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Partitioning of Ca to metastable precipitates in a Mg-rare earth alloy

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ABSTRACT

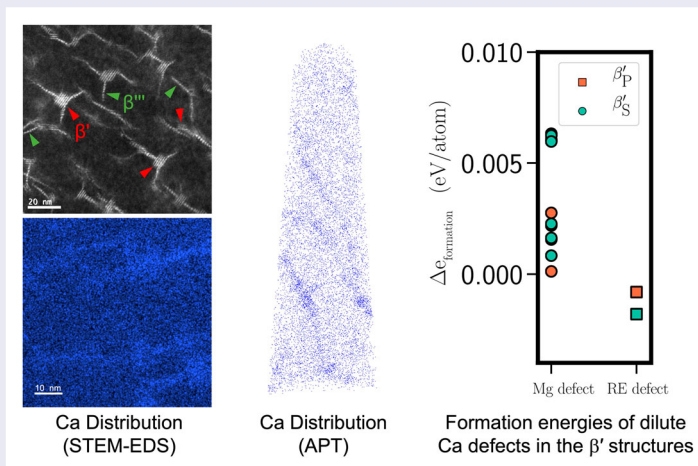
The potential effect of the element Ca on the precipitation behavior was investigated in an Mg-rare earth alloy. A combination of metastable β''' and β' precipitates was observed for the peak aging condition at 200°C. Ca addition was found to have no significant effect on the precipitating phases and evolution sequence. Composition analysis showed that the Ca partitioned to both β''' and β' precipitate phases. First-principles calculations indicated that Ca partitions to the rare-earth sublattice in the precipitate phase. This finding suggests the potential of Ca to partially replace costly rare-earth elements in precipitation-hardened Mg-rare earth alloys.

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KEYWORDS

Mg-RE alloy; Ca; precipitation; strength



IMPACT STATEMENT

Both experimental investigation and first-principal calculation in a Mg-Nd-Y-Ca alloy revealed the partitioning of non-rare-earth element Ca to Mg-RE precipitates, suggesting the potential of Ca to enhance precipitation and strength.

Introduction

Mg alloys containing rare earth (RE) elements have demonstrated exceptional strength from age hardening [1]. This is due to the formation of high-volume fractions of fine β -phase family precipitates during aging [2–4]. These Mg-RE precipitates have unique crystallographic orientation relationships with the Mg-matrix, i.e. the habit planes of precipitates are perpendicular to the easy-glide basal planes, which impedes dislocation motion more effectively compared to conventional Mg alloys [1]. However, the cost of RE elements limits their

commercial use for many applications. In order to reduce the amount of RE elements, it is of interest to explore the addition of non-rare-earth alloying elements to Mg-RE alloy systems to determine if comparable strengthening effects can be achieved.

Ca is a potentially important alloying element in Mg alloys. Ca has a lower density and a lower cost compared to RE elements and a positive effect on the refinement of grains. Ca also leads to an improvement in texture, formability and oxidation resistance [5–10]. Considering these benefits, Ca has been chosen for the design

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of many Mg alloy systems to improve material properties [11,12]. Alloys that contain Ca but no RE elements have been developed such as the commercially important MRI 230D, Diemag 422 and 633 alloys, which have comparable creep properties to those of the Mg-RE alloy AE42 [13,14]. A new processing technology, ECO-Mg, has been developed to produce Ca-containing Mg alloys. This technology is able to alloy Ca in molten Mg, which produces ECO-Mg alloys with high cleanliness and improved castability and mechanical properties of the final products [15–17].

The effect of Ca on the precipitation behavior in Mg alloys has been primarily reported for non-RE alloys such as the Mg-Al/Zn-based systems, where the beneficial effect of Ca addition on precipitation strengthening has been demonstrated [18–21]. It has been commonly reported that the intermetallic compounds of Mg_2Ca and Al_2Ca form in the as-cast and heat-treated microstructures of Mg-Al-Ca-based alloys [12,22–27]. Interestingly, it has been observed that a small amount of Ca (< 0.5 wt.%) does not produce any new phases in the as-cast microstructure [18,25,27], and that Ca is contained in the $Mg_{17}Al_{12}$ phase, which leads to the enhanced thermal stability of the $Mg_{17}Al_{12}$ phase [18,25,26]. A minor Ca addition was reported to result in refined and more uniformly distributed Zn-enriched precipitates for an Mg-Zn alloy [19]. In the Mg-Zn-Ag-Ca-Zr alloy system, Ca atoms have been observed to co-segregate with Zn atoms to form clusters in the early pre-precipitation stage, and subsequently partition in the Zn-enriched precipitates [20]. In addition, the interaction between Ca and Zn solute atoms and its relation to GP zone formation were recently investigated with first-principles electronic structure methods [21].

To reduce the amount of RE elements in Mg-RE alloys while retaining or further improving the significant precipitation strengthening effect from RE-enriched precipitates, Ca may be considered a good candidate for Mg-RE alloy modification. There has, however, been only a limited number of investigations of the effect of Ca on RE-enriched precipitates [28]. An encouraging result was reported in a study of precipitation in an Mg-Nd-Y-Zr-Ca alloy, where Ca was observed to segregate in Nd- and Y-enriched β_1 precipitates [28]. This motivates a study to understand whether Ca also partitions into the metastable β''' and β' RE-enriched precipitates that are generally responsible for the significant precipitation strengthening observed in Mg-RE alloys.

In the current study, an Mg-RE alloy containing Ca (Mg-Nd-Y-Ca quaternary alloy) was investigated to explore the potential interaction of Ca with the RE elements, Nd and Y. The aging response and precipitate evolution of this quaternary alloy during a

200°C aging process were examined by microhardness tests and advanced microstructural characterization techniques including high-angle annular dark-field (HAADF) imaging in scanning transmission electron microscopy (STEM) and atom probe tomography (APT) reconstruction.

Materials and methods

An extruded bar with nominal composition Mg-2wt.%Nd-4wt.%Y-0.5wt.%Ca was provided by CanmetMATERIALS, Canada. The bar was extruded from the 85 mm cast billet to a final diameter of 15 mm at 530°C with argon atmosphere at a speed of 63.5 mm/min. The cast billet was solution heat treated at 530°C for 3 h before the extrusion. The composition for this alloy was measured by the inductively coupled plasma (ICP) method to be Mg-2.34Nd-4.12Y-0.58Ca in weight percentage (Mg-0.42Nd-1.19Y-0.37Ca in atomic percentage). Solution heat treatment at 520°C for 24 h was performed on the as-received extruded bar. Solution-treated samples were subsequently aged in an oil bath at 200°C. Each heat treatment step was followed by water quenching. The aging response was characterized by microhardness measurements, which were performed using a Vickers microhardness indenter with a load of 100 g and a dwell time of 15 s. The structure of precipitates which formed at different stages of the 200°C aging process was characterized using a JEOL 2100F transmission electron microscopy (TEM) operated at 200 kV in STEM-HAADF mode. Energy dispersive X-ray spectroscopy (EDS) analysis was performed on a Thermo Fisher Talos F200X TEM equipment operated at 200 kV with a Super-X Quad windowless EDS detector. APT data collection was performed on a Cameca LEAP 5000XR instrument. The laser-pulsing mode with a pulse energy of 50 pJ and a specimen temperature of 30 K was used. Visualization and evaluation of APT data were carried out using the Integrated Visualization and Analysis Software (IVAS) package. Both thin TEM foils and needle-like APT tips were prepared using the focused ion beam (FIB) lift-out technique on a Thermo Fisher Helios 650 dual-beam system. This allowed selections of grains that facilitate the observation of precipitates using the low index zone axis $<0001>$ Mg.

In addition, first-principles electronic structure calculations were performed to shed light on the segregation tendencies of the alloying elements, Nd, Y and Ca, to the different precipitate phases that form in the alloy of this study. Total energy calculations were performed using the PBE parameterization of the generalized gradient approximation to density functional theory as implemented in the Vienna ab-Initio Simulation

Package (VASP). The plane wave basis energy cut-off was set to 450 eV and a Γ -centered k-point mesh of $25 \times 25 \times 13$ was chosen for the HCP primitive cell. Meshes were scaled appropriately for larger supercells to maintain roughly the same density of k-points. A frozen core pseudopotential was used for Nd and Y, while the pseudopotentials for Mg and Ca had 8 and 10 valence electrons. Structures were relaxed with respect to all degrees of freedom. Symmetrically-distinct decorations of all the elements on the hcp crystal structure were generated with the Clusters Approach to Statistical Mechanics (CASM) code [29,30]. Formation energies were calculated relative to HCP Mg, FCC Ca and β'' (Mg_3Nd , Mg_3Y) according to

$$\Delta e_{\text{formation}}(\text{Mg}_a\text{Nd}_b\text{Y}_c\text{Ca}_d) = \frac{E_{\text{total}}(\text{Mg}_a\text{Nd}_b\text{Y}_c\text{Ca}_d) - be(\text{Mg}_3\text{Nd}) - ce(\text{Mg}_3\text{Y}) - de(\text{Ca}) - (a - 3b - 3c)e(\text{Mg})}{a + b + c + d}$$

where $\Delta e_{\text{formation}}(\text{Mg}_a\text{Nd}_b\text{Y}_c\text{Ca}_d)$ is the formation energy per atom of a structure containing Mg atoms, b Nd atoms, c Y atoms and d Ca atoms. $e(\text{Mg}_3\text{Nd})$, $e(\text{Mg}_3\text{Y})$, $e(\text{Ca})$ and $e(\text{Mg})$ are the energies per atom of β'' (Mg_3Nd , Mg_3Y), FCC Ca and HCP Mg, respectively.

Results and discussion

Figure 1 shows the aging response and precipitation evolution for the age-hardened Mg-Nd-Y-Ca quaternary alloy. As can be observed in Figure 1(a), the hardness gradually increases until it reaches a peak at 96 h, and then a gradual decrease can be observed. Compared to a ternary Mg-Nd-Y alloy (Mg-1.64 wt.%Nd-3.72 wt.%Y) also aged at 200°C [31], the average hardness was higher and a faster time to peak aging was observed in the current Ca-containing alloy. Figure 1(b–e) shows the precipitate configurations after different aging time periods at 200°C. At the very early aging stage (shorter than 2 h), no obvious precipitation was observed. With longer aging times, very fine metastable phases including GP zones, β''' and β' started to form (the crystallographic structures for these two precipitates have been described in detail in references [2,32]), as shown in Figure 1(b). As aging time increased, the β''' and β' precipitates grew, and fewer GP zones were observed. When the aging time reached 96 h (Figure 1(c)), clusters combining plate-shaped β''' precipitates and globular β' precipitates formed. This unique type of precipitation configuration, $\beta''' + \beta'$ clusters with a high number density, significantly increased the hardness and accounted for the aging

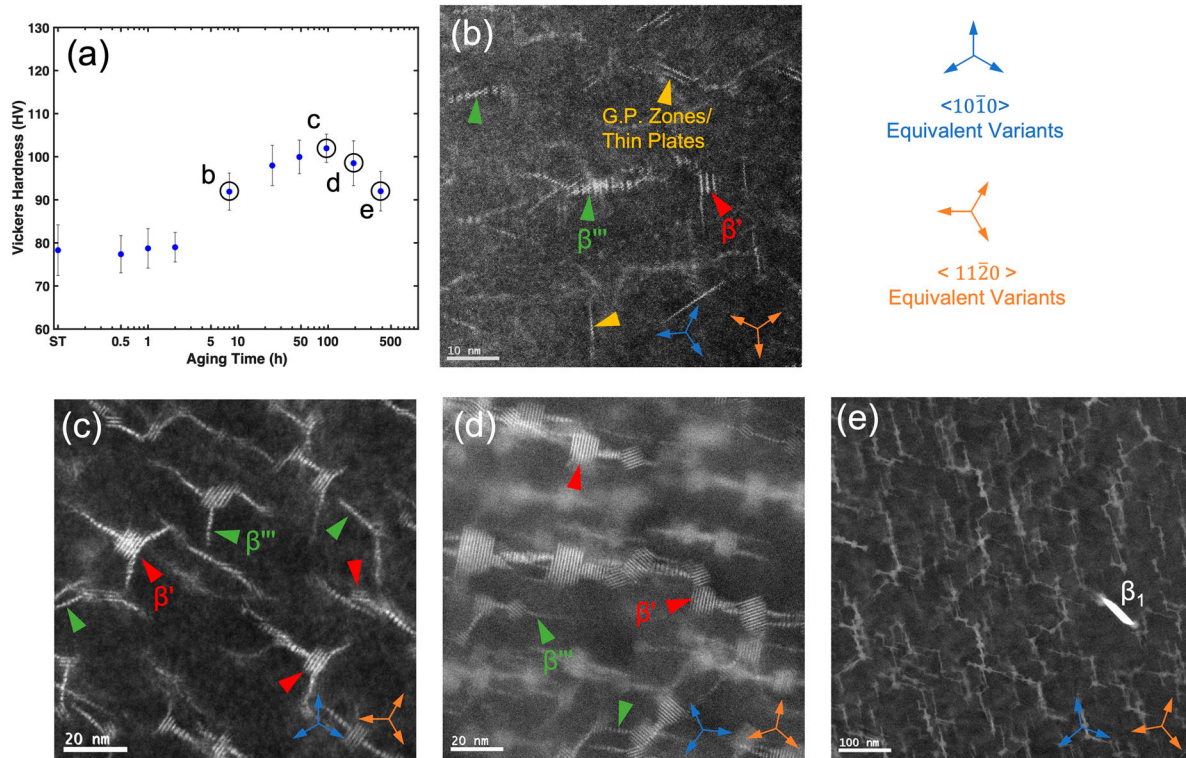


Figure 1. (a) Aging response of the investigated Mg-Nd-Y-Ca alloy at 200°C. Precipitation configurations at given aging times marked by black circles were characterized by STEM. (b)–(e) are STEM-HAADF images taken with $\langle 0001 \rangle$ Mg zone axis for aging conditions 200°C/8 h (under-aged), 200°C/96 h (peak-aged), 200°C/192 h and 200°C/384 h (over-aged).

peak. As the aging time was increased after the peak-aged condition, the $\beta''' + \beta'$ structure coarsened and the precipitate clusters grew such that a long chain-like structure connected by multiple β''' and β' precipitates formed (Figure 1(d,e)). After a long time of aging, plate-shaped β_1 precipitates were occasionally observed, as shown in Figure 1(e) for the over-aged condition (384 h at 200°C). The precipitation sequence observed in this Ca-containing alloy was very similar to the sequence previously observed in the ternary Mg-Nd-Y alloy without Ca [33]. This indicates that Ca addition induces no change in the precipitating phases or precipitation sequence.

In order to further understand the role that Ca plays in precipitation behavior, the elemental distribution of Ca in the matrix and precipitates was characterized using STEM-EDS and APT techniques. Figure 2 presents the EDS mapping results on an area containing the β''' and β' precipitate clusters produced at the aging condition

200°C/192 h and elemental line analysis across the precipitates for these two phases. The elemental line analysis from five precipitates of each phase was merged to improve the understanding of the results. As clearly exhibited in the elemental maps in Figure 2(b,c), rare earth elements Nd and Y are concentrated in both β''' and β' phases. By comparing Figure 2(e,f), a higher Nd concentration at the profile peak can be observed in the β''' precipitates than in β' . Interestingly, the mapping result in Figure 2(d) clearly shows that Ca is enriched in both the β''' and β' phases along with the rare earth elements Nd and Y. Since the Ca concentration is lower than that of Nd and Y, finer scale insets are shown in Figure 2(e,f) to show the Ca distribution within the matrix and the precipitates. The line analysis indicates that the average concentration of Ca in the β''' and β' precipitates increased to approximately ~ 0.4 at.%. Table 1 presents information about the composition of the β''' and β' phases extracted from this EDS analysis.

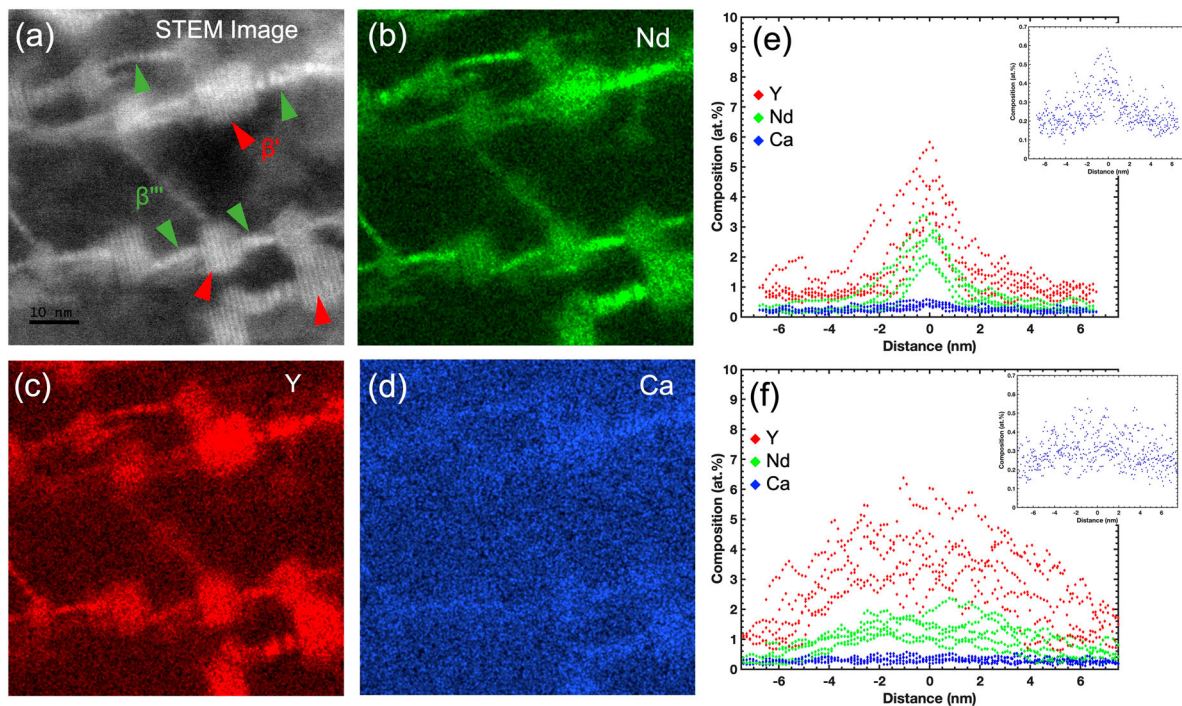


Figure 2. EDS mapping of an area containing β''' and β' precipitates with $\langle 0001 \rangle$ Mg zone axis. (a) Area image taken in STEM mode; (b)–(d) EDS mapping results for three alloying elements Nd, Y and Ca; (e) Line analysis merged from five β''' precipitates, which were positioned around the center of each line and (f) Line analysis merged from five β' precipitates, which were positioned around the center of each line. Note: inserts are provided showing Ca concentration across precipitate centers on a finer scale.

Table 1. Compositions of alloying elements for precipitates at aging condition 200°C/192 h extracted from STEM-EDS and APT analyses.

Composition (at.%)	Alloy (ICP)	Bulk	STEM-EDS			Bulk	APT		
			Matrix	β'''	β'		Matrix	β'''	β'
Nd	0.42	0.34 ± 0.04	0.10 ± 0.03	2.29 ± 0.56	1.37 ± 0.39	0.49 ± 0.09	0.04 ± 0.12	3.97 ± 1.73	3.76 ± 2.44
Y	1.19	1.31 ± 0.17	0.61 ± 0.07	3.79 ± 0.99	3.76 ± 1.04	1.64 ± 0.31	0.60 ± 0.49	5.40 ± 2.39	9.27 ± 3.82
Ca	0.37	0.04 ± 0.01	0.02 ± 0.01	0.40 ± 0.08	0.33 ± 0.09	0.09 ± 0.07	0.04 ± 0.11	0.10 ± 0.20	0.28 ± 0.65

Note: Standard deviation is used as the error margin.

The composition of the bulk and matrix was analyzed using the EDS spectrum collected from the entire area of interest or the matrix-only region. The composition of the precipitates was quantified from the line profile considering the size and shape of each phase. The β''' composition was determined as the average concentration over the region from -0.52 nm to $+0.52$ nm in the merged profile in Figure 2(e), while the β' composition was determined as the average concentration over the region from -2.08 nm to $+2.08$ nm in the merged profile in Figure 2(f). As shown in Table 1, the Ca concentration for the bulk was much lower than the overall alloy composition, which is attributed to compositional inhomogeneities that were not completely removed by the solution treatment [34]. Using the bulk and matrix composition as a reference, this semi-quantitative composition analysis for the β''' and β' phases indicates a partitioning of Nd, Y and Ca to the precipitates. However, it is difficult to determine whether Ca has a higher

concentration in β''' or in β' since the average Ca concentrations in the two phases were very similar and the scatter in EDS data was relatively high.

Atom probe tomography (APT) analysis was also performed to confirm the elemental distribution. Figure 3 shows the APT reconstruction and analysis results revealing the precipitate concentration at the aging condition $200^\circ\text{C}/192$ h. It can clearly be seen that, compared with the matrix, both of β''' and β' have increased concentrations of Nd and Y (Figure 3(a–c)). A higher concentration of Y than Nd in both phases was observed, with the ratio of Nb to Y being large in the β''' precipitates, as is evident in Figure 3(e,f). This is consistent with the EDS results shown in Figure 2. The partitioning of Ca to both phases was also observed in the APT results (Figure 3(d)). It should be noted that the composition profiles for β''' and β' in Figure 3(e,f) merged the one-dimension (cylinder shape) analysis results across three precipitates for each phase because significant statistical

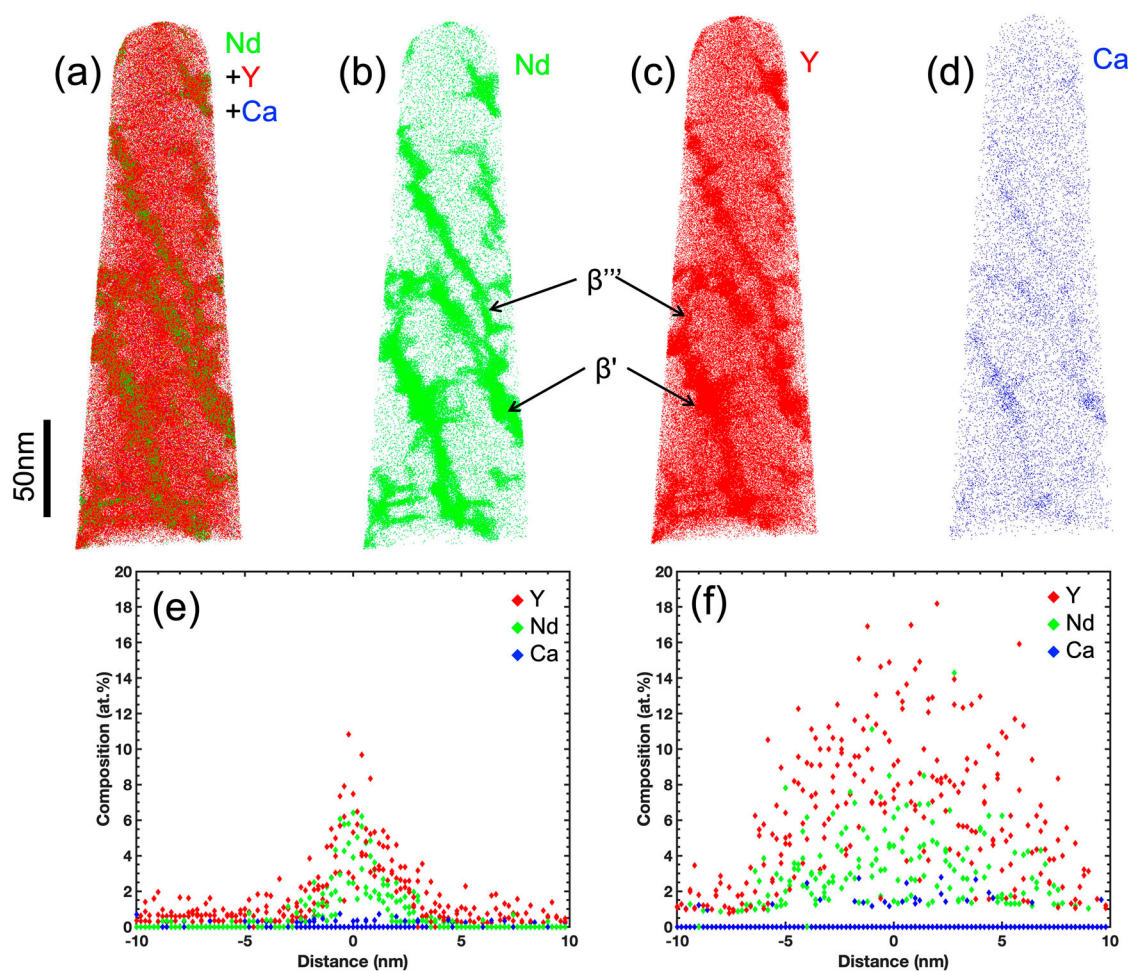


Figure 3. APT reconstruction and analysis for the precipitation concentration at the aging condition $200^\circ\text{C}/192$ h. (a)–(d) show the distribution of alloying elements ((a) Nd, Y and Ca atoms overlaid; (b) Nd atoms only; (c) Y atoms only; (d) Ca atoms only). (e) and (f) are the line analysis to extract the composition feature of β''' (e) and β' (f) by placing a cylinder across the precipitate. Information from three precipitates for each phase were merged.

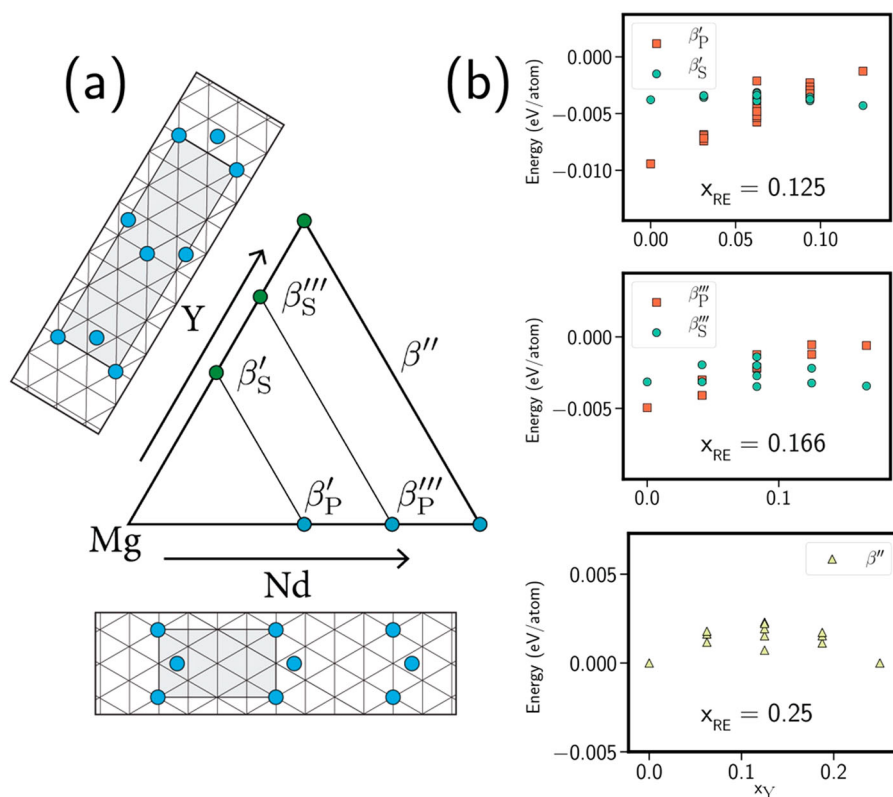


Figure 4. (a) 0 K metastable phase diagram of the Mg-Nd-Y ternary system. (b) Formation energies of orderings along constant rare-earth compositions. The concentration variable x_{RE} refers to the atomic fraction of the total amount of RE elements Nd and Y.

scatter was also found in APT results. This is similar to the EDS results in Figure 2(e,f). The composition information for the β''' and β' phases extracted from this APT analysis are also shown in Table 1. Consistent with the EDS analysis, the bulk Ca concentration for the APT tip was lower than the overall alloy composition presumably due to compositional inhomogeneity. The lift-out locations of both the APT tip and EDS analysis area were close to each other and within the same grain. The β''' composition from APT was determined as the average in a region from -0.6 nm to $+0.6$ nm in the merged profile in Figure 3(e), while the β' composition was determined as the average in a region from -2.0 nm to $+2.0$ nm in the merged profile in Figure 3(f). The partitioning of Ca along with Nd and Y in both β''' and β' phases is also reflected in Table 1. It should be mentioned that although both EDS and APT analyses presented the same elemental distribution trends, the concentration of Nd and Y in precipitates detected by APT is higher than that measured by STEM-EDS. Compared to the APT analysis, which is determined in a three-dimensional volume, the STEM-EDS analysis also interrogates a volume of material that is overlaid with the matrix where a lower concentration of Nd and Y would be expected. This would thus have the effect of lowering the measured apparent concentrations within the precipitate

regions. Regardless of this difference, the findings from both STEM-EDS and APT analyses confirm that Ca partitions to the RE-enriched precipitates, not only to the β_1 phase [28] but also to other metastable strengthening phases such as β''' and β' . This indicates the potential of Ca to promote the precipitation of coherent phases and enhance the corresponding strengthening effect for Mg-RE alloys.

In addition to the experimental study, first-principles electronic structure calculations were used to elucidate the thermodynamic driving forces for the distribution of Nd and Y and dilute Ca additions to the metastable β' and β''' precipitates, which are superlattice orderings on the HCP crystal structure. The orderings of β' and β''' precipitation phases that were observed in this study are illustrated in detail in reference [32]. The β' label refers to two distinct orderings, referred to as β'_P and β'_S that can be generated by periodically stacking zig-zag rows of RE atoms, which prefer to align in phase and out of phase, respectively. Both β' orderings have orthorhombic symmetry, however, the unit cell of the β'_P variant is primitive, while the orthorhombic unit cell of the β'_S variant is centered on one pair of faces. The β''' orderings (β'''_P and β'''_S) refer to a family of hybrid orderings that combine features of β' (either β'_P or β'_S) and β'' (i.e. DO19) [2,32]. In both the β'''_P and β'''_S structures, the

RE atoms arrange as zig-zags and strips of hexagons when viewed along the HCP c -axis [32].

Figure 4(a) shows the zero Kelvin metastable phase diagram in the ternary Mg-Nd-Y alloy. The β'''_P orderings are predicted to be stable along the Mg-Nd binary, while the family of β'''_S orderings is stable along the Mg-Y axis. No orderings are found to be stable at ternary compositions. Figure 4(b) shows the formation energies of orderings on β' , β''' and β'' families along lines of constant rare-earth composition. The replacement of Nb with Y in the β'_P -Mg₇(Nd_{1-x}Y_x) structure (corresponding to a total RE composition of $x_{RE} = 0.125$) results in an almost linear increase in formation energy with respect to x . Surprisingly the formation energies vary only slightly with the nature of ordering at a particular composition x . An almost linear variation of formation energies as a function of concentration, independent of ordering, suggests ideal solution behavior over the sublattice sites of β'_P that are being alloyed with Nd and Y. The free energy along the pseudobinary Nd-Y axis of β'_P -Mg₇(Nd_{1-x}Y_x) can, therefore, be described with an ideal-solution model, where mixing is entropically favored over the RE-sublattice. Similarly, the formation energies of structures where Y is replaced with Nd in β'_S also vary almost linearly with concentration and are more or less independent of the precise ordering of the two species, suggesting again ideal-solution-like behavior over the RE-sublattice sites of β'_S . A similar trend was found to persist at higher rare-earth compositions. The formation energies of orderings of Nd and Y in the β'' -Mg₃(Nd_{1-x}Y_x) structure show a very small positive enthalpy of mixing relative to β'' -Mg₃Nd and β'' -Mg₃Y. The positive mixing energies, however, are so small that they will be overcome by the ideal solution entropy at typical annealing temperatures. This indicates that this phase is likely also a complete solid solution along the pseudobinary composition axis x of β'' -Mg₃(Nd_{1-x}Y_x) at the elevated temperatures that are relevant for the precipitation aging of this alloy. Our calculations show that each individual family of β''' structures can be treated as a distinct phase with well-defined free energy that varies smoothly between the free energies of their Nd-rich and Y-rich orderings. Therefore, it is not surprising that, in our experimental characterization, small amounts of Y are found in the β''' precipitate, and a certain amount of Nd is observed in the β' precipitate since the rare-earth atoms are predicted to behave like a solid solution in each individual precipitate [32].

Calculations have shown that formation energies alone are not sufficient to rationalize experimentally observed orderings and consideration of misfit strains is also necessary for Mg-RE alloys [2,32]. The various β' and β''' orderings have very different misfit strains

with respect to the Mg HCP matrix phase. This leads to a strong dependence of the precipitate shape on the particular ordering within the precipitate [32]. The early RE alloying elements, {La, Ce, Pr, Nd, Pm and Sm} prefer β'''_P ordering and misfit strain arguments suggest that these alloys will form thin plate-like precipitates [32]. The late RE alloying elements, {Tb, Dy, Ho, Er, Tm, Lu, Sc and Y}, however, prefer β'_S ordering and should form more globular precipitates [32]. Therefore, a ternary solid solution (Mg-Nd-Y) that is age hardened is expected to phase separate into an Nd-rich β''' precipitate (β'''_P ordering) and a Y-rich β' precipitate (β'_S ordering). The Nd-rich β''' precipitate is expected to be plate-like due to the coherency strain of this precipitate relative to the matrix [2,3,32,35], while the Y-rich β' precipitate is more globular since it has lower transformation strains [4,32]. These predictions are in excellent agreement with experimental measurements for the ternary alloy without Ca [31–33,36,37] and the current study with Ca addition.

The addition of a large amount of Ca to an Mg alloy typically causes the precipitation of the equilibrium Laves phase (Mg₂Ca). The experimental results observed in the current study show that the small addition of Ca partitions preferentially to the precipitate phases rather than forming Mg₂Ca. To analyze the precise location of this Ca partitioning, first-principles calculations were performed to investigate the energetics of dilute Ca additions

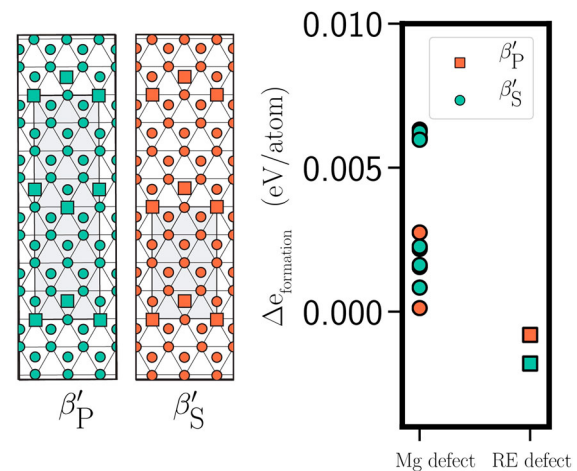


Figure 5. Formation energies of dilute Ca defects in the β' structures. Formation energies of configurations where Ca replaces Mg (denoted Mg defect) and RE (denoted RE defect) are calculated in a 96-atom supercell of the two β' structures. The circular markers are used to denote configurations where a single magnesium atom was replaced by Ca, while the square markers represent the energies of structures with a single RE atom being replaced by Ca. Points shown with the orange color correspond to defects in the β'_P ordering, while the green markers correspond to defects in the β'_S ordering.

to the β' precipitates. Defect formation energies were calculated in a cell of 96 atoms by replacing each symmetrically distinct site in the β'_S and β'_P orderings with Ca. Figure 5 shows the formation energies of these dilute substitutions relative to FCC Ca, HCP Mg, β'_S (Mg₇Y) and β'_P (Mg₇Nd). Replacing the Mg atoms with Ca leads to positive or slightly positive formation energy in both structures. However, replacing the rare-earth atoms with Ca leads to negative formation energy. This suggests that Ca partitions to rare-earth sublattices in the precipitate phase. Ca, Nd and Y have a much larger atomic radius than Mg. The lower energy produced by replacing rare-earth atoms is likely because of the similar size of Ca, Nd and Y with all three elements being significantly bigger than Mg.

Summary

A systematic characterization of the precipitation behavior during the aging process at 200°C was conducted for a Ca-containing Mg-RE alloy with the nominal composition Mg-2wt.%Nd-4wt.%Y-0.5wt.%Ca. High-resolution scanning transmission electron microscopy revealed the precipitation evolution for this alloy system. Compared to the Mg-Nd-Y ternary alloy system, very similar precipitating phases and evolution sequence was observed in this Ca-containing quaternary alloy system. A clustered combination of β''' and β' precipitates was observed for the peak aging condition at 200°C. Both STEM-EDS and APT characterization showed that Ca partitions to β''' and β' metastable precipitate phases. The effect of dilute Ca additions on the precipitates was investigated by first-principles electronic structure calculations. It is suggested that Ca partitions to rare-earth sublattice in the precipitate phase. These findings indicate the beneficial effect of Ca for promoting precipitation in Mg-RE alloys and enhanced precipitation strengthening. This suggests the possibility for use of Ca as an alternative element to replace a portion of the RE elements in Mg-RE alloys and expand the application of this important alloy system.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

The experimental data supporting this study are available on Materials Commons at <https://doi.org/10.13011/m3-c2rm-rc21>.

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