a fine duplex lamellar structure composed of fcc superlattice (D0$_3$) and 2H-Mg (hcp) structures. The D0$_3$/hcp duplex alloy transforms into LPSO structures during heating at ambient pressure. The transformation process starts in the dilute hcp-Mg region, because the alloying elements, Y and Zn, concentrate in the D0$_3$ structure rather than the hcp-Mg. This is an important difference from the experimental conditions in the previous studies. Thanks to this difference, analyzing this specimen makes it possible to gain new knowledge of the LPSO formation process in practical Mg alloys, which cannot be obtained by studying LPSO formation from a supersaturated amorphous structure.

With these points as background, the present study aims to investigate the transformation process from the D0$_3$/hcp duplex phase to the LPSO structure by means of in situ XRD, and to present an alternative explanation of the formation mechanism of the LPSO structure in the hcp-Mg matrix. The same experimental conditions used in the previous SAXS measurement for the amorphous alloy were used. In addition, a first-principles calculation was performed to elucidate the formation mechanism of the 18R-type LPSO in a dilute hcp matrix.

2. Procedures

2.1 Experimental procedures

A Mg$_{85}$Y$_9$Zn$_6$ master alloy with an 18R-type LPSO structure was prepared by casting, and its chemical composition was analyzed by inductively coupled plasma mass spectrometry. The alloy was cut to an appropriate size for the high-pressure experiments (φ (diameter) 2 × t (thickness) 2 mm$^3$). The alloy was subjected to 7 GPa and 923 K for 10 min, then the temperature was lowered, and subsequently the pressure was released. The high-pressure and high-temperature conditions were fixed by a multi-anvil high-pressure apparatus (Orange-1000, Sumitomo heavy industry). The XRD pattern and secondary electron imaging (SEI) from the scanning electron microscope observations of the specimen are shown in Fig. 1. The crystallographic information for the D0$_3$ phase obtained from the XRD profile is listed in Table 1. The lamellar structure was confirmed by SEI. The bright part of Fig. 1(b) corresponds to the D0$_3$ structure composed of Mg, Y, and Zn, and the dark part corresponds to the Mg-based hcp phase. These results coincide well with the previous work. This alloy was used as the starting material for the experimental procedure described below.

In situ XRD was performed using the P02.1 beamline of PETRA III at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. The wavelength was set to 2.0778 × 10$^{-2}$ nm, and the beam was reduced by a
0.5 \times 0.5 \text{mm}^2 \text{ slit. The alloy was cut and put in a quartz glass capillary with an inner diameter of 1.2 mm, and then placed in a Linkam THMS 600 furnace filled with argon gas. The XRD was performed on a bulk sample instead of ideal powder. A constant heating rate of 10 K/min was applied, which was the same heating rate used in the previous experiments.}

Microstructure variation because of the crystal structural transformation observed in the \textit{in situ} XRD was also investigated. The samples were inserted in a MgO capsule and annealed for 10 min in an evacuated silica tube at various temperatures, and then quenched. The samples were polished using an Ar ion beam, after which SEI observation and XRD measurements were performed.

### 2.2 Calculation procedures

Total energy calculations were performed using VASP, which is based on DFT. The exchange-correlation functional was given by the generalized gradient approximation as proposed by Perdew \textit{et al.}\cite{perdew1996generalized} The electron–ion interaction was introduced by the projector-augmented wave method, with plane-wave energies as high as 400 eV.\cite{bloch1994projector} The k-point meshes of the Brillouin-zone sampling in a primitive cell were based on the Monkhorst–Pack scheme with a Fermi broadening of 0.2 eV. The k-point meshes in real space were 28 \times 28 \times 15 for the 2H structure and 28 \times 28 \times 2 for the 18R structure. The convergence criteria for energy and force were 0.1 meV and 0.02 eV/Å, respectively.

The vibrational properties of the 2H and 18R structures were obtained by a direct method.\cite{paier1999phonon} In this method, phonon frequencies were calculated from the Hellmann–Feynman (HF) forces generated by nonequivalent atomic displacements in a supercell of the crystal structure. In the present study, the supercell dimensions were 3 \times 3 \times 2 and 3 \times 3 \times 1 for the unit cells of the 2H and 18R structures, respectively. For the calculations simulating these large systems, k-point sampling was limited to 0.15/Å, corresponding to, for example, a 6 \times 6 \times 1 mesh for the 18R structure. A dynamic matrix was constructed from the HF forces acting on all atoms in supercells with a displaced atom, and the phonon frequencies were calculated by solving the eigenvalue problem for the dynamic matrix. Thermal expansion was considered indirectly by performing the calculations for various lattice volumes.

### 3. Results and Discussion

#### 3.1 Analysis of XRD patterns

XRD patterns of the alloy obtained during heating are shown in Fig. 2. The peaks from the 18R- and 10H-type LPSO structures were indexed by the models with the space groups \(P3_121\) and \(P6_3/mcm\), respectively. The transformation process from D0\(_3\)/hcp to 18R- and 10H-type LPSO is roughly represented in the 2D false-color map shown in Fig. 2(a). With increasing temperature, several peaks suggesting the formation of the 18R-type LPSO emerged at 618 K; in contrast, those belonging to hcp-Mg
vanished. The peak diffracted by the \((0002)_{\text{hcp}}\) (i.e., the \((00018)_{18R}\) plane) was observed over the entire temperature range below the melting point. The peaks corresponding to the \(D0_3\) structure became weaker with increasing temperature and vanished after the peaks attributed to the \(18R\)-type LPSO appeared. Furthermore, some weak peaks labeled \(E\) in the figure emerged at 586 K and then disappeared soon afterward. The XRD patterns obtained at various temperatures are shown in Fig. 2(b). The XRD pattern at 536 K was characterized by the hcp-Mg and \(D0_3\) structures. Some of the peaks in the XRD pattern at 614 K can be explained by the hcp and \(D0_3\) structures, and there is no peak corresponding to the \(18R\)-type LPSO structure. The peaks labeled \(E\) cannot explain the crystal structure previously reported for this composition. However, the \(cF_{184}\)-type cubic structure listed in Table 2 can reasonably explain the XRD peak positions and intensities. The peak positions and intensities of the \(E\) phase calculated from the model are shown by red bars on the XRD pattern at 614 K. The details of this phase remain unclear at present, and further investigation is necessary. Above 750 K, major peaks appeared for the \(18R\)-type LPSO structure, together with a small peak for the \(10H\)-type LPSO structure. The XRD patterns obtained at various temperatures are shown in Fig. 2(b). The XRD pattern at 536 K was characterized by the hcp-Mg and \(D0_3\) structures. Some of the peaks in the XRD pattern at 614 K can be explained by the hcp and \(D0_3\) structures, and there is no peak corresponding to the \(18R\)-type LPSO structure. The peaks labeled \(E\) cannot explain the crystal structure previously reported for this composition. However, the \(cF_{184}\)-type cubic structure listed in Table 2 can reasonably explain the XRD peak positions and intensities. The peak positions and intensities of the \(E\) phase calculated from the model are shown by red bars on the XRD pattern at 614 K. The details of this phase remain unclear at present, and further investigation is necessary. Above 750 K, major peaks appeared for the \(18R\)-type LPSO structure, together with a small peak for the \(10H\)-type LPSO structure. The phase transformation to the \(18R\)-type LPSO structure was completed at around 750 K.

The lattice parameter values for the \(a\)- and \(c\)-axes of the specimen are shown in Figs. 3(a) and (b), respectively, with varying temperature. The \(a\) and \(c\) values were determined by using the \((10\bar{1}2)_{\text{hcp}}\) and \((10\bar{1}1)_{\text{hcp}}\) peaks for the hcp matrix as well as a combination of the \((2245)_{18R}\) and \((22410)_{3\text{sp}}\) peaks for the \(18R\)-type LPSO structure. The results are represented in these figures by a blue cross in the lower temperature region and a red cross in the higher temperature region. A clear gap in the \(a\) value is observed, which almost coincides with the difference in the lattice parameter between the hcp and \(18R\)-type LPSO structures observed in the Mg-Y-Zn system. The \(c\) value estimated from the \((0002)_{\text{hcp}}\) peaks collected over the entire experimental temperature range is shown by a gray cross in Fig. 3(b). The blue and red symbols coincide with the gray ones in Fig. 3(b), and there is no gap. This result suggests that the distance between the stacking planes gradually increased with the transformation from the hcp to the \(18R\)-type LPSO structure. The coefficient of thermal expansion (CTE) of \((0002)_{\text{hcp}}\) is shown in Fig. 3(c). The CTE started to increase above 460 K. Above 540 K, the CTE showed a drastic increase, and then reached a maximum at 570 K.

The change in the lattice constants can be explained by considering the solution of alloying elements in the hcp matrix after the collapse of the \(D0_3\) structure. The variation in integrated XRD peak intensities with temperature is shown in Fig. 4. The peak intensity for the \((0004)\) plane of the \(D0_3\) phase decreased at 460 K, indicated by \(T_A\) in Fig. 4, which almost corresponds to the temperature at which the CTE of the \(c\)-axis starts to increase anomalously in Fig. 3(c). This fact implies that a collapse of the \(D0_3\) phase results in a change in the composition of the hcp lattice and the expansion of its \(c\)-axis because of the larger atomic radius of \(Y\). Above 570 K, indicated by \(T_B\) in Fig. 4, the intensity of the \((0002)_{\text{hcp}}\) peak increased, while a significant decrease in the intensity of the \((10\bar{1}1)_{\text{hcp}}\) peak was observed. At this temperature, the CTE of the \(c\)-axis reaches a maximum, as shown in Fig. 3(c). This suggests that the hcp phase started to transform into another structure after an increase in the lattice volume. Incidentally, the \(E\) phase emerged at 584 K and then disappeared soon after, as shown in Fig. 1. The peak intensity of the \(E\) phase is also shown in Fig. 4. We consider the \(E\) phase to be metastable, consisting of the atoms released by the collapse of \(D0_3\), which dissolve into the hcp as well as the \(D0_3\) structures.

<table>
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<tr>
<th>Atom</th>
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<th>(y)</th>
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<th>Occupation</th>
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<td>0.5</td>
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<tr>
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<td>0.04</td>
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</table>

Table 2 The model structure of the \(E\) phase: \(Fd\bar{3}m\), \(a = 1.384\,\text{nm}\). Atomic coordinates and unit cell dimensions were estimated from the XRD profile.
are presented in Fig. 5(b). The (0003)18R peak originates from the 18R-type LPSO structure, respectively. The XRD peaks for the growth of the chemical and stacking modulations of the hcp lattice collapsed (Fig. 6(b)). The temperature variation of the (0110)hcp peak at 1.4° labeled E. The arrows on (22410)18R, (00018)18R, (0003)18R indicate 680, 700, and 730 K, respectively.

Based on these experimental results, the following transformation process from the hcp to the 18R-type LPSO structure possibly takes place in the specimen. At the beginning, the c-axis lattice parameter increases because of the solution of Zn and Y in the hcp phase, and then the hcp structure collapses. The 18R-type LPSO structure emerges at 618 K. A previous transmission electron microscope study of Mg97Gd2Zn1 alloy showed that the SFs were first inserted into the hcp matrix, and then the 14H-type LPSO structure emerged with increasing temperature. Stacking faults randomly inserted into 2H yield local 4H stacking. The previous study showed that the c value of 4H was longer than that of 2H even in pure Mg. This suggests that the large drop in the intensity of the (1011)hcp peak above 570 K in Fig. 4 could be explained by the insertion of SFs into the hcp lattice. The continuous increase in the stacking plane distance accompanied by the transformation to 18R as seen in (0002)hcp (i.e., (00018)18R) may also support the transformation process observed in the present study.

To discuss the relationship between the XRD patterns and the microstructure, the XRD patterns and the SEI observations of the alloys quenched at various temperatures are shown in Fig. 6(a) and (b), respectively. The XRD variation corresponds to that obtained by the in situ XRD measurements mentioned before. The XRD pattern and SEI for the sample quenched at 570 K are similar to those of the alloy before annealing (Fig. 1). In the sample quenched at 600 K, the peaks of the E phase labeled in Fig. 2(a) were observed in the XRD pattern; however, a clear lamellar structure was maintained in the microstructure. In the alloy quenched at 635 K, small peaks from the 18R-type LPSO were observed, and the lamellar structure collapsed (Fig. 6(b)). The temperature variations in the XRD measurement were similar to those obtained in the in situ XRD measurements mentioned above. The experimental fact that the D03/hcp duplex lamellar structure was retained even in the sample quenched at 600 K leads to a fundamentally different view of the formation process of LPSO from that suggested by Okuda et al.5) In these previous studies, small Y–Zn clusters formed in the amorphous phase and grew until the cluster size became equivalent to that of 18R. Then a spatial relocation of the clusters occurred with the transformation from the hcp to the 18R structure. In contrast, the present study shows that the change in the lattice constant and collapse of the hcp phase occurs even in the temperature range where the duplex structure of hcp and D03 maintains the same lamellar shape. Therefore, the hcp phase should not be in a supersaturated state, as in the stoichiometric composition of the 18R-type LPSO structure, but rather a dilute state, similar to the conditions for forming LPSO structures in practical alloys. Therefore, the formation of the LPSO structure is considered to have started from inside the
hcp phase, not with the growth of Y–Zn clusters in size similar to that of 18R-type LPSO in previous research.9,10)

3.2 Discussion on the transformation mechanism from the 2H to the 18R structure

In previous work,5) the volume expansion of the hcp lattice was confirmed to enhance the transformation to the 18R structure, showing that increasing the c-axis parameter value energetically favors the transformation. This is consistent with the present experimental results. To discuss the energy difference between the 2H and 18R structures, the calculated free energy differences between 18R-Mg (F18R) and 2H-Mg (F2H) with varying temperature are shown in Fig. 7(a). These values were evaluated from the temperature- and volume-dependent free energy calculations for pure Mg. The contribution of the lattice vibration effect at finite temperature was also considered. The equilibrium volumes were determined by fitting the Birch–Murnaghan equation21) to free energy–volume curves. The calculated result in Fig. 7(a) indicates the possibility of a transformation from hcp-Mg to an 18R structure above 420 K. This transformation has not been observed experimentally in pure Mg,19) probably because of the high activation energy required for atomic displacement, as discussed in the previous work.5)

The following calculation was performed to make a case for a change in the lattice constant of the hcp-Mg by the release of a solution of Y and Zn from the D03 phase. The lattice constants of the 2H structure were evaluated for the pure elements by first-principles calculations. The Mg29Y4Zn3 alloy was used to model the composition of an 18R-type LPSO structure, in which full L12 in-plane ordering in the SF layer was observed in the previous study.4) Thus, the lattice constants of the 2H structure of Mg29Y4Zn3 were calculated based on Vegard’s law using these values for pure elements. The lattice constants for the pure elements of the 18R structure were also evaluated, and the same approach yielded the lattice constants of the 18R structure of Mg29Y4Zn3. The calculated lattice constants for the 2H- and 18R-type Mg29Y4Zn3 alloys were respectively: \( a = 3.2005 \) Å and \( c = 5.2107 \) Å; and \( a = 3.1974 \) Å and \( c = 5.2280 \) Å. The temperature dependence of the lattice constants of pure 2H-type Mg was considered in terms of the effects of phonon dispersion and lattice expansion. A change in lattice constants with temperature for the 2H-type Mg29Y4Zn3 alloys was estimated by simply adding the difference in the lattice constants between the pure 2H-type Mg (\( a = 3.1932 \) Å and \( c = 5.1752 \) Å) and the 2H-type Mg29Y4Zn3 alloy. The same approach was applied to the 18R-type Mg29Y4Zn3 alloy using the lattice constants for 18R-type Mg (\( a = 3.1944 \) Å and \( c = 5.1817 \) Å). The variation in the \( a \)- and \( c \)-axis parameters of the Mg(2H), Mg29Y4Zn3(2H), and Mg29Y4Zn3(18R) phases with temperature is shown in Fig. 7(b) and (c). The \( c \) value of Mg29Y4Zn3(18R) was larger than that of Mg29Y4Zn3(2H); in contrast, the \( a \) value of Mg29Y4Zn3(18R) was smaller than that of Mg29Y4Zn3(2H). Figure 7(d) and (e) shows the correlations between the total energies of the \( a \)- and \( c \)-axes. The total energy of the \( a \)-axis abruptly changes when it departs from the equilibrium point, whereas that of the \( c \)-axis changes more smoothly. Therefore, when Y and Zn migrate in hcp, the \( c \)-axis expands much more easily than the

Fig. 5 (a) False-color map of the XRD between 600 and 750 K. The peaks from the hcp and D03 phases are indexed and labelled “h” and “D” in the upper part of the figure, respectively. The peak index and the calculated intensity from the 18R-type LPSO model4) are written in the lower part of the figure. (b) Calculated peak intensity from the 18R structure of pure Mg and the 18R-type LPSO structure models.4) (c) Peaks corresponding to (0003) and (22410) of the 18R-type LPSO structure and (1011) of the hcp structure at various temperatures.
This difference in the characteristics of the α- and c-axes is the origin of the difference in their temperature dependences.

The segregation of the solute elements to the SFs introduced by the transformation from 2H to 18R is well explained by the so-called Suzuki effect.\textsuperscript{22)} The SF in the hcp lattice is considered to be a fcc structure. Figure 8(a) shows the free energies of the hcp and fcc phases in the Mg-Y-Zn ternary system at 500 K, calculated using the reported thermodynamic parameters.\textsuperscript{23)} Here, we focus on the cross-section along the line through the Mg\textsubscript{85}Y\textsubscript{9}Zn\textsubscript{6} composition shown in Fig. 8(b). The Suzuki effect explains the segregation of solute atoms in SFs because of the difference in chemical potentials between the matrix phase and SFs.\textsuperscript{22)} In Mg\textsubscript{85}Y\textsubscript{9}Zn\textsubscript{6}, the amount of alloying elements, Y and Zn, segregated in the fcc SF sites can be estimated as shown in Fig. 8(b), where $x_1$ and $x_2$ represent the concentrations of...
alloying elements in the hcp matrix and in the SF layers, respectively. The value of \( x_2 \) is defined by the common tangent of the Gibbs free energy curves of the fcc (SF) phase and the hcp phase at the matrix concentration. As is evident from the figure, a marked amount of segregation, given by the difference \( x_2 - x_1 \), is expected in this system, yielding a plausible origin of the chemical modulation.

### 3.3 Overall formation process of the LPSO structure in Mg alloys

The proposed formation process of the 18R-type LPSO structure based on the present experimental results is shown in Fig. 9. A collapse of the D0₃ phase in the D0₃/hcp duplex structure starts above 450 K, and Zn and Y migrate into the dilute hcp phase. The c-axis of the hcp lattice expands in the vicinity of the enriched regions, because the radius of a rare earth element is, in general, 17–22% larger than that of Mg. According to our results, pure Mg transforms from hcp to other long-period structures in a finite temperature region, even if the system is not under any external effects. In addition, the introduction of large-radius atoms such as rare earth elements can accelerate the phase transition. Above 570 K, the hcp phase transforms into a long-period “disordered” structure as the SFs are introduced into the hcp matrix. This structure—a precursor of the 18R-type LPSO structure, as it were—forms at a temperature approximately 50 K higher than that at which the hcp phase collapses. Then, the Y and Zn atoms segregate to the SFs, mainly because of the difference in chemical potentials for each element between the hcp and the SF layers. According to the XRD measurements, the phase transformation to the LPSO structure completes at around 750 K.

### 4. Conclusions

The formation process of the 18R-type LPSO structure in Mg₈₅Y₉Zn₆ alloy was investigated by means of in situ XRD measurements as well as first-principles calculations to elucidate the structural transformation and the segregation behavior. The key findings in the present study were as follows:

1. A Mg₈₅Y₉Zn₆ specimen recovered after being subjected to a loading pressure of 7 GPa at 973 K showed a fine D0₃/hcp duplex structure. The hcp phase had a dilute composition, similar to the conditions for LPSO structure formation in practical Mg alloys. With an increase in the lattice volume because of the migration...
of Zn and Y into the hcp-Mg phase from the D0₃ phase during heating, a change in the hcp lattice occurs, triggering the transformation from the hcp to 18R-type LPSO structure. Furthermore, from a comparison of the intensity variations of the XRD peaks (0003)₁₈R and (22410)₁₈R, we deduce that the growth of 18R stacking occurs before the chemical modulation.

(2) The possibility that the lattice expansion of the matrix phase promotes the introduction of periodical SFs in hcp-Mg, i.e., stacking modulation in a higher temperature range, was reconfirmed in the present study. This suggests that the elongation of the c-axis of the host lattice energetically favors SFs. Calculation of the lattice constant in the composition of a typical 18R structure was attempted using Vegard’s law. It was found that the change in the c-axis was larger than that in the a-axis. This result reinforces the experimental fact revealed by XRD in this research. The cohesion of the solute element to the SFs introduced by lattice expansion, i.e., the chemical modulation, can be understood as segregation due to the chemical potential difference between the matrix phase and SFs. The segregated Zn and Y atoms on SF layers generate the characteristic LPSO microstructure caused by the stacking and chemical modulations.

(3) On the basis of the present study, the following overall formation process of the LPSO structure in Mg alloys is proposed. With a solution of Y and Zn from D0₃, the hcp phase transforms to a long-period “disordered” structure, in which SFs are introduced into the hcp matrix. This structure—a precursor of the 18R-type LPSO structure, as it were—forms at a temperature approximately 50 K higher than that at which the hcp phase collapses. Then, the Y and Zn atoms segregate to the SFs, mainly because of the so-called Suzuki effect.

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