Thermodynamic Stability of Mg-Based Laves Phases

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To investigate the stability of various Mg-based Laves phases, the formation enthalpy and phonon dispersion were obtained by first-principles calculation. The calculated formation enthalpy and phonon dispersion indicate that MgX\textsubscript{2} (X = Al, Co, Ni, Cu, Zn) and Mg\textsubscript{2}X (X = Ca, Sr, Y, Ba, La) are stable both statically and dynamically. These results are consistent with the experimental results except for MgAl\textsubscript{2} and Mg\textsubscript{2}La. These compounds are considered to be in a metastable state in each binary system. We also used the cluster expansion method to examine the possibility of adding a third element to MgZn\textsubscript{2}. Our theoretical investigations suggest attractive interaction between Zn and a third element such as Ag, Ca, and Zr in the MgZn\textsubscript{2} lattice. However, Ca and Zr replace a small amount of Zn in MgZn\textsubscript{2} owing to the instability of Mg\textsubscript{2}Ca\textsubscript{2} and Mg\textsubscript{2}Zr\textsubscript{2} in agreement with the experimental result. Furthermore, it is suggested that Zr becomes stable at the Mg site in the Mg\textsubscript{2}Zn\textsubscript{2} lattice owing to the stability of ZrZn\textsubscript{2}.

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1. Introduction

Mg-based alloys are expected to be applied in structural materials used in aircraft and vehicles because of their light weight and natural abundance. To date, the mechanical properties of Mg-based alloys have been improved by adding elements for imparting anticorrosion properties, grain refinement strengthening, precipitation strengthening, and so on. Despite the efforts at strengthening them, Mg-based alloys still have much lower strength than Al-based alloys; therefore, increasing their strength is important toward widespread use of Mg-based alloys. Among them, the precipitate-hardenable Mg–Zn-based alloys show relatively good mechanical properties.\textsuperscript{3,7} The precipitated phase in Mg–Zn-based alloys is the MgZn\textsubscript{2} Laves phase, which acts as a strengthening phase. Therefore, a promising strategy to improve the strength of Mg-based alloys is to use the MgZn\textsubscript{2} Laves phase effectively.

Outstanding physical properties can be obtained if a large amount of the precipitate is dispersed in the alloy; however, the low solubility of Zn in HCP suggests that this binary system has limitations. A promising strategy in materials design is to control the stability of the Laves phase by incorporating another element. For example, Mg–Zn-based alloys with added Zr are well-known commercial alloys owing to their relatively good mechanical properties. Mendis \textit{et al.} reported that Mg–Zn-based alloys containing Ag, Ca, and Zr also exhibit good mechanical properties.\textsuperscript{5,9} To determine the role of these additional elements, the precipitate phase has been investigated using a three-dimensional atom probe; the results suggested the existence of Ag and Ca associations as well as Zr inclusions.\textsuperscript{5,9} According to these previous studies, additional elements are distributed in the MgZn\textsubscript{2} Laves phase and they improve the alloy strength. We seek to identify additional elements which can be used to stabilize the Laves phase. To investigate the formation mechanism of the Laves phase and the interaction between Mg and Zn with additional elements in the Laves phase is useful for designing Mg–Zn-based alloys with potentially high mechanical properties.

For this purpose, first-principles calculation is suitable, because a systematic investigation of various replacement elements can be carried out more easily by this method than by experimentation. For example, Issa \textit{et al.} calculated the formation enthalpy using first-principles calculation to systematically examine the stability of the precipitation phase in Mg alloys containing rare-earth elements.\textsuperscript{4} Because their calculated thermodynamic stability is consistent with that determined experimentally, first-principles calculation is also attractive for investigating the Mg–Zn-based Laves phase. Furthermore, the Gibbs energy and atomic interaction in the solid solution phase obtained by first-principles calculation were reported by our group.\textsuperscript{5,7} These calculations can indicate the thermodynamic stability of the solid solution phase.

In this study, we investigated the stability of various binary Mg-based Laves phases. Using first-principles calculation, we systematically calculated the formation enthalpy and phonon dispersion. We also investigated the contribution of a third element added to MgZn\textsubscript{2} using first-principles calculation combined with the cluster expansion method (CEM). On the basis of the formation enthalpy of the MgZn\textsubscript{2} Laves phase, the formation of a metastable Laves phase and the contribution of Ag, Ca, or Zr to the stability of the Laves phase are discussed.

2. Calculation Procedure

We performed first-principles calculation based on the density functional theory (DFT) using the Vienna \textit{ab initio} simulation package (VASP) code.\textsuperscript{8,9} The interaction between the ion core and the valence electrons was described by the projector-augmented wave method.\textsuperscript{10,11} The exchange and correlation functions were given by the generalized gradient approximation, as proposed by Perdew \textit{et al.}\textsuperscript{12,13} For structural optimization and enthalpy calculation, we set the plane wave energy cutoff to 500 eV. Brillouin zone sampling
in a primitive cell was performed by a Γ-point-centered \( k \)-mesh that was limited to 0.1 Å\(^{-1} \), for example, a \( 14 \times 14 \times 8 \) mesh for MgZn\(_2\). The convergence criterion for electronic self-consistency and the ionic relaxation loop were set to 10\(^{-6} \) eV and 0.01 eV, respectively. The Methfessel–Paxton smearing method with a smearing width of 0.2 eV and the tetrahedron method with Blöchl corrections were used for structural optimization and the enthalpy calculation, respectively. The primitive cell was fully optimized with respect to the volume and shape of the unit cell and the atomic positions. For the partially substituted system, stable crystal structures were searched for using the CEM, which was implemented using the ATAT code with first-principles calculations. In the CEM, the energy of the structure is implemented using the ATAT code with first-principles calculations. In the CEM, the energy of the structure is estimated by the CEM. Then, the stable crystal structure is predicted by first-principles calculations and added to the set of energies for inverting the CEM process. Repeating this procedure can rapidly predict a stable crystal structure for the substituted system. In this study, we use a four-point cluster for the maximum number of points of a cluster. The parameters of the first-principles calculations for inverting the CEM are as follows: The plane wave energy cutoff was set to 500 eV and a Γ-point-centered \( k \)-mesh of 1000 points per reciprocal atom and the Methfessel–Paxton smearing method with a smearing width of 0.1 eV were used. The convergence criterion for electronic self-consistency and the ionic relaxation loop were set to 10\(^{-8} \) eV and 0.01 eV, respectively. This setting, 10\(^{-4} \) eV, is usually used to save on calculation time; however, this does not change the results for the stability of the solid solution.

To examine the dynamic stability of the Laves structures, we conducted a first-principles phonon calculation by the finite displacement method\(^{15,16} \) using the phonopy code\(^{17} \) combined with the VASP code. For this calculation, we used a \( 2 \times 2 \times 2 \) supercell containing 96 atoms and an atomic displacement distance of 0.01 Å. To estimate the force due to displacements within the DFT calculation, we used a plane wave energy cutoff of 500 eV, a convergence criterion for the electronic self-consistency loop of 10\(^{-6} \) eV, a Γ-point-centered \( k \)-mesh that was limited to 0.1 Å\(^{-1} \), and the Methfessel–Paxton smearing method with a smearing width of 0.2 eV. In the phonon calculations, the supercell was created from the fully optimized primitive cell.

3. Results and Discussion

Figure 1 shows the crystal structure of the C14-type Laves phase. The space group is P6\(_1\)/mmc (194), and the 12 atoms per primitive unit cell are located at the 2a, 4f, and 6h Wyckoff positions, (0, 0, 0), (0.33333, 0.66667, 0.56290), and (0.16970, 0.33940, 0.25000), respectively. In MgZn\(_2\), on one hand, Mg atoms occupy the 4f position, and Zn atoms occupy the 2a and 6h positions. On the other hand, Mg atoms occupy the 4f and 6h positions in Mg\(_2\)Ca. For these two types of Laves phases, viz., MgX\(_2\) and Mg\(_2\)X, static and dynamic stability are systematically investigated by first-principles calculations for X = Al, Si, Cu, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Sr, Y, Zr, Ag, In, Sn, Sb, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, which are mainly fourth-period and rare-earth elements.

Figure 2(a) and (b) show the calculated lattice constants of MgX\(_2\) and Mg\(_2\)X, respectively, compared with the available experimental data.\(^{18} \) The calculated lattice constants of MgX\(_2\) (X = Co, Zn) and Mg\(_2\)X (X = Ca, Sr, Y, Ba, Tb, Dy, Ho, Er, Tm, Yb, Lu) are consistent with those experimentally determined within 0.1 Å. Therefore, the optimized structures are reliable for estimating the formation enthalpy.

To investigate the stability of the Laves phase, we calculated the formation enthalpy \( H \), which is given by,

\[
H(A, B) = E_{\text{total}}(A, B) - \frac{xE_{\text{pure}}(A) + yE_{\text{pure}}(B)}{x + y}
\]

where, \( E_{\text{total}}(A, B) \), \( E_{\text{pure}}(A) \), and \( E_{\text{pure}}(B) \) are the total energies of an atom for the compound \( A, B \), pure state \( A \), and pure state \( B \), respectively. Figure 3(a) and (b) show the calculated formation enthalpy, \( H \) of various optimized Laves phases. A negative formation enthalpy implies that the Laves phase is statically stable at 0 K. Hence, the statically stable elements for MgX\(_2\) are X = Al, Co, Ni, Cu, Zn, Ga, and Ag, and those for Mg\(_2\)X are X = Ca, Sr, Y, Ba, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. In contrast, the other compounds show a positive formation enthalpy, implying that those elements have a statically unstable Laves phase.

The dynamical stability of the Laves phase was also examined by calculating the phonon dispersion of MgX\(_2\) (X = Al, Co, Ni, Cu, Zn, Ga, Ag) and Mg\(_2\)X (X = Ca, Sr, Y, Ba, La). Figure 4 shows the phonon dispersion and partial DOS of MgX\(_2\) (X = Al, Co, Ni, Cu, Zn, Ga, Ag) and Mg\(_2\)X (X = Ca, Sr, Y, Ba, La). The vertical axis represents the frequency, and the horizontal axis represents the wave vector for the phonon dispersion and the partial DOS, respectively. The partial DOS shows the vibrational contributions of Mg and X atoms. The wave vectors of the phonon dispersion are shown along the high-symmetry direction, A-H-L-A–Γ–K–M–Γ. In all, there are 36 phonon branches for MgX\(_2\) and Mg\(_2\)X. For MgAl\(_2\), the contribution of Mg and Al extends over a broad range of energy. As X elements become heavier, the higher frequency is mainly contributed by Mg, and the
lower frequency by X elements, as shown in the partial DOS. In particular, phonon branches distinctly separate into high- and low-energy parts for Mg$_2$Sr, Mg$_2$Y, Mg$_2$Ba, and Mg$_2$La.

In the phonon dispersion, an imaginary value of the frequency indicates that the structure is dynamically unstable. Therefore, the dynamically stable compounds are MgX$_2$ (X = Al, Co, Ni, Cu, Zn) and Mg$_2$X (X = Ca, Sr, Y, Ba, La), because no negative frequencies appear. In contrast, MgGa$_2$ and MgAg$_2$, which show some negative frequencies, are dynamically unstable compounds. These modes are assigned to $A_{2g}$ and $B_{2u}$ for MgGa$_2$ and $A_{2g}$, $B_{2u}$, and $E_{2u}$ for MgAg$_2$. Therefore, MgGa$_2$ and MgAg$_2$ exhibit a more stable structure. The calculated formation enthalpy and phonon dispersion suggest that the compounds that are both statically and dynamically stable are MgX$_2$ (X = Al, Co, Ni, Cu, Zn) and Mg$_2$X (X = Ca, Sr, Y, Ba, La).

Figure 5 shows the temperature dependence of the harmonic phonon energy, entropy, and Helmholtz free energy of the Laves phase for MgX$_2$ (X = Al, Co, Cu, Ni, and Zn) and Mg$_2$X (X = Ba, Ca, La, Sr, Y). The entropy term shows a larger material dependence than the harmonic phonon energy. This behavior can be understood by the phonon dispersion relation and DOS, as shown in Fig. 4. The entropy increases with the increasing number of phonons excited at a temperature. The phonon frequency of the Laves phase decreases with increasingly heavy elements, thereby increasing the number of phonons.

Here, we compare these calculated results with the experimental phase stabilities, and these are listed in

![Fig. 2](image-url) Calculated lattice constants of (a) MgX$_2$ and (b) Mg$_2$X compared with the available experimental data.

![Fig. 3](image-url) The calculated formation enthalpy of (a) MgX$_2$ and (b) Mg$_2$X.
Fig. 4 The calculated phonon dispersion and partial DOS of MgX$_2$ for X = (a) Al, (b) Co, (c) Ni, (d) Cu, (e) Zn, (f) Ga, (g) Ag, and Mg$_2$X for X = (h) Ca, (i) Sr, (j) Y, (k) Ba, and (l) La.

Fig. 5 Temperature dependence of the harmonic phonon energy, entropy, and Helmholtz free energy of the Laves phase for MgX$_2$ (X = Al, Co, Cu, Ni, and Zn) and Mg$_2$X (X = Ba, Ca, La, Sr, Y).
Table 1. The most stable phases of MgX₂ and Mg₂X at room temperature were determined from the phase diagrams.¹⁹²¹

Note that the Laves phase has three crystal structures. Close relationships between these three structures, which consist of stacks of six fundamental layers, was found by Berry and Raynor²² and Komura.²³ They found that C14 (prototype: MgZn₂) consists of ABBA stacking layers, C15 (prototype: MgCu₂) consists of ABC stacking layers, and C36 (prototype: MgNi₂) consists of ABABA stacking layers in the topologically close-packed structure. Because of their close topological relationship, the C14-, C15-, and C36-type Laves phases were treated as the same Laves structure in this study.

Table 1 shows that the calculated stable compounds are MgX₂ (X = Al, Co, Ni, Cu, Zn) and Mg₂X (X = Ca, Sr, Y, Ba, La). MgX₂ with X = Co, Ni, Cu, and Zn and Mg₂X with X = Ca, Sr, Y, and Ba are experimentally observed as the Laves phase; therefore, the calculated results are consistent with the experimental ones. In contrast, the calculated stable structure is inconsistent for MgAl₂ and Mg₂La, because the mixtures Al + Mg₂Al₄ and MgLa + Mg₃La are stable for the Mg–Al and Mg–La binary systems, respectively. Our calculated results indicate that MgAl₂ and Mg₂La are stable compounds, but experiments indicate that MgAl₂ and Mg₂La are not observed to be stable compounds. In the Mg–Al system, Mg₁₂Al₁₈ in the C14-type Laves phase has been
observed using a rapid cooling technique.\textsuperscript{24} In the Mg–La system, Mg\textsubscript{2}La in the C15-type Laves phase is the most stable phase at 620 to 769°C.\textsuperscript{25} These experiments and our results suggest that MgAl\textsubscript{2} and Mg\textsubscript{2}La are metastable compounds. Furthermore, the calculated result shows that the stably unstable compounds are MgX\textsubscript{2} with X = Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Ge, Sr, Y, Zr, In, Sn, Sb, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and Mg\textsubscript{2}X with X = Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Ag, In, Sn, Sb, and Ce, and the dynamically unstable compounds are MgX\textsubscript{2} with X = Ga and Ag. These results are also consistent with the experimental stabilities.

Next, using the CEM, we examined the possibility of adding a third element to the Laves phase, Mg-Zn-X (X = Ag, Ca, Zr), because these systems have been investigated experimentally.\textsuperscript{2,3,26–29} For example, on one hand, Wang \textit{et al.} reported that Ag is located at the 2a and 6h sites, resulting in the formation of Mg(Ag\textsubscript{1–x}Zn\textsubscript{x})\textsubscript{2}.\textsuperscript{26} On the other hand, as Zhang \textit{et al.} reported, a small amount of Ca is introduced into the MgZn\textsubscript{2} phase; instead, Ca forms Mg\textsubscript{2}Ca separately.\textsuperscript{28} Bhattacharjee \textit{et al.} reported that Zr is located at the 6h and 2a sites and forms Mg(Zn\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2}.\textsuperscript{27} Therefore, to study the ability to form the solid solution phase, we calculated the formation enthalpies of Mg(Zn\textsubscript{1–x}Ag\textsubscript{x})\textsubscript{2}, Mg(Zn\textsubscript{1–x}Ca\textsubscript{x})\textsubscript{2}, and Mg(Zn\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2}.

Figure 6 shows the calculated formation enthalpies of (a) Mg(Zn\textsubscript{1–x}Ag\textsubscript{x})\textsubscript{2}, (b) Mg(Zn\textsubscript{1–x}Ca\textsubscript{x})\textsubscript{2}, and (c) Mg(Zn\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2}. The crosses represent the formation enthalpies calculated using the first-principles technique, and the circles and solid lines represent the ground states of these enthalpies. As shown in Fig. 6(a), the formation enthalpy of Mg(Zn\textsubscript{1–x}Ag\textsubscript{x})\textsubscript{2} decreases with increasing Ag content in the range of 0 < x < 0.3 and has the minimum value at ~0.5. The interaction between Zn and Ag in Mg(Zn\textsubscript{1–x}Ag\textsubscript{x})\textsubscript{2} is attractive because the ground state is downward convex. These calculated results suggest that the solid solution of Mg(Zn\textsubscript{1–x}Ag\textsubscript{x})\textsubscript{2} is stable, which is consistent with the experimental results.\textsuperscript{26} As shown in Fig. 6(b) and (c), Zn–Ca and Zn–Zr also involve attractive interactions. However, because of the instability of the MgCa\textsubscript{2} and MgZr\textsubscript{2} Laves phases, the formation enthalpy of Mg(Zn\textsubscript{1–x}Ca\textsubscript{x})\textsubscript{2} and Mg(Zn\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2} increases monotonically with increasing Ca and Zr content. These results suggest that the solid solutions of Mg(Zn\textsubscript{1–x}Ca\textsubscript{x})\textsubscript{2} and Mg(Zn\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2} are unstable. The result for Mg(Zn\textsubscript{1–x}Ca\textsubscript{x})\textsubscript{2} is consistent with the experimental ones,\textsuperscript{28} therefore, our calculation correctly describes the solid solution state of the Laves phase containing Ag and Ca.

Fig. 6 Calculated formation enthalpies of (a) Mg(Zn\textsubscript{1–x}Ag\textsubscript{x})\textsubscript{2}, (b) Mg(Zn\textsubscript{1–x}Ca\textsubscript{x})\textsubscript{2}, and (c) Mg(Zn\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2}.

In case of Zr substitution, there is another experimental result. Ren \textit{et al.} reported that Zr is located at the 4f site and forms (Mg\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{Zn\textsubscript{2}}.\textsuperscript{29} Figure 7 shows the calculated formation enthalpies of (Mg\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{Zn\textsubscript{2}}. The interaction between Mg and Zr on the Mg sublattice is attractive, and the formation enthalpy decreases monotonically with increasing Zr content. Therefore, our calculations suggest that Zr tends to be located at the 4f site in terms of the energy of the ground state.

The calculated result for the system with added Zr apparently indicates the formation of (Mg\textsubscript{1–x}Zr\textsubscript{x})Zn\textsubscript{2}, which is supported by the experimental results reported in Ref. 29. Reference 3) concluded that Mg2.4Zn–0.1Ag–0.1Ca–0.16Zr (ZKQX) obtained by homogenization and hot extrusion has fine precipitates. We should discuss the relationship between the obtained formation enthalpy and the size of the precipitates. The growth of precipitates is generally considered in terms of Ostwald ripening.\textsuperscript{30} More large precipitates grow and small precipitates disappear owing to the flow of solute atoms from small to large precipitates, which is because of the differences in the solute concentration at the interface according to the radius of the precipitates. In this theory, the size of the precipitates is described by:

\[ r^3 - r_0^3 = Kt, \quad K \propto e^{DX}, \]

where, \( r \) and \( r_0 \) are the average radii at \( t \) and \( t = 0 \), respectively. \( D \) is the diffusion constant, \( \sigma \) is the interfacial energy, and \( X_e \) is the equilibrium concentration of the solute.
in the parent phase for precipitates with infinite radius, which is the solubility limit in the equilibrium phase diagram. From this equation, when \( \sigma, D, \) and \( X_e \) are small, grains grow slowly, and the precipitates remain small. To keep \( X_e \) small, the formation enthalpy of the precipitates should be low, which is trivial from the common tangential line between the parent phase and precipitation phase. Therefore, the experimental result, in which fine precipitates were formed in ZKQX, seems to indicate that the introduced Zr is located at the Mg site even in terms of the size of the precipitates. We note that our calculation may not indicate the stability of materials at finite temperatures owing to the limitations of the calculation techniques. To obtain a definitive result, it is necessary to include the effect of the finite temperature, for example, using the cluster variation method. In any case, data obtained by systematic calculations on the formation energy of the Laves phase are useful for controlling the precipitation of the Laves phase at a desired size.

4. Conclusions

To investigate the stability and mechanical properties of various Mg-based Laves phases, we performed first-principles calculation of the formation enthalpy and phonon dispersion. The formation enthalpy and phonon dispersion results indicated that \( \text{Mg}_2X (X = \text{Al, Co, Ni, Cu, Zn}) \) and \( \text{Mg}_3X (X = \text{Ca, Sr, Y, Ba}) \) have statically and dynamically stable structures, which is consistent with the experimental results. Furthermore, comparison with the experimental results indicates that \( \text{MgAl}_2 \) and \( \text{Mg}_2\text{La} \) are metastable phases of the Mg–Al and Mg–La systems, respectively. Using the CEM combined with DFT, we described the thermodynamic stability of the solid solution Laves phase. Our theoretical investigation suggests that attractive interaction contributes to the concentration of the additional element (Ag, Ca, or Zr) in the MgZn2 Laves phase.

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