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# Formation of high-strength $\beta'$ precipitates in Mg–RE alloys: The role of the Mg/$\beta''$ interfacial instability

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**Abstract**—Aging reactions in Mg–RE alloys strengthen magnesium, due to the formation of metastable $\beta''$ and $\beta'$ 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 $\beta'$ phases for Mg–RE systems across the RE series. (ii) Surprisingly, the Mg/$\beta''$ prismatic interfaces are unstable, with a negative interfacial energy. (iii) This interfacial instability implies the existence of a more energetically stable compound than $\beta''$, which we show to be the $\beta'$ precipitate. By exposing the link between Mg/$\beta''$ prismatic interfaces and the $\beta'$ structure, we propose that $\beta'$ phase formation is due to an energetic preference for an ordered arrangement of Mg and $\beta''$. (iv) Our Mg/$\beta''$ interfacial energy results also indicate that atomically thin $\beta''$ planar Guinier–Preston zones can form as a precursor to $\beta'$ precipitation.

*Keywords:* Magnesium alloys; Rare-earths; Precipitation strengthening; Density functional theory; Interfacial energy

## 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. [11,14–17,20–36]). In these systems, peak strength in the aged alloy often corresponds to the formation of $\beta''$ and $\beta'$ precipitates [14,16,17,32–36], which form prismatic plates and are coherent or semicoherent 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 that potential RE replacements should exhibit such an anisotropy. In this work, we investigate Mg/$\beta''$ interfacial energies, another important contribution which furthers our understanding of the precipitate morphology and elucidates the relation between the $\beta''$ and $\beta'$ precipitates. The combination of anisotropic strain energy and interfacial energy dictates the morphology of the $\beta''$ 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 concerning the early stages of the aging reaction. The disagreement centers around

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whether or not $\beta''$ 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 Guinier–Preston (GP) zones, followed by a $\beta''$ phase in the $D0_{19}$ structure, then a $\beta'$ phase [12,46–49]. The $\beta''$ ($D0_{19}$) structure, which is a superstructure of hexagonal-close packed (hcp) form (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 $Mg_3RE$ composition, while the $\beta'$ phase has a $Mg_7RE$ 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 $\beta''$. Another recent study [51], also using HAADF-STEM, reported the formation of planar GP zones followed by the $\beta'$ phase. The structure and morphology of the $\beta'$ phase has been less controversial, since it has been observed by most of the previous work [46–49,51] having a $Mg_7Nd$ 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 $\beta'$-short.

Reports on the Mg–Gd aging reactions, also summarized in Table 1, disagree about whether or not the $\beta''$-$D0_{19}$ phase forms [9,32,36,52,53]. TEM studies [9,32,36] report the formation of a $\beta''$-$D0_{19}$ phase in the earliest stages of precipitation. On the other hand, also using TEM, $D0_{19}$ short-range ordering was observed in Mg matrix immediately following solution treatment, followed by the formation of the $\beta'$ 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 $\beta'$ phase. This $\beta'$ phase, similar to that reported in Mg–Nd, is also body-centered orthorhombic with composition $Mg_7Gd$, 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 $\beta'$ structure is twice as long as the $\beta'$ structure reported in the Mg–Nd system above, we will refer to this structure as $\beta'$-long. Both $\beta'$ 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 $\beta''$-$D0_{19}$ phase forms and how it gives rise to the primary strengthener $\beta'$ is critical to well-controlled precipitation hardening in Mg alloys.

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 (e.g. [54–62]), 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 short-range order 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 $\beta''$, $\beta'$-short and $\beta'$-long phases across a series of Mg–RE systems and the interfacial energies of $\beta''$/Mg $[0001]$ and $[10\bar{1}0]$ interfaces. We find a surprising result: all the prismatic and some of the basal $\beta''$/Mg interfacial energies are negative. Because of negative interfacial energies, we predict that Mg/$\beta''$ interfaces are energetically favored to spontaneously form throughout the matrix, leading to ordered planes of Mg and $\beta''$. In other words, the Mg/$\beta''$ interfacial instability indicates that certain ordered arrangements of Mg and $\beta''$ units are more energetically stable than Mg+$\beta''$ phase separation. We show, through DFT calculations, that the energetically favored arrangement of Mg and $\beta''$ planes gives rise to $\beta'$ phase formation. The Mg/$\beta''$ interfacial instability, therefore, reveals the formation of prismatic $\beta''$ planes to be a precursor to the formation of $\beta'$ 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 [55,71,86–92]. 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/$\beta''$ coherent interfaces, we construct supercells of bulk of Mg and $\beta''$. 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 $\beta''$ 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, $\Delta E_f$[supercell], can be decomposed into these two contributions as [42,94]: