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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.

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-SiO_2 [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 Chatain 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:

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

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 became 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):

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

where $\Delta G_{ads(i\to 1)}$ 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),