Prediction of grain boundary chemistry in multicomponent alloys

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ABSTRACT
Hillert’s grain-boundary-phase (GBP) model is employed for predicting grain boundary (GB) chemistry in multicomponent alloys. The GB is approximated as a thin layer of a homogeneous phase with a constant thickness and its own Gibbs energy. The GB composition is computed to minimize the Gibbs energy of the mixture of a grain phase and the GB; the Gibbs energy of liquid phase is assigned to that of the GB. The calculation of phase diagram (CALPHAD) databases are employed to calculate the Gibbs energy of a phase of interest as a function of composition and temperature. To verify the calculation results’ validity, the predicted GB chemistry was compared with experimental data from previous research for nickel-based superalloys, an austenitic stainless steel, and a high-entropy alloy. It is demonstrated that the method combining Hillert’s GBP model and CALPHAD databases is effective for predicting the equilibrium solute segregation to stationary random high-angle GBs in multicomponent alloys, enabling the advanced compositional design of materials for GB segregation engineering.

1. Introduction

In polycrystalline metallic alloys, grain boundaries (GBs) influence several properties, including tensile strength, fatigue resistance, fracture toughness, strain hardening, brittleness, conductivity, and corrosion [1]. However, the solute segregation to GB changes GB properties, including cohesion, fracture resistance, electroconductivity, hydrogen embrittlement, mobility, and resistance to or sources of dislocations [1,2]. Thus, the GB design is critically significant, which involves not only the control of polycrystalline structures made of low-angle, random high-angle, and special high-angle GBs (GB engineering) but also the regulation of GB chemistry (GB segregation engineering) [1]. Recently, the GB segregation has been widely investigated in multicomponent alloys, including Ni-based superalloys [3–8], austenitic stainless steels [9–14], and high-entropy alloys [15]. The experimental characterizations of GBs offer us some tips on how to control the GB chemistry. However, for enabling the GB segregation engineering, theoretical and practical methods for predicting the GB chemistry in multicomponent alloys are also needed.

According to Gibbs’ adsorption equation [16], the GB excesses of element $i$ ($\Gamma_i$) are determined by the effects of chemical potentials ($\mu_i$) on the GB energy ($\sigma$) at a constant temperature: $d\sigma = -\sum_i \Gamma_i d\mu_i$ [17]. For a dilute solid solution, the GB excesses of element $i$ at a constant temperature $T$ are given by $\Gamma_i = -\left(\partial\sigma/\partial\ln x_i\right)_T/RT$ where $x_i$ represents the concentration of element $i$ in the grain interior and $R$ represents the universal gas constant [17]. The values of $\sigma$ as a function of $x_i$ and $T$ are needed to calculate the GB excesses. According to the Langmuir–Mclean equation [18], the relationship between the GB concentration ($X$) and the concentration in grain interior ($x$) in a binary system is described by $X/(1-X) = (x/(1-x)) \exp(\Delta E/RT)$ where $\Delta E$ represents the molar energy of segregation. The value $\Delta E$ is necessary to determine the GB concentration. The segregation energy is frequently determined using first-principles...
calculations [2]. Recently, there has been an effort to confirm the computed GB concentrations in a multicomponent alloy by comparing them with atom probe tomography (APT) measurement data [8]. Additionally, a method has been proposed to compute the segregation energy of distinct atomic sites in binary systems using interatomic potentials and an atomic model of polycrystal [19].

Hillert [20] supposed that the GB can be represented as a thin layer of a homogeneous phase of constant thickness and with its unique Gibbs energy. In a binary system, the equilibrium composition of the GB phase (GBP) can be found by a parallel-tangent construction to Gibbs energy curves of a grain phase and the GBP. It has been demonstrated that the Gibbs’ adsorption equation can be derived graphically using Gibbs energy–composition diagram in a binary system. Hillert [20] also considered an A–B binary system where the regular solution model [21,22] could be applied to both the grain phase and the GBP and demonstrated that a strong tendency for GB segregation (a large positive value of ΔE) is caused by a large negative value of the interaction parameter, i.e. a strong tendency for A and B atoms to mix in the GBP. According to the Hillert’s GBP model, the Gibbs energies of the grain phase and the GBP as a function of composition and temperature are necessary to calculate the equilibrium composition of the GBP.

In this research, Hillert’s GBP model is used for predicting GB chemistry in multicomponent alloys. Our main concern is the prediction of the equilibrium solute segregation to stationary random high-angle GBs. The fundamental idea behind our work is to fully use the calculation of phase diagrams (CALPHAD) [21,22] databases, which enable us to calculate the Gibbs energy of a phase of interest as a function of composition and temperature in a multicomponent system. To illustrate the general application of Hillert’s GBP model to multicomponent systems, the GB chemistry in Ni-based superalloys (Inconel718 and Inconel617B), an austenitic stainless steel (type 316L stainless steel), and a high-entropy alloy (Cantor alloy) is computed. To confirm the computation findings, the predicted GB chemistry is compared with experimental data from previous research. We demonstrate the effectiveness of the method combining Hillert’s GBP model and CALPHAD databases in the prediction of GB chemistry in multicomponent alloys.

2. Calculation method

We consider computing the GB chemistry according to Hillert’s GBP model [20]; the GB region is regarded as a thin film of a homogeneous phase of constant thickness. Here, we consider a grain phase (denoted as α) and a GBP (denoted as β) in an N-component system. The Gibbs energy of the (α + β) two-phase mixture is given by

$$G_c = G_c^\alpha(c_\alpha; T)f_{\alpha} + G_c^\beta(c_\beta; T)f_{\beta} + \lambda^\alpha(c_\alpha - c_0^\alpha - c_0^\beta),$$

where $G_c^\alpha$ and $G_c^\beta$ are the Gibbs energies of the α and β phases, respectively; $c_\alpha = (c_\alpha^1, c_\alpha^2, \ldots, c_\alpha^N)^T$ and $c_\beta = (c_\beta^1, c_\beta^2, \ldots, c_\beta^N)^T$ are the composition vectors of the α and β phases, respectively; $T$ represents temperature; $f_{\alpha}$ and $f_{\beta}$ are the volume fractions of the α and β phases, respectively; $f_{\alpha} + f_{\beta} = 1$; $c_0$ represents the average composition vector of the (α + β) two-phase mixture; and $\lambda \in \mathbb{R}^{N-1}$ represents the Lagrangian multiplier vector [23]. Note that $\bullet^T$ denotes the transpose of $\bullet$. The $c_\alpha$ and $c_\beta$ at constant temperature are determined to minimize $G_c$ under a fixed volume fraction of the β phase:

$$\frac{\partial G_c}{\partial c_\alpha} = \left(\frac{\partial G_c^\alpha}{\partial c_\alpha} - \lambda \right) f_{\alpha} = 0,$$

$$\frac{\partial G_c}{\partial c_\beta} = \left(\frac{\partial G_c^\beta}{\partial c_\beta} - \lambda \right) f_{\beta} = 0,$$

$$\frac{\partial G_c}{\partial \lambda} = c_0 - c_0 f_{\alpha} - c_0 f_{\beta} = 0.$$

From the above equations, the following relationships are derived:

$$\frac{\partial G_c^\alpha}{\partial c_\alpha} = \frac{\partial G_c^\beta}{\partial c_\beta},$$

$$c_0 = c_0 f_{\alpha} + c_0 f_{\beta}.$$

In a binary system, the relations are referred to as the parallel-tangent law, which can be interpreted as the parallel-tangent construction to the Gibbs energy curves of the α and β phases (see Figure 1(a)) [20].

A penalty function was defined as

$$J = \left(\frac{\partial G_c^\alpha}{\partial c_\alpha} - \frac{\partial G_c^\beta}{\partial c_\beta}\right)^2 = \left\{ (\mu_\alpha - \mu_\beta) - e(\mu_N^\alpha - \mu_N^\beta) \right\}^2,$$

where $e = (1, 1, \ldots, 1)^T$; $\mu_\alpha = (\mu_1^\alpha, \mu_2^\alpha, \ldots, \mu_N^\alpha)^T$ and $\mu_\beta = (\mu_1^\beta, \mu_2^\beta, \ldots, \mu_N^\beta)^T$ are the chemical potential vectors of the α and β phases, respectively. We focused on calculating the equilibrium solute segregation to random high-angle GBs (equilibrium composition of GBP) in a multicomponent system. Considering the atomic arrangement of random high-angle GBs, which have significant areas of poor fit and have a relatively open structure [24], the Gibbs energy of liquid phase was assigned to that of the β phase.
(GBP). The chemical potentials were computed using the Thermo-Calc software [25] and the CALPHAD databases TTN18 [26], TCFE11, and TCHEA5; TC-Python was used to couple the Thermo-Calc computations with our house-made Python code. Assuming that the volume fraction of the β phase (GBP) is infinitesimally small \( f_\beta = 0 \), we found an optimum \( c_\beta \) that minimizes \( J \) using the Nelder–Mead method [27]; \( c_\beta \) was updated until \( J \) became less than 1 J\(^2\) mol\(^{-2}\). The computation of \( c_\beta \) started from an elevated temperature, and the optimum \( c_\beta \) was sequentially explored around the optimum \( c_\beta \) at a higher temperature; this resulted in the computation of temperature dependence of \( c_\beta \). The multiple solution of Equation (5), which exist if there is a liquid–liquid phase separation, are beyond the scope of this research. In some multicomponent systems, there existed several types of equilibrium phases coexisting with the α phase (grain phase) depending on temperature conditions. In such situations, the phase equilibrium between all coexisting phases was determined first to obtain \( c_\beta \), and then, the optimum \( c_\beta \) was computed (see Figure 1(b)). When no bulk phases were coexisting with the α phase, the phase equilibrium computation was not required because \( c_\beta \) was identical to the alloy’s bulk composition (Figure 1(a)).

3. Results

3.1 Ni-Based superalloys

We consider predicting the GB chemistry of Inconel718 after service in an airplane engine by APT; the service temperature was considered to be up to 873 K, and the total service time was approximately 10,000 h or longer [3]. Figure 3 demonstrates the GB concentrations of solute elements at 873 K computed considering the phase equilibrium between \( \gamma \), \( \gamma' \), \( \gamma'' \), and \( M_{23}C_6 \). Note that \( M_{23}C_6 \) was

![Figure 1. Gibbs energy–composition diagrams demonstrating the concept of Hillert’s GBP model (parallel-tangent law) in an A–B binary system: (a) parallel-tangent construction to Gibbs energy curves of the grain phase (α) and the GBP (β), and (b) parallel-tangent construction to Gibbs energy curves of the grain phase (α) and the GBP (β) when the phase equilibrium between the α phase and a secondary phase (γ) is considered.](image-url)
presumed to precipitate based on the time-temperature-precipitation diagram for carbides in Inconel718 [29]. Mo and B are substantially enriched in GPB. In Figure 3, APT data of Mo, B, and C concentrations on a GB [3] are illustrated by solid circles for comparison; experimental data for other solute elements are influenced by fine γ' particles that occur in proximity to the GB and hence are challenging to compare with our calculation findings. The computed GB chemistry (3.9 at.% Mo, 2.6 at.% B, and 0.007 at.% C) is close to the experimental data (about 8 at.% Mo, 2.5 at.% B, and 0.2 at.% C). Since the TTN8 database lacks a P element, our estimation cannot predict the P segregation at the GB, which has also been proven by the experiment [3]. The P segregation could influence the Mo segregation and thus could reduce the difference in Mo concentrations between the estimation (3.9 at.% Mo) and the

Figure 2. Computation results for Inconel718 using the thermodynamic database TTN8 [26]: (a) temperature dependence of equilibrium phases, (b) temperature dependence of equilibrium concentrations of constituent elements in GBP when the γ single-phase polycrystalline state is assumed, and (c) temperature dependence of equilibrium concentrations of constituent elements in GBP when the γ phase is in equilibrium with other coexisting phases at each temperature. Note that MC carbide is modeled as C-rich γ (fcc-A1) phase [26] and hence is inevitably considered in the computation of (b).

Figure 3. Computed GB concentrations of solute elements at 873 K in Inconel718 using the thermodynamic database TTN8 [26]. The phase equilibrium between γ, γ', γ'', and \(M\)\(_{23}\)\(_{6}\) is considered. APT data [3] are shown by solid circles for comparison. Alloy concentrations are shown by solid diamonds.
experiment (8 at.% Mo). However, the existence of attractive interactions between P and other elements at GBs is unclear and further research is necessary.

We next consider predicting the GB chemistry in Inconel617B, which is a B-alloyed variant of Inconel617 and shows high creep strength and excellent weldability. Inconel617B is an alloy with the following composition Ni–24.7Cr–11.4Co–5.2Mo–2.1Al–0.4Ti–0.3C–0.02B in at.% [4]. Note that Fe, Si, N, Mn and Cu elements were excluded from our computation due to the high computing cost of calculating phase equilibrium in multicomponent systems. Figure 4(a) demonstrates the equilibrium phases computed using the thermodynamic database TTN18 [26]. At low temperatures, γ (solid solution phase with fcc structure), γ’-Ni3Al, μ (TCP phase [28]), M23C6, and M3B2 are predicted as the principal equilibrium phases. Figure 4(b) demonstrates the computed equilibrium concentrations of constituent elements in GBP when the γ single-phase polycrystalline state is assumed. Mo and B are enriched in GBP and their concentrations increase as temperature decreases, just like Inconel718. Figure 4(c) demonstrates the computed equilibrium concentrations of constituent elements in GBP when the γ phase is in equilibrium with other coexisting phases at each temperature. The Mo and B concentrations in the GBP are small compared to that demonstrated in Figure 4(b) since Mo and B are enriched in the M3B2 phase. Below 1050 K, the Co and Mo concentrations in GBP decrease with decreasing temperature because Co and Mo are enriched in the μ phase. Additionally, the Ti concentration in GBP decreases as temperature decreases due to the enrichment of Ti in the γ’ phase.

The GB chemistry of Inconel617B, which was homogenized at 1450 K and then quenched in water, was examined by Tytko et al. [4] using APT. Figure 5(a) demonstrates the GB concentrations of

Figure 4. Computation results for Inconel617B using the thermodynamic database TTN18 [26]: (a) temperature dependence of equilibrium phases, (b) temperature dependence of equilibrium concentrations of constituent elements in GBP when the γ single-phase polycrystalline state is assumed, and (c) temperature dependence of equilibrium concentrations of constituent elements in GBP when the γ phase is in equilibrium with other coexisting phases at each temperature. Note that MC carbide is modeled as C-rich γ (fcc-A1) phase [26] and hence is inevitably considered in the computation of (b).
solute elements at 1450 K calculated on the assumption of the γ single-phase polycrystalline state. Cr, Mo, B, and C are significantly enriched in GBP. As shown in Figure 5(a), APT data of Cr, Co, Mo, and B concentrations on a GB [4] are demonstrated by solid circles. The GB concentrations of Cr, Co, Mo, B, and C are similar between the computation (27.8 at.% Cr, 10.9 at.% Co, 11.6 at.% Mo, 8.9 at.% B, and 3.0 at.% C) and experiment (about 39 at.% Cr, 8 at.% Co, 19 at.% Mo, 13 at.% B, and 4 at.% C). The segregated elements of Cr, Mo, B, and C can be regarded as M<sub>23</sub>(B,C)<sub>6</sub>-forming elements. Tytko et al. [4] mentioned the possibility that a thin carbide film was precipitated at a GB region even during quenching at a high cooling rate. In this context, Figure 5(b) demonstrates the GB concentrations of solute elements at 1100 K estimated under the assumption of the γ single-phase polycrystalline state. The differences in Mo and B concentrations between the computation and experiment are substantially reduced compared to Figure 5(a). Therefore, it is assumed that the GB chemistry would change during the early stage of quenching from 1450 K, and the resulting GB segregation of Cr, Mo, B, and C will cause the M<sub>23</sub>(B,C)<sub>6</sub> formation at a GB region. The experimentally observed enrichment of Cr on a GB [4], which is significantly higher than our computation result (see Figure 5(a,b)), constitutes a precursory phenomenon of M<sub>23</sub>(B,C)<sub>6</sub> formation during quenching from 1450 K.

### 3.2 Austenitic stainless steel

We consider predicting the GB chemistry in type 316L stainless steel, which is a low-carbon variant of type 316 stainless steel and shows good corrosion resistance. Type 316L stainless steel has the following alloy composition in at.% Fe–0.04C–1.03Si–1.53Mn–0.050P–10.71Ni–18.37Cr–1.25Mo–0.14Co–0.0005B [12]. Note that S and N elements were excluded from our computation due to the high computational cost of calculating phase equilibria in multicomponent systems. Figure 6(a) demonstrates the equilibrium phases computed using the thermodynamic database TCFE11. At low temperatures, γ (solid solution phase with fcc structure), σ (Fe- and Cr-rich intermetallic phase), M<sub>23</sub>C<sub>6</sub>, and C14-type Laves are predicted as the principal equilibrium phases. Figure 6(b) illustrates the computed equilibrium concentrations of constituent elements in GBP when the γ single-phase polycrystalline state is assumed. P is enriched in GBP and the P concentration increases as temperature decreases. Figure 6(c) demonstrates the computed equilibrium concentrations of constituent elements in GBP when the γ phase is in equilibrium with other coexisting phases at each temperature. The existence of σ and M<sub>23</sub>C<sub>6</sub> phases at low temperatures has a negligible effect on the P concentration in GBP (compare Figure 6(b,c)).

The GB chemistry in type 316L stainless steel, which was solution-treated at 1316 K and subsequently quenched in water, was examined by Tomozawa et al. [12] using APT. Figure 7 depicts the GB concentrations of solute elements at 1316 K computed assuming the γ single-phase polycrystalline state. We can see that Mo, P, B, and C are substantially enriched in GBP. In Figure 7, APT data of Cr, Ni, Mo, P, B, and C concentrations on a GB [12] are demonstrated by solid circles. The computed concentrations of segregated elements (1.96 at.% Mo, 2.11 at.% P, 0.17 at.% B, and 0.21 at.% C) are close to the experimental data (about 3.5 at.% Mo, 0.7 at.% P, 1 at.% B, and 0.4 at.% C). The GB segregation factor was computed as the ratio of the concentration of a segregated element in GBP to that in the γ phase; 1.6 for Mo, 42 for P, 340 for B, and 5.3 for C. The segregation factor of B is significantly higher than that of other segregated elements, which is consistent with experimental data [12].
3.3 High-Entropy alloy

In the equiatomic quinary CrMnFeCoNi alloy (Cantor alloy), we consider predicting the GB chemistry. The composition of the Cantor alloy is 20Cr–20Mn–20Fe–20Co–20Ni in at.%. Figure 8(a) illustrates the equilibrium phases computed using the thermodynamic database TCHEA5. At low temperatures, $\gamma$ (solid solution phase with fcc structure), $\alpha$ (solid solution phase with body-centered cubic structure), and $\sigma$ (Fe- and Cr-rich intermetallic phase) are predicted as the equilibrium phases. Figure 8(b) demonstrates the computed equilibrium concentrations of constituent elements in GBP when the $\gamma$ single-phase polycrystalline state is assumed. Ni and Mn are enriched in the GBP and the Ni concentration slightly increases as temperature decreases. Figure 8(c) demonstrates the computed equilibrium concentrations of constituent elements in GBP when the $\gamma$ phase is in equilibrium with other coexisting phases at each temperature. Below 1200 K, the Ni concentration in GBP increases as temperature decreases, while the Cr concentration in GBP decreases as temperature decreases. This is due to the enrichment of Cr and depletion of Ni in the $\gamma$ phase; the resultant high concentration of Ni in the $\gamma$ phase results in the enrichment of Ni in GBP.

The GB chemistry in the Cantor alloy, which was annealed at 973 K for 800 h, was examined by Heczko et al. [15] using scanning transmission electron microscopy (STEM) energy-dispersive x-ray spectroscopy (EDS) (STEM-EDS). Figure 9(a) demonstrates the GB concentrations of constituent elements at 973 K computed considering the phase equilibrium
between γ and σ. As shown in the figure, experimental data of GB chemistry obtained by EDS line-scan elemental profiles across a GB [15] is demonstrated by solid circles. Although there are differences between the calculation findings and experimental data, experimentally observed depletion of Cr and enrichment of Ni and Mn in GBP are predicted by the computation. The enrichment of Ni and Mn can cause the formation of NiMn phase at GBs. It was established that a GB was partially decorated by many NiMn precipitates with sizes of 10–20 nanometers [15]. In Figure 9(b), the calculated GB concentrations of constituent elements at 973 K are compared with the experimental data obtained by EDS line-scan elemental profiles across a NiMn precipitate on a GB [15]. The composition of the NiMn phase is similar to the computed GB composition. This appears to be proof that the enrichment of Ni and Mn caused the NiMn phase to precipitate at the GB. The NiMn phase is not predicted to be the equilibrium phase at 973 K using the thermodynamic database TCHEA5 (see Figure 8(a)). Thus, the reassessment of the stability of NiMn phase appears to be needed for calculating the GB chemistry when the phase equilibrium between γ, σ, and NiMn are considered, i.e. for predicting the chemistry of a NiMn-precipitate-free GB.

4. Discussion

Hillert’s GBP model was used to estimate the GB segregation of Mo, B, and C at 873 K in Inconel718, and the GB segregation of Cr, Mo, B, and C at 1100 K and 1450 K in Inconel617B (see Figures 3 and 5). The segregation tendency of Mo and B has been also reported in several Ni-based superalloys [5–8]. Cr, Mo, B, and C are usually enriched in carbide/boride including M_{23}(B,C)_6, MC, and M_{23}B_{3} [6,30–33]; thus, the segregation of these elements would cause carbide/boride formation at GBs, which frequently influences mechanical properties of alloys. For example, Kontis et al. [31] demonstrated that adding B to a Ni-based superalloy reduces the formation of M_{23}C_{6} decorating GBs and the formation of M_{23}B_{3} along the GBs. Additionally, the B addition changed the GB character (formation of γ’ layers at GBs and serration of GBs), leading to the enhancement of high-temperature ductility of the superalloy [31]. The GB chemistry calculation based on Hillert’s GBP model would enable us to
regulate the GB chemistry and thereby promote/suppress the carbide/boride formation at GBs, enabling the design of GB microstructure in Ni-based superalloys.

In type 316L stainless steel, the GB segregation of Mo, P, B, and C at 1316 K was predicted according to Hillert’s GBP model (see Figure 7). Particularly, the substantial segregation of B was predicted. Similar tendencies of B segregation to austenite GBs has been also noted in several low-carbon steels [34–36]; B segregation would reduce the austenite GB energy and inhibit the austenite-to-ferrite transformation at GBs. Additionally, the segregation of P, which is promoted by irradiation and could enhance brittle intergranular fracture [13], has been also reported in several irradiated stainless steels [9–11,13,14]. As a whole, the solute segregation to austenite GBs influences the subsequent phase transformation behavior and/or mechanical properties of steels. The relationship between the alloy composition and the GB chemistry can be thoroughly analyzed by the method combining Hillert’s GBP model and CALPHAD databases, which would allow an advanced compositional design of steels with trace elements.

In the computation of GB chemistry, the volume fraction of the GBP was assumed to be infinitesimally small for simplicity, i.e. $f_\beta = 0$ in Equation (6). In type 316L stainless steel, the strong segregation tendency of P and B at 1316 K was predicted. However, when the GB concentrations of trace elements including P and B are computed, one may be interested in the effect of an actual value $f_\beta$ on the computation result. The relationship between $f_\beta$ and the grain size $d$ is expressed as $f_\beta = (3.165\Delta/d)(1 - 1.055\Delta/d)^2$ where $\Delta$ represents the GB thickness [37]. Thus, the GB composition at 1316 K in type 316L stainless steel was computed for five cases $f_\beta = 1.05 \times 10^{-5}$, $f_\beta = 5.27 \times 10^{-4}$, $f_\beta = 1.05 \times 10^{-3}$, $f_\beta = 3.16 \times 10^{-3}$, and $f_\beta = 6.32 \times 10^{-3}$, which correspond to the grain sizes of $d = 300 \mu m$, $d = 6 \mu m$, $d = 3 \mu m$, $d = 1 \mu m$, and $d = 0.5 \mu m$, respectively, when $\Delta = 1 \text{ nm}$ is assumed. Under the condition of $f_\beta \neq 0$, $c_\beta$ and $c_\alpha$ were alternately updated using Equation (5) and (6), respectively, until convergence. The computation findings of the dependence of GB composition on the volume fraction of the GBP are listed in Table 1. The GB composition computed for $f_\beta = 1.05 \times 10^{-5}$ ($d = 300 \mu m$) is nearly identical to that computed for $f_\beta = 0$. The GB compositions computed for $f_\beta = 5.27 \times 10^{-4}$ ($d = 6 \mu m$) and $f_\beta = 1.05 \times 10^{-3}$ ($d = 3 \mu m$) illustrate that when $d$ is within the range of a few micrometers, the Mo, P, and B concentrations slightly decrease with decreasing $d$. Additionally, the GB compositions computed for $f_\beta = 3.16 \times 10^{-3}$ ($d = 1 \mu m$) and $f_\beta = 6.32 \times 10^{-3}$ ($d = 0.5 \mu m$) illustrate that when $d < 1 \mu m$, the Mo, P, and B concentrations significantly decrease with decreasing $d$. Ohnuma [38] has reported a similar result for the GB concentration of P in Cu–0.1 at.-% P alloy. These findings show that the value $f_\beta$ has a small effect on the GB chemistry when $d$ is larger than a few micrometers but its effect should be explicitly considered when the GB chemistry in ultrafine-grained materials [39,40] is calculated according to Hillert’s GBP model.

The Langmuir–Mclean equation [18] is frequently used to discuss GB segregation. However, the segregation energy value, which is often determined using first-principles calculations [2], is needed for calculating the GB concentration. However, in Hillert’s GBP model, the GB is regarded as a separate phase (GBP) with its own Gibbs energy, and the composition of the GBP is determined by considering the Gibbs energy minimum condition under a fixed volume of the GBP (a fixed thickness of GBs) [20]. The use of CALPHAD databases enables us to calculate the Gibbs energy of a phase as a function of composition and temperature in a multicomponent system. Thus, the combination

**Figure 9.** Computed GB concentrations of constituent elements at 973 K in equiatomic quinary CrMnFeCoNi alloy (Cantor alloy) using the thermodynamic database TCHEAS. The phase equilibrium between γ and σ is considered. Solid circles are experimental data obtained using EDS line-scan elemental profiles across (a) a NiMn-precipitate-free GB and (b) a NiMn precipitate on a GB [15]. Alloy concentrations are shown by solid diamonds.
of Hillert’s GBP model and CALPHAD databases is effective for computing the composition of GBP. Our calculation findings for several multicomponent alloys reveal that the solute segregation to random high-angle GBs can be successfully predicted under the assumption that the Gibbs energy of liquid phase can be assigned to that of the GBP. This assumption has also been supported by Ohtani and Enoki [41], who calculated the segregation energies for solute elements in Fe–X binary systems using the thermodynamic parameters of liquid phase, and showed that the calculation results agreed with experimental data. Additionally, the use of CALPHAD databases enables us to predict the GB chemistry with considering the phase equilibrium between a grain phase and other coexisting bulk phases; solute partitioning to coexisting phases changes the chemical compositions of both the grain phase and the GBP (see Figure 1). The temperature dependence of the GB chemistry with/without considering the effect of coexisting phases (Figures 2, 4, 6 and 8) appears to be crucial information for regulating the GB segregation and the resultant formation of compounds on GBs during heat-treatment processes in multicomponent alloys.

The limitation of the method combining Hillert’s GBP model and CALPHAD databases is that it is unable to predict the solute segregation to low-angle GBs. The assumption that the Gibbs energy of liquid phase can be assigned to that of the GBP is reasonable only for random high-angle GBs. Modifying the Langmuir–Mclean equation so that it can incorporate the effect of both multiple solutes and multiple sites at GBs and using segregation energies from first-principles calculations as inputs [8] may be an alternative and effective method for predicting the solute segregation to low-angle GBs in multicomponent alloys.

5. Conclusion

We proposed a method combining Hillert’s GBP model and CALPHAD databases for predicting the equilibrium solute segregation to stationary random high-angle GBs in multicomponent alloys. The applicability of the method was evaluated by comparing the computed GB chemistry with experimental data from previous research for several multicomponent alloys. The obtained findings are summarized as follows.

1. The GB segregation of Mo, B, and C in Inconel718 after service at 873 K in an airplane engine, and the GB segregation of Cr, Mo, B, and C in Inconel 617B homogenized at 1450 K were predicted. The experimental data of GB chemistry in Inconel 617B from previous research was inconsistent with our computation result at 1450 K but rather consistent with that at 1100 K, showing that the GB chemistry changes during the early stage of quenching from 1450 K.

2. The GB segregation of Mo, P, B, and C in type 316L stainless steel solution-treated at 1316 K was predicted. The segregation factor of B was notably high compared with that of other segregated elements, which is consistent with experimental results from previous research. In the computation of GB chemistry based on Hillert’s GBP model, the assumption that the volume fraction of GBP is infinitesimally small is valid as long as the grain size is larger than a few micrometers.

3. The segregation tendency of Ni and Mn in the Cantor alloy annealed at 973 K for 800 h was predicted. The predicted GB chemistry was close to the composition of a fine NiMn precipitate on a GB reported in previous research, showing that the enrichment of Ni and Mn causes the formation of NiMn phase at the GB.

Disclosure statement

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Data availability statement

A sample code for computing the GB chemistry in the Cantor alloy is available on github: https://github.com/Y-Matsuoka-Material/GBseg-TCPython.

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