Thermodynamic Stabilization of Precipitates through Interface Segregation: Chemical Effects

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Abstract

Precipitation hardening, which relies on a high density of intermetallic precipitates, is a commonly utilized technique for strengthening structural alloys. At high temperatures, however, the precipitates coarsen to reduce the excess energy of the interface, resulting in a significant reduction in the strengthening provided by the precipitates. In certain ternary alloys, the secondary solute segregates to the interface and results in the formation of a high density of nanosized precipitates that provide enhanced strength and are resistant to coarsening. To understand the chemical effects involved, and to identify such segregating systems, we develop a thermodynamic model using the framework of the regular nanocrystalline solution model. For various global compositions, temperatures and thermodynamic parameters, equilibrium configuration of Mg-Sn-Zn alloy is evaluated by minimizing the Gibbs free energy function with respect to the region-specific (bulk solid-solution, interface and precipitate) concentrations and sizes. The results show that Mg$_2$Sn precipitates can be stabilized to nanoscale sizes through Zn segregation to Mg/Mg$_2$Sn interface, and the precipitates can be stabilized against coarsening at high-temperatures by providing a larger Zn concentration in the system. Together with the inclusion of elastic strain energy effects and the input of computationally informed interface thermodynamic parameters in the future, the model is expected to provide a more realistic prediction of segregation and precipitate stabilization in ternary alloys of structural importance.

Keywords: Statistical thermodynamics, Intermetallic precipitation, Coarsening, Solute segregation, Heterophase interface
I. INTRODUCTION

In structural alloys, one of the most commonly utilized strengthening mechanism involves the precipitation of ordered intermetallic compounds. For example, the precipitation of L12 Al3Sc [1, 2] and Al3Li [3, 4] intermetallics in aluminum has led to significant improvements in yield strength. Similar effects were observed in certain maraging [6, 7] and stainless steels [8]. The beneficial properties of intermetallic precipitation are not just confined to fcc alloy systems but have also been observed in hexagonal alloys of titanium [9, 10] and, more recently, in magnesium alloys [11–13]. Even in iron-based bcc alloys, L21 precipitates have resulted in significant improvements in yield strength [14, 16].

Precipitation hardening is usually attributed to two primary mechanisms - (i) dislocation cutting-through or bowing-around dispersed precipitate particles (dispersion hardening [17]) and (ii) dislocations interacting with the coherency strains of precipitates (coherency strain hardening [18, 19]).

In addition to mechanical properties, thermal stability of certain fcc alloys can be dramatically improved through the precipitation of ordered intermetallics. For example, precipitation of cubic L12 intermetallics, in nickel [20–24] and cobalt-based alloys [25, 26], results in an improved high-temperature yield strength [27]. While the improved mechanical properties have a non-trivial dependence on the size, density and crystallography of the precipitates, it is generally true that a higher density of smaller precipitates that are resistant to coarsening improves both the strengthening characteristics and high-temperature stability. For example, while the separate addition of Zr or Sc to Aluminum alloys results in increased tensile strength and resistance to recrystallization by forming ordered precipitates, the combined effect is considerably larger [28–34]. This is due to the formation of a higher density of small precipitates driven by Zr segregation to Al/Al3Sc hetero-phase interfaces [35].

Zr segregation in Al-Sc-Zr alloys has been attributed primarily to kinetic effects - the low diffusion coefficient of Zr compared to Sc restricts the partitioning of Zr to just the interface layer rather than the core of Al3Sc [35]. However, in general, both kinetic and thermodynamic factors may promote solute segregation to an interface. Some observed examples include: segregation of Mg [36], Zr [37] and Mg+Ag [38] to α-Al/Al3Sc interface; Sc [39], Si [40], Ag [41] and Si+Mg [42] to α-Al/Al2Cu interface; Gd+Zn [43] to Mg/Mg5Zn interface; Zn
to Mg/Mg$_2$Sn interface. The thermodynamic driving force for solute segregation to the interface is attributed to a reduction in the interfacial free-energy [46–52], which is attributed primarily to two factors: (a) favorable chemical interactions of solute element at the interface over that in the bulk; and (b) reduction of solute size misfit strain energy [53]. The reduction in the interfacial free-energy $\gamma$ further results in a decrease in the coarsening kinetics at elevated temperatures [54].

The afore-mentioned examples are but a few among a large number of binary alloy systems that favor intermetallic precipitation. For example, other commonly observed binary intermetallics in structural alloys include: Cu$_3$Al, Cu$_3$Sn, Cu$_3$Ti, Cu$_3$Au, Ni$_3$Al, Ni$_3$Ti, Ni$_3$Nb, Ni$_3$Si, MgZn, Mg$_2$Si, Mg$_3$Nd, Mg$_2$Cu, Mg$_2$Ni. By carefully introducing ternary atoms that will segregate to the the precipitate/matrix interface, it will be possible to stabilize much smaller precipitates that are resistant to coarsening at high-temperatures. To identify such systems, in section II, we develop a thermodynamic model that describes the energetics of simple ternary alloys (A-B-C), where the binary A-B system favors the precipitation of the ordered compound $A_mB_n$ and the impurity C atoms may segregate to the interface between the matrix and the $A_mB_n$ precipitate.

It is assumed that the segregation is promoted just through favorable chemical interactions at the interface. The important contribution of elastic strain is ignored, for now, so that we can build a simple thermodynamic model for the ternary alloy system. Future work will focus on incorporating the strain energy effects. Under these simplifying conditions, the model is assumed to be applicable to precipitating systems with incoherent interfaces (e.g. incoherent equilibrium $\theta$ phase in Al-Cu alloys [40]). In this article, we present the thermodynamic model using the ternary Mg-Sn-Zn alloy system, where recent experimental studies [44, 45] have shown the segregation of Zn to all Mg/Mg$_2$Sn interfaces irrespective of interface structure and orientation relationship and that the segregation is not limited by the kinetics of Zn diffusion. This observation suggests the presence of a chemical driving force for heterophase interface segregation. In section III the variations in equilibrium precipitate sizes and the Gibbs interfacial excess of the solute atoms, for the Mg-Sn-Zn ternary alloy, as a function of different interaction energy parameters and temperature are presented.
II. ANALYTICAL TREATMENT

In this section, we present a thermodynamic model to study solute segregation to the interface between a solid-solution bulk phase and a binary ordered-intermetallic-compound. The Gibbs free energies of the bulk and the interface regions of the system are described using a statistical-thermodynamic framework involving the regular solution assumptions of random mixing and nearest-neighbor pairwise interaction [55]. This follows the regular nanocrystalline solution model developed by Trelewicz and Schuh [56] and extended to ternary systems by Saber et al. [57]. Energy contribution of the precipitate region is described using the Gibbs free energy of formation of the intermetallic compound; this avoids the complexity involved in sublattice models. The model for a binary alloy system is presented first. The binary system consists of a solvent element, \( A \), and a solute element, \( B \), that favor precipitation of an intermetallic compound of the type \( A_m B_n \) from solid-solution. The model is subsequently extended to a ternary alloy system, wherein a secondary solute element, \( C \), is considered to be soluble in the bulk and the interface solid-solutions but assumed to be insoluble in the precipitate. The bulk and interface regions are provided with distinct descriptions of energetic parameters and compositions. This feature allows equilibrium segregation of solute to the interface for energetic parameters favoring the reduction in interfacial energy, and thus in the system free energy, on solute segregation. The free energy function, important relations and definitions pertaining to the model are presented below; the complete derivation is given in section S1 of Supplemental Materials.

A. Binary Model

The alloy system, consisting of a heterogeneous distribution of \( A \) and \( B \) atoms, is divided into three distinct regions—the bulk, the precipitate and the bulk/precipitate interface regions, denoted by \( b \), \( p \) and \( i \), respectively. The global concentration of \( B \) in the system, \( x_o \), can be expressed as a function of region-specific concentrations, \( x_b \), \( x_i \) and \( x_p \), and volume fractions, \( f_b \), \( f_i \) and \( f_p \), using the mass balance relation as:

\[
x_o = x_b (1-f_i - f_p) + x_i f_i + x_p f_p.
\] (1)
Here, \( f_b = 1 - f_i - f_p \), and since the precipitate is an intermetallic compound, concentration in \( p \) is stoichiometric with \( x_p = n/m \). For a closed system of given \( x_o \), this relation imposes constraint on the values that the variables \( x_b, x_i, f_i \) and \( f_p \) can take simultaneously.

The assumptions of random mixing and nearest-neighbor pairwise interaction between the atoms of bulk solid-solution result in the following expression for the Gibbs free energy of mixing of \( b \), \( \Delta \bar{G}^{mix}_b \):

\[
\Delta \bar{G}^{mix}_b = \left\{ \omega^{AB}_b (1 - x_b) x_b z_b + RT \left[ (1 - x_b) \ln (1 - x_b) + x_b \ln x_b \right] \right\} (1 - f_i - f_p),
\]

where, \( z_b \) is the coordination number and and \( \omega^{AB}_b \) is the regular solution interaction parameter, specific to region \( b \). The bar over \( \Delta \bar{G}^{mix}_b \) defines the quantity per mole of atoms in the system and applies to all quantities represented this way in this paper; \( \omega^{AB}_b \) is defined per mole of atoms in \( b \). This expression is essentially the free energy of mixing obtained in the regular solution model, scaled by the size of the bulk region relative to the system (i.e. \( f_b = 1 - f_i - f_p \)). The first term in the expression corresponds to the excess enthalpy of mixing, obtained from the internal energy of mixing assuming negligible volume change during mixing. Here, \( \omega^{AB}_b \) accounts for the energy difference involved in the formation of unlike \( AB \) bonds from like \( AA \) and \( BB \) bonds having energies characteristic of the bulk region; this is given by:

\[
\omega^{AB}_b = E^{AB}_b - \frac{E^{AA}_b + E^{BB}_b}{2}.
\]

The part of term multiplied to \( \omega^{AB}_b \), along with the bulk volume fraction \( f_b \), represents the number of \( AB \) bonds, \( N^{AB}_b \), in the bulk region. The first term thus corresponds to the enthalpy of forming unlike bonds from like bonds. The second term in Eq. (2) represents the ideal entropy of mixing in \( b \).

In general, the number of bonds of type \( kl \) in region \( r \), \( N^{kl}_r \), is obtained as:

\[
N^{kl}_r = N^{bonds}_r P^{kl}_r,
\]

where, \( r \) refers to the bonding regions of \( b \) and \( i \), and the transition regions \( ib \) and \( ip \), occurring between atoms of \( i \) and \( b \), and atoms of \( i \) and \( p \), respectively. \( N^{bonds}_r \) is the total
number of bonds in \( r \); \( P_{r}^{kl} \) is the statistical probability that the bond in \( r \) is of type \( kl \), and is obtained as a function of the composition in each region \( r \). For the binary system with a total number of \( N_{o} \) atoms of \( A \) and \( B \), expressions for various \( N_{r}^{bonds} \) and \( P_{r}^{kl} \) are presented in Table I.

TABLE I: Number of bonds, bond probabilities and bond energies of various bond-types specific to the different bonding-regions in the binary system.

| Region                        | Number of bonds in region \( r \), \( N_{r}^{bonds} \) | Bond type, \( kl \) | Bond energy | Bond probability, \( P_{r}^{kl} \) |
|-------------------------------|------------------------------------------------------|---------------------|-------------|----------------------------------|
| Bulk, \( b \)                 | \( N_{o} (1 - f_{i} - f_{p}) \frac{z_{i}}{2} \)      | AB                  | \( E_{b}^{AB} \) | \( 2 (1 - x_{b}) x_{b} \)       |
| Interface, \( i \)            | \( N_{o} f_{i} \frac{z_{i}}{2} \)                   | AA                  | \( E_{i}^{AA} \) | \( (1 - x_{i})^{2} \)           |
| Interface-bulk transition, \( ib \) | \( N_{o} f_{i} \frac{z_{ib}}{2} \)                  | BB                  | \( E_{i}^{BB} \) | \( x_{i}^{2} \)                |
|                               |                                                      | AB                  | \( E_{i}^{AB} \) | \( 2 (1 - x_{i}) x_{i} \)       |
| Interface-precipitate transition, \( ip \) | \( N_{o} f_{i} \frac{z_{ip}}{2} \)                  | BB                  | \( E_{i}^{BB} \) | \( x_{i} x_{p}^{i/f} \) \( x_{i} \) |
|                               |                                                      | AB                  | \( E_{i}^{AB} \) | \( (1 - x_{i}) x_{b} + (1 - x_{b}) x_{i} \) |

The Gibbs free energy of mixing for the formation of interface solid-solution, \( \Delta \bar{G}_{i}^{mix} \), is obtained similar to \( b \) following the regular solution model as:
\[ \Delta G_{mix}^i = \{ \omega_i^{AB} (1 - x_i) x_i z_{ii} + [\delta_i^{AA} (1 - x_i) + \delta_i^{BB} x_i] \frac{z_{ii}}{2} \] 
\[ + RT [(1 - x_i) \ln (1 - x_i) + x_i \ln x_i] \} f_i. \]  

Here, the interface interaction parameter, \( \omega_i^{AB} \), captures the energetics of formation of unlike bonds in region \( i \) from like bonds in pure element states characteristic of \( i \), and is given by:

\[ \omega_i^{AB} = E_i^{AB} - \frac{E_i^{AA} + E_i^{BB}}{2}. \]  

The formation of the interface solid-solution is considered from the same reference state as that for the formation of the bulk; i.e. the reference state is pure \( A \) and pure \( B \) with bond-energies and bond-coordination characteristic of \( b \). Therefore, in addition to the enthalpy of mixing (first term), an additional term (second term) arises—this corresponds to the energy associated with a change of state of components \( A \) and \( B \) from a state characteristic of \( b \) to one characteristic of \( i \). This change of state is captured by the parameters \( \delta_i^{AA} \) and \( \delta_i^{BB} \), and is defined per mole of \( A \) and \( B \), respectively, as,

\[ \delta_i^{AA} = E_i^{AA} \frac{z_b}{z_i} E_b^{AA} \quad \text{and} \quad \delta_i^{BB} = E_i^{BB} \frac{z_b}{z_i} E_b^{BB}. \]  

These parameters represent the difference between like bond energies characteristic of the interface and the bulk and can be directly related to the interface free energies of \( A \) and \( B \) (see Supporting Materials [S3]); \( z_b / z_i \) accounts for the different atomic coordination of \( b \) and \( i \). Analogous to Eq. 2, the terms multiplying the energy parameters in Eq. 5 are obtained form Table I. The term coupled to \( \omega_i^{AB} \) is \( N_i^{AB} \); and terms coupled to \( \delta_i^{AA} \) (i.e. \( f_i (1 - x_i) z_{ii} / 2 \)) and \( \delta_i^{BB} \) (i.e. \( f_i x_i z_{ii} / 2 \)) represent the number of AA bonds \( (N_i^{AA} + N_i^{AB} / 2) \) and BB bonds \( (N_i^{BB} + N_i^{AB} / 2) \), respectively, in the pure element reference state of \( i \). The terms coupled to the parameters \( \omega_b, \omega_i \) and \( \delta_i \) in subsequent equations can be interpreted in a similar manner.

The interface region is considered as one layer of atoms between the bulk and the precipitate regions. Thus, of the total coordination \( z_i \) per interface atom, \( z_{ii} \) connects to neighboring interface atoms, while \( z_{ib} \) and \( z_{ip} \) connect to \( b \) and \( p \) atoms, respectively, that lie adjacent to region \( i \). To account for the non-random distribution of atoms in \( p \) and the dependence on
the interface plane, concentration at the atomic layer of precipitate adjacent to $i$ is defined distinctly as $x_{p}^{i/f}$. Random distribution of atoms with a concentration of $x_{b}$ is assumed to be applicable to the atomic layer of $b$ adjacent to $i$. $ib$ and $ip$ bonds are defined to have bond-energies characteristic of $i$. Following these considerations, the Gibbs free energy for the formation of the transition regions $ib$ and $ip$, $\Delta \tilde{G}_{ib}$ and $\Delta \tilde{G}_{ip}$, respectively, are obtained as:

\[
\Delta \tilde{G}_{ib} = \omega_{i}^{AB} \left[ (1 - x_{b}) x_{i} + (1 - x_{i}) x_{b} \right] f_{i} \frac{z_{ib}}{2} \\
+ \left[ \delta_{i}^{AA} (1 - x_{i} + 1 - x_{b}) + \delta_{i}^{BB} (x_{i} + x_{b}) \right] f_{i} \frac{z_{ib}}{4},
\]

\[
\Delta \tilde{G}_{ip} = \omega_{i}^{AB} \left[ (1 - x_{p}^{i/f}) x_{i} + (1 - x_{i}) x_{p}^{i/f} \right] f_{i} \frac{z_{ip}}{2} \\
+ \left[ \delta_{i}^{AA} (1 - x_{i} + 1 - x_{p}^{i/f}) + \delta_{i}^{BB} (x_{i} + x_{p}^{i/f}) \right] f_{i} \frac{z_{ip}}{4}.
\]

Analogous to the interpretation of Eq. 5, the first terms of Eqs. 8 and 9 represent the enthalpy change associated with the formation of unlike bonds of the corresponding transition regions from like bonds of pure $A$ and pure $B$ states characteristic of $i$. The second terms corresponds to the additional enthalpy associated with the change of state of the pure elements from energies characteristic of $b$ to $i$.

While the free energy expressions presented in Eqs. 2, 5, 8 and 9 considered the reference states as pure $A$ and pure $B$ with crystal structures characteristic of the bulk solid-solution, $A$ or $B$ or both, however, may have a crystal structure preference different from the bulk. To enable treatment of such systems, the initial or standard state is chosen as pure $A$ and pure $B$ at $T$, having crystal structures specific to their Standard Element Reference State (i.e. the most stable state of an element at 298.15 K and $10^{5}$ Pa [58]). The molar free energies involved in the conversion of $A$ and $B$ from the standard state at $T$ to the reference state characteristic of $b$, at the same $T$, are defined as $\Delta \tilde{G}_{ref(b)}^{A}$ and $\Delta \tilde{G}_{ref(b)}^{B}$, respectively. The total free energy change associated with this change in reference state, $\Delta \tilde{G}_{ref}^{i/ref}$, for atoms forming $b$ and $i$ regions of the system is obtained as a mole fraction-weighted average of $\Delta \tilde{G}_{ref(b)}^{A}$ and $\Delta \tilde{G}_{ref(b)}^{B}$, scaled by the region-sizes as:
\[
\Delta \bar{G}_{b,i}^{\text{ref}} = [(1 - x_b) \Delta \bar{G}_{\text{ref}}^{A} + x_b \Delta \bar{G}_{\text{ref}}^{B}] (1 - f_i - f_p) \\
+ [(1 - x_i) \Delta \bar{G}_{\text{ref}}^{A} + x_i \Delta \bar{G}_{\text{ref}}^{B}] f_i. 
\] (10)

The Gibbs free energy for the formation of precipitate region, \(\Delta \bar{G}_p\), is obtained in terms of the molar Gibbs free energy for the formation of \(A_mB_n\) intermetallic, \(\Delta \bar{G}_{f}^{A_mB_n}\), from the pure element standard states of \(A\) and \(B\), and is scaled by the precipitate size.

\[
\Delta \bar{G}_p = \Delta \bar{G}_{f}^{A_mB_n} f_p 
\] (11)

The total Gibbs free energy, \(\Delta \bar{G}_{bin}\)—defined for the formation of the binary system configuration from initial pure element standard states of \(A\) and \(B\)—is obtained as the summation over free energy contributions corresponding to the formation of \(b\), \(i\), \(ib\), \(ip\) and \(p\) regions of the system from Eqs. 2, 5, 8, 9, 10 and 11, thus,

\[
\Delta \bar{G}_{bin} = \Delta \bar{G}_b^{\text{mix}} + \Delta \bar{G}_{i}^{\text{mix}} + \Delta \bar{G}_{ib} + \Delta \bar{G}_{ip} + \Delta \bar{G}_{b,i}^{\text{ref}} + \Delta \bar{G}_p. 
\] (12)

**B. Ternary Model**

The binary model presented in section II A is now extended to a ternary system containing an additional element in secondary solute \(C\). The ternary alloy system consists of a heterogeneous distribution of \(A\), \(B\) and \(C\) atoms and, as before, the system has three distinct regions of atom occupancy, viz. \(b\), \(p\) and \(i\), and bonding regions of \(b\), \(i\), \(p\), \(ib\) and \(ip\). We consider \(C\) to form ternary solid-solution with \(A\) and \(B\) in the bulk and the interface regions, while insoluble in the intermetallic compound. In addition to the mass balance relation for solute \(B\), given by Eq. 1 mass balance relation for solute \(C\) is obtained as:

\[
y_o = y_b (1 - f_i - f_p) + y_i f_i. 
\] (13)

Each of the variables \(x_i\), \(x_b\), \(y_i\), \(y_b\), \(f_i\) and \(f_p\) can take values between 0 and 1. For given values of \(x_o\) and \(y_o\), Eqs. 1 and 13 impose constraints on the values the above variables can take simultaneously. We will consider \(x_i\), \(y_i\), \(f_i\) and \(f_p\) as the independent variables.
The Gibbs free energy function, $\Delta G_{\text{tern}}$, for the formation of the ternary system from the standard pure element states of $A$ and $B$ is obtained, similar to that for the binary system, as the summation over free energy contributions corresponding to the formation of $b$, $i$, $ib$, $ip$ and $p$ regions of the system. Thus,

$$\Delta G_{\text{tern}} = \Delta G_{b}^{\text{mix}} + \Delta G_{i}^{\text{mix}} + \Delta G_{ib} + \Delta G_{ip} + \Delta G_{b,i}^{\text{ref}} + \Delta G_{p}, \quad (14)$$

where,

$$\Delta G_{b}^{\text{mix}} = \left\{ \left[ \omega_{b}^{AB} (1 - x_{b} - y_{b}) x_{b} + \omega_{b}^{BC} x_{b} y_{b} + \omega_{b}^{AC} (1 - x_{b} - y_{b}) y_{b} \right] z_{b} \right. \left. + RT \left[ (1 - x_{b} - y_{b}) \ln (1 - x_{b} - y_{b}) + x_{b} \ln x_{b} + y_{b} \ln y_{b} \right] \right\} (1 - f_{i} - f_{p}) ,$$

$$\Delta G_{i}^{\text{mix}} = \left\{ \left[ \omega_{i}^{AB} (1 - x_{i} - y_{i}) x_{i} + \omega_{i}^{BC} x_{i} y_{i} + \omega_{i}^{AC} (1 - x_{i} - y_{i}) y_{i} \right] z_{ii} \right. \left. + \left[ \delta_{i}^{AA} (1 - x_{i} - y_{i}) + \delta_{i}^{BB} x_{i} + \delta_{i}^{CC} y_{i} \right] \frac{z_{ii}}{2} \right. \left. + RT \left[ (1 - x_{i} - y_{i}) \ln (1 - x_{i} - y_{i}) + x_{i} \ln x_{i} + y_{i} \ln y_{i} \right] \right\} f_{i},$$

$$\Delta G_{ib} = \left\{ \omega_{i}^{AB} [(1 - x_{b} - y_{b}) x_{i} + (1 - x_{i} - y_{i}) x_{b}] + \omega_{i}^{BC} (x_{b} y_{i} + x_{i} y_{b}) \right. \left. + \omega_{i}^{AC} [(1 - x_{b} - y_{b}) y_{i} + (1 - x_{i} - y_{i}) y_{b}] \right\} \frac{z_{ib}}{2} \right. \left. + \left[ \delta_{i}^{AA} (1 - x_{i} - y_{i} + 1 - x_{b} - y_{b}) + \delta_{i}^{BB} (x_{i} + x_{b}) + \delta_{i}^{CC} (y_{i} + y_{b}) \right] \frac{z_{ib}}{4} ,$$

$$\Delta G_{ip} = \left\{ \omega_{i}^{AB} \left[ (1 - x_{p}^{i/f}) x_{i} + (1 - x_{i} - y_{i}) x_{p}^{i/f} \right] + \omega_{i}^{BC} x_{p}^{i/f} y_{i} \right. \left. + \omega_{i}^{AC} (1 - x_{p}^{i/f}) y_{i} \right\} \frac{z_{ip}}{2} \right. \left. + \left[ \delta_{i}^{AA} (1 - x_{i} - y_{i} + 1 - x_{p}^{i/f}) + \delta_{i}^{BB} (x_{i} + x_{p}^{i/f}) + \delta_{i}^{CC} y_{i} \right] \frac{z_{ip}}{4} ,$$

$$\Delta G_{b,i}^{\text{ref}} = \left\{ [(1 - x_{b} - y_{b}) \Delta G_{\text{ref}(b)}^{A} + x_{b} \Delta G_{\text{ref}(b)}^{B} + y_{b} \Delta G_{\text{ref}(b)}^{C}] (1 - f_{i} - f_{p}) \right. \left. + [(1 - x_{i} - y_{i}) \Delta G_{\text{ref}(b)}^{A} + x_{i} \Delta G_{\text{ref}(b)}^{B} + y_{i} \Delta G_{\text{ref}(b)}^{C}] \right\} f_{i},$$

$$\Delta G_{p} = \Delta G_{f}^{\text{mix}} B_{n} f_{p}.$$
energies of like bonds characteristic of the interface and that of the bulk is \( \delta_{kk}^i = E_{kk}^i - \frac{z_i}{z_b} E_{bb}^k \).

The terms multiplying \( \omega_b, \omega_i \) and \( \delta_i \) (including the volume fraction and the coordination number) correspond to the number of bonds of the type defined by \( \omega_b, \omega_i \) or \( \delta_i \), and were obtained, as described in section II A, using Eq. 4; the number of bonds specific to each bonding region, and the bond probabilities of the various bond types are presented in Table II. The \( \Delta \bar{G}_{\text{tern}} \) function given Eq. 14 is the main result of our model.
TABLE II: Number of bonds, bond probabilities and bond energies of various bond-types specific to the different bonding-regions in the ternary system.

| Region                  | Number of bonds in region $r$, $N^{bonds}_r$ | Bond type, $kl$ | Bond energy          | Bond probability, $P^{kl}_r$ |
|------------------------|---------------------------------------------|----------------|---------------------|-----------------------------|
| Bulk, $b$              | $N_o (1 - f_i - f_p) \frac{z}{2}$           | AB            | $E^{AB}_b$          | $2 (1 - x_b - y_b) x_b$     |
|                        |                                             | BC            | $E^{BC}_b$          | $2 x_b y_b$                 |
|                        |                                             | AC            | $E^{AC}_b$          | $2 (1 - x_b - y_b) y_b$     |
| Interface, $i$         | $N_o f_i \frac{z}{2}$                      | AA            | $E^{AA}_i$          | $(1 - x_i - y_i)^2$         |
|                        |                                             | BB            | $E^{BB}_i$          | $x_i^2$                     |
|                        |                                             | CC            | $E^{CC}_i$          | $y_i^2$                     |
|                        |                                             | AB            | $E^{AB}_i$          | $2 (1 - x_i - y_i) x_i$     |
|                        |                                             | BC            | $E^{BC}_i$          | $2 x_i y_i$                 |
|                        |                                             | AC            | $E^{AC}_i$          | $2 (1 - x_i - y_i) y_i$     |
| Interface-bulk transition, $ib$ | $N_o f_i \frac{z}{2}$               | AA            | $E^{AA}_i$          | $(1 - x_i - y_i) (1 - x_b - y_b)$ |
|                        |                                             | BB            | $E^{BB}_i$          | $x_i x_b$                   |
|                        |                                             | CC            | $E^{CC}_i$          | $y_i y_b$                   |
|                        |                                             | AB            | $E^{AB}_i$          | $(1 - x_i - y_i) x_b + (1 - x_b - y_b) x_i$ |
|                        |                                             | BC            | $E^{BC}_i$          | $x_i y_b + x_b y_i$         |
|                        |                                             | AC            | $E^{AC}_i$          | $(1 - x_i - y_i) y_b + (1 - x_b - y_b) y_i$ |
| Interface-precipitate transition, $ip$ | $N_o f_i \frac{z}{2}$               | AA            | $E^{AA}_i$          | $(1 - x_i - y_i) \left(1 - x_p^{if}\right)$ |
|                        |                                             | BB            | $E^{BB}_i$          | $x_i x_p^{if}$              |
|                        |                                             | AB            | $E^{AB}_i$          | $(1 - x_i - y_i) x_p^{if} + \left(1 - x_p^{if}\right) x_i$ |
|                        |                                             | BC            | $E^{BC}_i$          | $y_i x_p^{if}$              |
|                        |                                             | AC            | $E^{AC}_i$          | $y_i \left(1 - x_p^{if}\right)$ |
C. Geometric Relationship

FIG. 1: Right: Schematic of a spherical precipitate $p$, of radius $r_p$, within the bulk region $b$. The interface region, $i$, is a spherical shell of thickness $t$. Left: Region $p$ comprises an ordered arrangement of atoms $A$ and $B$. Region $b$ is a random solid-solution of $B$ and $C$ in $A$. The large concentration of $C$ in region $i$ illustrates interface solute segregation. Bonds in region $i$ correspond to bonds between the interface atoms, $ii$, between atoms of $i$ and $b$, $ib$, and between atoms of $i$ and $p$, $ip$.

The analytical model was developed considering that the interface atomic region constitutes a single layer of atoms. Thus, the interface volume fraction, $f_i$, can be expressed as a fraction of the precipitate volume fraction, $f_p$, as $f_i = \phi f_p$. A geometric representation of the system configuration can be obtained for these variables under certain assumptions of the shape and size of the precipitates. For a spherical morphology with equi-sized precipitates of
radius \( r_p \), the interface region is a spherical shell, of thickness \( t \) surrounding the precipitate; this is illustrated in Fig. [1]. Here, \( t \) is taken as 0.25 nm, which is characteristic of the atomic length scale in crystals. From geometric dependence of the volumes of the sphere and the encompassing spherical shell, a relation between the precipitate size \( r_p \) and the fraction of interface with respect to the precipitate, \( \phi \), is obtained as,

\[
r_p = \frac{3t}{\phi}.
\]  

(15)

D. Equilibrium Conditions

The equilibrium configuration of the ternary system, for a given set of global compositions \((x_o, y_o)\), temperature \((T)\) and parametric values \((\omega_b, \omega_i, \delta_i, z, x^i_p)\) can be obtained by minimizing the Gibbs free energy function for the system (Eq. 14) with respect to \( x_i, y_i, f_i \) and \( f_p \). The treatment of equilibrium between the the bulk, the precipitate and the interface regions is similar to that for equilibrium between three distinct phases. However, the interface region is different from a phase in that it cannot exist independent of the bulk and the precipitate phases. This constraint is incorporated by substituting the relation \( f_i = \phi f_p \), and by setting minimum and maximum values that \( \phi \) can take. System equilibrium is now obtained by minimizing \( \Delta \bar{G}_{tern} \) with respect to \( x_i, y_i, \phi \) and \( f_p \) as:

\[
\frac{\partial \Delta \bar{G}_{tern}}{\partial x_i} = 0, \quad \frac{\partial \Delta \bar{G}_{tern}}{\partial y_i} = 0, \quad \frac{\partial \Delta \bar{G}_{tern}}{\partial \phi} = 0 \quad \text{and} \quad \frac{\partial \Delta \bar{G}_{tern}}{\partial f_p} = 0.
\]  

(16)

The equilibrium system configuration obtained in terms of \( \phi \) and \( x_b, x_i, y_b \) and \( y_i \) can be represented by the equilibrium quantities, \( r_p^{eq} \) and \( \Gamma_i^C \), respectively. (Equilibrium in the binary system is similarly obtained by minimizing \( \Delta \bar{G}_{bin} \) (Eq. 12) with respect to \( x_i, \phi \) and \( f_p \).) Here, \( \Gamma_i^C \) is the excess concentration of \( C \) at the interface and represents the segregation state in the system. \( \Gamma_i^C \) for the ternary system is given by [59, 60]:

\[
\Gamma_i^C = \frac{1}{N_{avg} \Omega^{2/3}} \left[ y_i - y_b \frac{x_i - (1 - y_i) x_p}{x_b - (1 - y_b) x_p} \right],
\]  

(17)

where, \( N_{avg} \) is a mole of interface atoms, \( \Omega \) is the atomic volume, and \( N_{avg} \Omega^{2/3} \) represents the molar interface area. Defining the interface solute excess per interface area allows the
quantity to be used to compare different configurational states of the system having different interface volume fractions.

III. PARAMETRIC STUDY

With the thermodynamic model and the conditions for equilibrium established, we can solve for the equilibrium precipitate size \( r_{eq}^p \) and interfacial excess \( \Gamma_C^i \). For the binary alloy system, the equilibrium precipitate size as a function of global solute (B) concentration is obtained at either the largest or the smallest precipitate size allowed by the limits imposed on \( \phi \). The equilibrium states obtained at these limits do not represent a true equilibrium between the three regions as, in the absence of the limits, the equilibrium would be between just two regions of the system. In one case, equilibrium configuration tending towards just the bulk and precipitate regions arises when the interface energy is unfavorable compared to other two regions—this is representative of ideal binary precipitating systems where the precipitates coarsen to reduce the interfacial energy, provided it is kinetically feasible. In the other case, equilibrium between bulk and the interface occurs when the interface energy is favorable; this is obtained when the interface interaction energy, \( \omega_i^{AB} \), is set to a large negative value.

These equilibrium configurations obtained from the binary model can be rationalized by considering the different regions of the binary system as phases and invoking the Gibbs phase rule. For a two component system at constant temperature and pressure, the phase rule states the the equilibrium between three phases has zero degrees of freedom in the intensive thermodynamic variables (i.e. chemical potentials of the components, which in the present model relates to the concentrations). This means that true equilibrium between the three regions, represented by a precipitate size within the imposed limits, can only be obtained at a unique global composition. This is of limited interest to us, and hence we turn our attention to the ternary system. For a three component system, as per the phase rule, equilibrium between three phases is possible with one degree of freedom in the intensive variables (i.e. concentrations). This additional degree of freedom is due to the presence of C in the system. Indeed, we obtain a range of equilibrium precipitate sizes over a range of global compositions \( (x_0 \text{ or } y_0) \) from the ternary model; these results are presented below.
The equilibrium system configurations, $r_p^{eq}$ and $\Gamma^C_i$, for the ternary alloy system are presented in this section as functions of $T$, $x_o$ and $y_o$, and the interface energy parameters, $\omega_i^{AB}$, $\omega_i^{BC}$, $\omega_i^{AC}$, $\delta_i^{AA}$, $\delta_i^{BB}$ and $\delta_i^{CC}$. Equilibrium values of $x_i$, $y_i$, $f_p$ and $\phi$ are obtained by minimization of $\Delta \bar{G}_{tern}$ (Eq. 14) using an interior-point optimization routine [61, 62]. The optimized variables for a given set of parameters are then expressed in terms of $\Gamma^C_i$ and $r_p^{eq}$ through relations given in Eqs. 17 and 15 respectively.

We take Mg-Sn-Zn as an example system for this study as recent work by Liu et al. [44, 45] suggests a thermodynamic basis for Zn segregation to the ternary solid-solution/Mg$_2$Sn interface. Accordingly, the values for bulk interaction parameters defining the Mg-Sn-Zn solid-solution phase are used, and $\Delta \bar{G}_{f}^{A_mB_n}$ corresponds to the formation energy of Mg$_2$Sn of $-24.5$ kJ/mol [63] (Supplemental Materials S2). In the following study, except for the particular parameter whose values are varied, all other parameters are set to default values listed in Table III. The values of interface interaction parameters, $\omega_i^{kl}$, are chosen to favor the presence of Zn at the interface, and the interface penalty parameters, $\delta_i^{kk}$, are chosen to be positive to represent the energy penalty associated with an interface. The magnitude of $\delta_i^{AA}$ is based on an estimate of the average interface energy of Mg/Mg$_2$Sn interface (see Supplemental Materials S3).

TABLE III: Default values are presented for: bulk interaction ($\omega_b$), interface interaction ($\omega_i$) and interface penalty ($\delta_i$) parameters; coordination numbers ($z$); temperature ($T$); global concentration of $B$ ($x_o$); and precipitate $B$ concentration adjacent to the interface ($x^{i/f}_p$).

| $\omega_b$ (kJ/mol) | $\omega_i^{AB}$ | $\omega_i^{BC}$ | $\omega_i^{AC}$ | $\delta_i^{AA}$ | $\delta_i^{BB}$ | $\delta_i^{CC}$ | $z_b$ | $z_{ii}$ | $z_{ib}$ | $z_{ip}$ | ($T$) (K) | ($x_o$) (at.%) | ($x^{i/f}_p$) (at.%) |
|-------------------|---------------|---------------|---------------|----------------|----------------|----------------|------|--------|--------|--------|------------|----------------|----------------|
| -2.03             | +2.54         | -0.11         | -2.03         | +2.54         | -10            | 3.5            | 3.5  | 3.5    | 12     | 6      | 3          | 300            | 2.2             | 33.33          |

A. Global solute concentrations, $x_o$ and $y_o$

The equilibrium configurations are first analyzed by varying the concentrations of components B ($x_o$) and C ($y_o$) in the ternary alloy system. Default values listed in Table III are used for the remaining parameters. In the range of global concentrations analyzed in
In this study, the equilibrium radius, $r_{eq}^p$, of the precipitate was found to be of the order of a few tens of nanometers. As shown in Fig. 2(a), at dilute concentrations of solute $C$, a small increase in $y_o$ results in a dramatic decrease in $r_{eq}^p$. Since the interaction energy parameters remain constant in this analysis, equilibrium concentrations in the bulk and the interface regions do not change by much with a change in the global solute concentrations ($x_o$ or $y_o$). This is reflected by the constant value of $\Gamma^C_i$ in Fig. 2(b).

FIG. 2: Variation of (a) equilibrium precipitate size and (b) equilibrium interfacial secondary solute excess with global solute concentrations of B ($x_o$) and C ($y_o$). The default values of the other relevant parameters are $\omega_{AB}^b = -2.03$, $\omega_{BC}^b = +2.54$, $\omega_{AC}^b = -0.11$, $\omega_{AB}^i = -2.03$, $\omega_{BC}^i = +2.54$, $\omega_{AC}^i = -10$, $\delta_i^{AA} = 3.5$, $\delta_i^{BB} = 3.5$, $\delta_i^{CC} = 3.5$ and $T = 300K$ (the units of $\omega$’s and $\delta$’s is kJ/mol).

$\Gamma^C_i$ for the default parameters corresponds to a large interfacial concentration of $C$ atoms ($\sim 53$ at.%) and a low bulk $C$ concentration ($\sim 0.15$ at.%), and thus represents a strong segregation of $C$ atoms to the interface. From an initial non-equilibrium state of uniform concentration in the bulk and the interface, segregation of $C$ to the interface reduces the interface free energy and thus the overall free energy of the system. As $\omega_i^{AC}$ is assigned a highly negative interaction energy, the interfacial energy is reduced by maximizing the
number of energetically favorable $AC$ bonds at the interface—this is achieved at close to equiatomic interface concentration of $A$ and $C$ atoms.

As stated earlier, composition in the bulk solid-solution, the interface region and the precipitate remain almost constant as we change the solute concentration $x$ and $y$. Therefore, the volume fractions of the precipitate and the interface regions vary to accommodate for the variations in global solute compositions (this is similar to the lever-rule calculations in a binary eutectic-alloy). An increase in $y$ while keeping $x$ fixed will result in an increase in the volume fraction of interfaces ($f_i$) at a constant value of precipitate volume fraction ($f_p$). This is accomplished by reducing the size and increasing the number of precipitates, thus increasing the total interfacial volume fraction. Conversely, increasing $x$ at a fixed $y$ will result in an increase in $f_p$ while $f_i$ remains constant. This is accomplished by reducing $\phi$ since $f_i = \phi f_p$, which in-turn results in an increase in $r_p^{eq}$ according to Eq. 15.

### B. Interface interaction energy parameters, $\omega_{kl}^i$

To understand the influence of the interface interaction parameters, the equilibrium precipitate radius $r_p^{eq}$ and the interfacial solute excess $\Gamma_i^C$ are plotted as a function of the global secondary solute concentration $y$ as $\omega_{AB}^i$, $\omega_{BC}^i$ and $\omega_{AC}^i$ are varied in Figs. 3, 4 and 5, respectively. In general, an unlike bond of type $kl$ is preferred at the interface over the bulk if $\omega_{kl}^i + \frac{\delta_{kl} + \delta_{ll}}{2} < \omega_{kl}^b$. Thus, a large negative value of $\omega_{kl}^i$ allows a large volume fraction of interface to exist at equilibrium by promoting segregation of solutes that form $kl$ bonds to the interface. Equilibrium precipitates of nanoscale sizes are therefore achieved for $\omega_{AC}^i = -10$ kJ/mol through segregation of $C$ to the interface and formation of energy reducing $AC$ bonds. As shown in Figs. 3(a), 4(a) and 5(a), the equilibrium precipitate size increases with increasing $\omega_{kl}^i$ to account for the increase in the interfacial energy. In the following, as we justify the observed trends for $\Gamma_i^C$, it is important to note that almost all of the $B$ atoms are present in the precipitate due to the large driving force for intermetallic precipitation. With this in mind, the trends for interfacial solute excess can be understood as follows:

- In Fig. 3(b), it is shown that $\Gamma_i^C$ increases with increasing $\omega_{AB}^i$. This is because $A$ atoms de-segregate out of the interface to reduce the fraction of increasingly unfavorable $AB$
bonds in the \( ip \) transition region. Also, the \( C \) atoms substitute interfacial \( A \) atoms resulting in an increase in the favorable interfacial \( AC \) bonds (in the transition region), and hence, \( \Gamma_i^C \) increases with increasing \( \omega_i^{AB} \).

- Similar to the trend in \( \omega_i^{AB} \), an increase in \( \omega_i^{BC} \) will result in a reduction of the number of interfacial \( BC \) bonds. As most of the \( B \) atoms are present in the precipitate, the \( BC \) bonds are present in the \( ip \) transition region. Therefore, the only way to reduce the number of \( BC \) bonds in the \( ip \) region is by removing the \( C \) atoms from the interface. This results in a reduction in \( \Gamma_i^C \) as shown in Fig. 4(b).

- An increase in \( \omega_i^{AC} \) results in an increase in \( \Gamma_i^C \) as shown in Fig. 5(b). While this trend is non-intuitive, it is not entirely surprising given the relative magnitudes of the \( \omega_i \) parameters. The increase in \( \Gamma_i^C \) with increasing \( \omega_i^{AC} \) can be rationalized by fixing the volume fraction of the interface \( f_i \). This fixes the total number of interface bonds (of type \( ii \), \( ip \) and \( ib \)) in the system. When \( \omega_i^{AC} \) is increased, the system requires a larger number of interfacial \( AC \) type bonds to stabilize the same volume fraction \( f_i \). This is because the default values for \( \omega_i^{AB} = -2.03 \text{ kJ/mol} \) and \( \omega_i^{BC} = +2.54 \text{ kJ/mol} \) are much larger than the values of \( \omega_i^{AC} \) explored in this study (\( -14, -10.5, -10 \) and \( -9.7 \text{ kJ/mol} \)). Therefore, in order to stabilize the required volume fraction of interfaces in the system, \( \Gamma_i^C \) has to be increased if \( \omega_i^{AC} \) is increased.

In summary, increasing \( \omega_i^{kl} \) displaces \( r_p^{eq} \) vs. \( y_o \) curves to larger precipitate sizes; this is presented in Figs. 3(a), 4(a) and 5(a). As discussed above, the interface stability corresponding to the new parametric value of \( \omega_i^{kl} \) can be achieved by the system through a reduction in the unfavorable bond-types and an increase the favorable bond-types. However, in the absence of the required concentration of \( C \) in the system to partition to the interface, a larger \( \Gamma_i^C \) (for \( \omega_i^{AB} \) and \( \omega_i^{AC} \) variation) is achieved by decreasing the interface volume fraction; this is seen by the increase in precipitate size (note that \( f_p \) remains constant but the number density of precipitates decreases).
FIG. 3: Effect of parametric variation of $\omega_{i}^{AB}$ on: (a) equilibrium precipitate size versus $y_\circ$; (b) equilibrium interfacial secondary solute excess versus $y_\circ$. The default values of the other relevant parameters are $\omega_{b}^{AB} = -2.03$, $\omega_{b}^{BC} = +2.54$, $\omega_{b}^{AC} = -0.11$, $\omega_{i}^{BC} = +2.54$, $\omega_{i}^{AC} = -10$, $\delta_{i}^{AA} = 3.5$, $\delta_{i}^{BB} = 3.5$, $\delta_{i}^{CC} = 3.5$, $T = 300\text{K}$, $x_\circ = 2.2$ at.% (the units of $\omega$’s and $\delta$’s is kJ/mol)

FIG. 4: Effect of parametric variation of $\omega_{i}^{BC}$ on: (a) equilibrium precipitate size versus $y_\circ$; (b) equilibrium interfacial secondary solute excess versus $y_\circ$. The default values of the other relevant parameters are $\omega_{b}^{AB} = -2.03$, $\omega_{b}^{BC} = +2.54$, $\omega_{b}^{AC} = -0.11$, $\omega_{i}^{AB} = -2.03$, $\omega_{i}^{AC} = -10$, $\delta_{i}^{AA} = 3.5$, $\delta_{i}^{BB} = 3.5$, $\delta_{i}^{CC} = 3.5$, $T = 300\text{K}$, $x_\circ = 2.2$ at.% (the units of $\omega$’s and $\delta$’s is kJ/mol)
FIG. 5: Effect of parametric variation of $\omega_{i}^{AC}$ on: (a) equilibrium precipitate size versus $y_b$; (b) equilibrium interfacial secondary solute excess versus $y_b$. The default values of the other relevant parameters are $\omega_{b}^{AB} = -2.03$, $\omega_{b}^{BC} = +2.54$, $\omega_{b}^{AC} = -0.11$, $\omega_{i}^{AB} = -2.03$, $\omega_{i}^{BC} = +2.54$, $\delta_{i}^{AA} = 3.5$, $\delta_{i}^{BB} = 3.5$, $\delta_{i}^{CC} = 3.5$, $T = 300K$, $x_o = 2.2$ at.% (the units of $\omega$’s and $\delta$’s is kJ/mol)

C. Interface energy penalty parameters, $\delta_{i}^{kk}$

An energy penalty of $\delta_{i}^{kk}$ is associated with interface and transition bonds connected to interface atoms of type $k$. Each like-bond and unlike-bond has an energy penalty of $2\delta_{i}^{kk}$ and $\delta_{i}^{kk} + \delta_{i}^{ll}$, respectively, and each atom of type $k$ occupying the interface site has an energy of $\delta_{i}^{kk}z_i^2$ in excess of the bulk site (other energies being equal). To evaluate the effect of the interface energy penalty parameters on the the equilibrium system configuration, $\delta_{i}^{kk}$ for a specific like bond-type is varied, while the other two like bond-types are fixed at their default value of 3.5 kJ/mol.

With an increase in $\delta_{i}^{kk}$, interface stability is maintained by rejecting from the interface atoms that contribute to excess interface energy through $kk$-type bonds, and by the segregation to the interface, atoms that reduce the interface energy through favorable $kl$ interactions. Thus, an increase in $\delta_{i}^{CC}$ leads to the de-segregation of $C$ from the interface, as shown by the decreasing $\Gamma_{i}^{C}$ in Fig. 6b, to reduce the overall number of interface $AC$, $CC$ and $BC$ bonds. Increasing $\delta_{i}^{AA}$ leads to rejection of $A$ atoms to reduce the fraction of $AA$
(mostly) bonds, and segregation of $C$ to increase the fraction of favorable $AC$ bonds (there is a balance here between the favorable interaction energy and the energy penalty associated with $AC$ bonds); this is shown in Fig. 7b. Since the concentration of $B$ at the interface is negligible, the increase in interface energy with $\delta^{BB}$ corresponds mainly to $AB$ and $BC$ bonds in the $ip$ transition region. In this case, the interface energy is reduced by substituting atoms of $A$ with $C$, thereby increasing $\Gamma^C_i$ (as shown in Fig. 8b) and the fraction of interface energy reducing $AC$ bonds.

The segregation state of $C$ (i.e. $\Gamma^C_i$) changes with $\delta^{kk}_i$ to maintain the interface in equilibrium as discussed above. However, in the absence of sufficient concentration of $C$ in the system, the equilibrium interface volume fraction decreases as shown by the shift in $r^eq_p$ vs. $y_0$ curves to larger precipitate sizes (Figs. 6a, 8a and 7a). The precipitate can be retained to the same size (i.e. same $\phi$) by increasing $y_0$ at a fixed $x_o$.

**FIG. 6:** Effect of parametric variation of $\delta^{CC}_i$ on: (a) equilibrium precipitate size versus $y_0$; (b) equilibrium interfacial secondary solute excess versus $y_0$. The default values of the other relevant parameters are $\omega^{AB}_b = -2.03$, $\omega^{BC}_b = +2.54$, $\omega^{AC}_b = -0.11$, $\omega^{AB}_i = -2.03$, $\omega^{BC}_i = +2.54$, $\omega^{AC}_i = -10$, $\delta^{AA}_i = 3.5$, $\delta^{BB}_i = 3.5$, $T = 300K$, $x_o = 2.2$ at.% (the units of $\omega$’s and $\delta$’s is kJ/mol).
FIG. 7: Effect of parametric variation of $\delta^{AA}_i$ on: (a) equilibrium precipitate size versus $y_b$; (b) equilibrium interfacial secondary solute excess versus $y_b$.

The default values of the other relevant parameters are $\omega_{AB}^b = -2.03, \omega_{BC}^b = +2.54, \omega_{AC}^b = -0.11, \omega_{i}^{AB} = -2.03, \omega_{i}^{BC} = +2.54, \omega_{i}^{AC} = -10, \delta^{BB}_i = 3.5, \delta^{CC}_i = 3.5, T = 300K, x_o = 2.2 \text{ at.}\%$ (the units of $\omega$’s and $\delta$’s is kJ/mol).

FIG. 8: Effect of parametric variation of $\delta^{BB}_i$ on: (a) equilibrium precipitate size versus $y_b$; (b) equilibrium interfacial secondary solute excess versus $y_b$.

The default values of the other relevant parameters are $\omega_{AB}^b = -2.03, \omega_{BC}^b = +2.54, \omega_{AC}^b = -0.11, \omega_{i}^{AB} = -2.03, \omega_{i}^{BC} = +2.54, \omega_{i}^{AC} = -10, \delta^{AA}_i = 3.5, \delta^{CC}_i = 3.5, T = 300K, x_o = 2.2 \text{ at.}\%$ (the units of $\omega$’s and $\delta$’s is kJ/mol).
D. Temperature

Dependence of the system’s free energy function on temperature arises from the parameter \( T \) coupled to the entropy of mixing terms corresponding to the bulk and the interface solid-solutions. The temperature dependence of \( \Delta G_{\text{ref}}^{\text{ref}} \) is ignored and their values at 300 K are used as input. The interaction parameters \( (\omega) \) are temperature-independent in the regular solution approximation. Thus the variation in the equilibrium system configuration with \( T \) stems primarily from the entropic contributions.

With an increase in temperature, precipitates are stabilized at larger sizes as shown in Fig. 9(a). Correspondingly, concentration of \( C \) at the interface decreases as shown by the decrease in the interfacial secondary solute excess in Fig. 9(b). The results correspond to de-segregation of \( C \) from the interface with temperature, leading to a reduction in the equilibrium interface volume fraction, and therefore, an increase in stable precipitate size.
The cause of desegregation is the reduction in system free energy through an increase in the entropy of the bulk solid-solution region. While the total entropy of the system is a combination of configurational entropy of mixing of bulk and interface solid-solutions, since the volume fraction of the bulk is significantly greater than that of the interface ($f_b > 0.9$), the system entropy is dominated by the contribution from the bulk (second term in Eq. 2). Therefore, with increasing temperature, the free energy of the system is reduced by increasing the configurational entropy of the bulk, which is accomplished by the desegregation of $C$ from the interface to the bulk. Free energy minimization, however, is a trade-off between enthalpic and entropic contributions. A system with stronger interactions of $C$ atoms at the interface, over the bulk, will have a lower tendency to de-segregate if the enthalpic driving force for segregation to the interface is stronger than the entropic driving force for de-segregation.

IV. CONCLUSIONS

We developed an analytical model that captures the thermodynamic stabilization of nano-sized precipitates, through chemically driven solute segregation to the heterophase interface, in alloy systems precipitating an intermetallic compound from the solid-solution. In binary precipitate systems like Mg/Mg$_2$Sn, or in the absence of secondary solutes with energy reducing interface interactions, the interface always presents a positive energy penalty which can only be reduced through precipitate coarsening. While aging treatments can be optimized to produce an alloy with small-size and high number density of precipitates to provide beneficial mechanical properties at room temperature, these precipitates are only kinetically stable. At higher temperatures, the precipitates coarsen to large sizes (typically to micron length scales) and drastically degrade structural performance. On the other hand, in ternary (or quaternary) alloy systems, where secondary solutes are chosen to have strong interactions at the heterophase interface, thermodynamic stabilization through solute segregation can be effective at high temperatures. For example, results of the ternary model evaluated for Mg-Sn-Zn system show that precipitates can be stabilized through Zn segregation driven by thermodynamic interfacial energy minimization.

While this study presents a thermodynamic basis for the experimental findings [44] of Zn segregation to Mg/Mg$_2$Sn interface and an associated refinement of Mg$_2$Sn precipitate sizes,
actual values for the interface parameters are unknown. The parametric study presented in this paper shows a reduction in the equilibrium precipitate size when the global secondary solute concentration, \( y_o \), is increased or any of the interface interaction parameters are decreased. On the other hand, the equilibrium precipitate size increases with temperature due to the entropic contributions favoring a more random partitioning of concentration between bulk and interface regions. While the present model incorporates chemical interactions, extension to the model is necessary to capture segregation and precipitate stabilization resulting from elastic strain energy effects. Together with the input of interface parameters from methods like density functional theory calculations, and the inclusion of participate morphology as a variable, the model will allow a more realistic prediction of thermodynamically stable precipitate sizes and shapes in ternary alloy systems.

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Supplemental Materials

Thermodynamic Stabilization of Precipitates through Interface Segregation: Chemical Effects

S1. ANALYTICAL TREATMENT

A. Binary Model

1. Internal Energy Function

We consider a binary system consisting of three distinct regions—bulk solid-solution, intermetallic precipitate, and a single-atomic-layer of interface solid-solution between the bulk and the precipitate; these regions of atom occupancy are denoted by \( b \), \( p \) and \( i \), respectively. The total internal energy of the system in this configuration, \( U_{sys} \), is the sum of the individual internal energies of each of the three regions; \( U_{sys} \) is defined for the thermodynamic state at temperature \( T \), total volume of the system \( V \), and total number of atoms in the system \( N_0 \). Considering that an atom of a particular type \( k \) (i.e. \( A \) or \( B \)), within an atomic region \( \text{reg} \), has an average potential energy per atom \( E^k_{\text{reg}} \), the internal energy of the system with \( N^k_{\text{reg}} \) number of \( k \)-type atoms in each region \( \text{reg} \) is,

\[
U_{sys} = \sum_{\text{reg}=b,i,p} (N^A_{\text{reg}}E^A_{\text{reg}} + N^B_{\text{reg}}E^B_{\text{reg}}). \quad (S1)
\]

The initial or standard configuration of the system, at the same \( T \) as the system configuration, is taken as the pure components in their standard element crystal structures (the stable form at 298.15 K and 10^5 Pa). Per-atom energies in this standard state, \( \text{std} \), is denoted by \( E^k_{\text{std}} \). The internal energy of this unmixed, interface- and precipitate-free configuration is given by,

\[
U_{\text{std}} = N^A_{\text{total}}E^A_{\text{std}} + N^B_{\text{total}}E^B_{\text{std}}. \quad (S2)
\]

where, \( N^k_{\text{total}} \) is the total number of atoms of type \( k \) in the system, and is related to \( N^k_{\text{reg}} \) by,
The internal energy change, $\Delta U_{\text{bin}}$, for the formation of the binary system with the three regions $b$, $i$, and $p$ from the initial configuration of pure components is given by,

$\Delta U_{\text{bin}} = U_{\text{sys}} - U_{\text{std}} = \sum_{\text{reg}=b,i,p} \left[ N_{\text{reg}}^A \left( E_{\text{reg}}^A - E_{\text{std}}^A \right) + N_{\text{reg}}^B \left( E_{\text{reg}}^B - E_{\text{std}}^B \right) \right].$  

(S4)

According to Eq. (S4), the reference energies for all the three regions of the system are $E_{\text{std}}^A$ and $E_{\text{std}}^B$. The crystal structures of the solid-solution phases, however, may be different from that of the standard states, and the thermodynamic parameters of mixing available in thermodynamic literature/database correspond to a reference state that has the same crystal structure as the solid-solution. Therefore, we reformulate terms corresponding to $b$ and $i$ in Eq. (S4) to obtain reference states as the pure components with energies and crystal structures characteristic of $b$ and $i$. The energies of atoms of type $k$, specific to region $\text{reg}$, in their reference state is denoted by $E_{\text{ref(\text{reg})}}^k$. Next, the energy difference between the reference state of $i$ and the pure component standard state, $E_{\text{ref(i)}} - E_{\text{std}}$, is rewritten in terms of $E_{\text{ref(i)}} - E_{\text{ref(b)}}$ and $E_{\text{ref(b)}} - E_{\text{std}}$. The reference state for region $p$ is left unchanged as the standard state since the data for formation energies of intermetallics in literature/databases are defined with respect to the standard states. Thus, $\Delta U_{\text{bin}}$ is obtained as,
\( \Delta U_{\text{bin}} = \Delta U_{\text{mix}}^b + \Delta U_i + \Delta U_{\text{ref}}^b,i + \Delta U_p, \)

(S5)

where,

\[
\Delta U_{\text{mix}}^b = \left[ \left( N_A^b E_A^b + N_B^b E_B^b \right) - \left( N_A^b E_{\text{ref}(b)} + N_B^b E_{\text{ref}(b)} \right) \right], \quad \text{(S5a)}
\]

\[
\Delta U_i = \left[ \left( N_A^i E_A^i + N_B^i E_B^i \right) - \left( N_A^i E_{\text{ref}(i)} + N_B^i E_{\text{ref}(i)} \right) \right] + \left[ N_A^i (E_{\text{ref}(i)} - E_{\text{ref}(b)}) + N_B^i (E_{\text{ref}(i)} - E_{\text{ref}(b)}) \right], \quad \text{(S5b)}
\]

\[
\Delta U_{\text{ref}}^b,i = \left[ N_A^b \left( E_{\text{ref}(b)} - E_{\text{std}}^A \right) + N_B^b \left( E_{\text{ref}(b)} - E_{\text{std}}^B \right) \right] + \left[ N_A^i (E_{\text{ref}(i)} - E_{\text{std}}^A) + N_B^i (E_{\text{ref}(i)} - E_{\text{std}}^B) \right], \quad \text{(S5c)}
\]

\[
\Delta U_p = \left[ \left( N_A^p E_A^p + N_B^p E_B^p \right) - N_A^p E_{\text{std}}^A - N_B^p E_{\text{std}}^B \right]. \quad \text{(S5d)}
\]

\( \Delta U_{\text{mix}}^b \) and \( \Delta U_i \) represent the internal energy change associated with the formation of solid-solution regions \( b \) and \( i \), respectively, from the pure component reference state \( \text{ref}(b) \). By considering random mixing and pair-wise interactions, the mixing in \( b \) and \( i \) can be treated similar to the regular solution models [S1, S2]. Thus, Eqs. (S5a) and (S5b) are redefined from a formalism involving an average per-atom energy description to a bond energy description based on the nearest-neighbor pairwise interaction. \( N_{b/i}^k \) is expressed in terms of the number of \( kl \) bonds, \( N_r^k \), and \( E_{b/i}^k \) in terms of the corresponding bond energies, \( E_{b/i}^k \). The bonding regions (r) are designated as follows: \( ib \) for bonds between atoms of \( i \) and \( b \); \( ip \) for bonds between atoms of \( i \) and \( p \); \( ii \) for bonds within atomic region \( i \); \( b \) for bonds within atomic region \( b \).

\[
\Delta U_{\text{mix}}^b = \left( N_{\text{ref}(b)}^A E_{\text{ref}(b)}^A + N_{\text{ref}(b)}^B E_{\text{ref}(b)}^B \right) - \left( N_{\text{ref}(b)}^A E_{\text{ref}(b)}^A + N_{\text{ref}(b)}^B E_{\text{ref}(b)}^B \right) \quad \text{(S6)}
\]
\[ \Delta U_i = \left( N_i^{AA} E_i^{AA} + N_i^{BB} E_i^{BB} + N_i^{AB} E_i^{AB} \right) - \left( N_i^{AA} E_{\text{ref}(i)}^{AA} + N_i^{BB} E_{\text{ref}(i)}^{BB} \right) \\
\quad + \left[ N_i^A \left( E_{\text{ref}(i)}^A - E_{\text{ref}(b)}^A \right) + N_i^B \left( E_{\text{ref}(i)}^B - E_{\text{ref}(b)}^B \right) \right] \]  

(S7)

Relation between the number of atoms of type \( k \), the number of bonds of type \( kk \) between like atoms and type \( kl \) between unlike atoms, and the number of bonds in the reference state, for atomic regions \( b \) and \( i \) is given by,

\[ N_k^b z^b_b = 2 N_{ref(b)}^{kk} = 2 N_k^b + N_k^{kl}, \]  

(S8a)

\[ N_k^i z^i_i = 2 N_{ref(i)}^{kk} = 2 N_k^i + N_k^{kl} = \left( 2 N_{ii}^{kk} + N_{ii}^{kl} \right) + \left( 2 N_{ib}^{kk} + N_{ib}^{kl} \right) + \left( 2 N_{ip}^{kk} + N_{ip}^{kl} \right). \]  

(S8b)

Now, expressions for \( N_{ref(b)}^{kk} \) from Eq. (S8a) and for \( N_{ref(i)}^{kk} \), \( N_i^A \) and \( N_i^B \) from Eq. (S8b) are substituted in Eq. (S7). Also substituting \( E_{ref(r)}^{kk} = E_r^{kk} \) gives:

\[ \Delta U_{mix}^b = N_{AB}^b \left( E_{AB}^b - \frac{E_{AA}^b + E_{BB}^b}{2} \right) \]  

(S9)

\[ \Delta U_i = \sum_{r=ii,ib,ip} N_r^{AB} \left( E_r^{AB} - \frac{E_r^{AA} + E_r^{BB}}{2} \right) \\
\quad + \left( N_r^{AA} + \frac{N_r^{AB}}{2} \right) \frac{2}{z_i} \left( E_{ref(r)}^A - E_{ref(b)}^A \right) + \left( N_r^{BB} + \frac{N_r^{AB}}{2} \right) \frac{2}{z_i} \left( E_{ref(r)}^B - E_{ref(b)}^B \right) \]  

(S10)

In Eq. (S10), the energies of transition bonds are considered to be characteristic of interface bonds, i.e. for \( r = ii, ib \) and \( ip \), \( E_r^{kk/kl} = E_i^{kk/kl} \) and \( E_{r{ref(r)}}^k = E_{r{ref(i)}}^k \). This also applies to the energy parameters defined below.

The regular solution interaction parameters, capturing the energetics of formation of unlike bond types from like bond types, characteristic to \( b \) and \( i \) (i.e. \( ii, ib \) and \( ip \)) are defined as,
\[ \omega_{AB} = E_{b}^{AB} - \frac{E_{b}^{AA} + E_{b}^{BB}}{2}, \quad (S11a) \]
\[ \omega_{i}^{AB} = E_{i}^{AB} - \frac{E_{i}^{AA} + E_{i}^{BB}}{2}. \quad (S11b) \]

We define an energy penalty parameter, \( \delta_{kk}^{r} \), that represents the excess energy of interface-type bonds over bulk-type bonds. This is expressed as the difference between per-atom energies of interface and bulk reference states as,

\[ \delta_{AA}^{i} = \frac{2}{z_{i}} \left( E_{\text{ref}(i)}^{A} - E_{\text{ref}(b)}^{A} \right), \quad \delta_{BB}^{i} = \frac{2}{z_{i}} \left( E_{\text{ref}(i)}^{B} - E_{\text{ref}(b)}^{B} \right). \quad (S12) \]

Alternately,

\[ \delta_{AA}^{i} = E_{i}^{AA} - \frac{z_{b}}{z_{i}} E_{b}^{AA}, \quad \delta_{BB}^{i} = E_{i}^{BB} - \frac{z_{b}}{z_{i}} E_{b}^{BB}. \quad (S13) \]

Eq. (S12) for any bond-region \( r \) is represented by \( \delta_{r}^{kk} \) (\( \delta_{b}^{kk} = 0 \)) and by the coordination number \( z_{r} \). The energy difference between the pure component reference state of \( b \) and the pure component standard state is defined as,

\[ \Delta U_{\text{ref}(b)}^{A} = E_{\text{ref}(b)}^{A} - E_{\text{std}}^{A}, \quad \Delta U_{\text{ref}(b)}^{B} = E_{\text{ref}(b)}^{B} - E_{\text{std}}^{B}. \quad (S14) \]

Using the definitions of Eqs. (S11), (S12) and (S14), Eqs. (S9) and (S10) can be rewritten as:

\[ \Delta U_{b}^{\text{mix}} = N_{b}^{AB} \omega_{b}^{AB} \quad (S15) \]

\[ \Delta U_{i} = \sum_{r=ii,ib,ip} \left[ N_{r}^{AB} \omega_{r}^{AB} + \left( N_{r}^{AA} + \frac{N_{r}^{AB}}{2} \right) \delta_{r}^{AA} + \left( N_{r}^{BB} + \frac{N_{r}^{AB}}{2} \right) \delta_{r}^{BB} \right] \quad (S16) \]

Supposing uniform number density of atoms within the system and equal atomic volumes of the components, the global or system concentration of \( B \) \( (x_{o}) \) can be expressed in terms
of region-specific concentrations of $B$ ($x_b$, $x_i$ and $x_p$) and region-specific volume fractions ($f_i$ and $f_p$) through Eq. (S17). Since the precipitate region is chosen to be stoichiometric, $x_p = n/m$ for an $A_mB_n$ intermetallic.

$$x_o = x_b (1 - f_i - f_p) + x_i f_i + x_p f_p$$  \hspace{1cm} (S17)

The number of atoms of a given type and region affiliation, $N_{reg}$, in Eq. (S5c) can be expressed as,

$$N^A_b = (1-f_i-f_p) N_o (1-x_b), \hspace{0.5cm} N^A_i = f_i N_o (1-x_i),$$

$$N^B_b = (1-f_i-f_p) N_o x_b, \hspace{0.5cm} N^B_i = f_i N_o x_i.$$  \hspace{1cm} (S18)

Expressions for $N_{kl}^{r}$ in Eqs. (S15) and (S16) can be obtained using statistical consideration of the existential bond probability of $kl$ (like and unlike) bonds among the total number of all bond types in the given region ($N_{r}^{bonds}$) as,

$$N_{r}^{kl} = N_{r}^{bonds} P_{r}^{kl}.$$  \hspace{1cm} (S19)

Relations for $N_{r}^{bonds}$ and $P_{r}^{kl}$ are listed in Table I of the main paper. The bond probabilities are derived for $b$ and $i$ regions based on random site occupancy of atoms—the probability of occupancy of a lattice site by a component $k$ is the concentration of $k$.

The interface atoms are considered to contribute a part of their bond co-ordination, $z_{ib}$, to $ib$ transition region, and $z_{ip}$ to $ip$ transition region. The rest of the interface bond co-ordination, $z_{ii}$, connects interface atoms lying within the interface atomic region. The $ip$ transition bonds connect interface atoms with the precipitate atoms located at the layer of the precipitate region that is adjacent to the transition region. The concentration at this precipitate layer is uniquely defined by $x^{if}_i$.

The summation in Eq. (S16) is expanded over $r$, and the number of terms in the expansion is reduced by substituting $\delta^{kk}_b = 0$. Since $ib$ and $ip$ transitional bonds are assigned bond energies characteristic of the interface $(i)$,

$$\omega^{kl}_i = \omega^{kl}_{ib} = \omega^{kl}_{ip} = \omega^{kl}_{ii}, \hspace{0.5cm} \delta^{kk}_i = \delta^{kk}_{ib} = \delta^{kk}_{ip} = \delta^{kk}_{ii}.$$  \hspace{1cm} (S20)
Eq. (S5d) represents the internal energy for the formation of $A_m B_n$ from the standard state. The first part of this term is the internal energy of $A_m B_n$ and is defined by $U_f^{A_m B_n}$ as,

$$\frac{U_f^{A_m B_n}}{m+n} = x_p^A E_p^A + x_p^B E_p^B$$  \hspace{1cm} (S21)

The energy parameters of Eqs. (S20) and (S21) and the relations from Table II are substituted into $\Delta U_{mix}^b$ (Eq. S15), $\Delta U_i$ (Eq. S16), $\Delta U_{ref}^b,i$ (Eq. S5c) and $\Delta U_p$ (Eq. S5d). Rearranging the resulting expression, considering $N_0$ as a mole of atoms in the system, and redefining the energy parameters per mole yields the final expression for the internal energy function of binary system, $\bar{\Delta U}_{bin}$, per mole of atoms (represented by the bar over $U$) as:
\[ \Delta \bar{U}^{\text{bin}} = \Delta \bar{U}^{\text{mix}} + \Delta \bar{U} + \Delta \bar{U}^{\text{ref}} + \Delta \bar{U}_p, \quad (\text{S22}) \]

\[ \Delta \bar{U}_i = \Delta \bar{U}_i^{\text{mix}} + \Delta \bar{U}_i + \Delta \bar{U}_i, \quad (\text{S22a}) \]

where,

\[ \Delta \bar{U}_b^{\text{mix}} = \left[ \omega_b^{AB} (1 - x_b) x_b \right] (1 - f_i - f_p) z_b, \quad (\text{S22b}) \]

\[ \Delta \bar{U}_i^{\text{mix}} = \left[ \omega_i^{AB} (1 - x_i) x_i \right] f_i z_{ii} + \left[ \delta_i^{AA} (1 - x_i) + \delta_i^{BB} x_i \right] \frac{f_i z_{ii}}{2}, \quad (\text{S22c}) \]

\[ \Delta \bar{U}_i = \omega_i^{AB} \left[ (1 - x_b) x_i + (1 - x_i) x_b \right] f_i z_{ib} + \left[ \delta_i^{AA} (1 - x_i + 1 - x_b) + \delta_i^{BB} (x_i + x_b) \right] \frac{f_i z_{ib}}{2}, \quad (\text{S22d}) \]

\[ \Delta \bar{U}_i = \omega_i^{AB} \left[ (1 - x_p) x_i + (1 - x_i) x_p \right] f_i z_{ip} + \left[ \delta_i^{AA} (1 - x_i + 1 - x_p) + \delta_i^{BB} (x_i + x_p) \right] \frac{f_i z_{ip}}{2}, \quad (\text{S22e}) \]

\[ \Delta \bar{U}_{b,i}^{\text{ref}} = \left[ (1 - x_b) \Delta \bar{U}_{\text{ref}(b)}^A + x_b \Delta \bar{U}_{\text{ref}(b)}^B \right] (1 - f_i - f_p) + \left[ (1 - x_i) \Delta \bar{U}_{\text{ref}(b)}^A + x_i \Delta \bar{U}_{\text{ref}(b)}^B \right] f_i, \quad (\text{S22f}) \]

\[ \Delta \bar{U}_p = \left[ \frac{\bar{U}_m^{\text{A} B_n}}{m + n} - (1 - x_p) \bar{U}_\text{std} - x_p \bar{U}_\text{std} \right] f_p. \quad (\text{S22g}) \]
2. Free Energy Function

The molar free energy change for the formation of the binary system configuration, $\Delta \bar{G}_{\text{bin}}$, is written in terms of the molar enthalpy change, $\Delta \bar{H}_{\text{bin}}$, and the molar entropy change, $\Delta \bar{S}_{\text{bin}}$, as

$$\Delta \bar{G}_{\text{bin}} = \Delta \bar{H}_{\text{bin}} - T \Delta \bar{S}_{\text{bin}}.$$  \hspace{1cm} (S23)

Neglecting any change in volume, $\Delta \bar{H}_{\text{bin}}$ can be approximated to equal $\Delta \bar{U}_{\text{bin}}$ (Eq. S22). $\Delta S$ is taken as the change configurational entropy, $\Delta \bar{S}_{\text{mix}}^b$ and $\Delta \bar{S}_{\text{mix}}^i$, associated with the the random mixing involved in the formation of $b$ and $i$ regions of the system, respectively, from the pure component reference states. $\Delta \bar{S}_{\text{bin}}$ is obtained from the Boltzmann’s equation as an additive expression involving region-size scaled entropy contributions.

$$\Delta \bar{S}_{\text{bin}} = \Delta \bar{S}_{\text{mix}}^b + \Delta \bar{S}_{\text{mix}}^i$$ \hspace{1cm} (S24)

$$\Delta \bar{S}_{\text{mix}}^b = -R \left[ (1 - x_b) \ln (1 - x_b) + x_b \ln x_b \right] (1 - f_i - f_p)$$  \hspace{1cm} (S24a)

$$\Delta \bar{S}_{\text{mix}}^i = -R \left[ (1 - x_i) \ln (1 - x_i) + x_i \ln x_i \right] f_i$$ \hspace{1cm} (S24b)

In the above, the configurational entropy change associated with the formation of region $p$ is neglected considering that both $A$ and $B$ atoms in $A_mB_n$ compound occupy their corresponding sub-lattice sites. However, $\Delta S$ terms for $p$, and also for the change in state from standard to reference state for $b$ and $i$, are considered and coupled appropriately to the related $\Delta \bar{U}$ terms to obtain the Gibbs free energy function in Eq. (S25). While evaluating this function for an actual alloy system, free energy values/expressions are taken from thermodynamic literature/database. These values/expressions are generally obtained from empirical measurements or first-principles calculations and inherently account for configuration or vibrational entropy contributions, even though these are ignored in the model itself.
The molar free energy function for the binary system, $\Delta \bar{G}_{bin}$, is obtained from Eqs. (S22), (S23) and (S24) as:

$$\Delta \bar{G}_{bin} = \Delta \bar{G}^{mix}_b + \Delta \bar{G}^{mix}_i + \Delta \bar{G}_{ib} + \Delta \bar{G}_{ip} + \Delta \bar{G}^{ref}_{b,i} + \Delta \bar{G}_p, \quad (S25)$$

where,

$$\Delta \bar{G}^{mix}_b = \Delta \bar{U}^{mix}_b - T \Delta \bar{S}^{mix}_b, \quad (S25a)$$

$$\Delta \bar{G}^{mix}_i = \Delta \bar{U}^{mix}_i - T \Delta \bar{S}^{mix}_i, \quad (S25b)$$

$$\Delta \bar{G}_{ib} = \Delta \bar{U}_{ib}, \quad (S25c)$$

$$\Delta \bar{G}_{ip} = \Delta \bar{U}_{ip}, \quad (S25d)$$

$$\Delta \bar{G}^{ref}_{b,i} = \left[ (1 - x_b) \Delta \bar{G}^A_{ref(b)} + x_b \Delta \bar{G}^B_{ref(b)} \right] (1 - f_i - f_p)$$
$$+ \left[ (1 - x_i) \Delta \bar{G}^A_{ref(b)} + x_i \Delta \bar{G}^B_{ref(b)} \right] f_i, \quad (S25e)$$

$$\Delta \bar{G}_p = \Delta \bar{G}^{A_mB_n}_f f_p, \quad (S25f)$$

$$\Delta \bar{G}^{A_mB_n}_f = \frac{G^{A_mB_n}_f}{m+n} - (1 - x_p) \bar{G}^A_{std} - x_p \bar{G}^B_{std}, \quad (S25g)$$
B. Ternary Model

As with the binary system, we consider the ternary system to consist of atomic regions \( b, i \) and \( p \), and bonding regions \( b, ii, ib \) and \( ip \). Additional terms and relations arise due to the presence of the ternary component \( C \); these are presented below.

The internal energy of the system configuration and the initial configuration are given by:

\[
U_{sys} = \sum_{reg=b,i,p} \left( N_{reg}^A E_{reg}^A + N_{reg}^B E_{reg}^B + N_{reg}^C E_{reg}^C \right)
\]

(S26)

\[
U_{std} = N_{total}^A E_{std}^A + N_{total}^B E_{std}^B + N_{total}^C E_{std}^C
\]

(S27)

Since we consider \( C \) to be insoluble in the \( A_n B_n \) precipitate, the total number of \( C \) atoms in the system, \( N_{total}^C \), is given by:

\[
N_{total}^C = N_b^C + N_i^C
\]

(S28)

Relations between the number of atoms of \( A \) and the number of bonds connecting atoms of \( A \) and specific to various bonding regions are obtained as:

\[
N_b^A z_b = 2N_{ref(b)}^{AA} = 2N_b^{AA} + N_b^{AB} + N_b^{AC}
\]

(S29)

\[
N_i^A z_i = 2N_{ref(i)}^{AA} = 2N_i^{AA} + N_i^{AB} + N_i^{AC}
\]

\[
= \left( 2N_{ii}^{AA} + N_{ii}^{AB} + N_{ii}^{AC} \right) + \left( 2N_{ib}^{AA} + N_{ib}^{AB} + N_{ib}^{AC} \right)
\]

\[
+ \left( 2N_{ip}^{AA} + N_{ip}^{AB} + N_{ip}^{AC} \right)
\]

(S30)

Similar relations are obtained for components \( B \) and \( C \). Relations for \( N_{r}^{bonds} \) and \( P_{r}^{kl} \) for the ternary system are listed in the Table II in the main paper. \( N_b^k \) and \( N_i^k \) can be expressed in terms of region-specific volume fractions and concentrations and total number of atoms as given below; \( y_b \) and \( y_i \) are the concentrations of \( C \) in \( b \) and \( i \), respectively.

\[
N_b^A = (1 - f_i - f_p)N_o (1 - x_b - y_b), \quad N_i^A = f_i N_o (1 - x_i - y_i)
\]

(S31)

\[
N_b^B = (1 - f_i - f_p)N_o x_b, \quad N_i^B = f_i N_o x_i,
\]

\[
N_b^C = (1 - f_i - f_p)N_o y_b, \quad N_i^C = f_i N_o y_i.
\]
In addition to the mass balance relation for solute \( B \), which is given by Eq. (S17), the mass balance relation for solute \( C \) is obtained as:

\[
y_o = y_b (1 - f_i - f_p) + y_i f_i
\]  
(S32)

As with \( \omega_{r}^{AB} \) (Eq. S11), regular solution parameters for mixing of \( B \) and \( C \) and mixing of \( A \) and \( C \) are defined with energies characteristic of \( r \) (\( b \) or \( i \)) as:

\[
\omega_{r}^{AC} = E_{r}^{AC} - \frac{E_{r}^{AA} + E_{r}^{CC}}{2}, \quad \omega_{r}^{BC} = E_{r}^{BC} - \frac{E_{r}^{BB} + E_{r}^{CC}}{2}
\]  
(S33)

The interface energy penalty parameter for \( CC \) bonds at the interface or transition regions is defined by:

\[
\delta_{r}^{CC} = \frac{2}{z_i} \left( E_{r}^{C}_{\text{ref}(i)} - E_{r}^{C}_{\text{ref}(b)} \right)
\]  
(S34)

The energy difference for \( C \) between its pure component reference state characteristic of \( b \) and its pure component standard state is:

\[
\Delta U_{\text{std} \rightarrow \text{ref}(b)}^{C} = E_{\text{ref}(b)}^{C} - E_{\text{std}}^{C}
\]  
(S35)
1. **Internal Energy Function**

The internal energy function for the ternary system, $\Delta U_{\text{tern}}$, is now obtained using the modified and the additional relations for the ternary system and following the derivation presented for the binary model.

$$\Delta U_{\text{tern}} = \Delta U_{\text{mix}} + \Delta U_{i} + \Delta U_{ib} + \Delta U_{ip} + \Delta U_{ib_i} + \Delta U_{p} \quad (S36)$$

where,

$$\Delta U_{\text{mix}} = \left[ \omega_{b}^{AB} (1 - x_b - y_b) x_b + \omega_{b}^{BC} x_b y_b + \omega_{b}^{AC} (1 - x_b - y_b) y_b \right] (1 - f_i - f_p) z_b \quad (S37)$$

$$\Delta U_{i} = \left[ \omega_{i}^{AB} (1 - x_i - y_i) x_i + \omega_{i}^{BC} x_i y_i + \omega_{i}^{AC} (1 - x_i - y_i) y_i \right] f_i z_{ii}$$

$$\Delta U_{ib} = \left\{ \omega_{i}^{AB} [(1 - x_b - y_b) x_i + (1 - x_i - y_i) x_b] + \omega_{i}^{BC} (x_b y_i + x_i y_b) \right. \right.$$  
$$\left. + \omega_{i}^{AC} [(1 - x_b - y_b) y_i + (1 - x_i - y_i) y_b] \right\} f_i z_{ib}$$

$$\Delta U_{ip} = \left\{ \omega_{i}^{AB} [(1 - x_i^{i//f}) x_i + (1 - x_i - y_i) x_i^{i//f}] + \omega_{i}^{BC} x_i^{i//f} y_i \right. \right.$$  
$$\left. + \omega_{i}^{AC} [(1 - x_i^{i//f}) y_i] f_i z_{ip} \right\} \frac{z_{ip}}{2}$$

$$\Delta U_{ib_i} = \left\{ \delta_{i}^{AA} (1 - x_i - y_i + 1 - x_b - y_b) + \delta_{i}^{BC} (x_i + x_b) + \delta_{i}^{CC} (y_i + y_b) \right\} f_i \frac{z_{ib}}{4}$$

$$\Delta U_{ref} = [(1 - x_b - y_b) \Delta U_{ref}(b) + x_b \Delta U_{ref}(b) + y_b \Delta U_{ref}(b)] (1 - f_i - f_p)$$

$$\Delta U_{p} = \left[ \left( \frac{U_{f}^{A \cdot B}}{m + n} - (1 - x_p) U_{std}^{A} - x_p U_{std}^{B} \right) \right] f_p \quad (S42)
2. Free Energy Function

The configuration entropy for the ternary system, $\Delta \bar{S}_{\text{tern}}$, is obtained as:

$$\Delta \bar{S}_{\text{tern}} = \Delta \bar{S}_{b}^{\text{mix}} + \Delta \bar{S}_{i}^{\text{mix}}$$  \hspace{1cm} (S43)

where,

$$\Delta \bar{S}_{b}^{\text{mix}} = - R \left[ (1 - x_{b} - y_{b}) \ln(1 - x_{b} - y_{b}) + x_{b} \ln x_{b} + y_{b} \ln y_{b} \right] (1 - f_{i} - f_{p}) $$  \hspace{1cm} (S43a)

$$\Delta \bar{S}_{i}^{\text{mix}} = - R \left[ (1 - x_{i} - y_{i}) \ln(1 - x_{i} - y_{i}) + x_{i} \ln x_{i} + y_{i} \ln y_{i} \right] f_{i} $$  \hspace{1cm} (S43b)

The free energy change for the formation of the ternary system configuration, $\Delta \bar{G}_{\text{tern}}$, is given by:

$$\Delta \bar{G}_{\text{tern}} = \Delta \bar{U}_{\text{tern}} - T \Delta \bar{S}_{\text{tern}}$$  \hspace{1cm} (S44)

Using Eqs. (S36), (S43) and (S44), and coupling $\Delta \bar{U}$ terms in Eqs. (S41) and (S42) with corresponding $-T\Delta \bar{S}$ terms, the final expression of $\Delta \bar{G}_{\text{tern}}$ is obtained as:

$$\Delta \bar{G}_{\text{tern}} = \Delta \bar{G}_{b}^{\text{mix}} + \Delta \bar{G}_{i}^{\text{mix}} + \Delta \bar{G}_{ib} + \Delta \bar{G}_{ip} + \Delta \bar{G}_{b,i}^{\text{ref}} + \Delta \bar{G}_{p}$$  \hspace{1cm} (S45)

where,

$$\Delta \bar{G}_{b}^{\text{mix}} = \Delta \bar{U}_{b}^{\text{mix}} + \Delta \bar{S}_{b}^{\text{mix}}$$  \hspace{1cm} (S46)

$$\Delta \bar{G}_{i}^{\text{mix}} = \Delta \bar{U}_{i}^{\text{mix}} + \Delta \bar{S}_{i}^{\text{mix}}$$  \hspace{1cm} (S47)

$$\Delta \bar{G}_{ib} = \Delta \bar{U}_{ib}$$  \hspace{1cm} (S48)

$$\Delta \bar{G}_{ip} = \Delta \bar{U}_{ip}$$  \hspace{1cm} (S49)
\[ \Delta \bar{G}_{b,i}^{ref} = \left[ (1 - x_b - y_b) \Delta G_{ref(b)}^A + x_b \Delta G_{ref(b)}^B + y_b \Delta G_{ref(b)}^C \right] (1 - f_i - f_p) \]
\[ + \left[ (1 - x_i - y_i) \Delta G_{ref(b)}^A + x_i \Delta G_{ref(b)}^B + y_i \Delta G_{ref(b)}^C \right] f_i \]  
(S50)

\[ \Delta \bar{G}_p = \Delta \bar{G}_f^{A_mB_n} f_p \]  
(S51)

\[ \Delta \bar{G}_f^{A_mB_n} = \left[ \frac{G_{f}^{A_mB_n}}{m + n} - (1 - x_p) G_{std}^A - x_p G_{std}^B \right] f_p \]  
(S52)
S2. THERMODYNAMIC DATA

Input to the thermodynamic parameters for the ternary model are obtained for Mg-Sn-Zn system from thermodynamic databases and literature. These are presented in this section in units of kJ/mol. Mg, Sn and Zn correspond to A, B and C, respectively.

For hcp-Mg solid-solution phase, binary interaction parameters \( L_{kl}^0 \) of the Redlich-Kister-Muggianu free energy expression, describing the excess free energy contribution from non-ideal interactions, were evaluated by Meng et. al. [S3]. While higher order terms corresponding to ternary interactions were set to zero in their model, interaction parameters \( L_{kl}^{1} \) corresponding to composition dependent terms were included in the model and evaluated. However, \( L_{kl}^{1} \) parameters, describing the sub-regular solution behavior, are ignored in our study for simplicity, and thus only \( L_{kl}^0 \) terms are considered. The temperature dependent \( L_{kl}^0 \) obtained from [S3] are:

\[
\begin{align*}
L_{AB}^0 &= (-26256.5 + 6.234 T) \times 10^{-3}, \\
L_{BC}^0 &= 30453 \times 10^{-3}, \\
L_{AC}^0 &= (-3056.82 + 5.63801 T) \times 10^{-3}.
\end{align*}
\]

The regular-solution interaction parameters \( \omega_{kl}^{0} \) of the bulk region modeled in the present study are related to \( L_{kl}^0 \) through:

\[
\begin{align*}
\omega_{AB}^0 &= \frac{L_{AB}^0}{z_b}, & \omega_{BC}^0 &= \frac{L_{BC}^0}{z_b}, & \omega_{AC}^0 &= \frac{L_{AC}^0}{z_b}.
\end{align*}
\]

The free energy of formation of Mg\(_2\)Sn, denoted by \( G_{f}^{Am_{n}B_{m}} \) in the present model, was determined in [S3] from experimental heat capacity and heat content measurements reported in literature,

\[
\begin{align*}
G_{f}^{Am_{n}B_{m}} &= (-96165.9 + 339.999 T - 66.285 T \ln (T) - 0.0121662 T^2 \\
&\quad + 96000 T^{-1} + 3.33828 \times 10^{-7} T^3) \times 10^{-3}.
\end{align*}
\]

The standard state energies, \( G_{std}^k \), and the difference in free energies between the standard
state and the reference state, $\Delta G_{ref(b)}^k$, of the present model are obtained from the SGTE thermodynamic data compiled by Dinsdale [S4]. These respective quantities are defined in [S4] as the Gibbs energy evaluated with respect to enthalpy of the “Standard Element Reference” (which is the reference phase at 298.15 K for $k$), and the difference in Gibbs energy between the pertinent phase of $k$ and its reference phase. The expressions for Mg, Sn and Zn are given below:

$$G_{std}^A = (-8367.34 + 143.675547T - 26.1849782T \ln(T) + 0.4858 \times 10^{-3} T^2,$$
$$- 1.393669 \times 10^{-6} T^3 + 78950 T^{-1}) \times 10^{-3},$$
$$G_{std}^B = (-5855.135 + 65.443315T - 15.961T \ln(T) - 18.8702 \times 10^{-3} T^2,$$
$$+ 3.121167 \times 10^{-6} T^3 - 61960 T^{-1}) \times 10^{-3},$$
$$G_{std}^C = (-7285.787 + 118.470069T - 23.701314T \ln(T) - 1.712034 \times 10^{-3} T^2,$$
$$- 1.264963 \times 10^{-6} T^3) \times 10^{-3},$$

(S56)

$$\Delta G_{ref(b)}^A = 0,$$
$$\Delta G_{ref(b)}^B = (3900 - 4.4 T) \times 10^{-3},$$
$$\Delta G_{ref(b)}^C = 0.$$  

(S57)

**S3. INTERFACE ENERGY PENALTY**

The interface bond energy parameters, $\delta_i^{AA}$, representing the energy of interface-type $AA$ bond relative to the bulk-type $AA$ bond can be related to the free energy of the interface, $\gamma_i^A$, between $A$-rich solid-solution and $A_mB_n$ precipitate through,

$$\delta_i^{AA} = \frac{2}{z_i} \sigma \gamma_i^A.$$  

(S58)

Here, $\sigma$ is the molar surface area of the interface, which is given by $N_{avg} \Omega^{2/3}$, and $\Omega$ is the atomic volume of $A$. For an incoherent heterophase interface between Mg-rich solid-solution
and Mg$_2$Sn precipitate, Katsman et. al. [S5] reported an average value of 410 kJ/mol, which was estimated using a Langer-Schwartz model for precipitation and hardening, and an experimental measurement of aging response. Using this, $\delta_i^{AA}$ of 3.5 kJ/mol is obtained as a rough input for the present model.
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