Formation of High-Strength β' Precipitates in Mg-RE Alloys: The Role of the Mg/ β'' Interfacial Instability

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Abstract

Aging reactions in Mg-RE alloys strengthen magnesium, due to the formation of metastable β'' and β' precipitates. We use first-principles calculations to critically assess binary Mg-RE (RE=Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Y) aging reactions, metastable phases and interfacial energy. We find the following: (i) our calculations correctly predict the formation of different variants of β' phases for Mg-RE systems across the RE series. (ii) Surprisingly, the Mg/ β'' prismatic interfaces are unstable, with a negative interfacial energy. (iii) This interfacial instability implies the existence of a more energetically stable compound than β'' , which we show to be the β' precipitate. By exposing the link between Mg/ β'' prismatic interfaces and the β' structure, we propose that β' phase formation is due to an energetic preference for an ordered arrangement of Mg and β'' . (iv) Our Mg/ β'' interfacial energy results also indicate that atomically-thin β'' planar G.P. zones can form as a precursor to β' precipitation.

Keywords: magnesium alloys, rare-earths, precipitation strengthening, density functional theory, interfacial energy

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1. Introduction

There is a significant demand for structural magnesium alloys due to their low density compared to aluminum and steel [1]. While two thirds as dense as aluminum, [1] magnesium alloys typically have lower yield strength than their aluminum counterparts, a fact that has inhibited more widespread use of Mg in automotive and aerospace applications. Therefore, a large amount of research is being directed at Mg alloy strengthening [1–6]. Mg-rare earth (RE) alloys, either binary or with additional alloying elements, are of particular interest due to the high yield strengths achieved through precipitation hardening [7–19]. Consequently, their microstructure, aging response and mechanical properties have been extensively documented experimentally [e.g., see [11, 14–17, 20–36].] In these systems, peak strength in the aged alloy often corresponds to the formation of β'' and β' precipitates [14, 16, 17, 32–36], which form prismatic plates and are coherent or semi-coherent with the Mg matrix.

Understanding the exact precipitation sequence and the fundamental driving forces giving rise to precipitation sequences is a critical part of the effort to intelligently design high-strength Mg alloys. Precipitate morphology is controlled by the strain and interfacial energy between the precipitate and the matrix, in addition to kinetic factors, e.g. diffusion [37]. Uncovering the controlling factor in the precipitate morphology may aid in designing alloy compositions, possibly without expensive RE elements, that yield a specific, tailored precipitate morphology. For example, in our previous work [38], we found that the formation of prismatic plate shaped precipitates observed experimentally in Mg-RE alloys can be attributed to the elastic strain energy anisotropy between basal and prismatic planes, indicating potential RE replacements should exhibit such an anisotropy. In this work, we investigate Mg/ β'' interfacial energies, another important contribution which furthers our understanding of the precipitate morphology and elucidates the relation between the β'' and β' precipitates. The combination of anisotropic strain- and interfacial-energies dictates the morphology of the β'' precipitates. Precipitates may adopt an equilibrium morphology

dictated by the Wulff construction [39, 40] (when interfacial energies are dominant), thin plates [37] (when strain energy is dominant) or they may undergo a size-dependent change in morphology [41–45] (dictated by chemical interfacial energy at smaller length scales and strain energy at larger length scales). Quantifying *both* energetic contributions, strain and interfacial energies, thus provides a more complete understanding of the size- (and implicitly time-) dependent precipitate morphology in the Mg matrix.

Even though Mg-RE aging reactions have been extensively studied, some disagreement on the nature of the precipitates still exists, particularly in the early stages of the aging reaction. The disagreement centers around whether or not β'' forms in Mg-RE systems. The various precipitation reactions are summarized in Table 1. In some studies, the Mg-(Ce, Nd, Pr) systems are observed to first precipitate out G.P. zones, followed by a β'' phase in the D0₁₉ structure, then a β' phase [12, 46–49]. The β'' (D0₁₉) structure, which is a superstructure of HCP (i.e., a decoration of Mg and RE atoms on an HCP lattice), has dimensions $a_{D0_{19}}=2a_{Mg}$ and $c_{D0_{19}}=c_{Mg}$ and Mg₃RE composition, while the β' phase has a Mg₇RE composition. More recent work, however, using high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM) [50] reported the formation of Nd pillars in a Mg-2.5 at.%Nd alloy but no β'' . Another recent study, [51], also using HAADF-STEM, reported the formation of planar GP-zones followed by the β' phase. The structure and morphology of the β' phase has been less controversial, since it has been observed by most of the previous work [46–49, 51] having a Mg₇Nd composition in a body-centered orthorhombic structure with dimensions $a_{\beta'}=2a_{Mg}$, $b_{\beta'}=2\sqrt{3}a_{Mg}$ and $c_{\beta'}=c_{Mg}$. For reasons we explain below, we refer to this phase as β' -short.

Reports on the Mg-Gd aging reactions, also summarized in Table 1, disagree about whether or not the β'' -D0₁₉ phase forms [32, 36, 9, 52, 53]. TEM studies [32, 36, 9] report the formation of a β'' -D0₁₉ phase in the earliest stages of precipitation. On the other hand, also using TEM, D0₁₉ short range ordering was observed in Mg matrix immediately following solution treatment, followed by the formation of the β' phase [52]. Similarly, using HAADF-STEM and high

resolution transmission electron microscopy (HRTEM), Nishijima et al. [53] report the formation of local, short-range order followed by, and temporally overlapping with, the formation of the β' phase. This β' phase, similarly to that reported in Mg-Nd, is also body-centered orthorhombic with composition Mg₇Gd, but with different dimensions: $a_{\beta'}=2a_{Mg}$, $b_{\beta'}=4\sqrt{3}a_{Mg}$ and $c_{\beta'}=c_{Mg}$. As the $b_{\beta'}$ lattice parameter for this β' structure is twice as long as the β' structure reported in the Mg-Nd system above, we will refer to this structure as β' -long. Both β' structures, short and long, have been experimentally resolved [51, 53] and we discuss the relationship between them in the results section below. Knowing whether the β'' -D0₁₉ phase forms and how it gives rise to the primary strengthener β' is critical to well-controlled precipitation hardening in Mg alloys.

[Table 1 about here.]

First-principles calculations provide a valuable tool for studying precipitate formation and stability in Mg-RE systems. Density functional theory (DFT) calculations lend themselves to such an investigation for two reasons. First, it is possible to calculate quantities that may be difficult to measure experimentally, such as precipitate/matrix interfacial energy. Second, quantifying the two competing energetic contributions, strain and interfacial energy, provides an understanding of *why* certain precipitates form, and the morphology they adopt. First-principles calculations have provided valuable insight into precipitation in cubic, e.g. Al, alloys [see refs. [54–62], for example], as well as defects in Mg [63–69], and phase stability in Mg-RE-(Zn) systems [38, 70–74]. First-principles calculations have also been used to calculate short-range order in solid solutions, and critically analyze the connection (or lack thereof) between SRO and the underlying low-temperature long-range order [75–79].

In this work, we use DFT calculations to elucidate the energetic competition between the metastable precipitate phases in Mg-RE alloys. We calculate the formation energies of the β'' , β' -short and β' -long phases across a series of Mg-RE systems and the interfacial energies of β'' /Mg [0001] and [10 $\bar{1}$ 0] interfaces.

We find a surprising result: all the prismatic and some of the basal β''/Mg interfacial energies are negative. Because of negative interfacial energies, we predict that Mg/β'' interfaces are energetically favored to spontaneously form throughout the matrix, leading to ordered planes of Mg and β'' . In other words, the Mg/β'' interfacial instability indicates that certain ordered arrangements of Mg and β'' units are more energetically stable than $\text{Mg}+\beta''$ phase separation. We show, through DFT calculations, that the energetically favored arrangement of Mg and β'' planes gives rise to β' phase formation. The Mg/β'' interfacial instability, therefore, reveals the formation of prismatic β'' planes to be a *precursor* to the formation of β' precipitates.

2. Methodology

2.1. DFT Calculations

We perform first-principles DFT calculations using the Vienna Ab initio Simulation Package (VASP) [80, 81] and projector augmented wave potentials [82]. We utilized the PBE parameterization of the generalized gradient approximation (GGA-PBE) [83] for all calculations. All structures were relaxed with respect to all cell-internal and -external degrees of freedom at an energy cutoff of 350 eV. For each structure, gamma-centered k-point meshes were constructed to achieve at least 10,000 k-points per reciprocal atom. While RE metals have historically been difficult to model theoretically [84, 85], including the f-electrons in the core has been shown to be a viable and reasonably accurate approach, producing the correct ground state structure, energetic stability and elastic constants for RE intermetallic compounds [71, 55, 86–92]. Throughout this investigation, we will use the frozen potentials for all the calculations involving f-electron containing lanthanides.

2.2. Interfacial Energy Calculations

To calculate the energies of Mg/β'' coherent interfaces, we construct supercells of bulk of Mg and β'' . The formation energy of the supercell is defined as

the difference between the total energy of the supercell and the energy of the isolated bulk constituents, Mg and β'' in this case [93]:

$$\Delta E_f[\text{interface}] = E[\text{interfacial supercell}] - (E[\text{Mg}_{\text{bulk}}] + E[\beta''_{\text{bulk}}]). \quad (1)$$

If the two phases are perfectly lattice matched, the supercell formation energy will contain the contribution due to interfacial energy. On the other hand, the supercell formation energy in lattice-mismatched systems contains, in addition to the interfacial energy contribution, the energy penalty of straining the two phases so they are coherently matched across the interface. The supercell formation energy, $\Delta E_f[\text{supercell}]$, can be decomposed into these two contributions as [94, 42]:

$$\Delta E_f[\text{interface}] = \underbrace{N\Delta E_{CS}(\hat{k}, x)}_{\text{strain}} + \underbrace{2A\sigma}_{\text{chemical}}, \quad (2)$$

where the total strain and chemical energy components are labeled. In Eq. 2 ΔE_{CS} is the coherency strain energy per atom, N the total number of atoms in the supercell, A the area of the interface and σ the interfacial energy. (We note that $\Delta E_f[\text{supercell}]$ is the formation energy per supercell, not per atom.) To calculate the interfacial energy of forming the interface in a Mg/ β'' supercell, we must remove the strain energy contribution, $\Delta E_{CS}(\hat{k}, x)$, from the supercell formation energy. $\Delta E_{CS}(\hat{k}, x)$ is the strain energy penalty of deforming bulk Mg and Mg₃RE, with compositions 1-x and x, respectively, to maintain a coherent interface perpendicular to a direction $\hat{k}$ and is direction- ($\hat{k}$) and composition- (x) dependent. We have previously calculated [38], from first-principles, the coherency strain energy per atom, $\Delta E_{CS}(\hat{k}, x)$, for Mg-Mg₃RE (β'') systems in the basal ($\hat{k}=[0001]$) and prismatic ($\hat{k}=[10\bar{1}0]$) directions for the entire composition range from x=0 (pure Mg) to x=1 ("pure" Mg₃RE).

To elucidate the behavior of the interfacial formation energy in Eq. 2, we show a schematic of the formation energy of an X_qY_q supercell as a function of supercell size in Fig. 1. The supercell formation energy per atom,

$\Delta E_f[\text{supercell}]/N$, approaches a constant value, that of the coherency strain energy per atom, ΔE_{CS} , as N approaches infinity. The difference between $\Delta E_f[\text{supercell}]/N$ and ΔE_{CS} is the interfacial energy divided by N , a value that approaches zero as N approaches infinity. To get the interfacial energy, one must multiply $2A\sigma/N$ by N , resulting in a constant value as the supercell becomes infinitely large. In this work, X is Mg and Y is β'' . A unit of β'' has eight atoms: six Mg and two RE atoms.

[Figure 1 about here.]

For all Mg- β'' systems calculated, we performed convergence tests with respect to supercell size for the basal and prismatic interfacial energies. In Fig. 2, we show the supercell convergence calculations for the $[0001]$ and $[10\bar{1}0]$ interfacial energies in the Mg-Mg₃Ce (β'') system, where the interfacial energies are converged to about 1 mJ/m² for supercells of 80 atoms. The basal interfacial energy in this system has a value of 26 mJ/m², while the prismatic interfacial energy has a value of -25 mJ/m². For all systems calculated, 80 atom supercells had converged interfacial energies.

[Figure 2 about here.]

3. Results and Discussion

3.1. Energetic Stability

The formation energy of a phase is determined by the energy of that phase relative to the composition-weighted energies of its constituent elements. To explore the energetic stability of the β'' , β' -short, and β' -long phases, we calculate the formation energy per atom of each phase, ΔE_f , using:

$$\Delta E_{f/atom}[\text{Mg}_x\text{RE}_{1-x}] = E[\text{Mg}_x\text{RE}_{1-x}] - (xE[\text{Mg}] + (1-x)E[\text{RE}]). \quad (3)$$

In this equation, x is the atomic fraction of Mg, and $E[A]$ is the total energy per atom of structure A. The formation energies of the β' and β'' precipitates are

shown in Fig. 3, where we calculate the formation energies of β' -short, β' -long structures and $\text{Mg}+\beta''$ two-phase mixtures for the following systems: Mg-RE (RE=Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, Y). Since the β' and β'' phases have different RE compositions, Mg_7RE and Mg_3RE respectively, we compare the formation energy of $\frac{1}{2}\text{Mg}+\frac{1}{8}\text{Mg}_3\text{RE}$ two-phase mixture to the formation energies of $\frac{1}{8}\text{Mg}_7\text{RE}$ β' phases. We find that the $\text{Mg}+\beta''$ two phase mixture is higher in energy than either β' phase, consistent with experimental observation of β'' formation as a precursor to β' precipitation [32, 36, 12, 46–49]. We also find the β' -short phase to be more stable for the early REs, Mg-(Ce, Pr, Nd, Sm) phases, while the β' -long is more stable for the later REs, Mg-(Tb, Dy, Ho, Er, Tm, Y) systems. For the Mg-Gd system, the two phases are practically degenerate in energy. The change down the RE series from β' -short to β' -long is supported by experiment: β' -short is observed in Mg-Nd [51], while β' -long is observed in Mg-Gd [53, 13], Mg-Dy [95] and Mg-Y [96], in agreement with our calculations.

[Figure 3 about here.]

3.2. Mg/β'' Interfacial Energies

The Mg/β'' [0001] and $[10\bar{1}0]$ interfacial energies are shown in Fig. 4 for the Mg-RE (RE=Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y) binary systems. The basal interfacial energies are positive for the Mg-(Ce, Pr, Nd) binary systems, about zero for the Mg-Sm system and *negative* for the Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y) systems. *Also, the prismatic interfacial energies are negative for all systems calculated.* These negative interfacial energies are unexpected, as they indicate an interfacial instability in the Mg/β'' two-phase system. Negative interfacial energies indicate that a prismatic interface between β'' and Mg will lower the energy of the entire system, leading to the formation of another, more stable compound in the Mg matrix, which is also a decoration of the HCP lattice. Below, we show this more stable HCP superstructure to be the β' precipitate. With their positive basal energy and negative prismatic interfacial

energies, the Mg-(Ce, Pr, Nd) systems can lower their energy by maximizing Mg/ β'' prismatic interfaces and minimizing Mg/ β'' basal interfaces, thereby adopting prismatic plate morphologies that are exactly one unit cell thick in the basal plane, as shown in Figure 5. These atomically-thin plates are indeed observed by Saito et al. during the early stages of aging in Mg-Nd [51] and Mg-Ce [97] and are referred to as planar GP zones. On the other hand, since both basal and prismatic interfaces are negative for Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y) systems, β'' phase or GP zone formation is energetically unstable. We hypothesize that these systems lower their energy by maximizing both their basal and prismatic Mg/ β'' interface, β'' units may prefer to form in small clusters, surrounded by Mg matrix, and lacking any long-range ordering. These hypotheses are consistent with recent experimental observations in Mg-Gd [53] and Mg-Dy [95] systems, but disagree with other reports of β'' phases in Mg, as indicated in the introduction. Our interfacial calculations, summarized in Table 2, show β'' phase instability in all systems calculated, predicting instead prismatic planar GP zones in Mg-(Ce, Pr, Nd) systems and the possibility of small clusters of β'' in Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y) systems.

[Figure 4 about here.]

[Figure 5 about here.]

[Table 2 about here.]

3.3. Exploring the Mg/ β'' instability: The emergence of the β' structure

Since negative prismatic Mg/ β'' interfacial energies indicate the formation of a more stable phase in Mg-(Ce, Nd, Pr) systems, we now attempt to discover that phase by calculating the stability of different ordered arrangements of Mg and Mg₃Nd (β'') units in the Mg-Nd system. In Fig. 6 we plot the stability of Mg/ β'' ordered arrangements, with respect to pure Mg and β'' , as a function of composition. Three types of ordered arrangements are included in Fig. 6: (Mg₈)_q(β'')_q, (Mg₈)_q(β'')₁ and (Mg₈)₁(β'')_q structures. The (Mg₈)_q(β'')_q structures, where a unit of Mg₈ is an 8-atom supercell of pure Mg with the same

shape as β'' , are the supercells used for the interfacial energy convergence calculation and are all at a composition of 12.5 at.% Nd (50% β''). The $(\text{Mg}_8)_q(\beta'')_1$ ($q = 0.5, 1, 2, 3, 4, 5$) and $(\text{Mg}_8)_1(\beta'')_q$ ($q = 1, 2, 3, 4$) structures are ordered arrangements containing units of Mg_8 and β'' at compositions ranging from 4.2 at.% to 20 at.% Nd. As an example, we show one such arrangement in Fig. 7: $(\beta'')_1(\text{Mg}_8)_1$. The parabolic curve shown in Fig. 6 is that of the coherent phase separation (CPS) between Mg and β'' , defined as the strain energy penalty of forming a two-phase region of Mg and β'' , excluding interfacial energy contributions. This contribution is the coherency strain, which we calculated previously, [Eq. 2 in [38]]. Also included is the incoherent phase separation (IPS) curve, which is the line connecting pure Mg to pure β'' . The energy of coherent phase separation is given by the CPS curve, while the IPS line denotes the stability of incoherent Mg- β'' phase-separation containing no strain components. If the Mg-Mg₃Nd (β'') system preferred a coherent two-phase Mg+ β'' mixture, all the $(\text{Mg}_8)_q(\beta'')_q$ structures would have a formation energy at or above the Mg- β'' CPS curve. Instead, the $(\text{Mg}_8)_q(\beta'')_q$ supercells all have formation energies *below* the CPS curve, again indicating that the Mg/ β'' interfacial energy is *negative*. The Mg/ β'' prismatic energies in Fig. 6 follow the behavior of the blue curve, negative interfacial energy, in Fig. 1. The $(\text{Mg}_8)_1(\beta'')_1$ energies are lowest for $q=1$ and approach the coherency strain energy, CPS curve in Fig. 6, for $q=\infty$. The negative interfacial energy counteracts the positive strain energy contribution of forming a coherent interface, given by Eq. 2; in fact, the $(\text{Mg}_8)_1(\beta'')_1$ interfacial energy is about 10 meV *below the IPS phase separation line*, thus rendering even incoherent Mg- β'' phase separation energetically unstable. Clearly, the β'' phase is unstable and another ordered compound must be lower in energy between the Mg and Mg₃RE (β'') compositions.

The $(\text{Mg}_8)_1(\beta'')_1$ structure is the lowest energy arrangement of Mg+ β'' that we find. Interestingly, this arrangement forms *exactly* the β' -short structure observed by Saito et al. [51] in Mg-Nd, as shown in Fig. 7. Our calculations predict that it is this specific stacking of β'' units and Mg which is most favorable of those studied, giving rise to the β' -short structure that is observed at peak

hardness in aged Mg-Nd alloys [51]. This structure is more stable than $\text{Mg}+\beta''$ for all Mg-RE systems calculated, as we have shown in Fig. 3. The formation of GP zones which are exactly one unit cell thick in the basal plane can now be understood as a precursor to β' -short formation. Our results, therefore, reconcile the seeming discrepancy of experimental observations by showing that the so-called β'' phase is simply the initial phase of β' -short formation, which arises as a result of the energetic preference to form alternating layers of GP zones and Mg_8 .

[Figure 6 about here.]

[Figure 7 about here.]

The β' -long phase observed in Mg-Gd [53, 13], Mg-Dy [95] and Mg-Y [96] is also constructed of β'' and Mg_8 units, as shown in Fig. ???. The β' -long structure is $(\beta'')_1(\text{Mg}_8)_1(\beta'')_R(\text{Mg}_8)_1$, where $(\beta'')_R$ is a β'' unit rotated 90 degrees around the [0001] axis with respect to the other. We note here that the Mg/β'' and the $\text{Mg}/\text{R-}\beta''$ interfaces are equivalent.

Our results now provide an explanation for the negative interfacial energies between β'' and Mg. The β' phases, both long and short, precipitate after β'' in the aging reactions outlined in Table 1, meaning the β' phases are lower in energy than two-phase regions of $\text{Mg}+\beta''$. The planar β'' GP zones, experimentally reported in [51], are energetically favored to form an alternating, layered arrangement with Mg_8 planes sandwiched in between β'' zones, giving rise to β' . Since this arrangement maximizes Mg/β'' prismatic interfaces, it is only favored if that interface has a negative interfacial energy. Those β'' planar GP zones can now be viewed as a precursor to the formation of the metastable primary strengthener in Mg-Nd, β' .

4. Conclusions

We have used first-principles calculations to investigate and explain the experimentally reported Mg-RE metastable precipitates. We find that:

1. DFT calculations accurately predict energetic stability of three competing metastable structures: β'' , β' -short, and β' -long. We find β'' to be less stable than either β' phase for all Mg-RE systems calculated. Further, we accurately predict the structure competition between β' -short and β' -long, finding β' -short to be energetically preferred for the early REs, while β' -long is preferred for the later REs, in agreement with experimental observations.

2. The Mg/ β'' prismatic interfaces are not stable. This instability indicates the energetic preference for ordering between units of β'' and Mg. For the early REs, the basal interfaces are stable, allowing for planar GP zones at the earliest stages of aging in Mg-RE (RE=Ce, Pr, Nd) systems. For the later REs, the basal interfaces are unstable, precluding GP zone formation, but allowing for β'' clusters at the earliest stage of the aging reaction. These results are consistent with the most recent experimental investigations of Mg-RE binary systems.

3. Structures made of ordered units of (Mg₈) and (β'') naturally give rise to the β' -short and β' -long phases. It is precisely the negative interfacial energies between Mg and β'' that stabilize the β' phases with respect to Mg+ β'' two phase regions. The negative Mg/ β'' interfacial energies, then, form the crucial link between the formation of β'' clusters early in the aging reactions and the subsequent formation of the β' phase.

Our first-principles calculations shed light on the competing energetic contributions that lead to the formation of the β' phases and the close connection between the β'' structures and later β' phases. Understanding these links helps us grasp the mechanisms by which the Mg-RE aging reactions proceed, which in turn lead to an improved understanding of the strengthening behavior of RE precipitates in Mg.

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Table 1: Early stages of Mg-RE aging reactions, listing experimentally observed reactions up to β' . Questions marks denote disagreement.

Alloying Element	Precipitation Reaction
Ce [12], Nd [46–49], Pr [98]	$\text{Mg}_{ssss} \rightarrow \text{G.P. zones} \rightarrow \beta'' (\text{Mg}_3\text{RE D0}_{19}) (?) \rightarrow \beta' (\text{c-base centered orthorhombic, CBCO, Mg}_7\text{RE})$
Nd [51]	$\text{Mg}_{ssss} \rightarrow \text{G.P. zones} \rightarrow \beta' (\text{CBCO Mg}_7\text{RE})$
Gd [32, 36, 9]	$\text{Mg}_{ssss} \rightarrow \beta'' (\text{Mg}_3\text{RE D0}_{19}) (?) \rightarrow \beta' (\text{CBCO Mg}_7\text{RE})$
Gd [53, 52]	$\text{Mg}_{ssss} \rightarrow \text{Mg}_3\text{Gd-D0}_{19} \text{ clusters } (?) \rightarrow \beta' (\text{CBCO Mg}_7\text{RE})$
Y, Tb, Dy, Ho, Er, Tm, Lu [99]	$\text{Mg}_{ssss} \rightarrow \beta' (\text{CBCO, Mg}_7\text{RE})$
Y, Tb, Dy [95], Ho, Er [100], Tm [101], Lu [52]	$\text{Mg}_{ssss} \rightarrow \text{Mg}_3\text{RE-D0}_{19} \text{ clusters } (?) \rightarrow \beta' (\text{CBCO Mg}_7\text{RE})$

Interfacial energy components	Implication	Systems	Predicted shape
Positive basal and prismatic energies	stable basal and prismatic interfaces	none	3-dimensional precipitates
Positive basal, negative prismatic energies	stable basal interfaces, unstable prismatic interfaces	Mg-(Ce, Nd, Pr)	prismatic, planar GP zones
Negative basal and prismatic energies	unstable basal and prismatic interfaces	Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y)	cluster of β'' in Mg

Table 2: Summary of DFT interfacial energy results. We predict the formation of prismatic planar GP zones of β'' in Mg-(Ce, Nd, Pr) and β'' clusters in Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y). Our results in both cases are consistent with experiment [51, 53]

Schematic Decomposition of Interfacial and Strain Energies

Figure 1: A schematic of the formation energy per atom of an A_qB_q supercell of A and B phases. The dashed line denotes the coherency strain energy per atom of bringing the two lattice-mismatched systems together. The second contribution in the supercell formation energy is the interfacial energy, assumed here to also be a positive quantity, allowing for A-B phase separation.

Figure 2: Interfacial energy supercell convergence for the Mg/Mg₃Ce (β'') [0001] and $[10\bar{1}0]$ interfaces. The prismatic interfacial energy between Mg and β'' is negative, indicating the stability of another ordered compound, β' .

Figure 3: Formation energies of: two phase regions of $4Mg+Mg_3RE$ β'' , β' -long structures (Mg_7RE) and β' -short structures (Mg_7RE). The $Mg+\beta''$ two phase region is less stable than the β' phases, as expected since β' phases are observed to appear later in the aging reaction [Table 1]. The two β' structures and the two-phase region are in energetic competition, with the β' -short structure being more stable for the early RE systems (Ce, Pr, Nd, Sm), and the β' -long structure more stable for the later REs: (Tb, Dy, Ho, Er, Tm, Y). For the Mg-Gd system, the two β' structures are degenerate in energy.

Figure 4: Mg/ β'' interfacial energies. The basal interfacial energies are positive for the early RE systems, Mg-(Ce, Pr, Nd) and negative for the later REs, Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y). The prismatic interfacial energies are negative for all systems. These results preclude the formation of β'' as a separate phase, but predict the formation of GP zones in Mg-(Ce, Pr, Nd) systems and β'' short-range ordered clusters in Mg-(Gd, Tb, Dy, Ho, Er, Tm, Y).

Figure 5: A projection of the β'' G.P. zone, enveloped by Mg, onto the basal plane. The negative prismatic and positive basal interfacial energies in Mg-(Ce, Pr, Nd) systems favor the formation of prismatic β'' plates that are exactly one unit cell thick in the basal plane, as indicated by the dashed lines. The primitive unit cell of the β'' phase, the $\text{Mg}_3\text{RE D0}_{19}$ structure, is outlined by the solid black lines.

Figure 6: The stability of $(\text{Mg}_8)_q(\beta'')_p$ prismatic coherent interfaces (blue points) with respect to Mg and β'' reference states (red points). The coherent phase separation (CPS) curve is indicated in red and the incoherent phase separation (IPS) line is the zero line. The $(\text{Mg}_8)_q(\beta'')_p$ ($p, q=1, 2, 3, 4, 5$) structures have formation energies that are below the CPS line, indicating negative interfacial energies and prohibiting coherent phase separation of Mg and β'' . The $(\text{Mg}_8)_1(\beta'')_1$ ordered compound is more stable than the IPS line, indicating an energetic preference to order in that stoichiometry, this structure is the β' -short structure observed experimentally [51], as shown in Fig. 7. The $(\text{Mg}_8)_1(\beta'')_1$ structure is also shown.

Figure 7: The β'' precipitates projected onto the basal plane: (a) The β' -short structure [51] is outlined in thicker black lines from the supercell of the $(\beta'')_1(\text{Mg}_8)_1$ structure. (b) The β' -long structure [13] is outlined in thicker black lines from the supercell of the $(\beta'')_1(\text{Mg}_8)_1(\beta'')_R(\text{Mg}_8)_1$ structure. The $(\beta'')_R$ unit is a β'' structure that is rotated 90 degrees about the $[0001]$ axis with respect to the first β'' cell.