A unified description of ordering in HCP Mg-RE alloys

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Abstract

High throughput first-principles calculations were employed to unravel the thermodynamic stability of two sets of hierarchical phases, β_P''' and β_S''' , in Mg-RE (rare-earth) alloys. The β_P''' orderings (with compositions greater than $x_{RE} = 0.125$) are predicted to form in the Mg-{La,Ce,Pr,Nd,Pm,Sm} binary alloys, thus explaining experimental observations of RE atoms arranged as hexagonal rings in these alloys. Mg-{Sc,Y,Tb,Dy,Ho,Er,Tm,Lu} alloys are predicted to form β_S' ($x_{RE} = 0.125$) precipitates without hexagonal ring arrangements. The calculated misfit strains are used to infer the qualitative shapes of the precipitates and their relative aspect ratios. High aspect-ratio precipitates may be formed using alloying elements that encourage the formation of β_P''' . The predictions in this study can be used to inform alloy design of precipitation strengthened magnesium alloys.

Keywords: Magnesium alloys, Rare-Earth, Precipitation, First-principles, Thermodynamics

1. Introduction

Magnesium alloys are promising materials to aid in the “lightweighting” of many structural parts in automotive applications[1–6]. However, commercial use of these alloys is limited by their poor mechanical strength, creep resistance and corrosion properties[6]. Nevertheless, new alloy chemistries[7] and processing techniques[8] have led to advances that may make magnesium alloys commercially viable.

Magnesium alloys can be strengthened by the formation of ordered precipitates from a disordered solid solution during an aging heat treatment. This is especially true upon alloying with rare-earth (RE) elements, which leads to the formation of metastable precipitates that significantly improve mechanical properties[6]. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) studies have revealed a wide variety of HCP-based ordered phases in Mg-RE alloys[6, 9–14]. Though the precise ordering varies depending on the alloying element, the observed precipitates are found to contain RE atoms arranged as either zig-zags or hexagons when viewed along the [0001] direction. Recently, a family of orderings, labeled β''' , was discovered to form in the Mg-Nd binary alloy[14]. The β''' phases span a composition between $x_{Nd} = 0.125$ and $x_{Nd} = 0.25$ with Nd atoms arranged as zig-zags and hexagons. Though precipitates with similar RE orderings have been observed in other Mg-RE alloys, their exact crystal structure and thermodynamic stability has remained an open question.

Here we investigate the thermodynamic stability of hierarchical phases (β'''), similar to those reported in the Mg-Nd system, in all first-row binary Mg-RE alloys. A survey of the experimental literature reveals that all HCP-based metastable ordered phases in Mg-RE alloys observed to date belong to one of two families of hierarchical β''' phases. First-principles calculations predict that β''' phases are thermodynamically stable in all first row Mg-RE binary alloys when restricting the analysis to metastable HCP orderings. Furthermore, calculations of misfit strains allow us to rationalize experimentally observed precipitate orientations, shapes and compositions in the well studied binary Mg-{Nd,Y,Gd,Sm} alloys. We find that the presence or absence of hexagonal RE arrangements in a metastable precipitate is highly correlated with their tendency to decrease or increase misfit strains. The first-principles results of this study enable the formulation of design principles with which the properties of Mg-RE alloys can be further improved through precipitation strengthening.

2. Crystallographic Preliminaries

Magnesium alloys containing dilute additions of rare-earth elements show a rich variety of orderings on the HCP crystal structure when undergoing an aging heat treatment. Two classes of orderings are discussed in the literature[6]: β' and β'' . The first class, β' , actually refers to two different orderings generated by periodically stacking zig-zag rows (fig. 1a) of RE atoms as illustrated in fig. 1b and fig. 1c. Individual zig-zag rows are made of columns of RE atoms that extend along the [0001] direction of the underlying HCP crystal structure. Depending on the RE addition, the zig-zag rows prefer to align in

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phase as in fig. 1b or out of phase as in fig. 1c. Both orderings have orthorhombic symmetry, however, the unit cell of the variant of fig. 1b is primitive while that of the variant in fig. 1c is not primitive but has a Bravais lattice with an orthorhombic unit cell that is centered on one pair of faces. To distinguish between the two variants of β' , we will label the variant of fig. 1b as β'_P , where P signifies primitive, and the variant of fig. 1c as β'_S , where the subscript S is used as it is the Pearson symbol for a Bravais lattice that is centered on one pair of faces. The two variants, referred to collectively as β' , have a RE composition of $x_{\text{RE}} = 0.125$, corresponding to a stoichiometry of Mg_7RE .

The second class of orderings, β'' , is shown in fig. 1d and corresponds to D0_{19} , with the RE atoms forming a honeycomb pattern when viewed along the $[0001]$ direction of the underlying HCP crystal structure. D0_{19} has a composition of $x_{\text{RE}} = 0.25$ with stoichiometry Mg_3RE . While precipitates having D0_{19} ordering never appear in Mg-RE alloys[14, 15], isolated hexagons or linear strips of hexagons are observed in metastable precipitates of several Mg-RE alloys. The β'' label has, therefore, loosely been used to refer to these hexagonal features.

Figure 1: Schematic crystal structures of important metastable HCP orderings observed in Mg-RE alloys. All crystal structures are viewed along the $[0001]$ direction. Atoms shown on the triangular lattice are part of the “A” layer of the HCP crystal structure, while atoms at the center of the triangles belong to the “B” layer. Only RE atoms are shown for clarity. The figures show (a) zig-zag rows of RE atoms along the $[2\bar{1}10]$ direction that form the building blocks of the β' orderings, (b) β'_P (Mg_7RE), (c) β'_S (Mg_7RE), and (d) β'' (Mg_3RE)

The experimental literature shows a wide variety of β' -like orderings that have been referred to as “defected” due to the presence of strips of hexagons interleaving the zig-zag rows that characterize β' . It was recently shown that the β' -like phases containing hexagons in Mg-Nd alloys are in fact not defect structures, but rather belong to a family of stable hybrid orderings that can be con-

structed by combining β'_P and β'' [14]. A hierarchy of hybrid orderings can be generated by a “branching” algorithm[46]–[14, 16] whereby new orderings are constructed by combining two parent orderings. The starting parents are β'_P and β'' . Every new generation of orderings is formed by combining an ordering in the previous generation with one of the parent orderings. In the Mg-Nd alloy, these hybrid orderings were collectively referred to as β''' . Since the algorithm is inductive, the seed generation (or 0th generation) is formed by the parent phases, β'_P and β'' . Every ordering is given a unique name, determined by the number of parent orderings that was used to construct it and the order in which they were combined. In this convention, the parent orderings β'_P and β'' are denoted by 0 and 1 respectively. An ordering denoted by β'''_{021} , for example, is shown in fig. 2a and is generated by combining two β'_P units with one β'' unit.

While the family of hybrid β''' orderings was first identified in the Mg-Nd binary alloy, which is derived from β'_P , the observation of β'_S in several Mg-RE alloys[9–11] suggests the possibility that a family of hybrid phases that combine β'_S with β'' may also occur. The first few generations of the hierarchy of orderings generated algorithmically by combining β'_S with β'' is illustrated in Figure 2b. To distinguish the two possible families of hybrid orderings, we again use a subscript, with β'''_P referring to orderings generated by combining β'_P and β'' and β'''_S referring to orderings generated by combining β'_S and β'' . Both families have RE compositions that range between $x_{\text{RE}} = 0.125$ and $x_{\text{RE}} = 0.25$. We will use β''' to refer to the hybrid phases collectively. The family of phases includes the parent ordering used to generate them, however, for convenience and ease of understanding we will refer to the parent phases (β' and β'') as distinct orderings.

The experimentally observed coherent HCP precipitates in binary Mg-RE alloys, while only carefully characterized in a few systems such as the Mg- $\{\text{Nd}, \text{Gd}, \text{Y}, \text{Sm}\}$ binaries, can all be classified as belonging to one of the two β''' hierarchies of orderings. For instance, in the Mg-Nd alloy, recent work[13, 14, 17] has shown the formation of the β'_P orderings having compositions around $x_{\text{Nd}} \approx 0.15$. HAADF-STEM micrographs for this alloy show long plate-like precipitates containing hexagonal rows of Nd atoms interleaved between zig-zag rows, similar to the orderings in fig. 2a. Similar features are observed in the Mg-Sm alloy. A study by Nishijima *et al.*[12] on a Mg-Sm alloy reports on the formation of precipitates in which Sm atoms are also arranged as zig-zag rows and hexagons. The authors of the study noted that the precipitates consist of randomly arranged hexagons and zig-zags. In fact, the crystal structure prototype proposed by Nishijima *et al.*[12] as a representative ordering is identical to that of β'''_{01} (fig. 3). Interestingly, precipitates with rare-earth atoms arranged similar to β'''_P have also been reported to form in a quaternary magnesium alloy containing additions of Sm, Zn and Zr[18]. In gadolinium containing alloys the ordering is more complex. Large precipitates having β'_S orderings are

Figure 2: Hierarchy of structures (β''') that can be generated by combining β' and β'' along the $[010]_{\beta'}$ direction. In the schematic crystal structures, the regions that correspond to β' are colored yellow and the regions that correspond to β'' are colored gray. The first two generations of (a) β_P''' and (b) β_S''' are shown.

connected by thinner plate-like precipitates in which Gd atoms are arranged as hexagons and zig-zags. Although the precise orderings within the connecting regions has remained unnamed, the HAADF-STEM images of Nishijima *et al.*[9, 10] suggest β_P''' -like ordering. In contrast to the Mg-Nd, Mg-Sm and Mg-Gd alloys, the orderings in the Mg-Y alloy show no evidence of RE atoms arranged as hexagons. Instead, the precipitates have near perfect β_S' ordering with a composition of $x_Y = 0.125$.

Figure 3: Schematic illustration of the crystal structure of the $\beta_P''' \langle 01 \rangle$ ordering. This is identical to the crystal structure prototype proposed by Nishijima *et al.*[12] for the metastable precipitate in the Mg-Sm binary alloy.

In summary, all metastable HCP-based precipitates in Mg-RE alloys that have been experimentally observed so far belong to one of two β''' hierarchies of orderings. While

this classification provides a convenient framework with which to describe and compare precipitates in Mg-RE alloys, there are a number of questions that remain to be addressed. It is not clear, for example, if the hybrid orderings should be viewed as defective structures or as distinct phases that are energetically stable at low temperature in the absence of entropy. Furthermore, some alloys such as Mg-{Nd,Sm} form β''' orderings with $x_{RE} > 0.125$ while others such as Mg-Y form stoichiometric β_S' without any hexagonal RE arrangements. Experimental evidence suggests that precipitate shape is correlated to RE ordering and chemistry. The precipitates in Mg-{Nd,Sm}, for example, are plate-like in appearance while those in Mg-Y are more equiaxed. Clarifying these phenomena at a fundamental level will enable the formulation of design principles to guide the development of new Mg alloy chemistries that further increase strength.

3. Methods

3.1. Computational Methodology

We analyzed metastable phase stability in all first-row Mg-RE binary alloys by calculating the formation energies of the first three generations of β_P''' , first two generations of β_S''' and $\beta_S''' \langle 0^2 1^2 \rangle$ orderings from first principles. Total energies of each ordering ~~was~~^{were} calculated with density functional theory (DFT)[19] using the *Vienna ab-initio simulation package* (VASP)[20–24] and the

projector augmented wave (PAW) method. DFT calculations were performed within the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA)[25, 26] for the exchange-correlation functional. A cutoff energy of 450 eV was found to be sufficient to ensure a converged plane wave basis set. A Γ -centered k-point mesh of $25 \times 25 \times 13$ was chosen for the HCP primitive cell, and was scaled appropriately for larger supercells to maintain a roughly constant k-point density. The magnesium pseudopotential included the $2p$ levels among the valence. Frozen core potentials were used for all RE elements as these have been shown to replicate the ground states and elastic properties of rare-earth intermetallic compounds[27–31][28–32].

All formation energies were calculated relative to pure magnesium in the HCP structure and the β'' (D0₁₉) ordering having a stoichiometry of Mg₃RE. The formation energy (ΔE_f) of an arbitrary configuration containing N_{Mg} atoms of magnesium, and N_{RE} atoms of the rare-earth element can be written as:

$$\Delta E_f = \frac{1}{N} \left(E - (N_{\text{Mg}} - 3N_{\text{RE}})E_{\text{Mg}}^{\text{HCP}} - N_{\text{RE}}E_{\text{Mg}_3\text{RE}}^{\beta''} \right) \quad (1)$$

where E is the total energy of the ordering calculated with DFT, N is the total number of atoms, and $E_{\text{Mg}}^{\text{HCP}}$ and $E_{\text{Mg}_3\text{RE}}^{\beta''}$ are the total energies (per atom) of HCP-magnesium and Mg₃RE in the β'' (D0₁₉) ordering. The CASM software package was used to setup and automate the first-principles calculations[33].

3.2. Calculating transformation strains

Precipitates are formed coherently within the α -Mg matrix during age hardening. As a result their transformation strains relative to the matrix will play a crucial role in determining precipitate shape and relative phase stability among different orderings. The stress-free transformation strains can be calculated directly with DFT. The β' , β'' and β''' phases are superlattice orderings on HCP. In the absence of misfit strains, the supercell vectors, $\vec{A}_o$, $\vec{B}_o$ and $\vec{C}_o$, are integer linear combinations of the HCP Mg primitive unit cell vectors. However, rarely do ordered phases have lattice parameters that are identical to the undecorated crystal structure of the matrix phase within which they precipitate. When not constrained by coherency stresses of a surrounding matrix, the equilibrium supercell lattice vectors of the ordered phase adopt values that in general differ from $\vec{A}_o$, $\vec{B}_o$ and $\vec{C}_o$.

The deformation gradient, $\mathbf{F}$, relates the relaxed lattice vectors of an ordered phase, $\vec{A}$, $\vec{B}$ and $\vec{C}$, to the unrelaxed lattice vectors, $\vec{A}_o$, $\vec{B}_o$ and $\vec{C}_o$ according to:

$$\mathbf{S} = \mathbf{F}\mathbf{P} \quad (2)$$

where $\mathbf{S}$, $\mathbf{F}$ and $\mathbf{P}$ are 3×3 matrices with $\mathbf{P} = [\vec{A}_o, \vec{B}_o, \vec{C}_o]$ and $\mathbf{S} = [\vec{A}, \vec{B}, \vec{C}]$. In general, misfit deformations are not limited to just stretching of the lattice, but can also involve

rigid rotations as well. A common metric of deformation that is invariant to rigid rotations is the Green-Lagrange strain ($\mathbf{E}$) written in terms of $\mathbf{F}$ according to:

$$\mathbf{E} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}) \quad (3)$$

where $\mathbf{I}$ is the 3×3 identity matrix. When the strains are small, the components of $\mathbf{E}$ (E_{ij}) reduce to the familiar infinitesimal strains ϵ_{ij} .

In defining strain, it is necessary to specify the orientation of the Cartesian coordinate system in relation to the crystallographic axes. The β' and β''' phases have orthorhombic unit cells. Their three lattice vectors are conveniently oriented such that the A-axis ($[2\bar{1}\bar{1}0]$) is parallel to x , B ($[10\bar{1}0]$) is parallel to y and C($[0001]$) is parallel to z , as illustrated in fig. 4. The direction in parenthesis represent the directions in the HCP crystal that are along the orthorhombic axes. This choice of orientation of the Cartesian coordinate system along with the symmetry of the ordered phases ensures that there are no shear strains. Furthermore, the diagonal components of the Green-Lagrange strain metric (E_{11}, E_{22}, E_{33}) are directly related to the strains along the A, B, and C axis of these orderings.

Figure 4: Orientation of the β' orderings relative to the Cartesian coordinate system that is used to calculate the transformation strain. β''' orderings are oriented in a similar way, although they typically have longer unit cells along the $[010]$ direction.

4. Results

We restrict our focus to the metastable orderings that can form on the HCP crystal structure of dilute Mg-RE alloys. We therefore exclude the more stable phases that are slower to nucleate and grow during typical heat treatments and only consider the thermodynamic stability of the β' , β''' and β'' orderings. The formation energy of each ordering is referenced relative to that of Mg and β'' (Mg₃RE). The convex hull applied to calculated formation energies of different orderings determines thermodynamic phase stability at zero Kelvin. This is equivalent to

Figure 5: Calculated formation energies of β_P''' (yellow squares) and β_S''' (blue circles) orderings in the Mg-Nd alloy

Figure 8: Calculated formation energies of β_P''' (yellow squares) and β_S''' (blue circles) orderings in the Mg-Gd alloy

Figure 6: Calculated formation energies of β_P''' (yellow squares) and β_S''' (blue circles) orderings in the Mg-Sm alloy

Figure 7: Calculated formation energies of β_P''' (yellow squares) and β_S''' (blue circles) orderings in the Mg-Y alloy

the common tangent construction applied to free energies at finite temperature.

Figure 5 shows the formation energies of the β_P''' (yellow squares) and β_S''' (blue circles) orderings in the Mg-Nd alloy, as calculated with DFT at 0K. The [formation energies are calculated under boundary conditions of zero stress, corresponding to a “stress-free” state. This is the relevant boundary condition to evaluate incoherent phase stability. The \$\beta_P'''\$ orderings are predicted to be more stable than the \$\beta_S'''\$ hierarchy. In fact, all the \$\beta_P'''\$ orderings are \(to within numerical accuracy of our calculations\), on the Mg-Nd metastable convex hull. Figure 5 also shows that the \$\beta_S'''\$ orderings are not expected to form in this alloy. A rigorous study of the finite temperature free energies\[14\], using the cluster expansion method, showed that the phase stability predicted at zero Kelvin remains qualitatively unchanged at finite temperatures\[14\]. Thus, the calculated formation energies of fig. 5 suggest a two-phase coexistence between a dilute HCP disordered solid solution and \$\beta_P'\$ when aging dilute Mg-Nd alloys. \[Figures 6 to 8 show the formation energies calculated from first-principles for the Mg-{Sm,Y,Gd} binary alloys.\]\(#\) The formation energies of fig. 6 shows that the Mg-Sm system is similar to the Mg-Nd alloy, also having the \$\beta_P'''\$ orderings on the metastable HCP convex hull. The Mg-Y alloy in contrast, shows the \$\beta_S'''\$ orderings to be on the metastable convex hull \(Figure 7\), having formation energies that are lower than the \$\beta_P'''\$ hierarchy.](#)

Inspection of the formation energies of all first-row Mg-RE alloys summarized in appendix A shows that most of them are similar to either the Mg-Nd or the Mg-Y alloys. We exclude Eu and Yb from the analysis as these are well known to deviate from the rest of the lanthanide group elements[30]. The Mg-{La, Ce, Pr, Nd, Pm, Sm} alloys have β_P''' orderings on their metastable convex hulls, while alloys containing {Sc, Y, Tb, Dy, Ho, Er, Tm, Lu} have the β_S''' orderings on their hull. Furthermore, the formation energy plots of figs. 5 to 7 and appendix A, clearly show that β_S''' orderings are energetically unfavorable in systems

where β_P''' orderings are stable, and vice-versa.

The relative stability among the β''' orderings are also closely correlated to the relative stabilities between the two β' variants, β_P' and β_S' . This is evident in fig. 9, which plots the difference in energy, $\Delta E_{\beta'}^{\text{stab}}$ (per atom), between β_P' and β_S' for each Mg-RE alloy. A positive value of $\Delta E_{\beta'}^{\text{stab}}$ indicates that β_S' is more stable, and a negative value indicates that β_P' is more stable. As is clear in fig. 9, the early rare-earth elements, such as {La, Ce, Pr, Nd, Pm, Sm} prefer β_P' ordering to that of β_S' . Appendix A shows that all these binary alloys also have β_P''' orderings on their convex hull. The later rare-earth elements prefer the β_S' ordering. These binary alloys also have the corresponding β_S''' orderings on their convex hulls.

The Mg-Gd alloy system is an outlier amongst all the Mg-RE alloys. The calculated formation energies of Mg-Gd in fig. 8 show that the β_S''' and β_P''' hierarchies are energetically degenerate, to within the numerical accuracy of our calculations. This degeneracy is consistent with the prediction that β_P' and β_S' have almost identical formation energies (fig. 9). These results suggest that both hierarchies of orderings may even co-exist during the aging heat treatment in Mg-Gd alloys.

Figure 9: The difference in energy ($\Delta E_{\beta'}^{\text{stab}}$) between β_P' and β_S' for all Mg-RE alloys

Figure 10: The transformation strains as a function of neodymium composition (x_{Nd}) in the Mg-Nd alloy system for: (a) β_P''' and (b) β_S''' . The E_{11} component of the transformation strain is colored in red, E_{22} in cyan and E_{33} in purple. Lines are drawn as guides to show the linear dependence of the misfit strains on composition.

Figure 11: The transformation strains as a function of yttrium composition (x_Y) in the Mg-Y alloy system for: (a) β_P''' and (b) β_S''' . The E_{11} component of the transformation strain is colored in red, E_{22} in cyan and E_{33} in purple. Lines are drawn as guides to show the linear dependence of the misfit strains on composition.

Misfit strains are also important in understanding and rationalizing coherent precipitation. Figure 10 shows the misfit strains of the β_P''' (Figure 10a) and β_S''' (Figure 10b) orderings as a function of composition in the Mg-Nd alloy, with E_{11} labelled in red, E_{22} in cyan and E_{33} in purple. Figure 10 clearly shows that the components of the transformation strain of both the β_P''' and β_S''' orderings vary linearly with composition. Similar linear variations of misfit strains as a function of RE composition are predicted for all Mg-RE binary alloys as is evident in fig. 11 for the Mg-Y alloy and in appendix A for the other Mg-RE alloys.

Since the misfit strains for the β''' orderings vary linearly between those of β' at $x_{\text{RE}} = 0.125$ and β'' at $x_{\text{RE}} = 0.25$, it is informative to inspect trends in transformation strains across the lanthanide group for β' and β'' orderings. Misfit strains for the β' and β'' orderings as a function of RE chemistry are shown in fig. 12. The strain component along the C-axis (E_{33}) is very close to zero for the three orderings. With the exception of E_{22} for β_P' , all other strain components are positive, and decrease in magnitude across the group. A comparison of fig. 12a and fig. 12b suggests that the misfits are determined largely by the ordering of RE atoms. In β_P' , the E_{11} strain is large and positive, while E_{22} is typically small and sometimes negative. β_S' on the other hand, shows positive strains for both E_{11} and E_{22} in the basal plane. For the β'' ordering, the strain components in the basal plane, E_{11} and E_{22} , are equal due to symmetry. Interestingly, the transformation strains of the different orderings are closely related to misfits of the pure RE elements in an HCP crystal structure (relative to magnesium) shown in fig. 13. The transformation strains of all HCP RE crystals relative to HCP Mg are positive, consistent with the larger radii of the rare-earth element. The magnitudes of the strains, however, decreases across the ~~group~~^{period}, in line with the decrease in element size with increasing RE mass. Eu and Yb, however,

do not follow this trend and are well known to deviate from the rest of the group[30]. Since scandium and yttrium do not belong to the same period as the other elements, and are significantly smaller, they do not show the decrease in strain. The transformation strains for the ordered phases (β'_P , β'_S and β'') are found to closely mimic this decreasing trend across the group, suggesting that while the strains are largely determined by the ordering of RE atoms, the magnitude of the strains is affected by the size of the alloying element.

Figure 12: The transformation strains in Mg-RE binary alloys, relative to HCP Mg, are shown for: (a) β'_P (b) β'_S and (c) β'' orderings in all the Mg-RE alloying systems. The orientation of the crystal structures relative to the global coordinate system is also shown. The E_{11} component of the transformation strain is shown in red, E_{22} in cyan, and E_{33} in purple

5. Discussion

5.1. Precipitate orderings in Mg-RE alloys

A rich variety of HCP based ordered precipitates have been observed in Mg-RE alloys, leading to a proliferation of naming schemes[2, 3, 6, 9–13, 18, 34, 35]. Only a small subset of binary rare-earth alloys, however, have been investigated using HAADF-STEM. This includes the Mg- $\{\text{Nd, Sm, Y, Gd}\}$ binary alloys. It is therefore possible that additional orderings will be discovered in other Mg-RE binary alloys that have so far received less attention.

Figure 13: Transformation strains of the rare-earth elements in a HCP crystal structure, relative to HCP magnesium. The orientation of the crystal structures relative to the global coordinate system is also shown. The E_{11} component of the transformation strain is shown in red, E_{22} in cyan, and E_{33} in purple

In spite of the apparent complexity and variety among the HCP based Mg-RE ordered phases, section 2 showed that all metastable precipitates observed to date belong to one of two families of ordered phases. The first, which we have labeled β''' , is derived by combining β'_P and β'' . β'_P is the well-known orthorhombic ordering consisting of equally spaced zig-zag rows of RE atoms aligned in phase as illustrated in fig. 1b. The second family, labeled β'''_S , combines β'_S and β'' where β'_S consists of equally spaced zig-zag rows of RE atoms that are aligned out of phase as illustrated in fig. 1c. As described in section 2, both β''' families can be generated by a branching algorithm that interleaves the zig-zag rows from β' with hexagon strips from β'' generating a hierarchy of orderings that span a range of RE compositions between $x = 0.125$ and 0.25 . According to this branching algorithm, the two possible β' orderings and the β'' ordering are limiting cases of the β''' families, with β' emerging at $x = 0.125$ and β'' existing at $x = 0.25$.

First-principles calculations[30, 31] have shown that the β' and β'' orderings have negative formation energies in each Mg-RE binary alloy (relative to HCP Mg and the pure RE element in HCP). In this study, we have shown that many orderings from the β''' families are also favored energetically, their formation energies either breaking the common tangent between β' and β'' or having values that are within 1-2 meV per atom from this common tangent. Furthermore, as the formation energies in appendix A show, most binary Mg-RE alloys exhibit a clear preference for either β'''_P or β'''_S orderings. The β'''_P orderings are favored among the early RE alloying elements (La, Ce, Pr, Nd, Pm, Sm), while the β'''_S orderings are preferred among the late RE elements (Tb, Dy, Ho, Er, Tm, Lu). Similar to the late RE elements, the Mg-Sc and Mg-Y binary alloys also prefer β'''_S orderings. Only in the Mg-Gd binary do the two families of orderings have energies that are almost degenerate with each other.

An in depth study of precipitation in Mg-Nd alloys[14] showed that formation energies alone are not sufficient to rationalize experimentally observed orderings. Considera-

tions of misfit strains are also necessary. A strong dependence of misfit strains on RE ordering is evident in fig. 10, which shows the calculated misfit strains of the two β''' hierarchies for the Mg-Nd alloy. While both orderings have a negligible misfit strain along the C-axis (E_{33}), they have substantially different misfit strains in the basal plane (i.e. E_{11} and E_{22}). For the β_P''' orderings the E_{22} misfit strain is small and negative at low Nd concentrations, and increases almost linearly with composition until it reaches a large positive value for β_S''' . There is, therefore, a Nd concentration ($x \approx 0.15$) where the E_{22} misfit strain is zero for the β_P''' hierarchy. The misfit strain along the A-axis of the β_P''' orderings, E_{11} , is predicted to be very large, approaching values as high as 0.1, but it decreases slightly with increasing Nd concentration. Hence, as can be seen in fig. 10a, the misfit strains are overall smaller in β_P''' around $x \approx 0.15$ than they are in β_S' , thereby incurring a smaller coherency strain energy penalty than β_P' at $x_{\text{Nd}} = 0.125$. A similar trend is predicted for all early RE alloying elements (La, Ce, Pr, Nd, Pm, Sm).

Although the β_S''' hierarchy of orderings is not energetically favored in the Mg-Nd alloy, its transformation strains (fig. 10b) differ substantially from those of β_P''' ordering. A small lateral translation of adjacent zig-zag rows in β_P' , converting β_P' into β_S' ordering, makes all the basal plane transformation strains positive, thus lowering the anisotropy in basal plane misfits. Furthermore, both E_{11} and E_{22} increase with Nd concentration for β_S''' . Remarkably, the same trends are predicted for the Mg-Y alloy as is clear in fig. 11. As with the Mg-Nd alloy, the E_{11} and E_{22} misfit strains of the β_S''' orderings also increase with Y concentration in the Mg-Y alloy. This suggests that coherency strain energies for these orderings within a Mg matrix will only increase with increasing Y concentration. A comparison among the different Mg-RE binary alloys (appendix A) indicates that the qualitative trends of the misfit strains are more sensitive to the RE ordering pattern than to the RE chemistry. This can be attributed to the similarity in the valence structure of the RE elements. Since their f electrons do not participate in bonding, they all contain a single valence electron in their d -shell.

The calculated formation energies and misfit strains help clarify several puzzling experimental observations in the Mg-Nd, Mg-Sm, Mg-Y and Mg-Gd binary alloys. While the convex hulls for the Mg-Nd and Mg-Sm binary alloys predict a two-phase coexistence between HCP Mg and β_P' , aged samples of both alloys instead consist of β_P''' precipitates having concentrations larger than 0.125[12–14, 17, 34]. As was argued in a previous study[14], β_P''' orderings form in the Mg-Nd alloy as they have smaller misfit strains than β_P' . Indeed, as described above, the misfit strains of β_P''' decrease in absolute value relative to those of β_P' with increasing Nd concentration, with E_{22} becoming equal to zero at $x \approx 0.15$ (fig. 10). The misfit strains of β_P''' orderings in the Mg-Sm binary behave in a similar way. As with the Mg-Nd binary, the β_P''' hierarchy of orderings in Mg-Sm has compositions ($x_{\text{Sm}} \approx 0.16$)

where E_{22} becomes negligible (fig. 6). Since the β_P''' formation energies are essentially degenerate with those of β_P' and β_S''' (fig. 14a), the thermodynamic explanation underlying the experimental observations that β_P''' forms in the Mg-Sm binary [12, 34], instead of β_P' , is a drive to minimize the coherency strain energy.

Figure 14: The transformation strains as a function of samarium composition (x_{Sm}) in the Mg-Sm alloy system for: (a) β_P''' and (b) β_S''' . The E_{11} component of the transformation strain is colored in red, E_{22} in cyan and E_{33} in purple. Lines are drawn as guides to show the linear dependence of the misfit strains on composition.

The coherency strain arguments to rationalize the precipitation of β_P''' orderings as opposed to β_P' in Mg- $\{\text{Nd}, \text{Sm}\}$ can also be invoked to explain the absence of the β_S''' hierarchy in the Mg-Y binary where these orderings are preferred. HAADF-STEM micrographs of the precipitates in the Mg-Y alloy[10] do not show evidence of RE hexagons, indicating that β_Y''' orderings are not formed. Instead, all the precipitates in the study consisted of zig-zag rows of yttrium aligned out of phase as in β_S' . This is consistent with the first-principles predictions of fig. 11, which show that the misfit strains for the β_S''' family are larger than those of β_S' . Hence the coherency strain energy to form β_S''' should be larger than that to form β_S' in this alloy and only stoichiometric β_S' forms.

The Mg-Gd binary alloy is unique among Mg-RE alloys in that both families of β''' are predicted to be almost degenerate in energy (fig. 8). This suggests that both orderings may form concurrently as precipitates. As is clear in fig. 15b, the misfit strains of the β_S''' orderings increase with Y-Gd concentration, while those of the β_P''' (fig. 15a) ordering decrease in absolute value with small additions of Gd. Therefore, if the β_P''' family were to form in Mg-Gd, it would show Gd atoms arranged as hexagons, and if β_S''' were to form, only stoichiometric β_S' would be expected (i.e. no Gd atoms arranged as hexagons). Close scrutiny of HAADF-STEM images suggests that both orderings do in fact form in the Mg-Gd alloy. Studies by Liu et al[36] and Nishijima et al[10] show evidence of large precipitates with a crystal structure prototype identical to that of β_S' , with no hexagonal arrangements of Gd atoms. Further-

more, the large β'_S precipitates are connected by thin laths that consist of Gd hexagons and zig-zags reminiscent of β'''_P orderings. Both the lack of Gd hexagons in the larger β'_S precipitates and their presence in the connecting β'''_P regions are consistent with the calculated formation energies and misfit strains of the β''' hierarchies in the Mg-Gd binary.

Figure 15: The transformation strains as a function of gadolinium composition (x_{Gd}) in the Mg-Gd alloy system for: (a) β'''_P and (b) β'_S . The E_{11} component of the transformation strain is colored in red, E_{22} in cyan and E_{33} in purple. Lines are drawn as guides to show the linear dependence of the misfit strains on composition.

The above discussion for the Mg- $\{\text{Nd}, \text{Sm}, \text{Y}, \text{Gd}\}$ binaries clearly shows that the experimentally observed orderings are consistent with the orderings predicted as ground states on the HCP Mg-RE convex hull. Though incoherent phase equilibrium suggests a two-phase mixture between a disordered solid solution and β' in all Mg-RE alloys, additional considerations of misfit strains are necessary to determine which metastable precipitates will form during an aging heat treatment. Having established the consistency of first-principles predictions with experiment as well as the importance of coherency strains, we are now in a position to use the calculated formation energies and misfit strains to anticipate ordering tendencies in the other Mg-RE binaries that have not been explored. The first-principles formation energies (appendix A) predict that β'''_P should form in the early Mg-RE alloys (La, Ce, Pr, Nd, Pm, Sm) since this family of orderings reside on the convex hull. Furthermore, the calculated misfit strains for these orderings indicate that β'''_P will form instead of β'_P . Precipitates in the early Mg-RE alloys will therefore consist not only of RE zig-zags, but also of hexagon rings. For the late Mg-RE alloys (Tb, Dy, Ho, Er, Tm, Lu, Sc, Y), our calculations predict that β'_S should form. Since the misfit strains for β'_S are larger than those of β'_P , the precipitates in these alloys will only consist of RE zig-zags. This is summarized in fig. 16.

It should be noted that the predictions summarized in fig. 16 are expected for large precipitates. Due to the small differences in formation energy between β'''_P and β'_S

Figure 16: Summary of the predicted metastable phases in different Mg-RE alloys based on energetic and misfit strain considerations. The Mg- $\{\text{Eu}, \text{Yb}\}$ systems are not considered in this study since their behavior is known to deviate from the rest of the elements. These elements are therefore labeled in a white box.

hierarchies for all Mg-RE alloys, it is possible that in the early stages of precipitation, where the precipitates are still very small, a less stable β''' variant may form.

5.2. Precipitate shapes of Mg-RE alloys

While there are several factors that control the extent with which precipitates impede dislocation glide, a particularly important one in magnesium alloys is precipitate shape and orientation. Phase field simulations [36, 37] and first-principles studies [14] have shown that the misfit strain between the ordered precipitate and the Mg matrix plays a decisive role in determining precipitate shape. Our systematic first-principles study of all first-row Mg-RE binary alloys, has shown that misfit strains are very sensitive to the ordering of RE atoms in the precipitate. The misfit strains of the orderings predicted to form during an aging heat treatment are all small along the C-axis. However, misfit strains within the basal plane can differ substantially depending on whether β'''_P (with $x_{\text{RE}} > 0.125$) or β'_S (with $x_{\text{RE}} = 0.125$) forms. The β'''_P orderings have negligible misfit strains along their B-axis (i.e. E_{22}), but have a very large misfit strain along the A-axis (i.e. E_{11}). β'''_P precipitates will therefore minimize their strain energy by forming thin ellipsoidal plates perpendicular to the axis with the largest misfit strain [38] (i.e. their A-axis). The β'_S ordering, in contrast exhibits a more isotropic misfit strain within the basal plane. These precipitates will not lower their strain energy by forming as plates and will therefore likely strive to reduce their interfacial circumference within the basal plane to minimize interfacial free energy. Quantitative estimates of precipitate number density and morphology will require the investigation of the combined effects of strain and interfacial energy within a longer length-scale model such as the phase-field method [36, 37, 39, 40].

These misfit strain arguments are manifested experimentally by observations that β'''_P precipitates in Mg-Nd alloys form as thin plates [13, 14, 17] while the β'_S precipitates in Mg-Y alloys adopt more globular shapes [11, 36] with their long axis aligned parallel to the c -axis of HCP Mg. Likewise, the β'''_P precipitates that form in the Mg-Sm binary [12] are plate-like, while the β'_S precipitates of the Mg-Gd alloy [9, 10] form as rods. Interestingly, the correlation between precipitate shape and misfit strains are clearly evident in the study by Nishijima [40] [9, 10] of a

Mg-Gd alloy, where neighboring β'_S precipitates are connected to each other by significantly thinner (along the A-axis) β'''_P precipitates.

The strong correlations between experimentally observed precipitate shapes and calculated misfit strains allow us to apply the same misfit strain arguments to predict precipitate shapes for all first-row Mg-RE alloys. Since the early RE alloying elements, La, Ce, Pr, Nd, Pm, and Sm prefer β'''_P ordering, misfit strain arguments suggest that these alloys will form thin plate-like precipitates. The late RE alloying elements, Tb, Dy, Ho, Er, Tm, Lu, Sc and Y, however, prefer β'_S ordering and should therefore form more globular precipitates. While the misfit strains of β'_S are more isotropic than those of β'''_P , some degree of anisotropy emerges in β'_S as the size of the RE alloying element increases. The smaller elements like Y and Sc should exhibit more equiaxed precipitates while the larger elements such as Tb, Dy, Ho, Er, should have more elongated (along the B-axis) precipitates when viewed along the C-axis.

5.3. Implications for Alloy Design

Strengthening in magnesium and its alloys is determined by a variety of factors, including intrinsic mechanical properties[41], precipitate shape, orientation, number density, and surrounding strain field[36, 37, 39, 40, 42]. Precipitates that form as prismatic plates are known to have a much more significant strengthening effect than those that form as spherical or basal plates[42]. Recent work suggests that prismatic plates with a higher aspect ratio lead to larger increments in yield strength[36, 37, 42]. The aspect ratio, A , for a prismatic plate is defined as:

$$A = \frac{l_{[010]}}{l_{[100]}} \quad (4)$$

where $l_{[010]}$ is the length of the precipitate along the [010] direction and $l_{[100]}$ is the length along the [100] direction. Larger aspect ratios can be achieved by either increasing $l_{[010]}$ or decreasing $l_{[100]}$.

The results of this work suggest that the aspect ratio of precipitates can be tuned by the RE alloying addition. Based on calculated misfit strains, we expect the early RE alloying additions, {La,Ce,Pr,~~Sm~~,~~Nd~~,~~Nd~~,~~Pm~~,~~Sm~~}, to form precipitates having the highest aspect-ratio as they prefer β'''_P orderings, which have negligible misfit strains along their B axis (E_{22}) and large misfits along their A axis (E_{11}). Compared to precipitates of β'_S , all other factors remaining constant, the β'''_P precipitates are expected to give the largest increment to strength.

Changing the alloying chemistry however could modify many other properties that affect alloy strength. For instance, a shift in the metastable phase boundary due to additions of other rare-earth elements between the disordered solid solution and the metastable phase is expected to change the number density of the precipitates. The effect of alloy chemistry on the strength of the precipitates also remains unknown.

6. Conclusion

We have argued that all experimentally observed HCP based orderings in Mg-RE alloys characterized to date can be classified as belonging to one of two families of hybrid phases labeled β'''_P and β'_S . The hybrid phases combine features of β' (either β'_P , having a primitive orthorhombic cell, or β'_S , having a face centered orthorhombic cell) and β'' to generate a hierarchy of orderings in which the RE atoms arrange as zig-zags and strips of hexagons when viewed along the HCP c -axis. First principles DFT calculations predict that the Mg-{La, Ce, Pr, Nd, Pm, Sm} binary alloys prefer β'''_P , while the Mg-{Sc, Y, Tb, Dy, Ho, Er, Tm, Lu} binary alloys prefer β'_S . Comparisons to experimental observations demonstrate the importance of misfit strain in selecting particular β'''_P orderings in the Mg-Nd and Mg-Sm alloys, explaining the appearance of RE hexagons in addition to zig-zag rows in these alloys. Misfit strain arguments also explain the absence of hexagons in the ordered precipitates that form in the Mg-Y binary alloy. The predicted degeneracy between β'''_P and β'_S in the Mg-Gd binary clarifies the simultaneous occurrence of both phases, whereby large β'_S precipitates are connected by plate-like β'''_P secondary precipitates. The predicted formation energies taken in combination with calculated misfit strains suggest that Mg-{La, Ce, Pr, Nd, Pm, Sm} alloys will form precipitates that show RE atoms arranged as zig-zags and hexagons (corresponding to β'''_P), while Mg-{Sc, Y, Tb, Dy, Ho, Er, Tm, Lu} will only form β'_S precipitates consisting exclusively of zig-zags. The calculated misfit strains also suggest that β'''_P precipitates will exhibit the largest aspect ratio, while β'_S precipitates will be more globular.

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A. Formation energy and transformation strains for Mg-RE binary alloys

Calculated formation energies (left column) and transformation strains (right column) of the two hierarchies of orderings (β_P''' and β_S''') for first-row Mg-RE binary alloys are shown in this section. The figures are arranged in increasing atomic number of the rare-earth alloying element. The formation energies of the β_P''' orderings are shown as

yellow squares, while those of the β_S''' family are shown as blue circles. The transformation strains for these orderings, relative to HCP Mg, are also shown for each system. Sub-figure (b) corresponds to β_P''' , and sub-figure (c) is for the β_S''' orderings. For both figures, the E_{11} component of the transformation strain is shown in red, E_{22} in cyan, and E_{33} in purple. Lines are drawn as guides to show the dependence of these strains on composition. Configurations, such as $\beta_P'''(01^3)$ in the Mg-Tm binary, that underwent large deformations relative to HCP are not shown in the figure as it relaxed into a different crystal structure. The same ordering in the Mg-Ho is also not plotted as the calculations could not be converged.

Figure A.17:

Figure A.18:

Figure A.19: