Application of Grain Boundary Segregation Prediction Using a Nano-Polycrystalline Grain Boundary Model to Transition Metal Solute Elements: Prediction of Grain Boundary Segregation of Mn and Cr in bcc-Fe Polycrystals*1

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A prediction method for grain boundary segregation using a nano-polycrystalline grain boundary model is applied to the grain boundary segregation of Cr and Mn in bcc-Fe polycrystals for which experimental results exist, and the validity of the prediction method is verified. In this prediction method, focusing on the fact that the atomic structure of grain boundaries is almost independent of grain size, grain boundaries of polycrystals with grain sizes of the order of micrometers are modeled as grain boundaries of nano-polycrystals, for which structural relaxation calculations by molecular dynamics calculations are possible. For this grain boundary model, the grain boundary segregation energy of each site is calculated exhaustively using the interatomic potential. In addition, the average amount of grain boundary segregation in the polycrystal is calculated from the obtained grain boundary segregation energy. With this prediction method, the average amounts of grain boundary segregation and segregation energies of Cr and Mn in bcc-Fe polycrystals can be calculated and compared with the experimental results. Calculated results for both elements reproduced the experimental results well, suggesting that this prediction method is also effective in predicting the grain boundary segregation of other solute elements. [doi:10.2320/matertrans.MT-M2021205]

(Received October 13, 2021; Accepted December 14, 2021; Published February 4, 2022)

Keywords: grain boundary, segregation, steel, theoretical prediction, atomic modeling, iron alloys

1. Introduction

Steel is a widely used and important structural material. In recent years, the demand for high-strength steel, especially for automotive steel sheets, has been increasing, and the research and development of such steel has also increased.1–6) Impurity elements, such as P and S, or alloying elements, including Mn, induce embrittlement, thereby causing a significant reduction in the toughness of steel.7–12) For example, the addition of 500 wt.ppm of P increases the ductile–brittle transition temperature (DBTT) of bcc-Fe by approximately 100 K, and only a 30 wt.ppm addition of S increases the same by approximately 100 K.13,14) As the strength of a material increases, so does its susceptibility to grain boundary (GB) embrittlement.15) Therefore, a material design that suppresses GB embrittlement is required for the development of advanced steels.

The effect of GB segregation of an alloying element on the DBTT changes in proportion to the segregation amount of the alloying element in polycrystals.7) Therefore, the amount of segregation with respect to the amount of alloying elements added and heat treatment temperature is an important basic data in material design. However, as investigating this data experimentally is time-consuming, the experimental data has been reported only for a limited number of elements.16) Therefore, it is desirable to develop a non-empirical method for predicting the amount of GB segregation for a solute element in polycrystals.

For the non-empirical prediction of GB segregation, determination of the segregation energy using first-principles calculation16) is often used. The segregation energy of a GB is evaluated as the difference in energy between a system in which the solute element is present in the bulk and a system in which the solute element is present at the GB. By substituting the obtained segregation energy into the Langmuir-Mclean equation,17) the amount of GB segregation for the solute element in the thermal equilibrium state can be calculated. In bcc-Fe, the segregation energy determined using first-principles calculation using the Σ3(111) symmetric tilt GB reproduces the magnitude relationship of the segregation energy of various solute elements in polycrystals.18–23) First-principles calculations using the Σ3(111) symmetric tilt GB have been useful not only for investigating GB segregation tendencies of solute elements, but also for elucidating the mechanisms of GB segregation and GB embrittlement. However, it has been pointed out that the segregation energy obtained by calculation for the specific GB and the amount of segregation calculated from it are quantitatively different from the experimental values in polycrystalline GBs.24) Recently, highly accurate interatomic potentials for binary systems have been developed to reproduce the results of first-principles calculations, and many analyses of GB segregation in bcc-Fe using these potentials have been reported.25–28) Because the computational cost using the interatomic potential is extremely low compared with the first-principles calculation, it is easy to calculate the segregation energy of the GB model with a large number of atoms and to perform the calculation many times. Therefore, it is useful to comprehensively investigate the GB segregation tendencies of various solute elements and the dependence of GB segregation energy on the GB character and local atomic structure near the segregation site. A method that can predict GB segregation in polycrystals with sufficient accuracy has not yet been established.

To address this issue, we proposed a prediction method for GB segregation using a nano-polycrystalline GB model to improve the prediction accuracy of the amount of GB segregation in polycrystals.29,30) In this prediction method, focusing on the fact that the atomic structure of GBs is almost independent of grain size,31) GBs of polycrystals with grain

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*1 This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. 85 (2021) 421–429.
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sizes on the order of micrometers are modeled as GBs of nano-polycrystals, for which structural relaxation calculations by molecular dynamics calculations are possible. For this GB model, the segregation energy of a solute element is calculated comprehensively for all atomic sites constituting the GB model using an interatomic potential. Subsequently, each atomic site is classified based on its distance from the GB center and averaged to calculate the segregation profile of the solute element for that distance from the GB center. The developed prediction method was applied to the GB segregation of P in bcc-Fe polycrystals, and it was shown that the amount of GB segregation corresponding to the measurement region obtained by the prediction reproduced the experimental results well.\(^{29}\)

However, it is unclear whether the prediction method described above is valid for solute elements other than P. For example, many alloying elements are transition metal alloying elements, and it is necessary to investigate whether the experimental results can be well reproduced for these elements. The bonding between Fe and the transition metal solute elements in bcc-Fe is primarily metallic bonding between d-orbital electrons.\(^{21}\) Conversely, the bond with P has been shown to be a covalent-like bond.\(^{22}\) Because both bonds can be well described by interatomic potentials, it is unlikely that the predictability for transition metal solutes is reduced compared with the case of P in terms of bonding. However, transition metal solute elements such as Cr and Mn may have spins opposite to those of Fe in bcc-Fe.\(^{11,21}\) Thus, the magnetic properties of transition-metal solutes such as Cr and Mn are complicated, and it is unclear whether predictions based on the interatomic potential, which approximates quantum mechanical effects, can reproduce the experimental results well for these elements. In this study, we applied the prediction of GB segregation using the nano-polycrystalline GB model to transition metal solute elements to verify its validity. Specifically, we applied the prediction method to GB segregation of Mn and Cr in bcc-Fe, where accurate interatomic potentials are available and comparable experimental results exist. The paper is organized as follows: Section 2 describes the prediction of GB segregation using the nanoprecipitate GB model and the details of the calculation conditions. In Section 3, the obtained calculation results are compared with the experimental results, and the validity of the prediction method is discussed. Furthermore, the difference in the GB segregation behavior of Cr and Mn is discussed based on the calculation results. Finally, Section 4 presents the conclusions.

2. GB Segregation Prediction Using a Nano-Polycrystalline GB Model

In this section, we first describe how the amount of GB segregation and the segregation energy for polycrystals, which are the targets of prediction, are measured and evaluated. Then, the method for prediction of GB segregation using the nano-polycrystalline GB model is explained. Finally, the details of the calculation conditions are explained. For a more detailed discussion of the construction and validity of the prediction method, please refer to our previous report.\(^{29}\)

2.1 Method for prediction of segregation amount and segregation energy in polycrystalline GBs using a nano-polycrystalline GB model

Experimentally, the amount of GB segregation in a polycrystal is calculated as the average of the segregation amounts at several dozen different GBs, and the segregation energy in the polycrystal is determined from the amount of GB segregation.\(^{32}\) When measuring the amount of segregation at each GB, the distance from the GB center to be measured depends on the analysis method. Because the amount of segregation varies with the distance from the GB center,\(^{33}\) the amount of segregation may vary depending on the analysis method. Considering the calculation method for the amount of GB segregation of polycrystals in the experiments described above, in the present prediction method, a GB model simulating the polycrystals is constructed, and the amount of segregation is calculated according to the distance from each GB. The amount of segregation in the polycrystal is calculated by averaging them for the entire polycrystal. This makes it possible to calculate the amount of segregation and segregation energy corresponding to the measurement area and to calculate values that can be directly compared with the experimental values.

In this prediction method, focusing on the fact that the atomic structure of GBs is almost independent of grain size, GBs of polycrystals with grain sizes on the order of micrometers are modeled as GBs of nano-polycrystals, for which structural relaxation calculations by molecular dynamics calculations are possible. The initial atomic structure of a nano-polycrystal with random crystal orientation was created using the Voronoi tessellation,\(^{34,35}\) and the obtained initial structure was relaxed by molecular dynamics to obtain a nano-polycrystalline GB model. It has been shown that the atomic structure of the nanoprecipitate GB obtained in this manner is almost independent of the grain size.\(^{31}\) Therefore, if a sufficiently large number of grains are included, this GB model is expected to reproduce the GBs of polycrystals with grain sizes greater than micrometers. The segregation energy of a solute element was comprehensively calculated for all the atomic sites constituting the GB model. The GB segregation energy was calculated using a highly accurate interatomic potential constructed based on first-principles calculations and experimental results. Using the obtained GB segregation energy for each site, the segregation amount \(c_{gb}(D)\) in the region at a distance \(D\) from the GB center for each GB is calculated using the following equation:

\[
c_{gb}(D) = \frac{1}{NB} \sum_{i} \frac{c_{bulk} \exp \left(\frac{E_i^{seg}}{k_BT}\right)}{1 - c_{bulk} \exp \left(\frac{E_i^{seg}}{k_BT}\right)} \quad (D-(1/2dD) < D < D+(1/2dD))\]
\]

where \(E_i^{seg}\) is the GB segregation energy, defined such that as the positive value increases, so does the tendency for segregation. Additionally, \(k_B\), \(T\), and \(c_{bulk}\) are the Boltzmann constant, temperature, and bulk composition of the solute element, respectively. \(\Sigma\) implies the addition of sites \(i\) satisfying the inequality \(D - 1/2dD < D < D + 1/2dD\), where \(d\) is the GB width.
is the mesh size of $D_i$ and $N^D_i$ is the number of sites $i$ satisfying the inequality $D - 1/2D < D_i < D + 1/2D$. By substituting the segregation energy and distance from the GB of each site into this equation, the amount of segregation for each GB can be calculated corresponding to the distance from the GB, taking into account the atomic site dependence of the segregation energy. The segregation energy is then calculated from the average amount of segregation at the polycrystalline GBs. This segregation energy is directly comparable to the experimental segregation energy of the polycrystals. Equation (1) is an extension of the Langmuir–Mclean equation\(^{17}\) and the Coghlan–White equation, \(^{36}\) which are often used to describe GB segregation. Similar to the Coghlan–White equation, eq. (1) does not consider the interactions between solute elements. Therefore, the accuracy of the approximation is improved when the interactions between the solute elements are minimal or in the dilute limit.

2.2 Calculation details

The calculation conditions described below are the same as those used in the analysis of P segregation in bcc-Fe polycrystals, and they are known to predict well at least the amount of P GB segregation.\(^{39}\)

The Voronoi tessellation\(^{34,35}\) was used to create the initial structure of the nano-polycrystalline GB model. First, we randomly place a number of points that form the source of the grains in the calculation cell. Thereafter, considering the periodic boundary condition, the adjacent points are divided by perpendicular bisecting planes, and each point is divided into a region (corresponding to a grain), including one point. The initial structure is created by randomly assigning a crystal orientation to each region and placing atoms with the corresponding crystal orientation in each region. This procedure was carried out using AtomsK software.\(^{37}\) The initial structure of a nano-polycrystalline GB model consisting of 125 grains with dimensions of $28.6 \times 28.6 \times 28.6 \text{nm}^3$ was created.

To relax the GB structure, the model was annealed at 300 K for 300 ps and then cooled to 0 K using molecular dynamics, following the method of Swygenhoven et al.\(^{31}\) Subsequently, the atomic configuration was relaxed using the conjugate gradient method. These calculations were performed using the LAMMPS software\(^{38}\) and the second nearest-neighbor modified embedded atom method (2NN MEAM) interatomic potentials for Fe proposed by B.-J. Lee et al.\(^{39}\) If the molecular dynamics relaxation is carried out with the initial structure, some pairs of atoms are very close to each other and the calculation diverges. Therefore, we searched for atoms that were less than 2 Å apart from one another in the initial structure, and one of the pair was randomly deleted.

The obtained nanopoly-crystalline GB model is shown in Fig. 1. The white circles represent atomic sites whose atomic structures are not bcc, as determined by common neighbor analysis (CNA).\(^{40}\) The average grain size was 5.0 nm, and the number of GBs was 964. Figure 2 shows the histogram of the atomic sites near the GBs with the corresponding misorientation angle. The histogram is close to the Mackenzie distribution (dashed line in Fig. 2), indicating that a nano-polycrystalline GB model with near-random orientation was obtained.

The segregation energies of Cr and Mn at all constituent atomic sites of the nano-polycrystalline GB model were calculated. To calculate the segregation energies, we used the 2NN MEAM interatomic potentials for Fe–Cr\(^{41}\) and Fe–Mn,\(^{42}\) which were constructed based on the interatomic potential for Fe proposed by B.-J. Lee et al. These potentials reproduce not only the physical properties and phase stability of Cr and Mn, but also the experimental values of the mixing enthalpy of the binary system with Fe. The segregation energy was calculated from the difference between the change in energy when Fe was replaced with the solute atom at the site of interest and the change in energy when Fe was replaced with the solute atom at a site sufficiently far from the GB (a distance greater than 15 Å from the GB center). In these calculations, the atomic configuration was relaxed using the conjugate gradient method.

By substituting the obtained segregation energy into eq. (1), we obtained the GB segregation amount corresponding to the distance from the GB center for each GB. The GB center was set to the perpendicular bisecting plane used in
the Voronoi tessellation. The distance of each site from the GB center was defined as the shortest distance from each GB center. \( d_D \) is the mesh size of \( D \), which is set to 0.1 Å in this study. The experiments used for comparison in this study are the segregation energies of Cr and Mn in polycrystalline low-carbon steels measured by Guttmann et al., who investigated in detail the amount of segregation of Mn and Cr at GBs in low-carbon steels containing P. They evaluated the interaction energies of P–Mn and P–Cr at GBs and calculated the segregation energies of Mn and Cr in the absence of P based on the interaction energies. The segregation energies in the absence of P were used for comparison with the calculated results. In this experiment, the amount of segregation at each GB was calculated based on the Auger spectra obtained from the fractured surface of the GB using Auger electron spectroscopy. At this time, the effect of the inelastic mean free path of the Auger electrons is considered, and the amount of segregation is calculated by assuming that all the excess solute elements segregated at the GB exist within one atomic diameter from the center of the GB and correcting the measured peak intensity. The segregation energy is then calculated from the obtained segregation amount. Considering the method of evaluating the segregation energy in this experiment, we calculated the average amount of segregation for the entire polycrystal by calculating the segregation amount for each GB within one atomic diameter from the center of the GB and averaging them. The segregation energy was then calculated from the average segregation amount and compared with the segregation energy of the polycrystal obtained in the experiment. The validity of the assumption that the segregated solute elements are located within one atomic diameter from the center of the GB in the experiment and the effect of this assumption on the amount of segregation will be discussed in the next section based on the calculation results.

3. Results and Discussion

Figure 3 shows the segregation energies of Cr and Mn for each atomic site as a color map. In this figure, a white color indicates that the segregation energy is zero, and a darker red color implies a higher segregation tendency at the corresponding site. Figure 4 shows the dependence of the segregation energy of Cr and Mn on the distance from the GB center. For both Cr and Mn, the sites close to the GB show large positive or negative segregation energies, and the segregation energy approaches zero as the distance from the GB increases. Near the GB center, Mn shows positive segregation energy at most of the sites, while Cr shows negative segregation energy at many sites.

Figure 5 shows the Cr and Mn concentrations for the distance from the GB center obtained by substituting the segregation energies at each site into eq. (1). Three different GBs are shown as examples in this figure. Here, we calculated the equilibrium segregation at 823 K for the bulk center.
composition of each solute element. \( c_{\text{bulk}} \) was set to 1.0 at% to match the conditions for measuring the segregation energy in the experiments used for comparison. The amount of segregation increases monotonically toward the GB center for Mn, and the amount of segregation exceeds 3.0 at% at the GB center for three GBs. Conversely, for Cr, the change from the bulk composition is small even near the GB center, and the amount of segregation is only slightly greater than 1.0 at% at the GB center for three GBs.

Figure 6 shows the histograms of the amount of segregation within one atomic diameter (2.5 Å) from the GB center. For both Cr and Mn, the histograms in Fig. 6 are approximately similar to a normal distribution. These results were calculated from the segregation amount corresponding to the distance from the GB center, as shown in Fig. 5 for all GBs. These results are similar to the behavior of P segregation in the nanopolicyrstalline GB model,\(^{29}\) which suggests that the nano-polycrystalline GB model used in this study contained a sufficient number of GBs to obtain the average amount of GB segregation of Cr and Mn in polycrystals. The average amounts of segregation in the polycrystal obtained as the average of the segregation amount at each GB were 1.11 at% and 3.11 at% for Cr and Mn, respectively.

| Element | This work | Exp. \(^{43}\) |
|---------|-----------|---------------|
| Cr      | 0.01      | 0.00          |
| Mn      | 0.08      | 0.08          |

Table 1 shows the segregation energies calculated from the average amount of segregation in polycrystals and the segregation energies in polycrystals obtained from the experiments of Guttmann \( et al. \) for Cr and Mn. The obtained segregation energies for Cr and Mn are 0.01 eV and 0.08 eV, respectively, which are in good agreement with the experimental results. However, as mentioned in the previous section, the segregation energy in this experiment was calculated by assuming that all the excess solute elements segregated at the GB were within one atomic diameter from
the center of the GB, and by correcting the measured peak intensity. However, based on the calculation results shown in Fig. 5, it is possible that excess solute elements exist in the region beyond one atomic diameter from the center of the GB in the experiment, especially for Mn. Therefore, the experimental values may include these effects on the segregation amount and segregation energy. To evaluate this effect, we calculated the amount of segregation within one atomic diameter from the center of each GB, assuming that all the excess solute elements resulting from segregation calculated for each GB were all localized within one atomic diameter from the center of the GB. Then, the average segregation amount was calculated by averaging them, and the segregation energy was calculated from the average segregation amount. Using this calculation method, the calculated segregation amount naturally increased, but the average segregation amount for Mn was 3.94 at%, and the increase was small. The average segregation amount for Cr was 1.11 at%, which was almost unchanged. The segregation energies were calculated to be 0.01 eV and 0.10 eV for Cr and Mn, respectively. Thus, if the excess solute elements resulting from segregation are all localized within one atomic diameter, the calculation for Mn is slightly modified and deviates from the experimental results. However, the effect was small, and the calculated and experimental results were in good agreement for both calculation methods. These results suggest that the experimental values can be suitably reproduced by the present method of predicting the average amount of segregation using the nano-polycrystalline GB model simulating polycrystals and selecting the evaluation region corresponding to the measurement method for transition metal elements such as Cr and Mn. In the following paragraphs, we discuss the reasons for the good agreement with the experimental results obtained using this prediction method.

In the prediction of GB segregation of P using the nanopolycrystalline GB model, it was found that the histogram of the segregation amount of each GB followed a normal distribution in the nano-polycrystalline GB model created under the same conditions as in the present study, and the GB model contained a sufficient number of GBs to obtain the average value of the segregation amount of polycrystalline GBs. As a result, it was found that the same amount of segregation can be obtained under the same calculation conditions with little dependence on the random seed used to create the initial structure of the nanopolycrystalline GB model. Therefore, we investigated whether the same can be said for the GB segregation of Cr and Mn as in the case of the GB segregation of P.

Two new nano-polycrystalline GB models were constructed by changing the random seed in the Voronoi tessellation to create the initial structure of the nanopolycrystalline GB model, and the amount of segregation was calculated using each of the two models. Figure 7 shows the histograms for the amount of segregation within one atomic diameter from the center of each GB at equilibrium at 823 K when the bulk concentration of the solute element is 1.0 at%. Cases 2 and 3 show the results of the calculations for constructing the nanocrystalline GB model. (a) and (c) show the histograms of the GB concentration of Cr. (b) and (d) show the histograms of the GB concentration of Mn. The bulk composition of the solute elements is 1 at%, and the temperature is 823 K.

![Fig. 7 Dependence of histogram of grain boundary (GB) concentration of Cr and Mn in the thermal equilibrium state on a random seed for constructing the nanocrystalline GB model. (a) and (c) show the histograms of the GB concentration of Cr. (b) and (d) show the histograms of the GB concentration of Mn. The bulk composition of the solute elements is 1 at%, and the temperature is 823 K.](image-url)
using additional nano-polycrystalline GB models. For both Cr and Mn, the calculated results were similar to the histograms shown in Fig. 6. The average amount of segregation calculated from these results was 1.10 at% and 1.11 at% for Cr, which is very close to the value reported above (1.11 at%). The average segregation amounts for Mn were also 3.10 at% and 3.12 at%, which are very close to the value reported above (3.11 at%). These results indicate that the average amount of segregation and the segregation energy calculated from it are almost independent of the random seed. Thus, for Mn and Cr, the amount of segregation at each GB in the nano-polycrystalline GB model is different for each GB. However, the nano-polycrystalline GB model created under the conditions used in this study includes a sufficient number of GBs to obtain the average amount of segregation in polycrystals, and the amount of segregation and the segregation energy obtained using this model were found to be reasonable as an average value for polycrystals.

As described above, analysis using the nano-polycrystalline GB model reproduces the segregation behavior of Cr and Mn in polycrystals well. In this section, we discuss the differences in the segregation behavior of Cr and Mn from the calculated results. Figure 8(a) and (b) show the histograms of the segregation energy for the sites located within one atomic diameter from the center of the GB. Mn showed a positive segregation energy at most of the sites. Conversely, the histogram of the segregation energy of Cr shifts in the negative direction compared with that of Mn, and there are many sites showing negative segregation energy. As a result, the amount of segregation near the GB is larger for Mn than it...

Fig. 8 Relationship between grain boundary (GB) segregation energy and local atomic environment for Cr and Mn at sites within 2.5 Å of the GB center. (a) and (b) show the histograms of the segregation energy for Cr and Mn, respectively. (c) and (d) show the histograms of the Voronoi volume for each site. (e) and (f) represent the histograms of the coordination number for each site. In (c) and (e), the histograms for the sites with Cr segregation energy shown in blue in (a) are shown in blue. In (d) and (f), the histograms of the sites with Mn segregation energy shown in red in (b) are shown in red.
is for Cr, as shown in Figs. 5 and 6. To investigate the difference in the segregation behavior between Cr and Mn, we investigated the relationship between the segregation energy and the local atomic structure of each site. Regarding the local atomic structure of each site, the Voronoi volume and coordination number of each site, which are the most commonly used indices, were investigated. Figure 8(c) and (d) show the histograms of the Voronoi volume of the sites within one atomic diameter from the center of the GB in gray. Figure 8(e) and (f) show the histograms of the coordination number of sites within one atomic diameter from the center of the GB in gray. The coordination number was evaluated as the number of faces of the Voronoi polyhedron used in the calculation of the Voronoi volume. In this case, the coordination number of the bcc-Fe perfect crystal is 14, which is the sum of the eight nearest-neighbor atoms and the six second-nearest-neighbor atoms. The gray histograms shown in Fig. 8(c) and (d) indicate that the Voronoi volume of most of the near-GB sites is larger than that of the bulk site (11.6 Å²). The gray histograms in Figs. 8(e) and 8(f) show that the coordination numbers of the near-GB sites are distributed in the range of 12 to 17, compared with 14 in the bulk, and the average value is smaller than that in the bulk. Thus, the local atomic structure, as expressed by the Voronoi volume and coordination number, changes significantly in the near-GB sites, causing a positive segregation energy of Mn near the GB center. To investigate the relationship between the segregation energy of Mn and the local atomic environment in more detail, the histograms of the Voronoi volume and the coordination number of the sites with particularly high segregation energy are shown in red in Fig. 8(d) and Fig. 8(f), respectively. These results show that Mn has particularly high segregation energy at sites with small coordination numbers and small Voronoi volumes. Conversely, the fact that Cr shows negative segregation energy at many sites near the GB center indicates that, unlike Mn, the changes in the local atomic structure, such as coordination number and Voronoi volume relative to the bulk, do not necessarily lead to positive segregation energy near the GB center. To investigate the reason for this, the histograms of Voronoi volume and coordination number for the sites where Cr shows particularly high segregation energy are shown in blue in Fig. 8(e) and Fig. 8(e), respectively. These results show that Cr shows high segregation energy at sites where the coordination number is large and the Voronoi volume is large. Conversely, negative segregation energy is often observed at sites with small Voronoi volumes or coordination numbers, even near the GB. These behaviors of Cr and Mn are consistent with the results of first-principles calculations of the segregation energy of Mn and Cr at symmetric tilt GBs. In other words, the segregation energy of Mn at the GBs was positively larger than that of Cr. In addition, Cr tends to show positive segregation energy at sites where the Voronoi volume is larger than that of the bulk, whereas Mn shows a large positive segregation energy not only at sites where the Voronoi volume is larger than that of the bulk, but also at sites where the Voronoi volume is smaller than that of the bulk. As described above, changes in the local atomic structure, such as the coordination number and Voronoi volume, occur near the GB, which produces positive energies in most cases for Mn. For Cr, these changes do not necessarily lead to stabilization at the GB, and segregation tends to occur at sites with large coordination numbers and large Voronoi volumes. As a result, the amount of segregation near the GB center is larger for Mn than it is for Cr, as shown in Fig. 5. Thus, the prediction of GB segregation using the nanopolycrystalline GB model is also effective for a detailed analysis of the GB segregation behavior of solute elements in polycrystals.

As described above, for the GB segregation of Cr, Mn, and P in bcc-Fe, the prediction of GB segregation using the nanopolycrystalline GB model was found to be effective by comparison with experimental results. For other solute elements in bcc-Fe, the present method cannot be applied and validated directly because there are no experimental results or high-precision interatomic potentials. Therefore, in the following, we will discuss the applicability of the method to other elements from the viewpoint of the results for Mn, Cr, and P calculated so far and the calculation method used in the prediction of GB segregation using the nanopolycrystalline GB model.

Equation (1) for calculating the amount of segregation in this prediction method is an extension of the Langmuir-McLean equation (17) and the Coghlan-White equation, which are often used to describe GB segregation. Therefore, such equations do not consider the interaction between the same solute elements. For example, in the case of a solute element with a particularly large atomic size compared with Fe, there is a possibility of repulsive interactions between the same solute elements. In this case, not considering the interaction may lead to an overestimation of the segregation amount. However, the experimental results of GB segregation at polycrystalline GBs reported so far are well described by the Langmuir-McLean equation, which does not consider the interaction between the same solute elements. This indicates that the interaction between the same solute elements rarely affects the amount of GB segregation and the segregation energy obtained from it. Even if the interaction between the same solute elements is large, the effect can be described as a function of the segregation amount. Therefore, eq. (1) is a good approximation for small additions or high temperatures with a small segregation amount.

In this prediction method, the interatomic potential is used to calculate the segregation energy. The results obtained using the interatomic potentials of Mn, Cr, and P, which have been used in the past, reproduced the experimental results well, suggesting that the experimental results can be reproduced well for other solute elements using appropriate interatomic potentials. However, the number of binary systems for which high-precision potentials exist is currently limited. Recently, a number of methods have been proposed for constructing high-precision interatomic potentials using machine learning. If the development of high-precision interatomic potentials using these methods is promoted in the future, it is expected that the applications of our method will expand.

4. Conclusion

The prediction of GB segregation using the nano-
polycrystalline GB model was applied to the GB segregation of Mn and Cr in bcc-Fe polycrystals, where there is a high-accuracy interatomic potential and experimental results exist, and its validity was verified. It was found that the present prediction method can accurately predict the GB segregation energy of Mn and Cr in bcc-Fe polycrystals. These results suggest that this prediction method is also effective for predicting the GB segregation of other solute elements.

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