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Developing grain boundary diagrams for multicomponent alloys

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Abstract—Impurity-based, premelting-like, intergranular films (IGFs, a common type of grain boundary complexion) can form in various materials and influence sintering, creep, and microstructure development. A thermodynamic framework is presented to forecast the formation and stability of these premelting-like grain boundary complexions (*a.k.a.* interfacial "phases" that are thermodynamically two dimensional) in multicomponent alloys to consider the interactions of multiple alloying elements. Key thermodynamic parameters that control the interfacial segregation and disordering behaviors have been identified and systematically examined. Subsequently, ternary and quaternary grain boundary diagrams have been computed and used to forecast the sintering behaviors of W–Ni–*M* (*M* = Fe, Co, Cr, Zr, Nb and Ti) and Mo–Si–B–*M* (*M* = Ni, Co and Fe) systems. This work supports a long-range scientific goal of extending bulk computational thermodynamics and CALPHAD methods to interfaces and developing grain boundary complexion (interfacial "phase") diagrams as extensions to bulk phase diagrams, which can be a generally useful materials science tool.

Keywords: CALPHAD; Grain boundary complexion; Interfacial thermodynamics; Materials Genome Initiative; Premelting

1. Introduction

It is now well established that the surface of ice starts to "melt" well below 0 °C [1–3]. This phenomenon, known as *surface melting* or *premelting*, was also confirmed for other unary solids such as lead [1–3]. In the middle 19th century, Faraday originally proposed the existence of premelting and used it to explain why two blocks of ice can freeze together and a snowball can hold together below 0 °C [1–3], which are analogous to the *sintering* phenomenon studied by materials scientists. Geophysicists also believe that grain boundary (GB) premelting, enhanced by the presence of minor impurities, can play an important role in controlling glacier motion [1–3], which is related to the *Coble creep* phenomenon known in the materials research community. In 1980s, materials scientists had sought to confirm the existence of GB premelting in unary metals experimentally [4]; although GB premelting was later discovered in a colloidal crystal [5], the significance and importance of GB premelting in real unary materials remain elusive. Nevertheless, in multicomponent systems, the interfacial disordering can be enhanced by a concurrent GB adsorption (*a.k.a.* segregation); consequently, impurity-based, premelting-like, intergranular films (IGFs) can be stabilized over at larger undercoolings and influence a broad range of materials properties and fabrication processing [6–21]. Specifically, indirect measurements of GB diffusivity and chemistry suggested the existence of GB premelting-like behaviors in Cu [6–8] and Fe [7,9,10] based alloys. More recently, impurity-based, premelting-like IGFs have been observed directly by high resolution transmission electron microscopy (HRTEM) in W [15,16] and Mo [17–19] based alloys as well as several oxide systems [11–14].

Tang et al. [14] proposed that subsolidus IGFs in binary alloys form from coupled GB premelting and prewetting transitions [20] using a diffuse-interface model extended from the Cahn model [22], and this diffuse-interface model has been further elaborated by Mishin et al. using the Cu-Ag system as an example [21]. In a broader context, GB premelting and prewetting can be considered as the representative GB structural (disordering) and chemical (adsorption) transitions, respectively, and they are often coupled in multicomponent systems [14,21]. In 1968, Hart already proposed that GBs can be considered as *2-D interfacial phases* that may undergo transformations (*a.k.a.* transitions) [23,24]. Subsequent models developed by Hondros and Seah [25,26], Cahn [22,27–29], and many other researchers [18,20,21,30–42] further elaborated this concept. In ceramic materials, impurity-based IGFs can persist well above the bulk solidus lines with nanometer thicknesses limited by attractive van der Waals London dispersion interactions [14,30,31,43,44]. Clarke first proposed that such IGFs have an *equilibrium* thickness [30,31] and Cannon suggested that they can equivalently be interpreted as a class of structurally-disordered multilayer adsorbates [45]. Later, Tang,

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Carter and Cannon [20,32] named such "2-D interfacial phase" as "complexions" based on an argument that they are not "phases" according to the rigorous Gibbs definition, and related terminologies were discussed in two recent reviews [34,46]. In 2007, Dillon and Harmer [47–50] reported the discovery of a series of six discrete GB complexions in Al_2O_3 based ceramics, and similar complexions have also been observed in metals [18,19,46,51–54]; this series of Dillon-Harmer complexions can be considered as derivatives of IGFs (*a.k.a.* multilayer adsorbates) with discrete (equilibrium) thicknesses of 0, 1, 2, 3, x, and ∞ atomic layers [40,42,46,55]. Moreover, the existence of first-order GB complexion transitions was experimentally evident in Cu [6–8], Fe [7,9,10], Si [51] and TiO_2 [56] based systems and supported by recent atomistic modeling [57,58]; analogous first-order transitions have also been discovered at free surfaces [59–62].

Understanding GB complexions and transitions is both scientifically significant and technologically important. Specifically, enhanced mass transport in the impurity (sintering aid) based, premelting-like IGFs can lead to accelerated sintering below the bulk solidus lines, which explains a long-standing mystery regarding the origin of solid-state activated sintering [12,16,18,42]. The discoveries of GB complexions and transitions also provided new insights into the understanding of the atomic-level mechanisms for abnormal grain growth [47–49,63] and liquid metal embrittlement [52,53]. Generally, the formation of (relatively) disordered GB structures at high temperatures with enhanced transport properties can affect a broad range of GB-controlled materials properties, such as creep, corrosion and oxidation resistance, in addition to the microstructural evolution [14]. Furthermore, the GB structure and chemistry formed at the high processing temperature can often be (partially) retained upon cooling, thereby influencing a broad range of mechanical and physical properties at room temperature [14,46].

The development of bulk phase diagrams and calculation of phase diagram (CALPHAD) methods established one of the foundations for modern materials science. Since GBs can exhibit transitions that can affect a broad range of fabrication processing and materials properties (as discussed above), it is useful to develop the GB analogous to bulk phase diagrams and CALPHAD methods. Recently, premelting and other types of GB transitions have been simulated by atomistic [57,58], phase-field-crystal [64,65] and lattice [28,29] models; a limited number of GB complexion diagrams have been constructed by diffuse-interface models [20,21] and a lattice model [37]. In a series of recent studies, bulk CALPHAD methods were extended to model GBs to forecast the stability of impurity-based, premelting-like IGFs in binary alloys; subsequently, a type of GB λ diagrams has been developed to represent the thermodynamic tendency for general GBs to disorder and forecast related activated sintering behaviors in binary alloys (only) [18,41,42,66]. Although they are not yet rigorous GB complexion diagrams with well-defined transition lines and critical points, the correctness and usefulness of these binary GB λ diagrams have been validated by a series of experiments. First, the model predictions were corroborated with direct HRTEM and GB chemistry analysis for selected systems [16,18,19,42,67]. Second, the computed GB λ diagrams (with no free parameters) correctly predicted the onset sintering temperatures for a series of W based binary alloys as well as some trends in sintering rates [18,42,66]. Specifically, the predicted GB solidus temperature was consistent with a prior direct GB diffusivity measurement for W–Co (the primary element/phase is underlined) using radioactive tracers [42,68]. Third, the estimated GB diffusivity as a function of temperature and overall composition correlated well with the computed binary GB λ diagram for Mo–Ni [18]. Finally, a counterintuitive phenomenon of decreasing GB diffusivity with increasing temperature was predicted and subsequently verified experimentally in a Mo + 0.5 at.% Ni alloy [54].

Historically, bulk CALPHAD methods were first developed for binary alloys, for which phase diagrams have already been determined by experiments. CALPHAD methods become useful when they can utilize the thermodynamic data that are largely obtained from binary systems to extrapolate (by adding only a few multi-body interaction parameters) and predict behaviors of multicomponent alloys, where the Edisonian approach is no longer feasible. Likewise, after demonstrating the basic feasibility of constructing binary GB λ diagrams and their usefulness in predicting sintering behaviors, the challenging goal of this study is to extend and validate the model and computation methods to multicomponent ($N \geqslant 3$) alloys. This work is not only technologically important (since understanding such interactions can offer a way to control GB behaviors via developing co-alloying strategies) but also scientifically interesting (because interactions among multiple alloying elements can produce new interfacial phenomena).

It should be noted that these computed λ diagrams, which represent the thermodynamic tendency for average general GBs to disorder, are called "GB diagrams" in this article because they are not rigorous complexion diagrams with well-defined transition lines and critical points.

2. The model and computational methods

2.1. The interfacial thermodynamic model

In a phenomenological model adapted from the premelting and wetting models that were widely used by physicists [3,64,69,70], the excess free energy of a subsolidus, premelting-like IGF is expressed as:

$$\sigma^x(h) = \Delta G^{(\mathrm{vol})}_{\mathrm{amorph}} h + 2\gamma_{\mathrm{cl}} + \sigma_{\mathrm{interfacial}}(h), \tag{1}$$

where $\Delta G^{(\mathrm{vol})}_{\mathrm{amorph}}$ is the volumetric free energy for forming an undercooling liquid from the equilibrium solid phase(s), h is the film thickness and γ_{cl} is the crystal–liquid interfacial energy. The interfacial potential, $\sigma_{\mathrm{interfacial}}(h)$, includes the effects of all interfacial interactions and it vanishes as the film thickness (h) approaches infinity (by definition, so that $2\gamma_{\mathrm{cl}}$ can be well defined at $h \to +\infty$):

$$\sigma_{\mathrm{interfacial}}(+\infty) = 0. \tag{2}$$

We may re-write the interfacial potential as:

$$\sigma_{\mathrm{interfacial}}(h) = -\Delta\gamma \cdot [1 - f(h)], \tag{3}$$

where $f(h)$ is defined as a dimensionless interfacial coefficient that satisfies:

$$\begin{cases} f(0) = 0 \\ f(+\infty) = 1 \end{cases} \tag{4}$$

and

$$\Delta\gamma \equiv 2\gamma_{\mathrm{cl}} - \gamma^{(0)}_{\mathrm{GB}}, \tag{5}$$