CHARACTERISATION OF STRENGTHENING PRECIPITATE PHASES IN A Mg–Y–Nd ALLOY

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Abstract—Strengthening precipitate phases in a Mg–Y–Nd based alloy (WE54), aged at 250 °C, have been characterised using transmission electron microscopy. Precipitation at 250 °C involves formation of three separate metastable phases, (1120)0 platelets of an as yet unidentified phase, and the phases designated b′ and b, preceding formation of the equilibrium phase β. All three phases b′, b, and β are present in significant fractions in peak-aged samples. The β phase has a base-centred orthorhombic structure, with a potential point group of mmm. The b′ phase has an f.c.c. structure (space group Fm3m, a = 0.74±0.01 nm), which renders it isomorphous with a family of intermetallic compounds of the general form Mg3X, where X represents Nd, Ce, La, Pr, Dy and Sm. The equilibrium phase β has an f.c.c. structure (space group, F43m, a = 2.2±0.1 nm), which makes it isomorphous with Mg2Gd. The formation of the β phase is known to generate significant shear strain energy, and a mechanism of shear strain energy accommodation is proposed, involving nucleation in association with β′ phase. With prolonged ageing at 250 °C, the β phase transforms in situ to the equilibrium β phase. © 2000 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Magnesium alloys; Precipitation; Microstructure; Crystal structure; Phase transformations

1. INTRODUCTION

There has been a rapid growth in interest in recent years in the development of high strength, lightweight magnesium alloys for elevated temperature applications [1–7]. Among the more successful magnesium alloys developed in this category to date have been those based on the Mg–Y–Nd system [8–13]. The strength of such alloys, containing typically 5 wt% Y, 2 wt% Nd and 2 wt% heavy rare-earth elements (HRE) such as Th, Er, Dy and Gd, is produced by conventional age-hardening treatments, which typically involve a solution treatment of 8 h at 525 °C, a hot water quench and a subsequent ageing treatment of 16 h at 250 °C [11]. The aged microstructure at maximum hardness has been reported [8, 9] to contain metastable β′ and equilibrium β phases as dispersed precipitates, and both of these phases have been described as forming as plates on [1T00] planes of the magnesium matrix (a) phase. These prismatic precipitate plates have been suggested [14] to play an important role in strengthening by providing effective barriers to gliding dislocations. It is thus of interest to determine the structure, orientation and composition of such precipitate plates, and to identify those factors responsible for their presence in Mg–Y–Nd alloys.

Compared to similar plate-shaped precipitate phases in high strength aluminium alloys [15–18], the crystal structure(s) of precipitate plates in Mg–Y–Nd alloys have been much less extensively studied. Based on selected area electron diffraction (SAED) patterns, the metastable phase β′ has been determined [8, 9, 11] to have a composition of Mg12NdY and a face-centred cubic (f.c.c.) Bravais lattice, with lattice parameters a = 0.640 nm, b = 2.223 nm, c = 0.521 nm. The orientation relationship reported between β′ and the matrix phase has the form (100)β′// (1120)M, [001]β′// [0000]M. The proposed structure and orientation of the β′ phase are thus similar to those of the β′ formed in Mg–Y binary alloys [8]. The equilibrium phase β has been reported [8, 9, 11] to have a composition of Mg14Nd2Y and a face-centred cubic (f.c.c.) Bravais lattice, with a lattice parameter a = 2.223 nm. The orientation relationship reported between β and the matrix phase is such that (1T2)β// (1T00)M, [110]β// [0000]M, and is identical in form to that observed between β′ and the matrix phase in Mg–Nd binary alloys [8]. Although Bravais lattices have been proposed for the two precipitate phases, full crystal symmetries remain to be determined.

It is the purpose of the present paper to report
results of an examination of the structure and orientation of these strengthening precipitate phases using transmission electron microscopy and electron microdiffraction. Electron microdiffraction offers the opportunity of unambiguous identification of precipitate structure, since diffraction patterns may be collected from individual precipitates and the pattern symmetries that they contain may be systematically related to crystal symmetry. The forms of the precipitate phases are also examined and accounted for in terms of the point symmetries of the precipitate and matrix lattices, and the orientation relationship sustained between them. Compared to the results of previous studies [8, 9], the present work (i) clarifies the form of the metastable $\beta'$ phase, (ii) establishes the existence of a second metastable intermediate phase ($\beta_1$) not previously reported in this system, (iii) records, for the first time, the in situ transformation of the $\beta_1$ phase to equilibrium $\beta$, (iv) establishes the full crystal symmetry of the equilibrium phase $\beta$, and (v) sets forth a mechanism for the formation of plate-shaped $\beta_1$ phase.

2. EXPERIMENTAL PROCEDURES

Plates of cast alloy WE54, with a nominal composition of Mg–(5.0–5.5)Y–(1.5–2.0)Nd–(1.5–2.0)HRE–0.4Zr (wt%), were purchased from the Magnesium Elektron Company, England. The plates were received in the T6 condition (solution treated for 8 h at 525°C, hot water quenched and then aged for 16 h at 250°C). Specimens for transmission electron microscopy (TEM) were encapsulated in a glass tube under 0.3 atmosphere argon pressure. They were then solution treated for 8 h at 525°C, quenched by breaking the glass tube in cold water, then aged in salt baths at 250°C. Discs 3 mm in diameter were punched from the heat treated strips, ground to a thickness of 0.15 mm, and twin-jet electropolished in a solution of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 500 ml methanol and 100 ml 2-butoxy-ethanol, at −55°C and 0.1 A. Characterisation of precipitate phases was performed in a Philips CM20 TEM, equipped with an Oxford Instruments energy dispersive X-ray spectrometer and operating at 200 kV. Microdiffraction was performed in conventional TEM mode using a 30 μm condenser aperture and an electron probe nominally 7.5–15 nm in diameter.

3. EXPERIMENTAL RESULTS

3.1. Intermediate precipitate phases

A bright field micrograph typical of the microstructure in samples aged 4 h at 250°C is provided in Fig. 1. When viewed in an [0001]$_a$ orientation, the underaged microstructure contained globular particles surrounded by local arrays of thin $\{11\overline{2}0\}_a$ platelets with an aspect ratio of typically 10:1. The globular particles were identified by electron microdiffraction to be $\beta'$ phase [19].

Fig. 1. Transmission electron micrograph showing precipitates in samples of WE54 aged for 4 h at 250°C. Image was recorded parallel to [0001]$_a$.

Fig. 2. Transmission electron micrographs showing assemblies of plate-shaped and irregular globular precipitates in samples aged for 48 h at 250°C. Images were recorded parallel to [0001]$_a$, and (b) is enlargement of a local area in (a).
single array of internal fringes, lying perpendicular to \((\bar{1}00)_a\) directions, was visible within the \((11\bar{2}0)_a\) platelets. Accurate measurement of the fringe spacing proved difficult due to the precipitate size and the associated strain field. However, the fringe spacing was observed to vary within the range 1.1–1.5 nm, with an experimental error of ±0.1 nm. The size of the \((11\bar{2}0)_a\) precipitate platelets was such that it proved difficult to obtain electron microdiffraction patterns from individual particles to identify their crystal structure. Given the experimental difficulty, further work has not yet been carried out to establish the structure of the \((11\bar{2}0)_a\) platelets in underaged samples. However, it is to be noted that none of the precipitate phases identified to date in WE alloys has been reported to have a plate-like shape with habit plane parallel to \((11\bar{2}0)_a\).

With continued ageing at 250°C, the \((11\bar{2}0)_a\) platelets were rapidly replaced by \((\bar{1}00)_a\) precipitates. Figure 2 shows bright field images, recorded parallel to [0001]_a, typical of the microstructure in peak-aged samples (48 h at 250°C). The microstructure now contained a dispersion of coarser plate-shaped precipitates (aspect ratio typically 10:1), in contact with irregular, globular particles that were occasionally faceted. The projected images of the precipitate plates had the form of parallelopipeds, with the extended broad surfaces parallel to \([\bar{1}T00]_a\) planes. Three orientations of the precipitate plates were immediately visible in this projection, but closer examination of the edge-on plates revealed that, for each orientation of the plates, there were two independent variants which were twin-related across the habit plane, \([\bar{1}T00]_a\), and which were distinguishable on the basis of shape alone. All six variants are identifiable in Fig. 3(a) and the forms and crystallography of the six variants of the \([\bar{1}T00]_a\) plates are represented schematically in Fig. 3(b). It is to be noted from Fig. 2 that, in addition to the habit plane facets, these plate-like precipitates were closed by inclined planar facets which were invariably in contact with the more globular particles, on both opposing facets of the plates. These assemblies were commonly distributed in irregular clusters throughout the matrix phase.

Electron microdiffraction patterns obtained from individual particles of the irregular, globular precipitates and the overlapping matrix are provided in Fig. 4. As indicated, all such patterns could be indexed consistently according to the based-centred orthorhombic structure of \(\beta'\) phase [8, 9]. Further attempts to obtain convergent beam electron diffraction (CBED) patterns to determine the point group of \(\beta'\) proved unsuccessful due to the scale of the particles. The orientation relationship implied by the superimposed precipitate and matrix patterns was such that \((100)_{\beta'}/(1\bar{1}2\bar{1}0)_a\), \([001]_{\beta'}/[0001]_a\). Since \((100)_{\beta'}\) might be parallel to any one of three
(1T0) planes, there was a total of three crystallographically equivalent variants of $\beta'$ in a given grain of the matrix phase.

Examination of the (1T0) plates revealed that most of them were preferentially thinned during electropolishing of the thin foils, and the local foil thickness was such that it proved difficult to obtain from them CBED patterns in which the pattern symmetry elements were clearly defined. Figure 5 presents an electron microdiffraction pattern recorded from one such (1T0) plate, with the incident electron beam parallel to [000T]. The precipitate reflections could not be indexed according to any of the precipitate phases reported in previous studies of WE54 alloy [8, 9]. Examination of a number of the prismatic plates indicated that this pattern was representative, and that it could be indexed consistently according to an f.c.c. structure with a lattice parameter of $a = 0.74 \pm 0.01$ nm. The orientation relationship between this novel phase, designated $\beta_1$, and the matrix phase was of the form $(T12)_{h} // (1T0)_{d}$, $(110)_{h} // (0001)_{d}$, and is shown in stereographic projection in Fig. 6.

### 3.2. Equilibrium precipitate phase

A bright field micrograph typical of the microstructure in samples aged for 2400 h at 250°C is shown in Fig. 7, with the electron beam parallel to the [0001] direction. The microstructure now contains almost exclusively the (1T0) plates, which have a coarser distribution than that observed in samples aged for 48 h at 250°C. Figure 8 presents a series of zero order Laue zone (ZOLZ) electron microdiffraction patterns recorded from individual (1T0) plates. These patterns could be well indexed according to the equilibrium phase $\beta$ (f.c.c., $a = 2.2 \pm 0.1$ nm). The orientation relationship implied by superimposed precipitate and matrix patterns was such that $(T12)_{h} // (1T0)_d$, $(110)_{h} // (0001)_{d}$, and is thus similar to that observed between $\beta_1$ and the matrix phase.

The crystal point group of the $\beta$ phase was determined by noting the pattern symmetries in the ZOLZ and the whole pattern, and assigning the appropriate diffraction group [20–22]. The symmetries detected in the higher order Laue zone (HOLZ) patterns of Fig. 8 and the diffraction groups deduced for each zone-axis pattern are summarised in Table 1. There is ambiguity associated with assigning a crystal point group to the $\beta$ phase, since the point groups 43m, m3m and 62m are all consistent with the diffraction groups allowed for the two zone-axis patterns examined. However, such ambiguity could be overcome through the construction of the unit cell of the reciprocal lattice. In practice, this was achieved by projecting the reflections in the first order Laue zone (FOLZ) of the (001)ₜ pattern onto the ZOLZ pattern. The pos-
ditions of the projected higher order reflections were thus determined by those sites defined by the intersections of lines joining the reflections in the FOLZ. The reciprocal lattice of $\beta$ phase was thus defined by a body-centred unit cell, and the unit cell in real space was consequently inferred to be face-centred (F). Since the only possible Bravais lattice associated with the point group $\sigma_m \bar{6}2m$ is primitive (P), a face-centred unit cell is incompatible with this crystal point group. Furthermore, since the observed whole pattern symmetry (2mm) for the $\langle 001 \rangle_\beta$ zone axis is not consistent with that (4mm) expected for the point group $m3m$, the crystal point group of $\beta$ may thus be determined unambiguously to be $\bar{4}3m$.

The crystal space group of the $\beta$ phase was identified by consideration of the conditions limiting

Table 1. Symmetries observed in electron microdiffraction patterns in Fig. 8

<table>
<thead>
<tr>
<th>Zone axis</th>
<th>Whole pattern symmetry</th>
<th>Possible diffraction groups</th>
<th>Possible point groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>2mm</td>
<td>$4gmm_R, 2mm1_R, 2mm$</td>
<td>$\bar{4}3m, \bar{4}2m_R, 4/mmm, 4mm, 6/mmm, m3, m3m, mm2, \bar{6}2m$</td>
</tr>
<tr>
<td>(111)</td>
<td>3m</td>
<td>$3m, 3m1_R, 6gmm_R$</td>
<td>$\bar{4}3m, 3m, 5m2, 3m, m3m$</td>
</tr>
</tbody>
</table>

Fig. 8. (a–c) ZOLZ, and (d, e) HOLZ electron microdiffraction patterns recorded from $\beta$ phase. Electron beam is parallel to (a, d) [001], (b) [110], and (c, e) [111] zone axes.
possible reflections for all potential space groups and noting absent reflections in the observed electron microdiffraction patterns. Of the six space groups based on a point group $43m$, only two involve face-centred Bravais lattices, namely $F43m$ and $F43c$, and conditions defining permitted reflections for each of these two space groups are summarised in Table 2 [23]. A comparison of conditions for permitted reflections for these two space groups revealed that only an examination of $\{hhl\}$ type reflections could distinguish them. Examination of reflections in the $[011]_\beta$ electron microdiffraction pattern of Fig. 8 revealed that the $\{111\}_\beta$, $\{113\}_\beta$ and $\{331\}_\beta$ reflections were clearly detectable and thus not forbidden kinematically. The $\{111\}_\beta$ reflections could not be accounted for by double diffraction involving ZOLZ reflections because they have the minimum angular displacement from the transmitted beam. The occurrence of the $\{111\}_\beta$, $\{113\}_\beta$ and $\{331\}_\beta$ reflections limits the possible space groups exclusively to $F43m$ (Table 2). A careful examination of available electron microdiffraction patterns recorded from the phase $\beta$ indicated that all reflections were consistent with those expected for the space group $F43m$.

The dimension of the unit cell of $\beta$ was confirmed by measuring the radii of circles defined by HOLZ reflections in different high symmetry zone-axis patterns [22]. A consistent value of $2.2 \pm 0.1$ nm was obtained for $a$ from careful measurements of the diameters of the rings defined by the first order Laue zone reflections in different zone axes, such as those shown in Fig. 8. This value for $a$ was found to be consistent with those measured spacings in the ZOLZ of the $[001]$ pattern. The reflections with the minimum angular separation from the transmitted beam in the $[001]$ pattern were measured to represent an interplanar spacing of $1.1 \pm 0.1$ nm, corresponding well to that predicted for the $\{200\}$ planes of the proposed f.c.c. structure.

### Table 2. General conditions for permitted reflections for crystal space groups based on a $43m$ point group and a face-centred (F) Bravais lattice ($n$ are integers)

<table>
<thead>
<tr>
<th>Space group</th>
<th>hkl</th>
<th>hhl</th>
<th>0kl</th>
<th>00 l</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F43c$</td>
<td>$h+k, k+l, h+l=2n$</td>
<td>$h, l=2n$</td>
<td>$k, l=2n$</td>
<td>$l=2n$</td>
</tr>
<tr>
<td>$F43m$</td>
<td>$h+k, k+l, h+l=2n$</td>
<td>$h+l=2n$</td>
<td>$k, l=2n$</td>
<td>$l=2n$</td>
</tr>
</tbody>
</table>

#### 3.3. Phase transformation within the precipitate plates

Careful examination of images of $\beta$ plates projected parallel to $[001]_\beta$ revealed that a single plate often contained several domains of the $\beta$ phase (Fig. 9). These domains were distinguishable by a displacement of lattice fringes across the domain interface. The interfaces between the domains were commonly planar, parallel to $\{111\}_\beta$, although irregular, wavy interfaces were observed occasionally. Electron microdiffraction patterns recorded from individual domains within a single precipitate plate indicated that they were single variants of the $\beta$ phase and that each shared an identical orientation relationship with respect to the matrix phase. Given the similarity in the morphology, structure and orientation between the $\beta$ and $\beta_1$ phases, the presence of domains within individual precipitates of $\beta$ phase suggested the possibility of an in situ structural transformation from $\beta_1$ to $\beta$.

The $[0001]_\beta$ projected images of Figs 10 and 11 show $\beta_1$ precipitate plates which have transformed partially into $\beta$ phase in samples aged for only 48 h at 250°C. Regions of $\beta_1$ and $\beta$ within such plates could be readily distinguished, simply on the basis of contrast and/or lattice fringes alone. Careful measurements of fringe spacings and the angles between each array of fringes suggested that the lattice fringes were associated with those planes in an $(011)$ zone of $\beta$ phase. While there appeared to be only one domain of $\beta$ phase formed within the transformed volume in particle A (Fig. 11), several domains of $\beta$ phase (as indicated by arrows) were...
observed within particle B. An interesting observation was that in regions close to the rim of plate A, the lattice fringes characteristic of the $\beta$ phase effectively disappeared, implying that these regions were retained $\beta_1$ phase, with a lattice parameter approximately one third that of $\beta$ phase.

To identify the relationship between the two phases, electron microdiffraction patterns were recorded from regions with and without lattice fringes, respectively, and examples are provided in Figs 11(b) and (c). The pattern recorded from the
region without lattice fringes was consistent with that expected for $\beta_1$ phase, and the orientation relationship implied between $\beta_1$ and $\beta$ phases was such that the principal axes of $\beta_1$ were parallel to those of $\beta$. This implies that the orientation relationship between the resultant phase $\beta$ and the $\alpha$–Mg matrix phase is identical to that observed between $\beta_1$ and $\alpha$, i.e. $(T12)_\beta//(/\langle1T0\rangle_\alpha$, $[110]_\beta//[0001]_\alpha$.

Detailed examination of a large number of prismatic plates using microdiffraction and lattice imaging techniques revealed that it was also possible to detect two crystallographically equivalent and yet distinguishable variants of $\beta$ phase in a single precipitate plate. Figure 12 shows an $[0001]_\alpha$ projected image of such a precipitate plate. Within each of the two variants, the lattice fringes which had the smallest interplanar spacing and were yet visible in the micrograph, were associated with $\{111\}_\beta$ planes in the $(1T0)$ zone of $\beta$ phase. The two variants of the $\beta$ phase were separated by a planar interface, which was parallel to $(111)_\beta$ and normal to the habit plane of the plate, and were so arranged that they could be regarded as twin-related across $(111)_\beta$ planes of the $\beta$ phase.

3.4. Energy dispersive X-ray microanalysis

A comparison of energy dispersive X-ray spectra recorded from the $\beta'$, $\beta_1$ and $\beta$ phases and the $\alpha$ matrix is provided in Fig. 13. These spectra were obtained in TEM mode with a nominal probe size of 7.5–10 nm in diameter. X-ray microanalysis of the plate-shaped precipitates $\beta_1$ and $\beta$ was carried out with the habit plane approximately parallel to the electron beam in order to maximise the volume of precipitate phase within the interaction volume. However, care was taken to avoid analysis under conditions where either precipitate or matrix phase was strongly diffracting. Results obtained from the $\beta'$ phase indicated invariably that the concentration of Nd was significantly lower than that of Y [Fig. 13(a)]. Analysis of the matrix phase surrounding the $\beta'$ phase under similar analysis conditions indicated that the Nd content was below the level of detectability [Fig. 13(b)]. The Nd peak, which is detectable in Fig. 13(a), was thus not associated with the solid solution matrix phase. In contrast to the $\beta'$ phase, particles of $\beta_1$ and $\beta$ phases contained relatively high concentrations of Nd [Figs 13(c) and (d)]. Peaks of C and O, which were detectable in the low energy region of each of the four spectra, are attributable to contaminant surface films on the thin foils.

4. DISCUSSION

4.1. Structure of precipitate phases

In contrast to the results of previous studies [8, 9], it has been found that ageing at 250°C involves precipitation of at least three separate metastable phases preceding formation of the equilibrium phase $\beta$. These metastable phases include an unidentified phase formed as thin platelets on $(1120)_\alpha$, and the $\beta'$ and $\beta_1$ phases. The $\{1120\}_\alpha$ platelets are observed predominantly in underaged samples, while $\beta'$, $\beta_1$ and $\beta$ are the major precipitate phases present in peak-aged specimens. The structure of

![Fig. 13. Energy dispersive X-ray spectra recorded from phases of (a) $\beta'$, (b) $\alpha$–Mg matrix, (c) $\beta_1$, and (d) $\beta$ in a sample aged for 48 h at 250°C.](image-url)
the \{11\bar{2}0\}_z platelets remains unclear in the present study, but further characterisation of these precipitate platelets is beyond the scope of the present paper.

Contrary to previous suggestions [8, 9], the metastable phase \( \beta' \) does not form as plates parallel to \{11\bar{2}0\}_z planes, but takes the form of globular particles which appear irregularly faceted. Analysis of electron microdiffraction patterns recorded from individual globular particles of the \( \beta' \) supports the base-centred orthorhombic Bravais lattice and orientation relationship identified in previous studies [8, 9]. Of the two Bravais lattices proposed for \( \beta' \) [9, 24], the monoclinic structure [24] does not appear to be consistent with present experimental observations. The highest symmetry for a monoclinic Bravais lattice is 2/m. The intersection of this point group with that of the matrix phase in the observed orientation relationship is 2, and the order of the intersection point group with respect to the point group of the matrix phase is 24/2 [25]. This symmetry would thus require 12 crystallographically equivalent variants of \( \beta' \) in a given orientation of the matrix phase, which is clearly not supported by experimental observations of just three variants.

Independent determination of the point group of \( \beta' \) has proven difficult in the present study due to a lack of CBED patterns from this phase. Of the three possible point groups allowed for an orthorhombic Bravais lattice, namely mmm, mm2 and 222, the point group for \( \beta' \) can be identified as mmm if, indeed, there are only three crystallographically equivalent variants in a given matrix grain. For the point group mmm, the intersection point group is also mmm for the orientation relationship observed between \( \beta' \) and the matrix phase. Symmetry thus requires 24/8 or three crystallographic variants of \( \beta' \) in a given matrix orientation. For both of the point groups mm2 and 222, symmetry requires 24/4 or six variants of \( \beta' \), which is not supported by current experimental observations. If the observed number of variants of \( \beta' \) is accepted as accurate, then the point group for \( \beta' \) may be inferred to be mmm.

Microanalysis of \( \beta' \) using energy dispersive X-ray spectrometry indicates that the concentration of Nd is substantially lower than that of Y. This result thus differs significantly from previous measurements [11] of a stoichiometry of \( \text{Mg}_{2.2} \text{Nd}_y \) (Mg–27.5 wt% Nd–16.9 wt% Y). It is to be emphasised that, to measure the composition of the \( \beta' \) phase reliably, it is necessary to ensure that particles of \( \beta' \) are identified and isolated from surrounding precipitates of \( \beta_1 \) and the matrix phase and that the interaction volume defined by the beam is smaller than the volume of the precipitate. As the \( \beta' \) phase has been reported in previous studies [9, 11] to form as plates parallel to \{1\bar{1}00\}_z planes, the higher concentration of Nd reported for this phase [11] might be attributable to contributions from surrounding \{1\bar{1}00\}_z plates of \( \beta_1 \) or \( \beta \) phases. Given that the \( \beta' \) phase has a crystal structure similar to that of the \( \beta'' \) phase formed in Mg–Y binary alloys [8, 9], it is plausible that the concentration of Nd in this phase is lower than that of Y.

A previously unreported, metastable cubic phase, \( \beta_1 \), has been detected as a major intermediate phase during isothermal ageing at 250°C. Based on electron microdiffraction patterns acquired, the \( \beta_1 \) phase is proposed to be f.c.c. with \( a = 0.74 \pm 0.01 \) nm. Although it has proven difficult to obtain full crystal symmetry from electron microdiffraction patterns, the proposed structure is similar to that of \( \text{Mg}_2 \text{X} \), where X represents Nd, Ce, La, Pr, Dy and Sm. All such phases have an f.c.c. structure (space group Fm3m) and a lattice parameter in the range 0.74 ± 0.01 nm, and all form exclusively as plates parallel to \{1\bar{1}00\}_z planes [26–29].

The proposed structure of \( \beta_1 \) is further supported by the observed morphology and the number of variants. For the orientation relationship observed between \( \beta_1 \) and the matrix phase, the point symmetry elements common to the two structures are a two-fold axis ([110]_\beta // [0001]_1) and a mirror plane m normal to it. The intersection point group defined by such common elements is thus 2/m. The geometric forms consistent with this point group include [30] pinacoids (i.e. pairs of parallel, planar surfaces), either parallel or perpendicular to the two-fold axis, a prism perpendicular to the two-fold axis, or a combination of these forms. The observed precipitate shape is well described by a pinacoid parallel to the two-fold axis and is thus consistent with symmetry requirements. The point group of the matrix phase is 6/mmm and of order 24. Since the order of the intersection group is 4, symmetry thus requires 24/4 or six crystallographic variants of \( \beta_1 \) phase in a given orientation of the matrix phase, which is consistent with experimental observations (Fig. 3).

With extended ageing, the \{1\bar{1}00\}_z plates of metastable \( \beta_1 \) phase transform \textit{in situ} to the equilibrium \( \beta \) phase. Crystallographic analysis of the \( \beta \) phase, using symmetry observed in electron microdiffraction patterns, indicates that it has an f.c.c. crystal structure (space group I\bar{3}m) and a lattice parameter of 2.2 ± 0.1 nm. This crystal structure makes it isomorphous with the compounds \( \text{Mg}_2 \text{Gd} \), \( \text{Mg}_3 \text{Y} \text{La}_{1-x} \) (0.35 ≤ \( x \) ≤ 0.77) and \( \text{Mg}_{5.36} \text{Y} \text{Ce}_{1-x} \) (0.39 ≤ \( x \) ≤ 0.84, 0 ≤ \( y \) ≤ 0.60) [31–33]. The \( \beta \) phase exhibits 2mm whole pattern symmetry in (100) orientations. For the observed orientation relationship, \((\text{T12})_\beta // (1\bar{1}00)_z \), \{11\bar{1}0\}_\beta // [0001]_1, the intersection point group would be m if \( \beta \) formed directly from the matrix phase. The number of variants would then be expected to be 12, which is clearly at variance with experimental observations.

It has been demonstrated unambiguously in the present study that the prismatic precipitate plates of \( \beta \) phase are the product of direct transformation...
from metastable $\beta_1$ phase. The orientation relationship sustained during this in situ phase transformation is such that the principal axes of $\beta$ are parallel to those of $\beta_1$. For the orientation relationship observed between $\beta$ and $\beta_1$, the point symmetry elements common to the two structures are such that the intersection point group is defined as $\bar{4}m$. Since the intersection point group is identical to that of $\beta$ phase, symmetry thus allows 48/24 or two crystallographic variants of the $\beta$ phase to be produced within individual particles of $\beta_1$ phase, which is consistent with experimental observations (Fig. 12). The agreement between theoretical predictions and experimental observations again supports the structure proposed for the $\beta_1$ phase.

In contrast to the composition of $\beta'$ phase, concentrations of Nd in the $\beta_1$ and $\beta$ phases were significantly higher than those of Y. This result is qualitatively in agreement with the stoichiometry of Mg$_{14}$Nd$_{3}$Y (Mg:40.2 wt% Nd:12.4 wt% Y) reported for the equilibrium $\beta$ phase [11]. Since the $\beta_1$ phase has a structure similar to Mg$_{3}$Nd, it would not be unreasonable to expect a higher concentration of Nd in this phase. However, it remains unclear if there is compositional difference between the $\beta_1$ and $\beta$ phases.

4.2. Formation mechanism of $\beta_1$ plates

Although the $\beta_1$ phase has an f.c.c. structure, the orientation relationship observed between $\beta_1$ and the matrix phase is quite different from that commonly associated with h.c.p. (h)/f.c.c. (f) transformation, i.e. (111)$_h$/[0001]$_h$, [100]$_f$/[110]$_f$ [34–38]. Instead, the form of the orientation relationship between $\beta_1$ and the matrix phase is found to be equivalent to that of the Burgers orientation relationship, one of those commonly observed in h.c.p./f.c.c. transformation [39–44]. A close examination of atom distributions within the unit cell of $\beta_1$ [31] (Fig. 14) reveals that there exists a b.c.c. sub-lattice, defined by dashed lines, in the $\beta_1$ lattice and that the lattice parameter of this b.c.c. sub-lattice is half that of the $\beta_1$ lattice. Since the b.c.c. sub-lattice is so arranged that its principal axes are parallel to those of the $\beta_1$ lattice, the closest-packed plane of the $\beta_1$ lattice becomes [110]$_{\beta_1}$, while the closest-packed direction remains [111]$_{\beta_1}$. Therefore, it is perhaps not surprising to observe the Burgers orientation relationship between the $\beta_1$ and $\alpha$–Mg lattices.

If the lattice parameters of the $\beta_1$ and $\alpha$–Mg phases are assumed to be $a_{\beta_1}=0.74$ nm, and $a_{\alpha}=0.321$ nm and $c_{\alpha}=0.521$ nm, respectively, then for the observed orientation relationship, the two phases are near to perfectly coherent across the [100]$_{\beta_1}$ habit plane of the $\beta_1$ plates. Furthermore, the structure of $\beta_1$ phase may be considered to be generated phenomenologically from the $\alpha$–Mg lattice by a simple shear of magnitude ~0.22 on the [100]$_{\alpha}$ plane in the [110]$_{\alpha}$ direction, combined with an expansion of ~0.08 in the direction normal to the shear plane. As shown schematically in Fig. 15, the stacking sequence of the $\beta_1$ lattice can be considered to be produced by a shear of $a/[18][12][00]$, on successive ACAC planes, combined with shuffle displacements of atoms on BDBD planes by $a/[00][01][0]$. This formation mechanism for $\beta_1$ plates is similar to that proposed for proeutectoid $\gamma$ (b.c.c.) plates in a Ti–Cr (h.c.p.) alloy [42–44]. Using an orthonormal coordinate system (x, y, z) in which x/[110]$_{\alpha}$, y/[110]$_{\alpha}$, and z/[110]$_{\alpha}$, the lattice deformation, B, may be calculated as:

$$
B = \begin{pmatrix}
1.00 & 0.00 & 0.00 \\
0.00 & 1.00 & -0.22 \\
0.00 & 0.00 & 1.08
\end{pmatrix}
$$

The transformation strain thus defined is an invariant plane strain (IPS), with the invariant plane parallel to the shear plane (100)$_{\alpha}$, and the orientation relationship is thus confirmed as (12)$_{\beta_1}$/(100)$_{\alpha}$, [110]$_{\beta_1}$/[0001]$_{\alpha}$. Similar IPS transformations have been observed in the formation of precipitate plates of $\gamma'$ (Ag$_2$Al, h.c.p.) in Al–Ag (f.c.c.) alloys [35–37, 45], 0' (Al$_2$Cu, tetragonal) in Al–Cu alloys [45, 46], T$_1$ (Al$_2$CuLi, h.c.p.) in Al–Cu–Li(–Mg–Ag) alloys, and $\Omega$ (Al$_2$Cu, orthorhombic) in Al–Cu–Mg–Ag alloys [38, 47, 48].

Figure 16 shows a schematic representation of an initial $\beta_1$ platelet, with a thickness value corresponding to that formed by one unit cell, constrained within $\alpha$–Mg matrix phase. If there is no deformation of the precipitate phase, the formation of this platelet of $\beta_1$ will give rise to regions of expansion (E) and contraction (C) in the matrix surrounding precipitate plate, and to the associated accumulation of significant shear strain energy [49]. It might thus be expected that some mechanism
might be required to operate to minimise the shear strain energy during nucleation (and growth) of the \( \beta_1 \) phase.

Since there is a mirror plane normal to the \([11\bar{2}0]\) direction, the \( \beta_1 \) lattice may also be generated by shearing the Mg lattice with a shear strain of \( \pm 0.22 \) in the \([11\bar{2}0]\) direction, i.e. by an opposite shear (Fig. 17). The successive operation of these two opposite shears will produce a platelet with no net shear. In this case, the minimum thickness of a \( \beta_1 \) platelet would be equivalent to a displacement of \([11\bar{2}0]_{\beta_1} \) (~1.81 nm) (Fig. 17). Alternatively, the shear strain energy could be reduced or eliminated by an extrinsic supply of relatively large solute atoms to the regions E, and of corresponding concentrations of vacancies to the regions C. Such an environment might be found in the vicinity of pre-precipitate clusters combining large solute atoms with a local excess of vacancies. Recent studies using a three-dimensional atom probe [50–54] have demonstrated unambiguously that such pre-precipitate clusters of solute atoms exist in a range of precipitation-hardened aluminium alloys. Such a mechanism appears, for example, to be operating in the formation of precipitate plates of \( \theta' \) phase in Al–Cu alloys microalloyed with Sn, Cd, In, Mg and Si, T1 phase in Al–Cu–Li alloys microalloyed with Mg and Ag, and \( \Omega \) phase in Al–Cu alloys microalloyed with Mg and Ag [38, 55].

Although there is currently no evidence for such pre-precipitate clusters in Mg–Y–Nd alloys, it is to be noted that Nd and Y atoms have relatively high binding energies with vacancies (Nd: 0.25 eV, Y: 0.11 eV) [56] and are both larger than Mg atoms. The shear strain associated with an embryo precipitate plate might be reduced or removed if Nd or Y atoms segregate to the extended regions and associ-

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**Fig. 15.** Schematic diagram showing the lattice correspondence defined between f.c.c. \( \beta_1 \) and h.c.p. Mg matrix, i.e. \([0001]_{\beta_1} \rightarrow 1/2[11\bar{0}]_p \), \( 2/3[1\bar{1}20]_p \rightarrow 1/2[1\bar{1}1]_p \), \( 2[1\bar{0}0]_p \rightarrow 1/2[\bar{1}13]_p \). Open circles represent atoms in the zero layer, and squares represent atoms displaced one layer normal to the plane of projection.

**Fig. 16.** Schematic diagram showing a platelet of \( \beta_1 \) constrained in \( \alpha \)-Mg matrix. The normal to the plane of the diagram is \([0001]_{\beta_1} \parallel [\bar{1}100]_p \). For clarity only atoms on the zero layer are shown.

**Fig. 17.** Schematic diagram showing two interpenetrated lattices of \( \beta_1 \) and \( \alpha \)-Mg matrix. The structure of \( \beta_1 \) can be generated with zero net shear strain by shearing two identical h.c.p. structural blocks abcf and jihe by \( a/18[1\bar{1}20]_p \) in opposite directions (marked by arrows). Open circles represent atoms in \( \beta_1 \) lattice, and filled circles represent atoms in \( \alpha \)-Mg lattice. For clarity only atoms on the zero layer are shown. The normal to the plane of the diagram is \([0001]_{\beta_1} \parallel [\bar{1}100]_p \).
ated vacancies to the compressed regions during nucleation. Presumably those vacancies associated with these solute clusters would be attracted away from them and into the compressed region associated with any embryo forming within proximity of the solute-vacancy clusters. If such a mechanism were to operate, then it is plausible that any particles evolved from such solute-rich clusters would be expected to form at the end-facets, rather than the broad surfaces, of the $\beta_1$ plates. This is in perfect agreement with experimental observations that $\beta_1$ plates form invariably in association with $\beta'$ particles which are in contact with the end-facets of $\beta_1$ plates (Fig. 2). It is to be noted that similar phenomena have been documented in Al–Cu–Sn alloys, where the formation of $\theta'$ plates involves a large shear strain [45–48] and Sn particles are invariably located at the end facet of $\theta'$ plates when they form in association with the $\theta'$ plates [50, 55].

Although it has been suggested [14] that an increased number density of intrinsically-strong, prismatic precipitate plates will increase the tensile yield strength of magnesium alloys, there has been a lack of theoretical guidelines for achieving such microstructures. The present model suggests that, to promote the nucleation of precipitate plates of $\beta_1$ phase, it appears essential to select those elements which have an atomic size larger than Mg and which have, where possible, high binding energies with vacancies.

5. CONCLUSIONS

In magnesium alloy WE54 (Mg–5 wt% Y–2 wt% Nd–2 wt% HRE) solution treated, quenched and aged at 250°C, the precipitation sequence involves initial formation of globular particles of metastable $\beta'$ phase, with associated fine-scale $\{12\overline{2}0\}_s$ platelets of a metastable phase that is as yet unidentified. With increased ageing time, the $\{12\overline{2}0\}_s$ platelets are replaced by irregular networks of metastable $\beta'$ particles in contact with $\{1\overline{1}00\}_s$ plates of a $\beta_1$ phase not previously identified in this alloy. The $\beta_1$ plates appear to nucleate preferentially in association with the $\beta'$ particles. With extended ageing, the $\beta'$ phase decomposes, and the $\beta_1$ plates transform in situ to the equilibrium $\beta$ phase. The peak-aged microstructure contains predominantly the phases $\beta'$, $\beta_1$ and $\beta$, and key features of these strengthening precipitate phases include:

1. The metastable $\beta'$ phase has a base-centred orthorhombic structure, with a potential point group of mmm. The orientation relationship between $\beta'$ and the matrix phases is of the form $(100)_{\beta'}/(1\overline{1}20)_s$, [001]$_{\beta'}/[0001]_s$. Contrary to previous observations [8, 9], the $\beta'$ phase does not form as plates parallel to $\{1\overline{1}00\}_s$ planes, but takes the form of globular particles which appear irregularly faceted.

2. A previously unidentified phase $\beta_1$ has been revealed as a major intermediate precipitate phase in this system. It has an f.c.c. structure (space group Fm$\overline{3}$m, $a = 0.74 \pm 0.01$ nm), which makes it isomorphous with a family of intermetallic compounds of the general form Mg$_3$X, where X represents Nd, Ce, La, Pr, Dy, Sm. The $\beta_1$ phase forms as plates with habit plane parallel to $\{1\overline{1}00\}_s$, and an orientation relationship such that $(\overline{1}2\overline{1}0)_{\beta_1}/(1\overline{1}00)_s$, [110]$_{\beta_1}/[0001]_s$.

3. The equilibrium $\beta$ phase has an f.c.c. crystal structure (space group F$\overline{4}3$m, $a = 2.2 \pm 0.1$ nm), which renders it isomorphous with Mg$_3$Gd. The orientation relationship between $\beta$ and matrix $\alpha$ is such that $(\overline{1}2\overline{1}2)_{\beta}/(1\overline{1}00)_a$, [110]$_{\beta}/[0001]_a$.

4. The structure of the $\beta_1$ phase can be considered phenomenologically to be generated from the Mg lattice by a simple shear of magnitude $\sim 0.22$ on the $(1\overline{1}00)_s$ plane in the $\{\overline{1}1\overline{2}0\}$ direction and an expansion of $\sim 0.08$ in the direction normal to the shear plane. Preferential nucleation of $\beta_1$ phase in association with the $\beta'$ particles, which are invariably located at the end-facets of the $\beta_1$ plates, is suggested to be the consequence of shear strain energy accommodation.

5. With extended ageing, the metastable $\beta_1$ phase transforms in situ to the equilibrium $\beta$ phase. The orientation relationship sustained between the two phases is such that the principal axes of $\beta$ are parallel to those of $\beta_1$.

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