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Theoretical Prediction of Grain Boundary Segregation Using Nano-Polycrystalline Grain Boundary Model*1

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The importance of controlling grain boundary (GB) segregation is increasing, especially with the strengthening of steel nowadays. In this study, a theoretical prediction method for the amount of GB segregation for a solute element in polycrystals is established. This prediction method entails the development of a nano-polycrystalline GB model for simulating GBs in polycrystals, and the segregation energy of a solute element is comprehensively calculated for all atomic sites constituting the GB model by using an interatomic potential. From the obtained segregation energies, the segregation amount of the solute element at each atomic site is determined. Subsequently, each atomic site is classified based on its distance from the GB center and averaged to determine the segregation profile of the solute element for that distance from the GB center. By applying this method to the GB segregation of P in bcc-Fe and comparing the results with experimental findings, it is determined that this prediction method can deliver excellent prediction accuracies. [doi:10.2320/matertrans.MT-M2020352]

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1. Introduction

The grain boundary (GB) segregation of alloying and impurity elements significantly affects the properties of polycrystalline metals. In particular, impurity elements, such as P and S, or alloying elements, including Mn, induce GB embrittlement, thereby causing a significant reduction in the toughness of steel.[1–6] 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.[7,8] In recent years, the strengthening of steels has been accelerated to reduce their environmental burdens and improve safety. As the strength of a material increases, so does its susceptibility to GB embrittlement.[9] Therefore, a material design that suppresses GB embrittlement is required for the development of advanced steels.

One possible material design approach to suppress GB embrittlement is to add alloying elements that segregate to GBs and strengthen them. The effect of GB segregation of an alloying element on the DBTT changes in proportion to the amount of segregation of the alloying element in polycrystals.[1] 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 exists only for some elements. Therefore, in this study, we develop a method for predicting the amount of GB segregation for a solute element in polycrystals.

To predict GB segregation, the segregation energy is often determined using first-principles calculations.[10] Notably, GB segregation energy is evaluated as the difference in energy between the system wherein the solute element is present in the bulk and the system in which the solute element is present at the GB. By substituting the obtained segregation energy into the Langmuir–Mclean equation,[11] to be described later, the amount of GB segregation for the solute element in the thermal equilibrium state can be calculated. In bcc-Fe, the segregation energy calculated with the first-principles calculation using the Σ3(111) symmetric tilt GB reproduces the magnitude relationship of the segregation energy of solute elements, such as B, C, P, and S, in polycrystals. 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 GB segregation mechanisms and embrittlement.[12] However, it has been pointed out that the segregation energy obtained by the calculation for the specific GB and the amount of segregation calculated from it are quantitatively different from the experimental values in polycrystalline GBs.[13] A method that can be used to predict GB segregation in polycrystals with sufficient accuracy has not yet been established.

There are two main reasons for the deviation from the experimental values: (1) the GB model used to calculate the segregation energy cannot simulate the GBs in polycrystals, and (2) the Langmuir–Mclean equation is too simplistic to calculate the amount of GB segregation from the calculated segregation energy. The segregation energy calculated by the first-principles calculations depends on the GB character and segregation site.[14,15] However, because of the computational cost, the segregation energy is often evaluated for GBs with low Σ values that can be calculated with a crystal structure having a small number of atoms, such as the Σ3(111) symmetric tilt GB. In addition, the Langmuir–Mclean equation is a formula for calculating the amount of GB segregation based on a single value of segregation energy and

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cannot consider the dependence of the segregation energy on the GB characteristics and GB sites.

Therefore, in this study, we developed a new prediction method for the amount of GB segregation for a solute element in polycrystals, whereby the GB model used to evaluate the segregation energy and calculation method for the amount of segregation from the determined segregation energy are improved. In our prediction method, we use a GB model of randomly oriented nano-polycrystalline grains generated by the Voronoi tessellation[16,17] to simulate a polycrystalline GB. In other words, because it is computationally infeasible to deal directly with a grain size of the order of micrometers, we simulate this with a computable atomic model of a nano-polycrystal. It has been established that the GB structure of nano-polycrystals created by the Voronoi tessellation is similar to that of common polycrystals with grain sizes in the order of micrometers.[18] It is expected that this GB model can be used to fully consider the effects of GB character and GB sites. Although the developed prediction method is applicable to GB segregation in various binary alloys, we apply the prediction method to P segregation in bcc-Fe polycrystals, for which experimental data exist[1] to confirm the validity of the technique.

2. Development of a Prediction Method for the Amount of GB Segregation in Polycrystals

In this section, how the amount of GB segregation is measured and evaluated in polycrystalline materials is first described, taking the example of P segregation in bcc-Fe polycrystals, which is used to verify the prediction accuracy. Considering this, we discuss: (1) the GB model for calculating the segregation energy and (2) the method for evaluating the amount of segregation from the calculated segregation energy to improve the prediction accuracy.

2.1 Factors to be considered in predicting the amount of GB segregation in polycrystals

In the experiment of the GB segregation of P in bcc-Fe polycrystals, the sample was cooled to liquid nitrogen temperature and the GB fracture surface was exposed under vacuum conditions in an Auger electron spectrometer. The obtained GB fracture surface was analyzed by Auger electron spectroscopy. Because the amount of GB segregation generally varies from one GB to another, the analysis is carried out for approximately several dozen GBs, and the amount of segregation in the polycrystalline GB is calculated by averaging them. Thus, the amount of GB segregation in polycrystals is calculated as the average value for GBs with different amounts of segregation. Therefore, it is necessary to prepare a GB model that simulates polycrystals for prediction, calculate the segregation amount for each GB, and average them.

In the measurement of segregation for each GB, the amount of segregation in the monoatomic layer (2.5 Å) region from the GB center (fractured GB surface) is obtained by considering the mixed signals from the bulk and correcting them.[19] In general, the amount of GB segregation decreases with increasing distance from the GB center.[20] Therefore, to predict or compare with the experimental data, it is necessary to calculate the amount of GB segregation in the region corresponding to the analysis method, considering the change in the amount of GB segregation according to the distance from the GB center. Although we have taken the Auger electron spectroscopy experiments as an example, the above-mentioned factors must also be considered when predicting the amount of GB segregation in polycrystals measured by transmission electron microscopy[21] and atom probe tomography.[22]

Considering the calculation method for the amount of GB segregation of polycrystals in the experiments as described above, in the present prediction method, a GB model simulating the polycrystals was constructed and the amount of segregation was calculated according to the distance from each GB. The amount of segregation in the polycrystal was calculated by averaging them for the whole polycrystal. This enables the calculation of the amount of segregation corresponding to the analysis area of various analysis methods. In the evaluation of GB segregation by Auger electron spectroscopy, GBs appearing as a GB fracture surface may be limited to those with a large amount of P and brittle, while GBs with a small amount of P may not be considered in the calculation of the average value. This leads to an overestimation of the average amount of segregation in polycrystals. This effect will be discussed later, based on our calculation results.

2.2 GB model to simulate polycrystals

As mentioned above, it is necessary to construct a GB model that simulates polycrystals. In this study, we consider a nano-polycrystalline GB model composed of grains with random orientations created by the Voronoi tessellation.[16,17] The Voronoi tessellation divides a computational cell spatially and randomly assigns a crystal orientation to each region. Thereafter, the initial structure is created by arranging atoms to fill each region. The obtained initial structure is relaxed by molecular dynamics to obtain a polycrystal with a stable GB structure. The crystal grain size is generally in the order of nanometers due to the need for structural relaxation by molecular dynamics. The detailed analysis of the GB structure suggests that the GBs of the nano-polycrystals obtained through this method have a GB structure similar to that of common polycrystals with grain sizes greater than micrometers.[18] In addition, Holm *et al.* analyzed the grain growth of nano-polycrystals prepared by the Voronoi tessellation using molecular dynamics and showed that nanocrystalline grain growth followed the same $t^{1/2}$ kinetics (where t is time), which was observed for polycrystals with grain sizes greater than micrometers.[23] Because the grain growth behavior is known to be strongly influenced by the nature of GBs,[24] the similarity in the behaviors of the nano-polycrystals made by Voronoi partitioning and that of general polycrystals suggests that the GBs of nano-polycrystals made by the Voronoi tessellation are similar to those of general polycrystals with grain sizes greater than micrometers.

2.3 Calculation method for the amount of GB segregation in polycrystals

As described in the previous section, we study the prediction of the amount of segregation using the nano-

polycrystalline GB model. Although the segregation energy at each segregation site can be calculated through first-principles calculations, it is impractical to adopt first-principles calculations for prediction using the nano-polycrystalline GB model because of the computational cost.

In the present prediction method, the interatomic potential is used to calculate the segregation energy for each site. In the Fe–P binary system, an interatomic potential[25] has been developed to reproduce the results of first-principles calculations, and the analysis of GB segregation using this potential has been reported.[26] Because the computational cost is extremely low when using the interatomic potential relative to the first-principles calculations, it is easy to calculate the segregation energy of the GB model with a large number of atoms many times. Therefore, the segregation energies of all the atomic sites in the nano-polycrystalline model were comprehensively calculated using the interatomic potential, and the average amount of segregation was determined considering the site dependence of the segregation energy and the distance from the GB.

The Langmuir–Mclean equation[11] is often used to calculate the amount of segregation from the segregation energy as described above. The amount of GB segregation of a solute element c_{gb} is given by the following equation:

$$c_{gb} = \frac{c_{bulk}\exp\left(\frac{E_{seg}}{k_B T}\right)}{1 - c_{bulk} + c_{bulk}\exp\left(\frac{E_{seg}}{k_B T}\right)} \quad (1)$$

where E_{seg} is the GB segregation energy, defined such that the higher the positive value, the higher the tendency for segregation. Additionally, k_B, T, and c_{bulk} are the Boltzmann constant, temperature, and bulk composition of the solute element, respectively. Therefore, this equation cannot consider the dependence of segregation energy on the atomic site. Conversely, Coghlan and White proposed an equation that could consider the dependence of segregation energy on atomic sites.[27] In this equation, the amount segregation for the solute element at the GB site i c^i_{gb} (or probability of existence) is expressed by the following equation:

$$c^i_{gb} = \frac{c_{bulk}\exp\left(\frac{E^i_{seg}}{k_B T}\right)}{1 - c_{bulk} + c_{bulk}\exp\left(\frac{E^i_{seg}}{k_B T}\right)} \quad (2)$$

where E^i_{seg} is the segregation energy for site i. The amount of segregation for the solute element at the GB is expressed by the following equation:

$$c_{gb} = \sum_i (F_i c^i_{gb}) \quad (3)$$

where F_i is the ratio of the site with a segregation energy of E^i_{seg} to the total GB sites. In this equation, it is necessary to determine which atomic sites are considered to be GBs in the GB model. For example, decisions based on the crystal structure nature of each atomic site[28–30] using the common neighbor analysis (CNA)[31] or based on the value of the segregation energy of each atomic site are used.[32] Nonetheless, to predict the amount of segregation obtained experimentally, it is necessary to calculate the amount of segregation corresponding to the distance from the GB center, as described above. In this study, eq. (3) is modified and the amount of segregation $c_{gb}(D)$ at the distance D from the GB center is calculated by the following equation:

$$c_{gb}(D) = \frac{1}{N^D} \sum_{\substack{i \\ (D-(1/2)dD<D_i \\ <D+(1/2)dD)}} \frac{c_{bulk}\exp\left(\frac{E^i_{seg}}{k_B T}\right)}{1 - c_{bulk} + c_{bulk}\exp\left(\frac{E^i_{seg}}{k_B T}\right)} \quad (4)$$

where D_i is the distance from the GB center of site i; Σ implies the addition of sites i satisfying the inequality $D - (1/2)dD < D_i < D + (1/2)dD$; dD is the mesh size of D, which is set to 0.1 Å in this study; and N^D is the number of sites i satisfying the inequality $D - (1/2)dD < D_i < D + (1/2)dD$. The average amount of segregation in polycrystals considering the site dependence of the segregation energy can be calculated by substituting the segregation energy and the distance from GBs into eq. (4). Similar to the Coghlan–White equation, eq. (4) does not consider the interactions between solute elements. Therefore, the accuracy of the approximation is improved when the interactions between solute elements are minimal or in the dilute limit.

3. Calculation Details

3.1 How to create a nano-polycrystalline GB model

In this section, we describe the construction of a nano-polycrystalline GB model using the Voronoi tessellation. Firstly, we randomly place a number of points that form the source of the grains in a 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 laying down atoms with the corresponding crystal orientation to each region. This procedure was carried out using the Atomsk software.[33] The initial structure of a nano-polycrystalline GB model consisting of 125 grains with dimensions of $28.6 \times 28.6 \times 28.6\,\mathrm{nm}^3$ was created. To relax the GB structure, the model was annealed at 300 K for 300 ps and then cooled down to 0 K using molecular dynamics following the method of Swygenhoven *et al.*[18] Subsequently, the atomic configuration was relaxed using the conjugate gradient method. These calculations were performed using the LAMMPS software.[34] 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 them was randomly deleted.

The obtained nano-polycrystalline GB model is illustrated in Fig. 1. The white circles represent atomic sites whose atomic structures are not bcc determined by the CNA. The average grain size and average GB energy were 5.3 nm and $1.53\,\mathrm{J/m}^2$, respectively. Figure 2 shows the histogram of atomic sites near 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 is obtained.

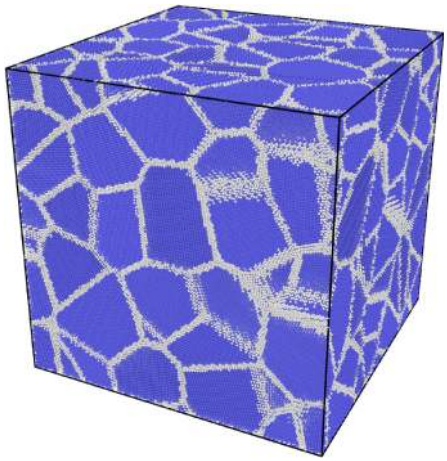

Fig. 1 Nano-polycrystalline grain boundary model. The white circles represent atomic sites whose atomic structures are not bcc. Cell dimensions are 28.6 nm × 28.6 nm × 28.6 nm.

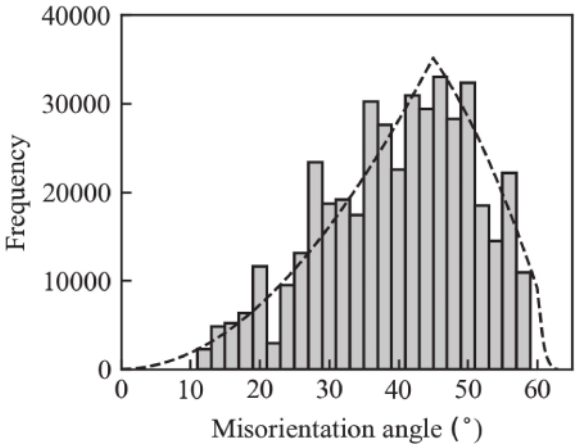

Fig. 2 Histogram of atomic sites near grain boundaries with the corresponding misorientation angle. The dashed line represents the distribution for a completely random case.

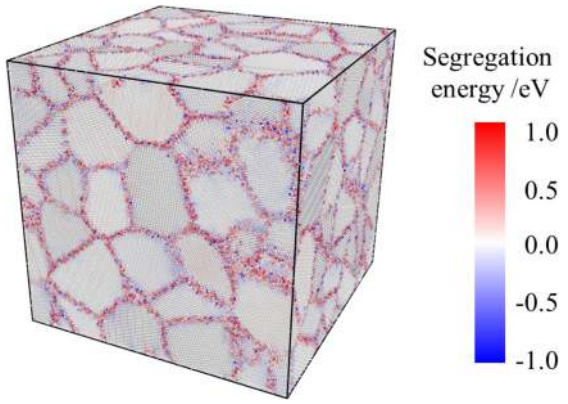

Fig. 3 Color map of segregation energy at each atomic site. Darker red represents a higher segregation energy at the corresponding site.

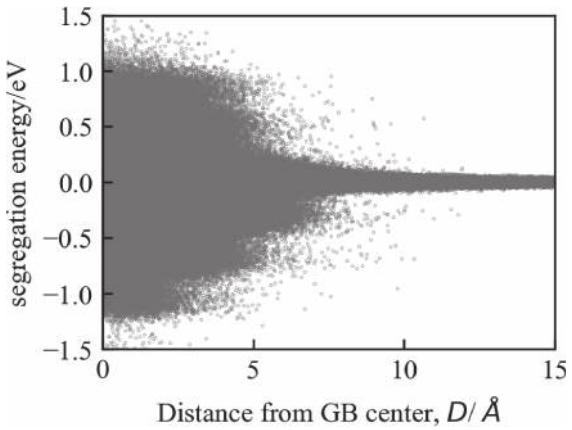

Fig. 4 Relationship between segregation energy and distance from the grain boundary (GB) center for each atomic site.

3.2 Method for calculating the segregation energy and amount of segregation

The segregation energies of P at all the constituent atomic sites of the nano-polycrystalline GB model were calculated using the embedded atom method (EAM) potential of the Fe–P system.[25] The segregation energy of P was calculated from the difference between the change in energy when Fe was replaced with P at the site of interest and the change in energy when Fe is replaced with P at a site sufficiently far from the GB (at a distance of more than 10 Å from the GB center). Atomic position relaxation was also performed in these calculations. Tschopp *et al.* used this potential to calculate the segregation energy of P at ⟨110⟩ symmetric tilt GBs comprehensively and showed that the dependence of the segregation energy of P on the GB character and atomic site could be described by this potential.[26] The results of this calculation satisfactorily reproduce the segregation energy of the Σ3(111) symmetric tilt GB calculated using first-principles calculations.[14]

By substituting the obtained segregation energy into eq. (4), we obtained the GB segregation amount corresponding to the distance from the GB center. 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.

4. Results and Discussions

Figure 3 shows the segregation energies of 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 to the corresponding site. Figure 4 shows the dependence of the segregation energy on the distance from the GB center. 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.

Figure 5 shows the P concentrations for the distance from the GB center obtained by substituting the segregation energies at each site into eq. (4). Here, we calculated the equilibrium segregation at 1073 K for Fe–0.05 wt.%P, Fe–0.1 wt.%P, Fe–0.2 wt.%P, and Fe–0.3 wt.%P, for which experimental data were available. The grain size of each alloy used in the experiment was greater than several tens of micrometers, and the effect of the GB segregation of P on the bulk composition of P was negligible. Therefore, the alloy composition was used as the bulk composition of the solute element c_{bulk} in eq. (4). It should be noted that the results

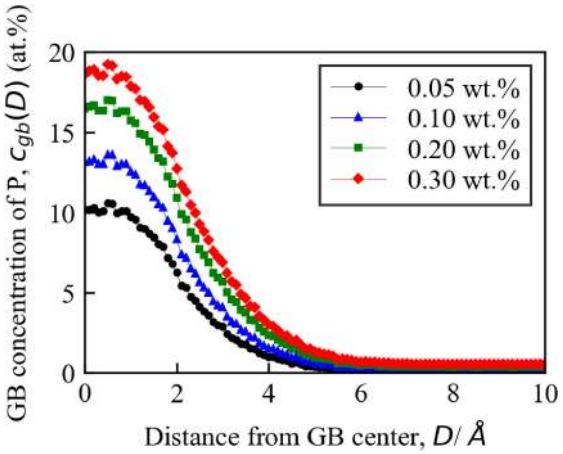

Fig. 5 Dependence of grain boundary (GB) concentration of P on the distance from the GB center in the thermal equilibrium state at 1073 K.

represented in Fig. 5 are the amount of segregation averaged over all GBs. The P concentration increases with decreasing distance from the GB center, which is consistent with the results generally observed in experiments.[20] The segregation area of P is concentrated in a region of approximately 5 Å from the center of the GB, i.e., about a diatomic layer. This result also shows that the amount of segregation is strongly dependent on the distance from the GB center, indicating that the prediction of segregation should consider the measurement area in the experiment.

From the results given in Fig. 5, the average segregation up to the monolayer region (<2.5 Å) was determined for comparison with the results of Auger electron spectroscopy by Kimura.[1] Figure 6 shows the comparison between the calculated and experimental results on the dependence of GB concentration of P on P concentration in the bulk at the thermal equilibrium state at 1073 K. The red line (NP GB, 2.5 Å) represents the calculation result for the single atomic layer region using the nano-polycrystalline GB model. The black line (Σ3 GB, 2.5 Å) denotes the calculation result for the single atomic layer region using the Σ3(111) GB model. The green line (NP GB, 5.0 Å) indicates the calculation result for the double atomic layer region using the nano-polycrystalline GB model. The blue trend represents the experimental result for one atomic layer region measured via Auger electron spectroscopy. For comparison, the black line (Σ3 GB, 2.5 Å) denotes the calculation result for the single atomic layer region using the Σ3(111) GB model, while the green line (NP GB, 5.0 Å) indicates the calculation result for the double atomic layer region using the nano-polycrystalline GB model. The calculation results of the amount of segregation in the monolayer region through the present prediction method duly reproduce the experimental values and the dependence on the amount of P added. Although it can be qualitatively reproduced that P tends to segregate at the GBs in the calculation using the Σ3(111) GB, the segregation amount is considerably larger than the experimental results of polycrystals. In the calculation results for the diatomic region using the present prediction method, the amount of segregation is underestimated. From these results, it was found that the experimental values could be suitably reproduced by the prediction method of the average amount of segregation using the nano-polycrystal GB model simulating polycrystals and selecting the evaluation region corresponding to the measurement method. In the following paragraphs, we discuss the validity of this prediction method.

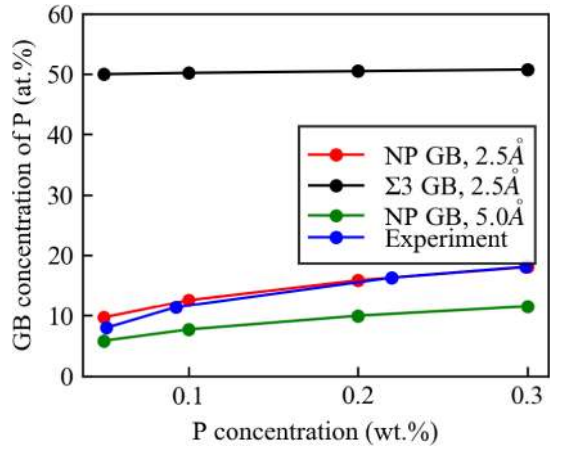

Fig. 6 Comparison between calculated and experimental results on the dependence of grain boundary (GB) concentration of P on P concentration in the bulk in the thermal equilibrium state at 1073 K. The red line (NP GB, 2.5 Å) represents the calculation result for the single atomic layer region using the nano-polycrystalline GB model. The black line (Σ3 GB, 2.5 Å) denotes the calculation result for the single atomic layer region using the Σ3(111) GB model. The green line (NP GB, 5.0 Å) indicates the calculation result for the double atomic layer region using the nano-polycrystalline GB model. The blue trend represents the experimental result for one atomic layer region measured by Auger electron spectroscopy.

As mentioned above, the calculated average amounts of segregation are in good agreement with the experimental values. However, because the amount of segregation generally depends on the GB, it is possible that the average amount of segregation of the present nano-polycrystalline GB model may be close to the experimental value by chance. To investigate this possibility, two new nano-polycrystalline GB models were constructed by changing the random seed in the Voronoi tessellation to create the initial structure of the nano-polycrystalline GB model, and the amounts of segregation were calculated using each of the two models. In Fig. 7, Cases 2 and 3 are the results of additional calculations, and Case 1 is the result shown in Fig. 5. The results of the three calculations are very consistent with one another. From these concentration profiles, we calculated the average amount of segregation in one atomic layer region for Cases 1–3, which were 10.9 at.%, 11.1 at.%, and 11.2 at.%,

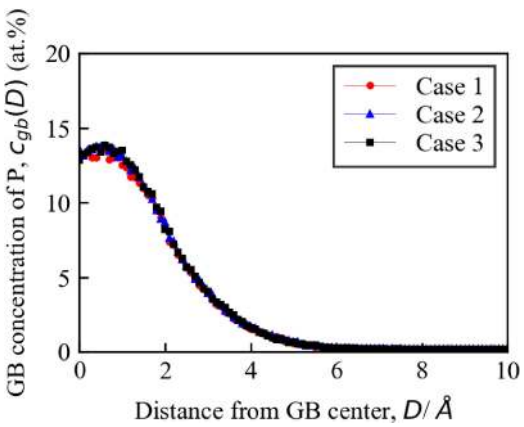

Fig. 7 Dependence of grain boundary (GB) concentration of P in Fe–0.1 wt.%P in the thermal equilibrium state at 1073 K on the random seed for constructing the nanocrystalline GB model.

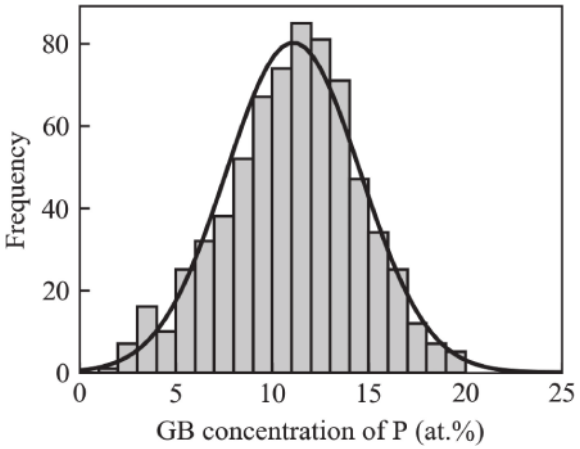

Fig. 8 Histogram of grain boundary (GB) concentration of P at each GB in Fe–0.1 wt.%P in the thermal equilibrium state at 1073 K. The solid line represents a normal distribution.

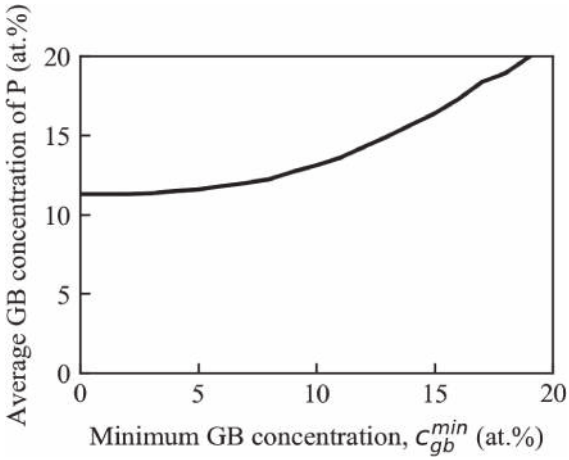

Fig. 9 Dependence of average grain boundary (GB) concentration of P on c_{gb}^{min} in Fe–0.1 wt.%P in the thermal equilibrium state at 1073 K. c_{gb}^{min} is the minimum value of GB concentration considered in the calculation of the average GB concentration.

respectively, indicating that the obtained results were almost independent of the random seed.

To investigate why the average amount of segregation calculated from the present prediction method is independent of the generated nano-polycrystalline GB model, we calculate the amount of segregation at each GB in the nano-polycrystalline GB model for Case 1 and analyze how it contributes to the average amount of segregation. Figure 8 shows the histogram of the amount of segregation for the monolayer region of each GB. The histogram is only included for GBs with more than 50 atomic sites for a single GB to prevent GBs with a small number of constituent atomic sites and a large amount of segregation variability from affecting this histogram. It should be noted that the GB with a small number of atomic sites removed has an inconsiderable effect on the average amount of segregation. The histogram of the segregation in Fig. 8 is approximately close to the normal distribution, and the median value of 11.0 at.% obtained by fitting to the normal distribution is close to the average value of 10.9 at.% described above. These results show that the segregation of each GB in the nano-polycrystalline GB model differs from one GB to another, but the nano-polycrystalline GB model used in this study included a sufficient number of GBs to obtain the average amount of segregation in polycrystalline structures.

However, as mentioned in Section 2.1, the evaluation method via Auger electron spectroscopy may overestimate the average amount of segregation in polycrystals, which may lead to inappropriate experimental values for comparison. Therefore, based on the results presented in Fig. 8, we discuss the effect of the GB with a small amount of P without considering it in the calculation of the average amount of segregation in polycrystals. We discuss the case where GBs below a certain amount of P segregation do not appear as a GB break surface in Auger electron spectroscopy experiments and, consequently, these GBs are not considered in the calculation of the average amount of segregation. Figure 9 shows the average amount of segregation obtained by changing the minimum amount of segregation c_{gb}^{min} at the GB considered in the calculation of the average amount of segregation. As c_{gb}^{min} increases, so does the calculated average amount of segregation, but the calculated average amount of segregation is 13.5 at.% even when c_{gb}^{min} is 11.0 at.%, which is the median value when fitting the normal distribution in Fig. 8. The actual c_{gb}^{min} value should be smaller than this value. For example, even if c_{gb}^{min} is 8 at.%, the average amount of segregation changes by 1 at.%, indicating that the effect of c_{gb}^{min} is minor. This is because the histogram of the amount of segregation at each GB follows a normal distribution and the dispersion is small. Thus, the experimental results for the GB segregation of P in bcc-Fe were approximately close to the true average amount of segregation, indicating that the results were valid for comparison.

The calculation results of the amount of segregation based on the present prediction method depend on the interatomic potential used to calculate the segregation energy. The interatomic potential used in this study reproduces the segregation energy[12] for each site of the Σ3(111) symmetric tilt GB evaluated through first-principles calculations,[14] thereby suggesting that this interatomic potential is also reasonable for the calculation of the segregation energy in the nano-polycrystalline GB model. In recent years, the development of high-precision interatomic potentials using first-principles calculations and machine learning has been carried out, which will enable the calculation of the segregation energy more accurately.

Equation (4) presents an extension of the Coghlan–White equation and does not consider the interaction between solutes at GBs. In the present calculation, the amount of segregation may exceed 10.0 at.% as shown in Fig. 8. Therefore, depending on the magnitude of the interaction, it is possible that the interaction between solutes cannot be ignored. However, the relationship between the amount of P added and the amount of segregation in the experimental results used for comparison is well explained by Mclean's equation, which does consider the interactions between solute elements. This suggests that the influence of solute element interactions on the amount of segregation is inconsiderable at the level of the calculated segregation. This effect can be considered, for example, by utilizing the semi-grand canonical Monte Carlo simulation.[35] However, when this method is

applied to a nano-polycrystalline GB model, GB movement is induced by the extremely high driving force of grain growth. Therefore, it is difficult to evaluate the amount of segregation, which cannot be used to predict the amount of segregation in polycrystals with grain sizes in the order of micrometers, as in the present study. If it is possible to determine representative GBs based on the calculation results of the present nano-polycrystalline GB model, the problem will be solved by semi-grand canonical Monte Carlo simulations on the bicrystal model of those GBs.

The effect of GB triple junctions is overestimated due to the use of the nano-polycrystalline GB model. It has been reported that the amount of segregation of GB triple junctions differs from that of GBs,[36] which may lead to errors in the prediction of the segregation amount using the nano-polycrystalline GB model. According to the equation proposed by Palumbo *et al.*,[37] the ratio of the triple junctions to GBs was approximately 20% when the GB width was defined as 0.5 nm and the average grain size was 5.3 nm. Therefore, although the grain size was small, the ratio of the GB triples was still approximately 20%, and it was presumed that the amount of segregation was not greatly influenced by the grain size. The effect of the triple junctions on the amount of segregation can be investigated by analyzing the grain size on the dependence of the amount of segregation. By correcting this effect, it is possible to predict the amount of segregation more precisely, but this is a subject for further study.

The present prediction method is expected to improve the accuracy further by using high-precision interatomic potentials and considering the effects of the interaction between solute elements and GB triple junctions. However, in this study, it was found that the prediction accuracy of the amount of GB segregation in polycrystals was significantly improved by developing a GB model that simulated the polycrystals and calculating the average amount of segregation by selecting the evaluation region corresponding to the measurement method.

5. Conclusion

An improved method for predicting the equilibrium GB segregation of a single element in polycrystalline GBs is developed based on: (1) a nano-polycrystalline GB model that simulates polycrystalline GBs and (2) an equation for calculating the amount of segregation that considers the site dependence of the segregation energy and the distance from the GB center.

By applying this method to the GB segregation of P in bcc-Fe and comparing its results with experimental findings, it is determined that this prediction method can attain a good prediction accuracy. The present prediction method is expected to be effective in predicting the amount of GB segregation in various polycrystalline binary alloys.

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