Early precipitate morphologies in Mg-Nd-(Zr) Alloys

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Aging of Mg-Nd alloys involves the formation of Guinier-Preston zones followed by β''' precipitation that is associated with peak hardness. Using atom probe tomography and high-angle annular dark-field scanning transmission electron microscopy, the three-dimensional morphologies of the coherent Guinier-Preston zones and β''' precipitates were quantified. The Guinier-Preston zones form equiaxed plates while the β''' precipitates are elongated along the $[0001]_{Mg}$ direction thereby minimizing elastic strains. The β''' precipitates exhibit additional faceting along the $[0001]_{Mg}$ direction and along the $\langle 1\bar{1}01 \rangle_{Mg}$ and $\langle 1\bar{1}02 \rangle_{Mg}$ directions when viewed along the $\langle 11\bar{2}0 \rangle_{Mg}$ zone axes, which can be affected by strain field interactions from nearby precipitates.

Keywords: Magnesium alloy; precipitation; atom probe tomography; scanning/transmission electron microscopy (STEM)

Magnesium alloys containing rare earth elements such as Nd are well known for their significant aging response and formation of precipitates with prismatic habit planes [1-5]. WE43 and WE54 are two commonly used Mg-rare earth (RE) element alloys containing Nd and Y as the major strengthening elements, and a significant amount of research has focused on characterizing precipitate phases in these alloys [3-8]. However, the different alloying elements make the microstructure complex and the role of each element on the precipitate processes difficult to identify. A more meaningful approach involves the analysis of model alloys, as illustrated through previous experimental [9-14] and computational [15-18] studies.

In the Mg-Nd system, the precipitation sequence involves the formation of metastable phases from the supersaturated solid solution and is understood to be [3, 9-11, 14, 19, 20]:

Guinier-Preston (GP) zones include the so-called “N”, “V”, and hexagon arrangements either as individual units or single layer sheets [9, 11, 20]. Precipitates often referred to as β' are more accurately labeled here as β''' according to [20]. The GP zones and β''' precipitates form in the early stages of aging in Mg-Nd alloys and are responsible for the increased alloy strength when aged between 170°C [9] and 250°C [21]. Therefore, characterization of these phases is essential in order to understand the microstructure-property relationships in Mg-RE alloys.

While transmission electron microscopy (TEM) studies of Mg-Nd alloys have successfully characterized the atomic structure of the precipitates forming in the early stages of aging [9, 11, 19-21], their three-dimensional shape remains to be established. With the exception of Ref. [9, 20, 21], all previous work using transmission electron microscopy (TEM) have imaged these precipitates along the $[0001]_{\text{Mg}}$ direction. As a consequence, a more detailed description including the three-dimensional morphology and size distributions for each dimension is needed to understand the mechanisms controlling precipitate shape and size evolution and to relate the microstructure to the strengthening behavior. Phase field calculations of the 3D morphology suggested β''' to be plate-shaped with the longest dimension along the $\langle 1\bar{1}00 \rangle_{\text{Mg}}$ directions [17], yet these predictions have remained inconclusive due to the lack of experimental evidence.

To answer this question, this paper provides a quantitative description of the shapes of GP zones and β''' precipitates in a Mg-Nd alloy using atom probe tomography (APT) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM).

The alloys examined in this paper were provided by Magnesium Elektron [North America Inc. Ltd.](#) The compositions of the two alloys were measured by inductively coupled plasma mass spectrometry and found to be Mg-2.35 wt.% Nd (Mg-0.40 at.% Nd) and Mg-2.18 wt.% Nd-0.32 wt.% Zr (Mg-0.38 at.% Nd-0.09 at.% Zr at.%). Results from APT were collected from the Mg-Nd-Zr alloy while results from HAADF-STEM were obtained from the binary Mg-Nd alloys. Precipitation is not affected by the presence of Zr thereby allowing direct comparisons to be made between the two alloys. The alloys were encapsulated in quartz tubes in an argon atmosphere and solution treated at 560°C for 24 hours followed by water quenching. [The solution treatment was chosen to ensure the sample was sufficiently homogenized. Although the temperature is above](#)

[that of the eutectic, the sample did not experience any melting.](#) Samples were then aged in an oil bath at either 200°C for 1 hour and 16 hours or 250°C for 3 minutes, 15 minutes, and 1 hour followed by water quenching. The APT specimens were electropolished with a solution of 25% perchloric acid in acetic acid using 14-20 V and then fine polished with a solution of 2% perchloric acid in butoxyethanol with 5-10 V. The APT data was collected on a Cameca LEAP XHR4000 instrument operated in voltage mode with a specimen temperature of 50 K. The data was collected at detection rates varying between 0.005 to 0.01 atoms per pulse on average using a voltage pulse fraction of 20% and a repetition rate of 200 kHz. The data was then reconstructed using the Integrated Visualization and Analysis Software (IVAS) package. The reconstruction parameters, geometric factor, and image compression factor were chosen to ensure that the planar spacings observed at identified poles and the angles between such planes match that of the hexagonal magnesium matrix. Crystallographic analysis methods developed for APT [22] were used to determine the orientation of the APT data. TEM specimens were prepared using the method described in Ref. [23]. Micrographs were taken using a JEOL 2100 with a collection angle of 52 mrad and a double-corrected JEOL 3100R05 microscope operated at 300 kV with a collection angle of 74 mrad.

Examination of the morphology and size in 3D is experimentally challenging for TEM, especially for GP zones where the dimension along $\langle 1\bar{1}00 \rangle_{Mg}$ directions is only a couple atomic layers thick. However, the 3D nature of APT data provides a means to measure shape and dimensions. Since APT cannot always resolve the atomic structure of the precipitates, the GP zones and β''' were distinguished by their crystallographic orientations.

Selected images illustrating the 3D morphology of GP zones using APT and HAADF-STEM are shown in **Figure 1**. As previously reported [9], the GP zones are thin platelets of Nd atoms, parallel to $\{1\bar{1}00\}_{Mg}$ planes. The N and V arrangements observed by STEM are not recognizable by APT, despite the slight difference in habit plane orientation (**Figure 1**). This difference in habit plane is related to the staggering of the N and V units. The V units (**Figure 1a**) alternate such that their apex is pointing up in one unit and down in the neighboring unit. Each matching unit lies on the same $\{1\bar{1}00\}_{Mg}$ plane. Conversely, the N units (**Figure 1b**) have identical atomic arrangements and each subsequent N unit sits on different but parallel $\{1\bar{1}00\}_{Mg}$ planes creating an angle of 10.9° from the $\{1\bar{1}00\}_{Mg}$ plane. Size distributions and aspect ratios of the GP platelets

were measured independently by APT and STEM and are shown in **Figure 2**, revealing comparable dimensions from the two techniques. Most of the GP platelets are slightly longer in the $[0001]_{Mg}$ directions and occasionally in the $\langle 11\bar{2}0 \rangle_{Mg}$ directions. The dimension along $\langle 1\bar{1}00 \rangle_{Mg}$ directions is fixed by the atomic structure and therefore not plotted. The linear correlation between the dimensions along the $[0001]_{Mg}$ and the $\langle 11\bar{2}0 \rangle_{Mg}$ directions suggests that GP zones are thin plates with a constant aspect ratio that is independent of size.

The 3D size distributions and morphology of β''' precipitates obtained from APT and HAADF-STEM observations are presented in **Figure 2** and **Figure 3**. Isolated β''' precipitates are longest in the $[0001]_{Mg}$ direction, shortest in the $\langle 11\bar{2}0 \rangle_{Mg}$ directions, and intermediate in the $\langle 1\bar{1}00 \rangle_{Mg}$ directions. The thickness along $\langle 11\bar{2}0 \rangle_{Mg}$ directions more strongly correlates with the length along the $\langle 1\bar{1}00 \rangle_{Mg}$ directions. We note that the size distributions presented in **Figure 2** do not take into account the finite thickness of the TEM samples.

The $\{010\}_{\beta'''}$ planes have two possible arrangements of Nd atoms, which are zigzag chains or rows of hexagonal rings, as previously discussed [9]. Interestingly the thickness along $\langle 11\bar{2}0 \rangle_{Mg}$ directions is related to the atomic structure such that the platelets are thinnest when the ratio of the rows of hexagonal rings to zigzag chains is largest and vice versa. Also, when viewed along the $\langle 11\bar{2}0 \rangle_{Mg}$ zone axes, the edges of the precipitates appear faceted, as shown in **Figure 3c** and in the Supplementary Material-**Movie 1**. The faceted morphology observed with APT is illustrated in **Figure 3d** where the facets are parallel to the $\langle 1\bar{1}01 \rangle_{Mg}$ and $\langle 1\bar{1}02 \rangle_{Mg}$ directions. In some cases, the presence of neighboring precipitates and associated strain fields might influence faceting, as shown in **Figure 3e** and **f**, where the two precipitates have matching facets along the $[0001]_{Mg}$ direction.

Previous observations showed that β''' is often connected to the ends of GP zones, indicating that β''' can nucleate from existing GP zones [21]. However, it was unclear how the two phases were connected along the $[0001]_{Mg}$ direction. GP zones and β''' precipitates connected edge to edge are shown in **Figure 4**. These phases are connected along the $[0001]_{Mg}$ direction, and the GP zone in this figure extends farther along this direction than the β''' precipitate (**Figure 4c**).

Assuming thermodynamic equilibrium, coherent precipitate shapes minimize the sum of the interfacial and elastic strain energies. In general, when the precipitates are small, the interfacial energy would contribute more to the overall shape because the area to volume ratio is large. Here however, the plate-like morphologies of the GP zones and β''' are the result of a strong elastic strain energy contribution as explained in the next paragraphs. Despite their different habit planes, the GP zones and β''' precipitates are both platelets lying on prismatic planes and therefore, the same argument used to explain the shape of β''' can be extended to describe the shape of the GP zones.

Previous computational work showed that the interfacial energies for β''' are very small [17] and would therefore have a negligible contribution to the precipitate shape. In fact, previous phase field models of the β''' precipitates based only on interfacial energy values and neglecting any contribution from strains created precipitates with relative dimensions such that $l_{\langle 1\bar{1}00 \rangle_{Mg}} > l_{\langle 0001 \rangle_{Mg}} > l_{\langle 11\bar{2}0 \rangle_{Mg}}$ [19], which are inconsistent with the present experimental observations. Alternatively, the previously calculated misfit strains [20] agree with the experimental observations of plate-shaped precipitates having relative dimensions such that the platelets are longest along $[0001]_{Mg}$, shortest along $\langle 11\bar{2}0 \rangle_{Mg}$ directions, and intermediate along $\langle 1\bar{1}00 \rangle_{Mg}$ directions.

While elastic strain energy explains the overall dimensions along the three principle axes, it does not currently reflect the presence of facets that are visible when viewed along the $\langle 11\bar{2}0 \rangle_{Mg}$ zone axes. Further modeling may be required to explain these facets and determine whether these features are equilibrium or transient growth features. The interpretation of the observed shapes is further complicated when considering possible interactions between strain fields from neighboring precipitates. Precipitates located within close proximity to one another causes their strain fields to interact and alter the precipitate morphologies.

The nucleation of β''' can be inferred from its relationship to the GP zones. It is clear that β''' nucleates heterogeneously on the GP zones at hexagonal rings, as shown in **Figure 4**. The hexagonal rings exist in both the GP zones and the β''' and are consistently located where the two phases connect, suggesting that the strain field at the rings makes it easier for β''' to form. The

β''' precipitates might then grow by the so-called ledge mechanism through the nucleation of new $\{010\}_{\beta''''}$ planes.

Figure 2 suggests that the overall shapes for both GP and β''' precipitates are independent of size for the aging condition selected. However, the question remains whether the observed shapes are equilibrium shapes or transient morphologies that could change during the aging process due to kinetics limitations. Growth kinetics depends on the ability for solute atoms to diffuse to the growing precipitate and to attach at the interface. Considering the roughness and microfaceting visible along the precipitate interfaces (**Figure 3a-c**), it seems reasonable to expect the precipitates to grow along the $\langle 11\bar{2}0 \rangle_{Mg}$ and $[0001]_{Mg}$ directions by atoms attaching randomly to the ends of existing $\{010\}_{\beta''''}$ planes, while growth along the $\langle 1\bar{1}00 \rangle_{Mg}$ directions would require a new $\{010\}_{\beta''''}$ row to nucleate on the surface and possibly grow by the so-called ledge mechanism. As a result, when ignoring the energetic constraints, growth would be expected to be faster along the $\langle 11\bar{2}0 \rangle_{Mg}$ and $[0001]_{Mg}$ directions compared with growth along the $\langle 1\bar{1}00 \rangle_{Mg}$ directions. Growth along the $[0001]_{Mg}$ will be more favorable than growth along $\langle 11\bar{2}0 \rangle_{Mg}$ because of the high misfit strains [20]. The slowest growth rate is expected along $\langle 1\bar{1}00 \rangle_{Mg}$ directions due to the required nucleation event. As an illustration, although most of the β''' precipitates have hexagonal rings located at the ends of the precipitates (**Figure 3a**), occasionally there is a small segment of a new zigzag chain that has formed at the end, as shown in **Figure 3b**. Finally, the ledge mechanism may contribute to the observed facets (**Figure 3c and d**), however their presence in the majority of the observed precipitates and orientation along low index directions would rather suggest that they are characteristic of an equilibrium configuration.

In summary, we have examined the 3D shapes of GP zones and β''' in Mg-Nd alloys using complementary APT reconstructions and HAADF-STEM images. The GP zones are plate-shaped with $\{1\bar{1}00\}_{Mg}$ habit planes and extend along the $[0001]_{Mg}$ and $\langle 11\bar{2}0 \rangle_{Mg}$ directions. The β''' precipitates are elongated platelets with $\{11\bar{2}0\}_{Mg}$ habit planes and their longest dimension along the $[0001]_{Mg}$ direction. In addition, most β''' precipitates exhibit faceted edges that lie parallel to $\langle 1\bar{1}01 \rangle_{Mg}$ and $\langle 1\bar{1}02 \rangle_{Mg}$ directions. The overall dimensions of both GP and β''' precipitates are in general agreement with elastic strain energy minimization. However the oblong shape in the $[0001]_{Mg}$ direction and the faceting in the $\langle 1\bar{1}01 \rangle_{Mg}$ and $\langle 1\bar{1}02 \rangle_{Mg}$ directions of the β'''

precipitates require further work to determine whether these are equilibrium features, the result of overlapping strain fields from neighboring precipitates, or transient characteristics from the growth mechanism. Characterization of the precipitates at different aging times to follow their evolution will address this question.

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Figure 1

Figure 1 a) and b) HAADF-STEM images of the two GP variants after aging at 200°C for 16 hours with the incident beam parallel to the $[0001]_{Mg}$ zone axis. c and d) APT data of a GP variant after aging at 250°C for 15 minutes. Precipitates are viewed along the c) $\langle 1\bar{1}00 \rangle_{Mg}$ and d) $[0001]_{Mg}$ directions. Nd atoms are shown in red

Figure 2

Figure 2: Size distributions and aspect ratios of a-c) GP zones and d-g) β''' precipitates after aging at 200°C (for GP zones) or 250°C (for β''') for 1 hour. Dimensions along $\langle 11\bar{2}0 \rangle_{Mg}$ are in grey, $\langle 1\bar{1}00 \rangle_{Mg}$ in white, and along $[0001]_{Mg}$ are in black. The data was obtained from a) APT b) HAADF-STEM c) APT d-g) HAADF-STEM.

Figure 3

Figure 3: a-c) HAADF-STEM images and d-f) APT reconstructions of β''' precipitates after aging at 250°C for a-c) and e-f) 1 hour and d) 3 min. Precipitates are viewed along the a), b), and e) $[0001]_{Mg}$ and c), d), and f) $\langle 11\bar{2}0 \rangle_{Mg}$ zone axes.

Figure 4

Figure 4 a) HAADF-STEM image after aging at 200°C for 16 hours. b and c) APT data after aging at 250°C for 3 minutes. Precipitates are viewed along the a) and b) $[0001]_{Mg}$ and c) $\langle 11\bar{2}0 \rangle_{Mg}$ zone axes.