Precipitation Sequence in the Mg–Gd–Y System Investigated by HRTEM and HAADF-STEM

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In this work, the early stage of precipitation have been investigated in a Mg–2.9 at% Gd–0.8 at% Y by high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and high resolution transmission electron microscopy (HRTEM).

At the underaged condition, precipitates observed by HRTEM were classified as follows; mono-layer, a part of βγ, β. By HAADF-STEM, zig-zag structure, small hexagonal network, and β' could be recognized. The small “super hexagons” are the first precipitates in this alloy. This structure, referred to as the pre βγ-phase, displays a short range similar to the one present in the D019 structure. This phase is formed during quenching and prevails over the zig-zag structure at the beginning of aging. The zig-zag contrast is one of the variations of this small hexagonal network or heterogeneous nucleation during aging. Finally, we concluded that the proposed precipitation sequence is as follows: SSSS → βγ-phase having D019-SRO → β'→ β-phase. The comparison of HRTEM, HAADF-STEM and simulated images have helped to clarify the meaning of HRTEM features. [DOI:10.2320/matertrans.L-M20140824]

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1. Introduction

Among the Mg–rare earth metals (RE) alloys, which demonstrate the age-hardenability, we distinguish 2 subgroups of alloys depending on the precipitation sequence involved upon aging. In the alloys belonging to Ytrium sub-group, the first metastable structure is designated as β'' phase, which later transforms into β before an equilibrium β phase is formed at the end of the precipitation sequence. The alloys of Ce sub-group follow almost the same sequence of decomposition. However, Guiner Preston (GP) zones are observed before the precipitation of β'' phase.1,2

According to the literature,3–8 the following precipitation sequences have been reported in Mg–RE systems:

Mg–Nd3,4): supersaturated solid solution (s.s.s.s.) → GP zone → β' phase(D019) → β' phase(bco) (fcc) → β phase(bct) (bcc)

Mg–Nd5,6): s.s.s.s. → GP zone → β' phase(orth) → β1 phase(fcc)

Mg–Gd7,8): s.s.s.s. → ordered GP zone → β' phase(D019) → β phase(orth) → β1 phase(fcc) → β phase(tetra) → β2 phase(tetra)

Mg–Gd–Y9,10) s.s.s.s. → ordered G.P. zones → β' phase(D019) → β phase(orth) → β1 phase(fcc) → β phase(fcc)

Mg–Y–Nd11,12) s.s.s.s. → ordered G.P. zones → β' phase(D019) → β phase(orth)

Mg–Gd3): s.s.s.s. → short range order (SRO) → β phase (bco)

Mg–Gd–Zr3): s.s.s.s. → β phase(D019) → β phase (bco) → β phase (bcc) → β phase (fcc) → β phase (fcc)

The precipitation sequence in Mg–Gd–Y system and the early path of precipitation still remains unclear. In comparison to the binary Mg–Gd alloys, Mg–Gd–Y (GY series), developed for practical Mg alloys by Kamado et al.9,10) to reduce the density, exhibit an increased creep resistance up to 523–573 K. In this work, the early stages of aging in Mg–Gd–Y alloy have been observed by HAADF-STEM in order to elucidate the mechanisms involved during the early stages decomposition of the supersaturated solid solution, and the comparison between HRTEM and HAADF-STEM images obviously shows the possibility of HAADF-STEM to clarify the precipitation sequence.

2. Experimental Details

2.1 Alloy and heat treatment

Mg–2.9 at% Gd–0.8 at% Y alloy (Gd/Y ≈ 3) was prepared by casting using 99.9% Mg, Gd and Y purity ingots. The obtained alloy was homogenized at 773 K for 43.2 ks, and then hot rolled at 773 K to 1 mm in thickness. The rolled sample was capspulated into the pyrex glass tube with argon gas. Then, it was solution heat-treated at 773 K for 3.6 ks and...
quenched in warm water at 353 K, and aged in a silicone oil bath at 473 K.

2.2 Sample preparation for TEM

TEM specimens were cut from plate samples and thinned by the twin-jet electro polishing technique using an electrolyte of 10 percent perchloric acid-ethanol solution at about 243 K. HRTEM observations were performed by using a TOPCON EM-002B operated at 120 kV. The specimen thickness for TEM observation was estimated using EELS, and it is usually less than 50 nm. STEM observations were performed on JEOL ARM 200F operating at 200 kV and using a Shottky type electron gun. Images were recorded on a 3-mm-diameter specimen mounted on a double-tilt holder in all HAADF images were obtained using a probe size of 0.1 nm (FWHM) and a half-objective aperture angle of 15 mrad. The HAADF detector was set to collect electrons between 40 and 150 mrad.

2.3 Simulation for HRTEM and HAADF-STEM images

The defocusing to obtain HRTEM image was about \( \Delta f = -30 \sim -50 \) nm. Calculated HRTEM and HAADF-STEM images were obtained by the conventional multi-slice method using a rectangular cell of 1.92 nm \( \times \) 2.22 nm \( \times \) 0.52 nm including 96 atoms based on the hcp structure of Mg by MacTempus. The condition for HRTEM image simulation was as follows: high voltage = 120 kV, convergent angle = 0.5 mrad and Cs = 0.34 mm. The condition for HAADF-STEM image simulation was as follows: high voltage = 200 kV, Cs = 0 mm, convergence angle = 12.5 mrad, probe sampling = 0.05 Å/px, probe semi-angle = 12.5 mrad, inner aperture = 89.63 mrad and outer aperture = 170.0 mrad.

3. Results and Discussion

Figure 1 shows TEM images for 2.9Gd-0.8Y alloy aged at 473 K. Even in as quenched condition, diffuse scattering is visible at 1/2 (1100)-type spots. This is consistent with the reported short range ordering elongated to \( \langle 11 \bar{2} 0 \rangle \) direction.\(^7\) Aging times of 1.8 and 7.2 ks are the under aged condition and those samples include \( \beta'' \)-phase according to the previous report.\(^6\) The sample aged for 7.2 ks includes the \( \beta \)-phase because of split of diffraction spots in its SAED pattern.

Figures 2 and 3 show HRTEM images for samples aged at 473 K for 1.8 and 7.2 ks. According to our previous work, there are \( \beta'' \) and some \( \beta \)-phase in there. \( \beta'' \) has the D0\(_{19}\) and \( \beta \) is an orthorhombic structure. The enlarged pictures of Figs. 2(b) and 2(c) correspond to regions of X and Y in Fig. 2(a). The lattice fringe including brighter and darker dots are visible in Fig. 2(b) and this has been recognized as the mono-layer zone in our previous reports.\(^5,6\) A half of the hexagonal network for \( \beta'' \)-phase is also visible as marked by Y in Fig. 2(c). These are beginning of precipitation in this alloy. In Fig. 3, the typical feature for \( \beta'' \)- and \( \beta \)-phases in HRTEM image are revealed in a region of A and B in Fig. 3(a). Figure 3(b) is an enlarged picture of the region B in Fig. 3(a) and it is a typical rectangle periodicity of 2.22 nm.

![Fig. 1](image1.png)

![Fig. 2](image2.png)
in the $\beta^\prime$-phase. Figure 3(c) shows an enlarged picture of the region A, which is in good agreement with a part of the hexagonal network of $\beta''$-phase with a spacing of 0.64 nm.

Figure 4 shows the HAADF-STEM image obtained for the sample aged for 1.8 ks at 473 K. Brighter dots are corresponding to atomic columns of heavy element in this alloy (i.e., Gd or Y). Mostly, three different features are visible, which are identified as A, B and C in Fig. 4. Figure 5 shows enlarged images of A, B and C regions of Fig. 4. The feature A exhibits a "W" shape of arrangement of bright dots, so-called zig-zag contrast. Particular spacings of 0.37 and 0.64 nm are identified in this feature. The region B shows a hexagonal network of bright dots. As for the region C, it shows a straight line of bright columns with a spacing of 0.32 nm parallel to [1100] direction of the matrix. It is noted that the region B shows a spacing of 0.64 nm, if two hexagons connects each other.

Figure 6 shows the HAADF-STEM image obtained for the sample aged for 7.2 ks. The straight bright lines parallel to $\langle 1100 \rangle$ direction of the matrix are more remarkable than Fig. 4. There are 4 regions marked by D, E, F and G and those enlarged images are shown in Fig. 7. The region D of Fig. 7(a) is a small hexagonal network similar to the region B in Fig. 4. The region E of Fig. 7(b) is the same as the zig-zag contrast in the region A in Fig. 4. The region F in Fig. 7(c) shows the hexagonal network with spacing of 0.64 nm and it corresponds to the $\beta''$ of D0$_{19}$. Figure 7(d) shows the region G in Fig. 6, wherein a typical periodicity of 2.22 nm of $\beta''$-bco structure is visible.

In order to avoid any misleading conclusion based on the simple interpretation of HAADF and HRTEM images, image simulations have been conducted. The simulated cells are presented in Fig. 8. Results of the simulations are displayed in Figs. 9–11. Only Gd atoms were used as RE element in these simulations. A simulated HRTEM image for the zig-zag structure in Fig. 9(b) shows a $\{1010\}$ lattice plane having bright dots of 0.64 nm separation distance which corresponds to the length of the $a$-axis in the $\beta''$-phase. A darker band has been also shown at the center of Fig. 9(b) and this corresponds to the layers of Gd atoms parallel to $[1210]$ direction comparing with Fig. 8(a). A calculated HAADF image clearly reveals the zig-zag arrangement of Gd atomic columns which exhibit first and second neighbouring distance between columns of 0.37 and 0.64 nm respectively. As a conclusion, the zigzag structure revealed by HAADF displays a mono-layer contrast in HRTEM according to imaging condition.

The hexagonal networks of thin dotted line in Figs. 10(a), 10(b) and 10(d) correspond to the hexagonal network of 0.64 nm in Fig. 10(a), and hexagons drawn by thick broken line shows a unit cell of the $\beta''$-phase in Fig. 8(b). Both
experimental and simulated HRTEM images in Figs. 10(a) and 10(b) show a hexagonal network of bright dots having a spacing of 0.64 nm. On the other hand, both experimental and simulated HAADF images in Figs. 10(c) and 10(d) also show a hexagonal network of bright dots, but its spacing is 0.37 nm which is smaller than that in HRTEM images. It is pointed out that the smaller hexagons were observed in the Mg–Nd system, where they are designated as super-hexagons. As for the $\beta'$-phase, which observations are displayed in Fig. 11, HRTEM and HAADF images mostly consist in a succession of mono-layer or zig-zag structure already described in Fig. 9. Intensities of images depend on the arrangement of Gd atomic columns in the unit cell. According to the simulations and their comparison to experimental observations, the following conclusions can be drawn (i) The mono-layer structure revealed in HRTEM images are most likely to correspond to the zig-zag structure; (ii) $\beta''$-phase consists of small hexagonal network of 0.37 nm side, previously designated as super-hexagons; (iii) $\beta$-phase can be distinguished in HRTEM images based on the characteristic periodicity of 2.22 nm.

Finally, image simulations have been conducted for a super-hexagon cell as shown in Fig. 12(e). The superhexagon is a hexagonal prism of a part of D0$_{19}$ structure consisting of Mg and Gd atoms. Its chemical composition is Mg : Gd $= 3 : 1$. A simulated HRTEM image in Fig. 12(b) shows a similar contrast as the one visible for $\beta''$-phase in Fig. 10(b). Figure 12(d) shows a HAADF simulation reproducing a contrast close to the one visible in Fig. 12(c). Such super-hexagons could not be identified in the previous work by HRTEM, because it shows similar contrast to a part of $\beta''$ according to the simulation. The present observations highlight the difficulty of imaging such features by HRTEM only and demonstrate that the same features can be identified unambiguously by means of HAADF.

According to those results, super-hexagons (of 0.37 nm side) are the first precipitate to be formed in the alloy investigated. It must be pointed out that this metastable structure exhibits a short range order similar to a part of D0$_{19}$ structure. These super-hexagons are hereafter designated as the pre $\beta''$-phase. This phase is formed during quenching and is predominant compared to the zig-zag contrast at the

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**Fig. 6** A HAADF-STEM image obtained for the sample aged for 7.2 ks.

**Fig. 7** Enlarged pictures of Fig. 6. (a), (b), (c) and (d) correspond to D, E, F and G regions.

**Fig. 8** Unit cells used for calculations of HRTEM and HAADF-STEM images. (a) Zig-zag structure, (b) $\beta''$- and (c) $\beta$-phases.
beginning of aging. At a later stage, this phase grows to large normal $\beta''$. The zig-zag contrast is one of the variations of this small hexagonal network as shown in Fig. 13. If three super-hexagons combine with each other, forms a hexagonal network of 0.64 nm is formed (see Fig. 10). This later distance it becomes a lattice constant of the $\beta''$-phase. Small hexagons of the pre $\beta''$-phase consume to form the zig-zag contrast or transform to the $\beta'$ after enough aging time.

Nishijima and Hiraga$^7$ used a cast Mg–5%Gd alloy without rolling and solution heat treatment. After casting, their ingot was homogenized at 773 K for 6 h, quenched and then aged at 473 or 523 K. They concluded that the arrangement of bright dots indicates the short range ordered state and the $\beta''$ phase nuclide in the short range ordered structure. It this later study, the authors had doubts about the existence of the $\beta''$ phase. In the present study however, lower solute content and lower ageing temperature were used, in order to reveal the initial stage of precipitation of this alloy system. It is hence likely that the conditions applied by Nishijima and Hiraga$^7$ could lead to an advanced stage of the precipitation sequence.

In another alloy system, a Mg–0.99 at% Sm alloy aged at 473 K,$^{13}$ some isolated hexagonal contrasts and short zigzag lines similar to those reported in the present work were reported. In reference 13 the authors concluded that the hexagonal arrangement of Sm atoms is stably formed as nuclei in the early stage of the formation of precipitates. This result supports our conclusions. It is also suggested that the HAADF-STEM images can compensate for misleading HRTEM details.

Based on HRTEM and HAADF observation, supported by image simulations, it is hence possible to derive the following precipitation sequence involved at 473 K for the Mg–2.9 at% Gd–0.8 at% alloy:

$$SSSS \rightarrow \text{pre } \beta''\text{-phase having } D0_{19}\text{-SRO} \rightarrow \beta''\text{-phase} \rightarrow \beta'\text{-phase}$$

For larger supersaturation of the solid solution (i.e., larger solute content) and/or higher aging temperature, the $\beta''$-phase would be skipped. The bond overlap population (BOP) between atoms was calculated by the discrete-variational DV-Xa method using the BONDOD program$^{17}$ to understand the stability of pre $\beta''$-phase for the hexagonal prism of pre $\beta''$-phase as shown in Fig. 14. This method has been also mentioned in our recent report.$^{16}$ The BOP value for binding
between central atom and surrounding atoms are summarized in Table 1. BOP values for 
Mg–Mg or Mg–RE bindings for the first nearest (M-1) and second neighbors (M-2) are mostly the same value of 0.16 eV\(^{-1}\). The BOP values for the third nearest neighbors (M-3) are smaller than the first and second ones, however, BOP values of Gd–Gd and Gd–Y bindings for the third nearest neighbors are 0.019 and 0.021 eV\(^{-1}\). This is 4 times larger than that for 0.005 eV\(^{-1}\) of Mg–Mg binding. This means that Gd–Gd or Gd–Y binding provides more stable state for this phase. Kimizuka and Ogata\(^{18}\) have proposed the effective multibody potential model for changing stacking of the close-packed planes on dilute Mg–Gd and Mg–Al–Gd alloys. In the Mg–Gd system, they concluded that the linear zigzag and localized hexagonal patterns were observed in their simulation for clustering and zigzag patterns become dominant over the hexagonal ones as the aging time increased as a reflection of lower formation energy of the \(\beta^*\)-phase. For the Mg–Al–Gd system, the linear zigzag patterns disappeared and only rather isolated hexagonal patterns survived because the addition of Al stabilized the local D\(_{019}\)-type structure. Their result is quite similar to
our result for Mg–Gd–Y system, namely, Mg–Gd system including smaller atomic number of Y than Gd forms the localized hexagonal pattern.

4. Conclusions

The precipitation sequence involved in a Mg–2.9Gd–0.8Y alloy aged at 473 K has been revealed by a combination of HRTEM and HAADF-STEM observations with image simulations. Results obtained are summarized as follows:

1. In the under-aged condition, precipitates observed by HRTEM were classified as follows; mono-layer, a part of \( \beta'' \), \( \beta \). HAADF-STEM observations revealed a zig-zag structure, small hexagonal network (or super hexagon\(^{14}\)) and \( \beta' \).

2. The small hexagons of 0.37 nm is the first precipitate to be formed in this alloy. Since it exhibits a short range order close to \( \text{D}0_{19} \) structure, it is referred as the pre-\( \beta'' \)-phase. This phase is formed during quenching, and prevails over the zig-zag structure at the beginning of aging.

3. The proposed precipitation sequence is as follows:

\[
\text{SSSS} \rightarrow \text{pre } \beta'' \text{-phase having } \text{D}0_{19}\text{-SRO} \\
\rightarrow \beta'' \text{-phase } \rightarrow \beta' \text{-phase}
\]

4. According to image simulations, it is concluded that the mono-layer structure observed in HRTEM image corresponds to the zig-zag structure. \( \beta'' \)-phase consists of small hexagonal network of 0.37 nm. \( \beta' \)-phase can be recognized by HRTEM image because of the characteristic periodicity of 2.22 nm. The zig-zag contrast is one of the variations of this small hexagonal network, or heterogeneous nucleation during aging.

5. The calculated BOP value for Gd–Gd or Gd–Y binding in the hexagonal prism of the pre-\( \beta'' \)-phase showed the higher value than Mg–Mg binding in that cluster. This demonstrates the relative stability of such solute rich structures.

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