

Grain boundary complexions in multicomponent alloys: Challenges and opportunities



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ABSTRACT

Grain boundaries (GBs) can undergo first-order or continuous phase-like transitions, which are called complexion transitions. Such GB transitions can cause abrupt changes in transport and physical properties, thereby critically influencing sintering, grain growth, creep, embrittlement, electrical/thermal/ionic conductivity, and a broad range of other materials properties. Specifically, the presence of multiple dopants and impurities can significantly alter the GB complexion formation and transition. This article reviews and discusses several GB adsorption (segregation) and prewetting/premelting type complexion models in multicomponent alloys, in which the interactions among multiple adsorbates not only provide a route to control GB properties but also produce novel phenomena. Specifically, various ternary GB diagrams, including both GB adsorption complexion diagrams with well-defined transition lines calculated from a lattice model (without considering interfacial disordering) and GB λ diagrams that predict useful trends for average general GBs to disorder at high temperatures and related sintering phenomena, are constructed to quantitatively describe the GB behaviors as functions of bulk compositions. Finally, we propose a new opportunity of utilizing “high-entropy GB complexions” to stabilize nanocrystalline alloys.

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1. Introduction

Grain boundaries (GBs) in crystalline materials can be treated as “interfacial phases” that can undergo first-order or continuous transitions with varying thermodynamic potentials, such as temperature (T), pressure (P), and chemical potentials (μ). Recently, a new term “complexion” was introduced to differentiate such interfacial phases, which are thermodynamically two-dimensional (2D, while the variations in composition and structure in the third dimension is thermodynamically-determined and fixed) and cannot exist alone without abutting bulk phases, from the bulk phases defined by Gibbs [1–5].

A variety of GB complexions have been observed via high resolution electron microscopy (HREM) and aberration-corrected scanning transmission electron microscopy (AC STEM). One common type of GB complexions is represented by the equilibrium intergranular films (IGFs) that are widely observed in ceramics [6]. Similar impurity-based, quasi-liquid, interfacial films have also been observed at GBs in metals such as W-Ni and Mo-Ni (where the primary phase is underlined) [7–10] and on oxide surfaces [11–23]. Dillon and Harmer [24–27] further discovered a series

of discrete GB complexions in Al_2O_3 -based ceramics, which may be considered as derivatives to IGFs with (nominal) discrete thicknesses of 0, 1, 2, 3, x , and $+\infty$ atomic layers, respectively [3,28–30]. This series of Dillon-Harmer complexions have also been observed in other materials such as TiO_2 -CuO-SiO₂ [28]; moreover, bilayer complexions have been directly observed by AC STEM in metallic alloys such as Ni-Bi [31] and Cu-Bi [32], as well as in Si-Au [33].

GB complexion transitions can often result in the abrupt changes in GB structure and chemistry, which can in turn drastically alter various properties such as GB cohesion (embrittlement) [31,32], ductility [34], GB mobility (normal and abnormal grain growth) [24–27], GB diffusivity (activated sintering) [7,9,10,21,29,35–38], and ionic conductivity [39].

To tailor microstructures and materials properties through controlling GBs, a comprehensive understanding of the formation and transition of GB complexions is desirable and imperative. Various interfacial thermodynamic models have been developed to describe GB complexion formation and transition. In 1968, Hart first postulated that GBs can be considered as 2-D interfacial phases that may undergo first-order transformations [40]. This concept was further elaborated by Hondros and Seah [41] and by Kikuchi and Cahn [42–44]. More recently, Wynblatt, Shi, and Chaitain developed a sophisticated regular-solution type lattice model to describe multilayer adsorption at metallic GBs [45–47], and they

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demonstrated the existence of a GB prewetting (thin-thick adsorption) transition line [47], analogous to that shown by Cahn in his critical-point wetting model for a binary de-mixed liquid [48]. In parallel, Tang et al. [1,2] and Mishin et al. [49] used diffuse-interface (phase-field type) models to describe coupled GB prewetting and premelting transitions. The formation and stability of premelting-like GB complexions (enhanced by concurrent GB adsorption or prewetting) in multicomponent alloys have also been treated by a sharp-interface model, where a new type of GB λ diagrams have been constructed to present the thermodynamic tendency for average general GBs to disorder [7,29,35–38]; although GB λ diagrams are not rigorous GB complexion diagrams with well-defined transition lines and critical points, they have been validated by direct HRTEM and proven useful for predicting trends in activated sintering [7,29,35–38]. Later, a hybrid model has been formulated, which produced layering transitions that leads to the formation of six Dillon-Harmer complexions [30]. Rickman et al. also demonstrated the existence of a series of first-order layering GB transitions using a lattice model by considering elastic interactions between GBs and adsorbates [50]. GB transitions have also been modeled by Frolov et al. [51–54].

Most of the prior studies of GB complexions are conducted for either unary or binary systems. Yet, most polycrystalline materials for engineering applications contain more than one type of alloying elements (plus unintentional impurities). In such multicomponent systems (with three or more components), interactions among different GB adsorbates can significantly affect GB complexion and transition behaviors via attractive or repulsive interactions between them, as well as site competition and induced structural transitions (e.g., disordering). For example, in Fe based alloys, interactions between Si-P [55], Si-C [56], Sn-C [57], and B-P [58] are repulsive, whereas the interactions between B-N [56], Fe-Sb [59], and Ti-P [60] are attractive. Investigating the effects of such interactions is not only scientifically interesting but also technically important.

This article first reviews two types of thermodynamic models to investigate GB adsorption and complexions in multicomponent systems. Subsequently, we construct and discuss two types of multicomponent GB diagrams, including both rigorous GB complexion diagrams for prewetting (adsorption) transitions (without considering interfacial disordering) and GB λ diagrams that can predict useful trends in GB disordering (via coupled GB premelting and prewetting) and related sintering phenomena. One general scientific theme is to discuss the effects of interactions among different adsorbates on GB adsorption, disordering and complexion transitions. Since the GB layering transitions and related GB complexion diagrams are reviewed in a separate article in this special issue (for binary systems) [61], this article will focus on prewetting and premelting transitions without discussing layering transitions. Finally, several challenges and opportunities are discussed. Specifically, we propose, for the first time to our knowledge, a new opportunity of using “high-entropy GB complexions” to stabilize nanocrystalline alloys at high temperatures.

2. Interfacial thermodynamic models

In a multicomponent system, the GB energy is the GB excess of the grand potential ($\Phi_G = E - TS - \sum \mu_i N_i$, where E is internal energy, S is entropy, T is temperature, and μ_i and N_i are the chemical potential and amount of the i -th component), which can be expressed as:

$$\gamma_{GB} = e^{xs} - s^{xs} T - \sum_i \mu_i \Gamma_i, \quad (1)$$

where e^{xs} (excess internal energy), s^{xs} (excess entropy), and Γ_i (adsorption of the i -th component) are the interfacial (GB) excess

quantities per unit area. At given temperature (T), pressure (P), and equilibrium chemical potentials (μ_i 's, which are typically specified by the chemical potentials of the adjacent grains), the GB adopts the spatially-varying compositional and structural profiles that minimize γ_{GB} , which specifies a GB thermodynamic state (i.e., a “complexion” as defined by Tang et al. [1–5]); other metastable complexions can often exist, which can become stable via first-order or continuous GB transitions with varying thermodynamic potentials (T , P , and μ_i). For example, Eq. (1) suggests the possible occurrence of GB transitions to form more disordered GB complexions (of high s^{xs}) with increasing temperature (e.g., via GB premelting [1,62–64]) or to form GB complexions with high adsorption (Γ_i) with increasing chemical potentials (e.g. via prewetting [47] or layering [30,61] adsorption transitions). In multicomponent systems, GB premelting and prewetting transitions are often coupled to form disordered GB complexions with high levels of GB adsorption concurrently [2,7,29,35–38,49].

In multicomponent systems, GB adsorption of multiple solutes may

- compete for the adsorption sites (in fixed-site models),
- interact each other via (equivalent) attractive or repulsive interactions between different pairs of adsorbates,
- induce interfacial disordering at high temperatures (which may subsequently accommodate more adsorption),
- produce layering transitions due to the discrete nature of atoms (as discussed in a separate article in this special issue [61]) and associated roughening, both of which can be significantly influenced by the presence of multiple adsorbates of different sizes, and
- generate extra (effective) GB configurational entropies under certain conditions that may produce novel phenomena, e.g., nanoalloys stabilized by high-entropy GB complexions.

A quantitative description of GB complexion formation and transition in multicomponent systems requires statistical thermodynamic models that consider all above factors. Specifically, realistic modeling of the coupling between adsorption and structural transitions (e.g., interfacial disordering at high temperatures) in systems with three or more components is challenging. Consequently, various approximations and simplifications have to be adopted, some of which are discussed subsequently.

2.1. Classical GB adsorption models

Various classical GB adsorption/segregation models exist (noting that thermodynamically the terms “segregation” and “adsorption” are identical; see an elegant discussion of these two terms by Wynblatt and Chatain [46]; in this article, we adopt the term GB adsorption in most discussion); many of the classical models can be extended to multicomponent alloys.

In 1957, McLean proposed a statistical thermodynamic model for GB adsorption following the famous Langmuir surface monolayer adsorption model [65]. Treating both the bulk and the GB as ideal solutions, the Langmuir-McLean adsorption equation can be derived for a binary system, which can be readily generalized to multicomponent systems (assuming no interactions among different components):

$$\frac{X_i^{GB}}{X_1^{GB}} = \frac{X_i^{Bulk}}{X_1^{Bulk}} \exp \left(- \frac{\Delta G_{ads(i-1)}}{RT} \right) \quad (2a)$$

where $\Delta G_{ads(i-1)}$ is the molar free energy of adsorption. In Eq. (2), X^{Bulk} and X^{GB} , respectively, are bulk and GB compositions, respectively, where the subscript denotes the component; here we (somewhat arbitrarily) select Component 1 as the matrix (solid solvent),

which serves as the reference for defining $\Delta G_{ads(i-1)}$, and Component i ($i = 2, \dots, N$) as solutes (adsorbates or segregants, which are used interchangeably). Specifically,

$$\Delta G_{ads(i-1)} = N_A \Delta g_{ads(i-1)} \approx N_A \Delta h_{ads(i-1)} = \Delta H_{ads(i-1)}, \quad (2b)$$

where N_A is the Avogadro constant and $\Delta g_{ads(i-1)}$ (or $\Delta h_{ads(i-1)}$) represents the Gibbs free energy (or enthalpic) change associated with an exchange of one atom of the i -th component in the bulk with one atom of the 1-st component at the GB for a substitutional solution. The selection of matrix Component 1, which serves as the referencing component, is somewhat arbitrary (even if we typically select the primary component that has the highest concentration), but $\Delta G_{ads(i-1)}$ should always be defined with respect to the correct reference. Noting that configurational entropies of mixing are excluded in the term $\Delta G_{ads(i-1)}$; any extra entropic terms (beyond the ideal mixing) are relatively small and typically neglected in most models (in part because they are difficult to quantify) so that we replace $\Delta G_{ads(i-1)}$ with $\Delta H_{ads(i-1)}$ as an approximation in the subsequent discussion. Please see a discussion by Wynblatt and Chatain [46] about these extra entropic contributions, which may come from chemical and elastic/vibrational origins. Please also note that significant interfacial disordering at high temperatures may result in additional entropic terms, making this approximation ($\Delta G_{ads(i-1)} \approx \Delta H_{ads(i-1)}$) inaccurate.

When interactions among different components are prominent, the segregation behaviors no longer follow the ideal Langmuir-McLean adsorption equation. Such interactions were considered in the Fowler-Guggenheim model [66]; Guttman [67] further extended the Fowler-Guggenheim model to multicomponent systems and derived the following adsorption equation:

$$\frac{X_i^{GB}}{X_1^{GB}} = \frac{X_i^{Bulk}}{X_1^{Bulk}} \exp \left(- \frac{\Delta H_{ads(i-1),0} - 2\alpha_{ii}X_i^{GB} + \sum_{j=2,\dots,N,j \neq i} \alpha'_{ij}X_j^{GB}}{RT} \right) \quad (3a)$$

where $\Delta H_{ads(i-1),0} \approx \Delta G_{ads(i-1),0}$ is the intrinsic segregation enthalpy of the i -th component (with respect to Component 1), α_{ii} denotes the interaction between the 1-st and i -th complements, and α'_{ij} ($\alpha'_{ij} \equiv \alpha_{ij} - \alpha_{i1} - \alpha_{j1}$; $i \neq j$, $j \neq 1$) denotes the relative interaction between i -th and j -th components (with respect to Component 1; see Eq. (3c)). The above adsorption equation reduces to the Langmuir-McLean adsorption equation if all $\alpha_{ii} = \alpha'_{ij} = 0$.

The interaction parameters in the Guttman model can be related to the pair-interaction or regular-solution parameters in a simplified model (with several approximations, such as the negligence of the effects of compositional gradients, which are treated more rigorously in a generalized Wynblatt type model described subsequently) with the following relations:

$$\alpha_{ii} = zN_A\omega_{i1} \quad (3b)$$

$$\alpha'_{ij} \equiv \alpha_{ij} - \alpha_{i1} - \alpha_{j1} = zN_A(\omega_{ij} - \omega_{i1} - \omega_{j1}) \quad (3c)$$

where z is the coordination number and the pair-interaction parameter is defined as:

$$\omega_{ij} = e_{ij} - (e_{ii} + e_{jj})/2, \quad (4)$$

where e_{ij} , e_{ii} , and e_{jj} , respectively, are bond energies of i - j , i - i , and j - j bonds ($i, j = 1, \dots, N$), respectively. Thus, α 's in the above equations are essentially the molar regular-solution parameters ($\alpha_{ij} = \Omega_{ij} = zN_A\omega_{ij}$), even if they may be considered as the effective GB regular-solution parameters in the Guttman model, which can be different from the bulk regular-solution parameters. Specifically, a negative α'_{ij} ($i \neq j$) implies an effective attractive interaction between the i -th and j -th species, whereas a negative α_{ii} implies attractive

interaction between the i -th and 1-st species (i.e., an effective self-repulsion among i - i adsorbates). A similar derivation that treated the GB as a regular solution of a standalone phase (as an approximation) to derive the binary Fowler-Guggenheim equation is given in Section 2.3.1 in Ref. [3] (noting that the parameter α has a different definition and sign in that article [3]).

2.2. GB adsorption without interfacial disordering: A generalized Wynblatt type lattice model for multicomponent alloys

Using a lattice model, Wynblatt, Shi, and Chatain [45,46] developed an elegant and more rigorous multilayer GB adsorption model that considers the multilayer adsorption (with different adsorption enthalpies for each layer), the influence of composition gradients (perpendicular to GBs), and the anisotropy of GB adsorption. The formulae of the Wynblatt-Shi-Chatain model in Refs. [45,46] were developed for binary alloys. To illustrate the effects of interactions among multiple adsorbates, here we extend the Wynblatt-Shi-Chatain model to multicomponent alloys ($N \geq 3$), but only for a special case of a symmetric twist GB with $J_{\max} = 1$ [45,46] (meaning that all bonds are either in the atomic plane or between the immediate adjacent planes) for simplicity. Subsequently, we obtain the following GB adsorption equation for a generalized Wynblatt type lattice model for multicomponent alloys:

$$\frac{X_i^k}{X_1^k} = \frac{X_i^{Bulk}}{X_1^{Bulk}} \exp \left(- \frac{\Delta H_{ads(i-1)}^k}{RT} \right), \quad (5a)$$

where the superscript k represents the k -th GB layer, and the (molar) segregation enthalpy of the solute i at the k -th GB layer is expressed (in a form that can be compared with the Guttman model) as:

$$\begin{aligned} \Delta H_{ads(i-1)}^k &= \Delta H_{ads(i-1),0}^k + zN_A \left[-2(X_i^k - X_i^{Bulk})\omega_{1i} \right. \\ &\quad + \sum_{j=2,\dots,N,j \neq i} (X_j^k - X_j^{Bulk})(\omega_{ij} - \omega_{1j} - \omega_{1i}) \\ &\quad + z_v N_A \left[-2(X_i^{k-1} - 2X_i^k + X_i^{k+1})\omega_{1i} \right. \\ &\quad \left. \left. + \sum_{j=2,\dots,N,j \neq i} (X_j^{k-1} - 2X_j^k + X_j^{k+1})(\omega_{ij} - \omega_{1j} - \omega_{1i}) \right] \right] \quad (5b) \end{aligned}$$

where $\Delta H_{ads(i-1),0}^k$ is the intrinsic segregation enthalpy (originating from the differential bonding energies and the strain energy of solutes [45,46]), z is the total coordination number (numbers of bonds per atom), z_v is the number of bonds between adjacent layers (so that $z = 2z_v + z_1$, where z_1 is the lateral coordination number within the same atomic plane; noting that $J_{\max} = 1$ [45,46] for this simplified case), and ω_{ij} is the pair-interaction parameter defined in Eq. (4) (for the bulk solid-solution phase). Please note that $X_i^0 = X_i^1$ for the symmetrical twist GB since the 0-th layer is essentially the 1-st GB layer on the other side and the effects of “broken bonds” at the GB core are considered separately in the $\Delta H_{ads(i-1),0}^k$ term.

This generalized Wynblatt type lattice model for multicomponent systems has a similar form as the Guttman model with a few refinements. First, this is a multilayer adsorption model with different adsorption enthalpies for each layer (vs. that the Guttman model is essentially a monolayer model). Second, the Guttman model was derived for a dilute solution so that all $X_i^{Bulk} \approx 0$ ($i \neq 1$), and this approximation is not adopted in Eq. (5). Third, the third term in Eq. (5b) represent energies related to the compositional gradients (noting that the $(X_j^{k-1} - 2X_j^k + X_j^{k+1})$ terms

in Eq. (5b) is proportional to $(dX_j/dx)^2$, the square of compositional gradient, where x is the spatial coordinate perpendicular to the GB, which is not considered in the Guttman model. Finally, more realistic $\Delta H_{ads(i-1),0}^k$ functions are used in this generalized Wynblatt type lattice model to represent the intrinsic segregation enthalpies originated from the differential bonding energies and strain energies, following Refs. [45,46].

The above segregation equation was solved numerically for several hypothetical ternary regular-solution systems and the results are discussed in the subsequent sections to illustrate the effects of interactions between two solute/adsorbate species (i.e., the effects of the sign and magnitude of ω_{ij}) on simple adsorption behaviors as well as complexion transitions.

2.3. A sharp-interface model for coupled GB premelting and prewetting

The lattice models discussed above do not consider the effects of GB structural transitions, particularly the possible occurrence of premelting-like interfacial disordering (near, but still below, the bulk solidus lines/curves) that can be important at high temperatures. Coupled GB adsorption (prewetting) and interfacial disordering (premelting) in binary alloys have been modeled using diffuse-interface models by Tang et al. [1,2] and Mishin et al. [49]. Furthermore, the possible occurrence of layering transitions to produce a series of discrete Dillon-Harmer complexions has been demonstrated in a hybrid interfacial thermodynamic model via adopting a hard-sphere type, oscillatory, structural, interfacial interaction resulted from the finite atomic size [30]. To date, no study has been conducted to extend the above models beyond binary systems.

Alternatively, we can model coupled GB disordering and adsorption by extending a sharp-interface phenomenological thermodynamic model that was originally developed for premelting in unary systems [64] to multicomponent alloys. Recently, this model has been combined with bulk CALPHAD (calculation of phase diagram) data and methods and the model predictions have been validated by experiments both directly via HRTEM and indirectly via sintering experiments [7,29,35–38]. Most recently, this model and approach have been successfully generalized to multicomponent alloys with three or more components [35].

In this phenomenological interfacial thermodynamic model [7,29,35–38], a disordered GB complexion is regarded as a confined liquid-like interfacial film, with their thermodynamic properties being modified by the presence of various interfacial interactions. The excess grand potential as a function of the effective interfacial width (h , which is often called “film thickness”) can be written as:

$$\sigma^x(h) = \Delta G_{amorph}^{(vol)} \cdot h + 2\gamma_{cl} + \sigma_{interfacial}(h), \quad (6)$$

where $\Delta G_{amorph}^{(vol)}$ is the volumetric free energy for forming an undercooling liquid from the equilibrium solid phase(s) and γ_{cl} is the crystal-liquid interfacial energy. The interfacial potential, $\sigma_{interfacial}(h)$, represents the effects of all interfacial interactions ($\sigma_{interfacial}(+\infty) = 0$ by definition). A premelting-like GB complexion can be stabilized if the energy penalty for forming an undercooled quasi-liquid film is overcompensated by the reduction in the interfacial energy:

$$-\Delta\gamma \cdot f(h) > \Delta G_{amorph}^{(vol)} h \quad (7a)$$

where

$$\Delta\gamma \equiv 2\gamma_{cl} - \sigma^x(0) \quad (7b)$$

and $f(h)$ is a dimensionless interfacial coefficient:

$$f(h) = 1 + \sigma_{interfacial}(h)/\Delta\gamma \quad (7c)$$

with the boundary conditions: $f(0) = 0$ and $f(+\infty) = 1$. The equilibrium thickness, h_{eq} , corresponds to the minimum of Eq. (6) with respect to h (so that $d\sigma^x(h)/dh|_{h=h_{eq}} = 0$), which is difficult to be quantified because the exact form of $f(h)$ or $\sigma_{interfacial}(h)$ is typically unknown. Thus, we introduced a thermodynamic parameter:

$$\lambda \equiv \frac{-\Delta\gamma}{\Delta G_{amorph}^{(vol)}}, \quad (8)$$

which scales the actual interfacial width (h_{eq}) and can be quantified by combining bulk CALPHAD data with statistical interfacial thermodynamic models [7,29,35–38].

Subsequently, the computed lines of constant λ values can be plotted into bulk phase diagrams to represent the thermodynamic tendency for average general GBs to disorder. These GB λ diagrams can predict useful trends in GB disordering in binary and multicomponent alloys at high temperatures that have been validated by experiments [7,29,35–38], even if they are not rigorous GB complexion diagrams with well-defined transition lines and critical points. Most recently, GB λ diagrams have been constructed multicomponent alloys with three or four components, including $\underline{W}$ -Ni-M (where M is a transition metal such as Fe, Co, Cr, Zr, Nb, or Ti) and $\underline{Mo}$ -B-Si-M [35].

Several computed examples for both hypothetical ternary regular-solution systems and real $\underline{W}$ -Ni-M ($M = \text{Fe, Cr, or Ti}$) alloys are shown and discussed here in an effort to understand how interactions of multiple adsorbates can influence on GB disordering at high temperatures in ternary alloys and to further compare the results with those predicted from the lattice model of GB adsorption without considering interfacial disordering.

2.4. Thermodynamic parameters used

To illustrate how the interactions of multiple adsorbates may affect GB complexions, numerical experiments were conducted to compute Figs. 1–3 and 6 for regular solutions of a ternary ABC system with the following parameters: $z = 12$, $z_v = 4$, and $\Delta H_{ads(i-1),0}^1 = 0.1$ eV/atom. To calculate the GB λ diagrams shown in Fig. 3, we also assumed the following parameters: $\Delta S_{fuse}^1 = 10$ J/mol K, $T^{melt} = 1000$ K, and $V_m = 8$ cm³/mol for all elements (A, B, and C) and $\gamma_{GB}^{(0)} = 0.4$ J/m²; moreover, all non-zero Ω 's are specified explicitly in the text and figures whereas other Ω 's were assumed to be zero (ideal mixing).

Real CALPHAD data as well as other structural and other data were used to compute GB λ diagrams for $\underline{W}$ -Ni-Fe, $\underline{W}$ -Ni-Cr, and $\underline{W}$ -Ni-Ti ternary alloys, as shown in Figs. 4 and 5. Please see Ref. [35] and references therein for the specific CALPHAD parameters used.

3. Effects of co-doping on adsorption and complexion transitions

In earlier studies, various researchers already demonstrated the interactions of different individual solutes in multicomponent (particularly Fe based) alloys [41,67,68]. If we do not consider the effects of interfacial disordering and other types of GB structural transitions, the two major factors at play are: (1) the competition of different solutes/adsorbates for limited sites at GBs and (2) attractive or repulsive chemical interactions between dissimilar solutes/adsorbates (represented by the molar regular-solution parameter $\Omega_{ij} = zN_A \omega_{ij}$, where a negative Ω_{ij} indicates an attractive interaction that enhances the GB adsorption of both species, whereas a positive Ω_{ij} indicates a repulsive interaction that inhibits the adsorption of one solute in the presence of the other).

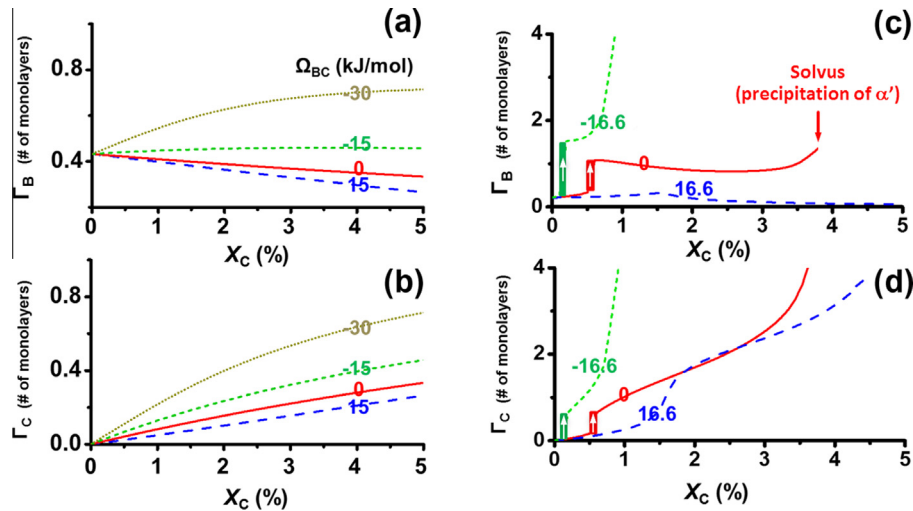


Fig. 1. Computed GB excesses of solutes B and C (Γ_B and Γ_C) vs. the molar fraction of C in the bulk phase (X_C) curves for hypothetical ternary (B + C) co-doped A alloys with different B–C interactions (represented by the Ω_{BC} values labeled on the curves) for (a and b) four cases where $\Omega_{AB} = \Omega_{AC} = 0$ (ideal A–B and A–C mixing), $X_B = 5\%$ (fixed), and $\Omega_{BC} = -30, -15, 0$, and $+15$ kJ/mol, respectively (representing attractive to repulsive B–C interactions) and (c, d) three additional cases where $\Omega_{AB} = \Omega_{AC} = 16.6$ kJ/mol (repulsive A–B and A–C interactions that lead to first-order GB prewetting transitions, which correspond to the jumps in Γ_B and Γ_C indicated by the vertical arrows in the figure), $X_B = 1\%$ (fixed), and $\Omega_{BC} = -16.6, 0$, and $+16.6$ kJ/mol, respectively (labeled in the figure).

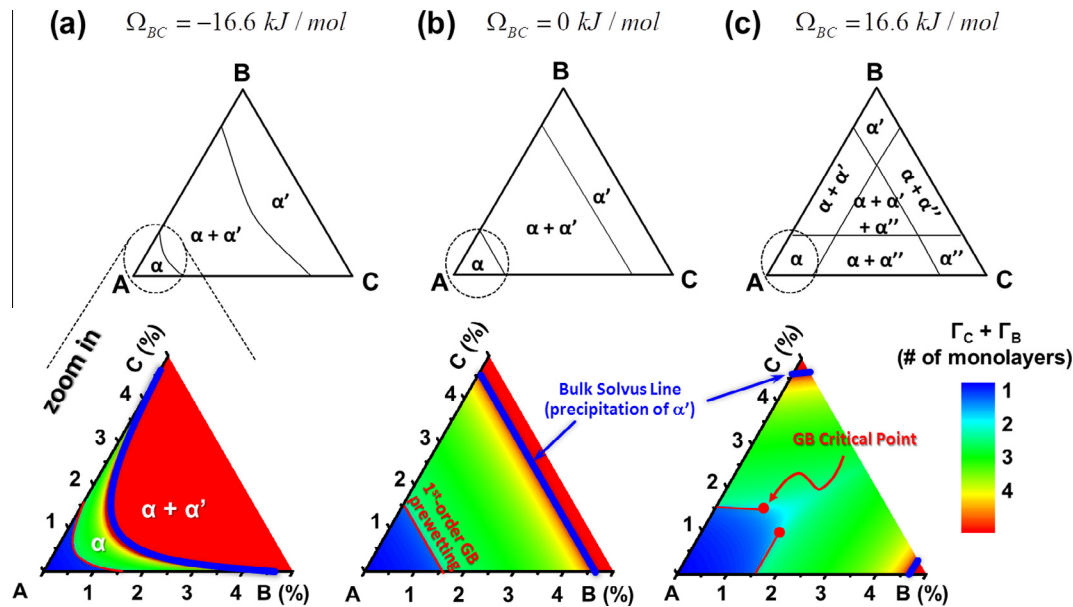


Fig. 2. Computed GB complexion diagrams for three hypothetical ternary (B + C) co-doped A alloys, where $\Omega_{BC} =$ (a) -16.6 , (b) 0 , and (c) $+16.6$ kJ/mol, respectively, with the following other parameters: $\Omega_{AB} = \Omega_{AC} = 16.6$ kJ/mol and $T = 600$ K. The first-order GB prewetting (adsorption) transitions are represented by the thin red lines, while the bulk solvus lines are represented by the thick blue lines. The three black-and-white figures on the top are the corresponding (complete) ternary bulk phase diagrams, for which only the A-rich corners are zoomed in for computing GB complexion diagrams. These three GB complexion diagrams are computed based on a generalized Wynblatt type lattice adsorption model (with our modifications to extend the model from binary to multicomponent alloys; see Section 2.3; assuming no interfacial disordering). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Let us first consider a simple case of a ternary ABC alloy, where we assume, for simplicity, that both solutes B and C mix with the matrix A ideally ($\Omega_{AB} = \Omega_{AC} = 0$). In this system, we vary the composition of the second solute, X_C , with a fixed $X_B = 5\%$. Fig. 1(a) and (b) illustrates the computed GB excesses (adsorptions) of B and C vs. the bulk composition of C (Γ_B vs. X_C and Γ_C vs. X_C) curves for four different Ω_{BC} ($= -30, -15, 0$, and $+15$ kJ/mol, respectively), representing different levels of attractive to repulsive interactions between solutes B and C). For the case where there is no B–C interaction ($\Omega_{BC} = 0$), solutes B and C compete for the GB adsorption sites; i.e., Γ_C increases with increasing bulk X_C , at the expense of a simultaneous decrease of Γ_B , as indicated by the solid red lines in

Fig. 1(a) and (b). For the case where there is a moderate attractive B–C interaction ($\Omega_{BC} = -15$ kJ/mol), Γ_C increases more rapidly with increasing bulk X_C (as compared with the case where $\Omega_{BC} = 0$ in Fig. 1(b)), while Γ_B is almost a constant (independent of X_C , as shown in Fig. 1(a)). When the B–C interaction becomes more attractive ($\Omega_{BC} = -30$ kJ/mol), both Γ_C and Γ_B increases rapidly with increasing bulk X_C , indicating that the attractive interaction overcomes the site competition effect and the total adsorption, $\Gamma_C + \Gamma_B$, increases beyond the monolayer region (noting that this is not possible in a monolayer adsorption model). Conversely, the site competition effect is enhanced if the interaction is repulsive (e.g., as illustrated in Fig. 1(a) and (b) for a case where $\Omega_{BC} = +15$ kJ/mol).

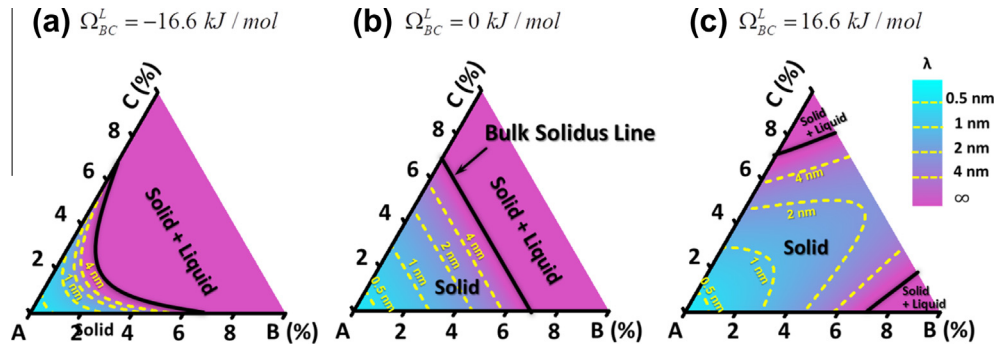


Fig. 3. The effects of varying Ω_{BC}^L on the computed GB λ diagrams for three hypothetical ternary (B + C) co-doped A alloys. The lines of constant λ are plotted as yellow dashed lines to represent the thermodynamic tendency for average general GBs to disorder, where the computed λ value scales the actual interfacial width (h_{eq}) of quasi-liquid GB complexions. The following parameters are used in the calculations: $\Omega_{BC}^L = 0$ or ± 16.6 kJ/mol; $\Omega_{AB}^L = \Omega_{AC}^L = \Omega_{AB}^S = \Omega_{AC}^S = \Omega_{BC}^S = 0$; $T_A^{melt} = T_B^{melt} = T_C^{melt} = 1000$ K; and $T = 600$ K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

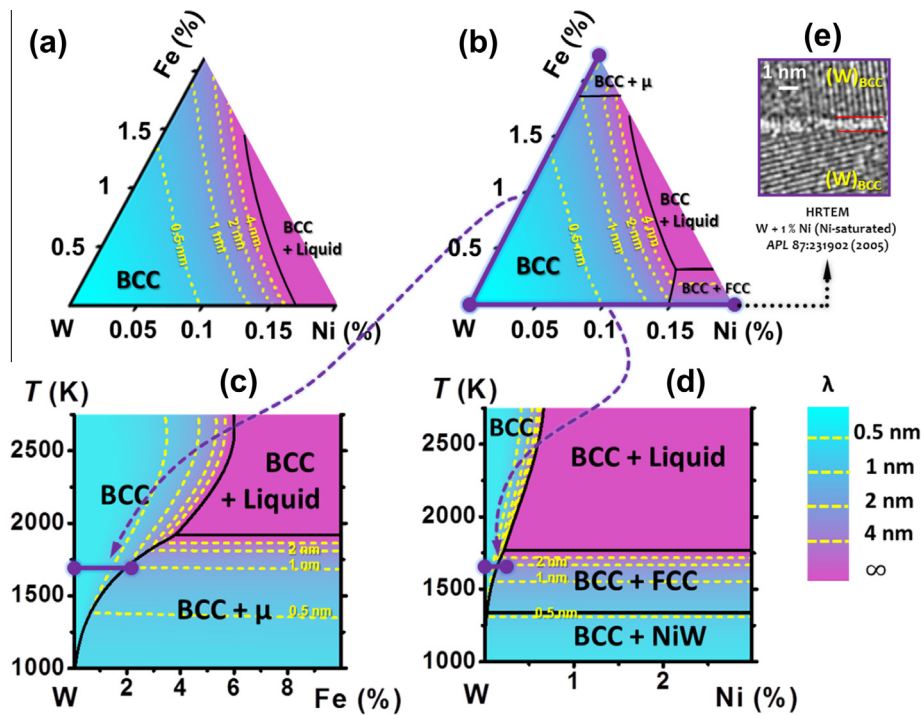


Fig. 4. Schematic illustration of a two-step procedure to construct an isothermal section of a ternary GB λ -diagram for (Ni + Fe) co-doped W ternary alloy ($\underline{W}$ -Ni-Fe) at 1673 K. (a) First, λ values are computed according to bulk compositions and plotted without considering the precipitation of any secondary crystalline phase(s). (b) Subsequently, the precipitation of other equilibrium secondary phases (FCC and μ -FeW in this specific case), which limit the bulk chemical potentials and λ values in two- and three-phase coexistence regions, are considered. The corresponding binary GB λ diagrams for (c) $\underline{W}$ -Fe and (d) $\underline{W}$ -Ni. (e) A HRTEM image showing a nanometer-thick, quasi-liquid, GB complexion reported in Ref. [10]. This figure is re-plotted, with revisions, after Ref. [35] with permission.

Furthermore, Fig. 1(c) and (d) illustrates cases where repulsive interactions between matrix and solutes ($\Omega_{AB} = \Omega_{AC} = 16.6$ kJ/mol) lead to first-order prewetting transitions that correspond to the discontinuous jumps in Γ_B/Γ_C vs. X_C curves (for a lower fixed $X_B = 1\%$). Likewise, an attractive interaction between solutes B and C ($\Omega_{BC} = -16.6$ kJ/mol) promotes the occurrence of the first-order prewetting transition (by shifting the transition to a lower bulk X_C , as compared with the case of $\Omega_{BC} = 0$), whereas a repulsive B-C interaction ($\Omega_{BC} = +16.6$ kJ/mol) suppresses the occurrence of the first-order prewetting transition. In the latter case ($\Omega_{BC} = +16.6$ kJ/mol), the prewetting adsorption transition in Γ_C vs. X_C curve not only is delayed to a higher X_C but also becomes continuous, whereas the GB adsorption of solute B is largely suppressed.

To further demonstrate the effects of different solute-solute interactions on prewetting complexion transitions, we have calculated the total absorption of solutes as a function of bulk

compositions (both X_B and X_C) for three cases ($\Omega_{BC} = 0, \pm 16.6$ kJ/mol). The corresponding complexion diagrams are shown in Fig. 2, where the thin red lines represent the first-order prewetting transition lines (separating two GB complexions with lower and higher levels of total GB adsorption with discontinuous changes in Γ 's, similar to the jumps indicated by the errors in Fig. 1 (c) and (d)); in the same diagrams, the thick blue lines represent the bulk solvus lines and the color represents the total adsorption ($\Gamma_B + \Gamma_C$). When solutes B and C have no interaction ($\Omega_{BC} = 0$), both GB prewetting transition line and bulk solvus line are straight, as shown Fig. 2(b); in this case, the first-order prewetting transitions occur when $X_B + X_C \approx 1.6\%$. As shown in Fig. 2(a), an attractive B-C interaction ($\Omega_{BC} = -16.6$ kJ/mol) promotes GB prewetting transitions in the mixing region (with the occurrence of first-order prewetting transitions at $X_B + X_C \ll 1.6\%$), reducing the stable region of the nominally “clean” GB complexion (with low

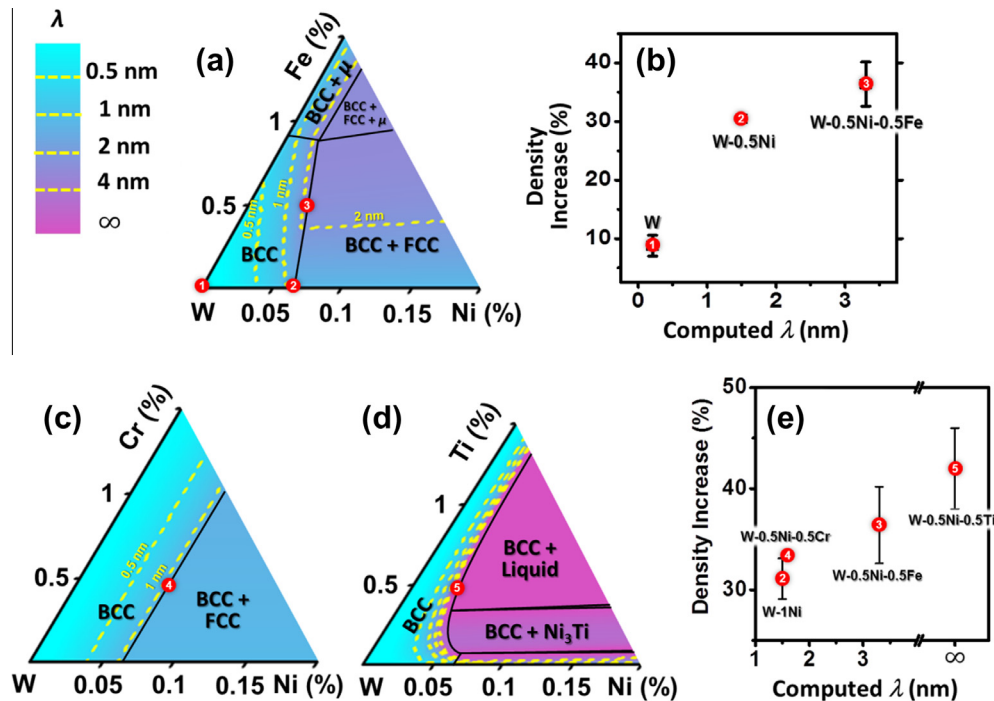


Fig. 5. (a) A computed isothermal section of GB λ diagram for $\underline{W}$ -Ni-Fe at 1573 K, suggesting that the addition of 0.5 at.% Ni as a sintering aid will boost the sintering of W and the addition of 0.5 at.% Fe as the second/additional sintering aid can further enhance the densification. (b) The density increases for three specimens (W, $\underline{W}$ -0.5Ni, and $\underline{W}$ -0.5Ni-0.5Fe at.%) after isothermal sintering at 1573 K for two hours vs. the computed λ values for these three compositions, verifying the above prediction. Additional computed isothermal sections of GB λ diagrams for (c) $\underline{W}$ -Ni-Cr and (d) $\underline{W}$ -Ni-Ti at 1573 K, which, along with the GB λ diagram for $\underline{W}$ -Ni-Fe shown in panel (a), suggest the relative effectiveness of co sintering aids (Ti > Fe > Cr > none) for $\underline{W}$ -Ni. (e) Measured density increases of four W-0.5Ni-0.5M (at.%, M = Ni, Cr, Fe, and Ti, respectively), specimens after isothermal sintering at 1573 K for two hours, which correlate well with the computed λ values. The equilibrium compositions of the primary BCC phases (instead the overall compositions) of the five specimens shown in panels (b) and (d) are labeled in three GB λ diagrams using the numbered red disks. This figure is re-plotted, with revisions, after Ref. [35] with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

adsorption levels). In contrast, Fig. 2(c) shows that a repulsive B-C interaction ($\Omega_{BC} = +16.6$ kJ/mol) inhibits GB prewetting transitions; moreover, the first-order transition becomes continuous near the region of $X_B \approx X_C$, between the two critical points (red dots in Fig. 2(c)); one of such continuous adsorption transitions is illustrated in the computed Γ_C vs. X_C curve (for a fixed $X_B = 1\%$) in Fig. 1(c) for the case of $\Omega_{BC} = +16.6$ kJ/mol. Moreover, the GB transition lines are generally parallel to the bulk solvus lines, suggesting a correlation between the GB complexation transition (leading to the formation a prewetting α' -like GB complexion) and the bulk phase transformation (leading to the formation a wetting α' bulk secondary phase).

While the GB complexion diagrams shown in Fig. 2 are computed from a lattice model for GB adsorption without considering the effects of interfacial disordering, regular-solution parameters can also have similar impacts on the stability of liquid-like GB complexions, as shown in the GB λ diagrams in Fig. 3 ($\Omega_{BC}^L = 0$, ± 16.6 kJ/mol; all other Ω 's are assumed to be zero for simplicity). Fig. 3 illustrates that an attractive B-C interaction in the liquid phase ($\Omega_{BC}^L = -16.6$ kJ/mol) promotes GB disordering in the mixing region, whereas a repulsive B-C interaction in the liquid phase ($\Omega_{BC}^L = +16.6$ kJ/mol) inhibits GB disordering. Interestingly, the observed trends in Figs. 2 and 3 are similar. In both cases, the GB complexions can be considered as 2-D GB precursors to 3-D bulk phases – i.e., (prewetting) adsorption complexion as the 2-D GB precursor to the (wetting) bulk crystalline α' phase in Fig. 2 vs. the quasi-liquid (coupled premelting and prewetting) GB complexion as the 2-D GB precursor to the (wetting and “melting”) bulk ternary liquid phase in Fig. 3. Thus, these two sets of GB diagrams shown in Fig. 2 vs. Fig. 3 exhibit phenomenological similarities.

Moreover, the co-alloying effects on GB disordering have been investigated systemically via numerical experiments using

$\underline{W}$ -Ni-X (where X is a hypothetical element for which we can assign arbitrary thermodynamic properties) as the model systems in a recent study [35]. Specifically, five key thermodynamic parameters of X, i.e., the melting temperature of X (T_X^{melt}) and the four regular-solution parameters for the W-X and Ni-X interactions in solid and liquid phases (Ω_{W-X}^S , Ω_{Ni-X}^S , Ω_{W-X}^L , and Ω_{Ni-X}^L), are varied independently to examine their effects on influencing GB disordering. It was found, somewhat counterintuitively, that T_X^{melt} has little influence on GB disordering. However, a repulsive interaction between X and W in the solid phase (positive Ω_{W-X}^S) or attractive interactions between X and W or Ni in the liquid phase (negative Ω_{W-X}^L or Ω_{Ni-X}^L) generally promotes GB disordering. Please see Ref. [35] for results and discussion.

4. Multicomponent GB λ diagrams for real alloys and their applications in forecasting experimental trends in GB-controlled activated sintering

A useful, long-range, scientific goal is to develop GB diagrams, including GB λ diagrams that have been proven robustly useful for predicting some trends in GB disordering and more rigorous GB complexion diagrams with well-defined transition lines and critical points, for real materials. It is particularly useful and important to develop GB diagrams for real multicomponent materials. Historically, bulk CALPHAD methods were first developed for binary alloys, for which measured phase diagrams already existed. CALPHAD methods become practically useful only when they can utilize the thermodynamic data that are largely obtained from binary systems to extrapolate and predict behaviors of multicomponent alloys, where the Edisonian approach is no longer feasible. Likewise, it is imperative to develop various GB diagrams for

multicomponent alloys ($N \geq 3$) to make them practically useful, which will be a very challenging, yet highly fruitful, task.

A recent study [35] successfully developed GB λ diagrams to forecast useful trends in GB disordering, as well as related GB-controlled activated sintering behaviors, for several W- and Mo-based ternary and quaternary alloys. Fig. 4 illustrates a two-step procedure to construct a ternary GB λ diagram for $\underline{W}$ -Ni-Fe at 1673 K. First, λ values were computed as a function of bulk compositions without considering the precipitation and plotted in Fig. 4(a). The computed λ values increase monotonically with increasing X_{Ni} and X_{Fe} in the W-rich corner, which indicates that both Ni and Fe promote GB to disorder (but noting that the scales of X_{Ni} and X_{Fe} are different in Fig. 4 so that the GB disordering increases much faster with increasing X_{Ni}). Second, the precipitation of secondary bulk phases (the Ni-rich FCC phase and FeW μ phase in this particular case) was taken into account, which limits the equilibrium bulk chemical potentials and the associated equilibrium λ values in multiphase regions, as shown in Fig. 4(b). Considering the competition between GB transitions and bulk precipitation of secondary phases are practically important; for example, a quantitative understanding in this regard can help to design strategies to use a “gettering” effect to remediate GB embrittlement, such as addition of Mg, Ca, Mn, Zr to Fe- and Ni- based alloys to reduce the embrittlement by GB adsorption of S [69,70]. Fig. 4(c) and (d) also display the corresponding binary bulk and GB λ diagrams for $\underline{W}$ -Ni and $\underline{W}$ -Fe, and Fig. 4(e) shows an HRTEM image verifying the formation of Ni-enriched, quasi-liquid, GB complexion [10].

Furthermore, GB λ diagrams were constructed for several ternary $\underline{W}$ -Ni-M ($M = \text{Cr, Fe, Ti}$) alloys at 1573 K and shown in Fig. 5(a), (c), and (d). Since the rate of densification of GB-controlled activated sintering should increase with increasing GB disorder [29,35], the calculated results suggested the increasing densification rates for the series of W, $\underline{W}$ -0.5Ni and $\underline{W}$ -0.5Ni-0.5Fe specimens in the $\underline{W}$ -Ni-Fe ternary system (Fig. 5(a)) and for $\underline{W}$ -1Ni, $\underline{W}$ -0.5Ni-0.5Cr, $\underline{W}$ -0.5Ni-0.5Fe, and $\underline{W}$ -0.5Ni-0.5Ti diagrams in the $\underline{W}$ -0.4Ni-M ($M = \text{Ni, Cr, Fe, and Ti}$) series, which were experimentally verified; Specifically, Fig. 5(b) and (d) shows excellent correlation between the measured densifications after 2-h isothermal sintering at 1573 K and the computed λ values for both sets of specimens [35].

5. Utilizing high-entropy GB complexions to stabilize nanocrystalline alloys at high temperatures

The presence and interaction of multiple (many) components in GB complexions may also produce novel physical phenomena that are unattainable otherwise. Here, we propose one such new opportunity of utilizing high-entropy GB complexions to stabilize nanoalloys. In a bulk-phase analogy, recent studies showed that solid solutions of high entropy alloys (HEAs) with five or more components may exhibit exceptional thermodynamic stability against precipitation (due to a “high-entropy” effect) and low diffusion rates (via so-called “sluggish kinetics”) as well as other unique properties such as enhanced strength and corrosion resistance [71–73].

Here, we propose, for the first time to our knowledge, that we can utilize high-entropy GB complexions to achieve exceptional stability of nanocrystalline alloys via:

- thermodynamic effects: by means of reducing GB energies more significantly than that can be achieved in binary alloys without precipitation (thru both bulk and interfacial high-entropy effects, as discussed below) and
- kinetic effects: by means of sluggish GB migration kinetics due to the presence and solute-drag of many different adsorbates.

Thermodynamic stabilization of nanocrystalline alloys, based on the idea that the thermodynamic driving force for grain growth can be reduced by reducing GB energy via GB adsorption, was first proposed by Weissmüller in 1993 [74,75]. Specifically, a nanocrystalline alloy can be stabilized as the effective GB energy approaches zero, after which an equilibrium grain size can be achieved. Kirchheim et al. [76,77] further elaborated this theory and showed that in binary alloys, the “stable” nanocrystalline alloys typically represent *metastable states* in supersaturated regions, occurring only when precipitation is hindered kinetically [76]. A recent study further combined full CALPHAD data and methods with the Wynblatt-Shi-Chatain multilayer GB adsorption model to develop a stability map for poly/nanocrystalline Fe-Zr alloys, which also showed that the equilibrium grain sizes are achieved in supersaturated regions at *metastable equilibria* with kinetic inhibition of precipitation [78].

Here, we propose that high-entropy effects can be utilized to alter the above competition between precipitation and GB adsorption (by both promoting GB adsorption and inhibiting bulk precipitation) so that we can reduce GB energy more significantly before the precipitation of a secondary bulk phase, particularly at high temperatures. First, using a high-entropy solid solution as the bulk phase can suppress precipitation, thereby allowing more GB adsorption to further reduce the GB energy before reaching the solvus lines/curves. Second, our calculation (Fig. 6) has shown that along the multicomponent solvus line (at the saturation limit before the precipitation of any secondary phase), adding more (multiple) solutes/adsorbates can effectively reduce GB energy more at high temperatures; subsequently, it is possible to reduce GB energy to zero in a multicomponent system (see Fig. 6) to achieve a true thermodynamically-equilibrium nanocrystalline alloy (without kinetic inhibition of precipitation). Moreover, the computed results shown in Fig. 6 also suggest the feasibility of

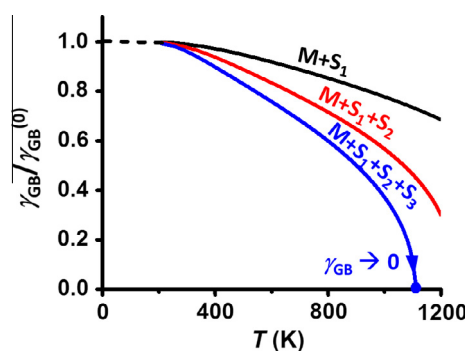


Fig. 6. Illustration of a proposed new opportunity of utilizing “high-entropy GB complexions” to stabilize nanocrystalline alloys. Computed normalized GB energy vs. temperature curves along the bulk solvus lines (i.e., for equilibrium saturated specimens on the “tips” of multicomponent solvus lines) for a regular solution with one, two, and three segregating solutes (S_1 , S_2 , and S_3) with identical adsorption enthalpies and pair-interaction parameters with the matrix element M . This numerical experiment demonstrates that it is theoretically possible to use GB adsorption of multiple solutes to achieve effective zero GB energy to stabilize nanocrystalline alloys at a true (instead of metastable) thermodynamic equilibrium (without going into the super-saturation region via kinetic inhibition of precipitation) at high temperatures. High-entropy GB complexions may also stabilize nanocrystalline alloys via two other (one thermodynamic and one kinetic) mechanisms discussed in text. To compute this figure using the (generalized) Wynblatt type model described in Section 2.2, we assumed, for simplicity, that: (1) all solutes form regular solutions with matrix elements with $\Omega_{ii} = 6$ kJ/mol; (2) the matrix element (M) and solute (S) form a line compound M_5S , with $\Delta G_{\text{formation}} = -5$ kJ/mol; (3) ideal solutions form between different solute elements with $\Omega_{ij} = 0$ ($i, j \approx 1$); (4) all solutes have an identical segregation enthalpy: $\Delta H_{\text{ads}}^{k(i \rightarrow 1),0} = 0.3$ eV/atom; (5) the bonding energy between identical element atoms $|e_{ii}| = 0.46$ eV (with $z = 12$ and $z_v = 4$); and (6) there are 1/6 broken bonds at the GB core to represent a general GB (so that $\gamma_{\text{GB}}^0/\gamma_{\text{S}}^0 = 1/3$).

stabilizing nanocrystalline alloys at high temperatures (vs. the typical low-temperature stabilization of binary nanocrystalline alloys due to the needs of kinetic inhibition of precipitation). Finally, the intrinsic sluggish kinetics associated with high-entropy alloys (and presumably high-entropy GB complexions) may also provide beneficial effects for stabilizing nanocrystalline alloys (while we do recognize a possible detrimental effect as a result of interfacial disordering, which may compete with the high-entropy sluggish kinetics), in addition to the two thermodynamic effects discussed above.

6. Concluding remarks and future directions

In this article, we have reviewed several interfacial thermodynamic models for modeling GB adsorption and complexion formation/transition in multicomponent alloys. Two specific focuses are placed on (1) discussing the effects of interaction between different adsorbates and (2) developing GB diagrams for multicomponent systems. Finally, we propose a new opportunity of stabilizing nanocrystalline alloys via utilizing high-entropy GB complexions, particularly at high temperatures.

We propose a major scientific goal for our community to develop various types of GB diagrams, including robustly-useful GB λ diagrams that can predict trends in activated sintering and other GB controlled properties such as Coble creep as well as more rigorous GB complexion diagrams with well-defined transition lines and critical points. Guided by such GB diagrams, fabrication recipes can be designed to control microstructures and optimize interfacial structures to improve properties. It is particularly important to develop various types of GB diagrams for multicomponent systems, where Edisonian approaches are inefficient.

Albeit promising opportunities in this field, major challenges still remain, which dictate several future research directions, as follows:

- First, we should further refine and validate various existing models for multicomponent alloys (for $N \geq 3$), where only limited prior studies have been conducted.
- Second, we need to develop and refine statistical thermodynamic models that can describe coupled adsorption and structural transitions (interfacial disordering) as well as represent various types of GB transitions (including coupled prewetting and premelting as well as layering and roughening) to construct (more rigorous) GB complexion diagrams that can be verified/validated by experiments for multicomponent systems.
- Third, current models are developed mostly for representing metallic alloys; thus, we should extend them and/or develop more sophisticated models that can predict some useful trends for ceramic materials, where the interfacial interactions are more complex.
- Furthermore, we should further integrate statistical interfacial thermodynamic models with quantum-mechanical density functional theory (DFT) and atomistic (molecular dynamics and Monte Carlo) simulations, as well as continuum-level simulations of mechanical, transport, and physical properties.
- Yet another major challenge is represented by the experimental validation of computed GB complexion diagrams, which are often too time-consuming; thus, it is imperative to develop novel accelerated or combinational experimental approaches.
- Another major obstacle for computing GB complexion diagrams is represented by the lacking of reliable thermodynamic data; thus, we should develop reliable database by combining experiments with DFT and atomistic simulations using an Materials Genome Initiative (MGI) approach to build an open-access “Materials Interface Genome” data bank to collect not only

related thermodynamic data but also items like (computed and/or experimentally verified) GB complexion diagrams, interfacial models, various useful algorithms, and open-access codes.

- Finally, we also aim to discover novel phenomena via the interaction of multiple (many) components at GBs to achieve properties unattainable otherwise. One such exciting possibility is represented by the possible stabilization of nanoalloys via utilizing high-entropy GB complexions to achieve exceptional thermal stability at high temperatures unattainable by conventional binary nanoalloys (as proposed and discussed in Section 5). Many other opportunities should also exist. Here, the guidance from quantitative interfacial thermodynamic models for the many-component systems, even if the models can only predict some useful trends, become vital for success, since the Edisonian approaches for optimizing many-component systems will be infeasible.

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