Thermodynamic and Kinetic Modeling of Grain Boundary Equilibrium Segregation of P in α -Fe

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Abstract

Phosphorus is a primary contributor to interface fracture and embrittlement in steels because of its strong segregation tendency at grain boundaries (GBs). The lack of consistency in literature data imposes great difficulties in performing segregation modeling that is compatible with both the Langmuir-McClean segregation theory and the thermodynamic description of the Bcc(Fe,P) phase. This work carefully evaluated experimental data for phosphorus segregation at GBs in α -Fe and provided a new formula for converting the auger electron spectroscopy (AES) peak height ratio to GBs. Based on newly assessed literature data, this work proposes that the major driving force for phosphorus segregation is the formation of Fe₃P-type clusters at GBs, which is supported not only by the almost equivalent Gibbs energy of α -Fe using the Bcc(Fe,P) substitutional model and the Bcc(Fe,Fe₃P, P) associate model, but also by the good agreement between thermodynamic/kinetic modeling results and experimental data.

Introduction

Earlier studies on equilibrium grain boundary (GB) segregation in steels found that metalloid elements, such as P, S, Si, Ge, Sn, and so on, embrittle materials when they enrich at GBs [1]. Among the various elements, phosphorus (P) is one of the most frequent impurities in steels. It can strongly segregate at GBs and affect the materials properties even at small bulk concentrations of 100 ppm. Therefore, GB segregation of P in steels is one of the most widely studied subjects, and it is known to be a primary contributor to embrittlement, intergranular fracture, and intergranular corrosion and stress corrosion cracking of low-alloying steels [2-9]. Not only equilibrium segregation but also irradiation-enhanced P segregation at GBs has been related to irradiation-enhanced embrittlement of pressure vessel steels in nuclear reactors [10-16]. Equilibrium segregation (ES) is concerned about equilibrium distribution of solutes between boundary and bulk governed by the minimum of the total free energy of the whole system at a given temperature. In contrast, non-equilibrium segregation (NES) is concerned about non-equilibrium solute distribution induced by quenching, radiation, etc. Faulkner et al. developed a model for non-equilibrium P segregation at GBs by introducing a radiation enhanced ratio to the

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diffusion activation energy [17]. However, a more rigorous model based on the linear response theory, with a clear correspondence between the D-coefficients and the L-coefficients to describe the effect of interaction and correlation among elements is needed for multicomponent alloys. Progress in this regard has been made recently in the modeling of radiation-induced segregation of Fe-Cr-Ni alloys [18]. The details of modeling radiation induced segregation is beyond the scope of this work. Our research in this work was focused on the equilibrium GB segregation of P in α -Fe, and on the kinetics of this process. This model will be used in a future study connected with the Radiation-Induced-Segregation model to provide a complete description of GB segregation of P under both irradiation and thermal conditions.

1. Literature review

Tipler et al.[19]. first found dilute alloys of iron (Fe) with P suffered from a marked intergranular brittleness at temperatures from 600 to 1000°C. Quantitative measurements of GB segregation levels of P in α -Fe have mainly used auger electron spectroscopy (AES) in the literature [3, 20-22]; however, the results differ greatly from one work to another. Ramasubramanian and Stain [22] estimated that the P concentration at GBs can be as high as 100 at. %. Matsuyama and Suto [20] performed a systematic quantitative AES analysis of GB segregation of P for Fe-(0.05~1.7) wt % P alloys. These alloys were annealed at different temperatures (1150~500°C) for different durations (14~1800 h). The researchers found that in low-P alloys, the segregation levels of P at GBs increased with increasing bulk concentrations and decreasing annealing temperatures. In high-P alloys, the P composition at GBs reached a saturation level of ~15 at. % P, and Fe₃P precipitates at GBs were observed. Erhart and Grabke [3] performed another systematic study of P segregation in α -Fe in Fe-(0.003~0.33) wt % P alloys [3]. The samples were made from melting high-purity elements; solutionized at 1050°C for 1 h, followed by water quenching and tempering treatment at 850°C for 1 h; and then furnace-cooled to the aging temperature. The specimens were held at the aging temperature for different periods of time and then water quenched for AES analysis. The AES analysis was done at the interfaces of GBs that had been fractured at -120°C. The study confirmed that the P segregation increased with increasing bulk concentrations and decreasing annealing temperatures. However, the measured P concentrations were in the range of 5~95 at. %, much higher than the saturation value of 15 at. % found in Matsuyama and Suto's work [20]. Such a drastic difference in the GB composition measurement is probably due to the different methods that were used to convert the peak height ratio of the AES spectrum into the composition.

Suzuki et al. [7, 21, 23] and Egert et al. [24] published several papers on the chemical state of P segregated at GBs of α -Fe, using a combination of AES with x-ray photoelectron spectroscopy (XPS) or electron energy-loss spectroscopy (EELS). They found that P segregated at GBs of α -Fe was in a similar chemical state to P in Fe₃P for Fe-0.1wt % P and Fe-0.05 wt % P alloys. Hashimoto [25, 26] and Ishida [27] performed atomistic simulation on structural transitions at GBs due to P segregation and confirmed the local atomic environment surrounding P atoms is similar to that of crystalline Fe₃P.

In view of the large differences between the Erhart et al.[3] and Matsuyama et al.[20] datasets, only one set of data will be used to validate the modeling results. The alloys in Matsuyama's work [20] had higher P concentrations, causing the formation of Fe₃P precipitates. It is difficult to determine the true remaining P concentration in the α -Fe solid solution. The alloys in Erhart and Grabke's work [3] had less P content and did not form Fe₃P precipitates. The nominal P concentrations in alloys represented the true P concentration in the α -Fe solid

solutions. Therefore, the Erhart and Grabke results were preferred. However, only the AES peak height ratio from Erhart and Grabke [3] was used in this work. The reported GB compositions were not adopted, because their approach for converting the AES peak height ratio into the chemical composition of P is questionable. They used an Fe-1P (wt %) single crystal as a standard and performed AES and low energy electron diffraction (LEED) on the saturated layer of absorbed phosphorus on the (100) surface. The LEED pattern indicated a c(2×2) structure, based on which they assumed a concentration of 50 at. % P for the surface layer. The AES measurements showed an average peak height ratio of P to Fe is around 1. Therefore, they obtained the relationship of $xPs = 0.5 IPIFe$, where xPs is the P concentration at surface and IP and IFe are the auger peak intensities of P and Fe. This derivation has two major problems. First, the LEED c(2×2) pattern can provide only information regarding surface structure, not composition. It tells the number of sites with a specific symmetry, but cannot give the information on the fraction of elements in each site. Second, the AES measurement includes signals from both the surface layer and a few subsurface layers, whereas LEED provides only surface structure information. Yoshihara et al. [28] measured sulfur segregation in α -Fe and found that when the saturated surface displayed a c(2×2) structure, the maximum concentration obtained from AES measurement was ~30 at. % sulfur, corresponding to the Fe₂S chemical state.

In this work, we converted the AES peak height ratio from Erhart and Grabke [3] following the approach in the AES analysis handbook [29], by taking the sensitivity factors of elements into consideration, as shown in Eq. (1):

$$xP = IPSP / (IFeSFe + IPSP) \quad (1)$$

S_i is the sensitivity factor of element i . Erhart and Grabke [3] used a 3 KeV beam, at which the sensitivity factor of P at 120 eV is 3.0834 and the sensitivity of Fe at 650 eV is 0.7878. By inserting the values of sensitivity factors into Eq. (1), we obtain

$$xP = 1 / (1 + 3.91 IFeIP) \quad (2)$$

We can see from Eq. (2) that when $IPIFe = 1$, the maximum atomic composition of P is ~0.2, which is lower than the 0.25 suggested by the chemical state of Fe₃P. This is because Eqs. (1) and (2) assume the composition depth profile of P is flat. Yoshihara et al. [28] suggest that the concentration of P is exponentially decreasing from the surface and introduce a calibration factor αP to account for such an effect:

$$xPs = xP\alpha P, \quad (3)$$

where xPs is the true surface composition with an exponential depth profile and xP is the composition with a flat depth profile. For Erhart and Grabke's data, at saturation, $IPIFe = 1$, where $xP = 0.2$, and $xPs = 0.25$ based on the chemical state of Fe₃P, we get $\alpha P = 1.25$. This is in reasonable agreement with the 1.5 reported by Yoshihara et al. [28]. Therefore, the following formula is used in this work to convert the AES peak height ratio to the surface composition:

$$xPs = 1.25 / (1 + 3.91 IFeIP) \quad (4)$$

We plotted the raw AES peak height ratio as shown on the left scale in Fig. 1 and used Eq. (4) to convert the AES peak ratio to the composition, as shown on the right scale in Fig. 1. The newly derived compositions are much less than those calculated by Erhart and Grabke [3]. Using the new compositions, the derived segregation energy is $-34469+22.9T$ (J/mol), which is close to the reported value of $-34300+21.5T$ (J/mol) from Erhart and Grabke [3].

Fig. 1. Experimental data for the raw peak height ratio [3] and the derived P composition at GBs considering the sensitivity factors of P and Fe. The bulk composition of P in wt % is denoted along each curve in the plot.

To summarize the literature information, although the reported experimental results for P segregation at the GBs of α -Fe differ greatly from one work to another, because of the different cooling rates (e.g., furnace cooling or water quench) and aging periods, the AES calibration method, the conversion method from AES peak ratio to composition, and so on, there are general trends that can be captured from the experimental results: (1) the segregation level of P increases with the bulk concentration; (2) the segregation level of P decreases with increasing aging temperature; (3) the chemical state of P at GBs is similar to that of Fe_3P ; (4) P segregation at GBs occurs in merely a few atomic layers; and (5) both small-angle and low- Σ symmetric boundaries correspond to low levels of P segregation. Recognizing that the GB structure has an important role in the segregation process, the current modeling will focus on thermodynamic and kinetic aspects of P segregation at general GBs, because most available experimental data were obtained from fractured polycrystalline materials in which no detailed information about GB structure was available. Few studies using bicrystal samples generated very useful information on GB orientation–segregation relationships [30], which can be used to develop future more-sophisticated GB segregation models with consideration of the GB structure modeling.

2. Thermodynamic and kinetic modeling

2.1 The Langmuir-McLean segregation equation

Thermodynamic modeling of equilibrium segregation is based on the **Langmuir-McLean segregation** approach [31-33]. There exist several ways to derive the segregation isotherms

based on this approach. The method used by duPlessis and van Wyk [34] is briefly discussed here. Consider a closed system containing the GB inside the crystalline surrounding. The GB is considered as a region of finite thickness, while the bulk of the crystal is of infinite size. GB segregation is then defined as a redistribution of solute atoms between the crystal and the interface. From this point of view, both parts of the system are considered as open, enabling an exchange of solutes. The basic condition for chemical equilibrium between the solute P and solvent Fe at the grain boundary φ and the bulk B is $FeB + P\varphi = Fe\varphi + PB$. The Gibbs energy of reaction at equilibrium is

$$\Delta G = \mu_{P\varphi} - \mu_{PB} - \mu_{Fe\varphi} + \mu_{FeB} = 0, \quad (5)$$

where μ_{sl} represents the chemical potential of the s element in the l state, s represents element P or Fe, and l represents phase φ or B . Because

$$\mu_{sl} = \mu_{sl}^0 + RT \ln(a_{sl}), \quad (6)$$

μ_{sl}^0 is the standard chemical potential of the s element in the l state, and a_{sl} denotes the activity coefficient of s in l . Combining Eqs. (5) and (6), we obtain

$$a_{P\varphi} a_{Fe\varphi} = a_{PB} a_{FeB} \exp(-\Delta G_{PO} / RT), \quad (7)$$

where $a_{P\varphi}$ denotes the activity of P in φ , $a_{Fe\varphi}$, a_{PB} and a_{FeB} were similarly defined, and ΔG_{PO} is the standard molar Gibbs energy of segregation, as described by Eq. (8). It is a composition-independent quantity.

$$\Delta G_{PO} = (\mu_{FeB}^0 - \mu_{PB}^0) - (\mu_{Fe\varphi}^0 - \mu_{P\varphi}^0). \quad (8)$$

Because $a_{sl} = \gamma_{sl} x_{sl}$, with γ_{sl} as the activity coefficient and x_{sl} the atomic concentration of s in l , Eq. (7) can be written as

$$x_{P\varphi} (1 - x_{P\varphi}) = x_{PB} (1 - x_{PB}) \exp(-(\Delta G_{PO} + \Delta G_{PE}) / RT), \quad (9)$$

where ΔG_{PE} is the excess molar Gibbs energy of segregation, which equals to

$$\Delta G_{PE} = RT \ln(\gamma_{P\varphi} \gamma_{FeB} / \gamma_{Fe\varphi} \gamma_{PB}). \quad (10)$$

For an ideal solution, the excess Gibbs energy is zero. For a non-ideal solution, the excess Gibbs energy is not zero and shall not be ignored. The solid solution of α -Fe with a small amount of P is a non-ideal dilute solution. Based on a recently assessed thermodynamics database [35], Bcc(Fe,P) is a regular substitutional solid solution with the interaction parameter ω_{Fe_P} as $-182800 + 25.6$ (J/mole). Because

$$RT \ln \gamma_P = \Delta H_P = \omega_{Fe_P} (1 - x_P)^2, \quad (11)$$

$$RT \ln \gamma_{Fe} = \Delta H_{Fe} = \omega_{Fe-P} (1 - x_{Fe})^2 . \quad (12)$$

ΔH_P and ΔH_{Fe} are the partial mole enthalpy of P and Fe in Bcc(Fe,P), respectively. Substituting Eqs. (11) and (12) into Eq. (13), the excess segregation energy can be described by

$$\Delta G_{PE} = 2\omega_{Fe-P} (x_{PB} - x_{P\varphi}) . \quad (13)$$

Then the total segregation energy is

$$\Delta G_P = \mu_{FeB, O} - \mu_{PB, O} - \mu_{Fe\varphi, O} - \mu_{P\varphi, O} + 2\omega_{Fe-P} (x_{PB} - x_{P\varphi}) . \quad (14)$$

Equation (14) suggests that the segregation energy of P in α -Fe is highly dependent on the magnitude of ω_{Fe-P} and $x_{P\varphi}$. x_{PB} can be ignored for a dilute solution. With a large negative ω_{Fe-P} , and the $x_{P\varphi}$ as high as 25 at. % [3], the excess segregation energy of P is highly negative, is composition dependent, and shall not be ignored. However, in almost all literature, the P segregation energy in diluted Bcc(Fe,P) is assumed to be equal to ΔG_{PO} with no contribution from excess Gibbs energy. This assumption is supported by Erhart and Grabke [3], who derived the GB segregation energy of P in α -Fe by fitting experimental $x_{P\varphi}$ into Eq. (9). They obtained a composition-independent total segregation energy of $34300 + 21.5T$ (J/mole) that can well reproduce all the experimental data. On the other hand, the ω_{Fe-P} agreed with available thermodynamic property and phase diagram data. How can we reconcile this contradiction?

As discussed in the literature review section, the experimentally observed P chemical state at the GBs is similar to that of Fe_3P . If we assume that at GBs, the negative interaction energy between Fe and P is mainly used to form Fe_3P -type clusters, and the chemical interaction between Fe and Fe_3P is ideal, i.e., $\omega_{Fe-Fe_3P} = 0$, then the excess Gibbs energy between them can be ignored. To test this assumption, we replaced the substitutional model of the Bcc(Fe,P) solid solution with an associate model Bcc(Fe, Fe_3P , P). The Gibbs energy description of the substitutional model is

$$G_{Bcc} = x_{Fe} G_{FeO, Bcc} + x_P G_{PO, Bcc} + RT x_{Fe} \ln x_{Fe} + x_P \ln x_P + \omega_{Fe-P} x_P x_{Fe} . \quad (15)$$

For the associate model, assuming no interactions between species of Fe, P and Fe_3P , i.e., an ideal solution, the Gibbs energy is

$$G_{Bcc} = y_{Fe} G_{FeO, Bcc} + y_P G_{PO, Bcc} + y_{Fe_3P} G_{Fe_3PO, Bcc} + RT y_P \ln x_P + y_{Fe} \ln x_{Fe} + y_{Fe_3P} \ln x_{Fe_3P} . \quad (16)$$

In this equation, y_{Fe} denotes the mole fraction of species. It is different from the mole fraction of elements. The only unknown parameter is $G_{Fe_3P, Bcc}$, which denotes the Gibbs energy of the Fe_3P cluster. It can be described by

$$G_{Fe_3P, Bcc} = 3G_{FeO, Bcc} + G_{PO, Bcc} + \Delta G_{Fe_3P, f}, \quad (17)$$

where $\Delta G_{Fe_3P, f}$ denotes the formation energy of the Fe_3P cluster. We derive the formation energy of the Fe_3P associate from the mixing energy of the substitutional $bcc(Fe, P)$ model at the stoichiometric composition $Fe_{0.75}P_{0.25}$. The detailed derivation is described in Appendix II. We plotted and compared the Gibbs energy of $\alpha_{-}Fe$ and the Fe-P phase diagram in Fig. 2 using the substitutional regular solution model and the ideal associate model. The results show slight difference in the Gibbs energy curve and the bcc solvus and solidus. Since we didn't make any attempt to optimize model parameters, the direct conversion from the mixing energy of the regular solution model at $Fe_{0.75}P_{0.25}$ to the formation energy of the Fe_3P associate resulted in good agreement between two models within experimental uncertainties. It should be noted that the similarity between the regular solution model (Fe, P) and ideal associate model (Fe, Fe_3P, P) breaks up when the P composition is beyond 25 at%, as shown the comparison of integral and partial Gibbs energy for the full composition range in Appendix III. However, for the Fe-P bcc solid solution with a solubility less than a few atomic percent in the bulk case, and the maximum 25 at% in the GB case, the Gibbs energy difference is small. These results suggest that the thermodynamic driving force to form Fe_3P clusters in $\alpha_{-}Fe$ at GB is highly competitive, if not the most favorable. Therefore, it is reasonable to assume that the GB structure in combination with the strong thermodynamic driving force favors the formation Fe_3P clusters and thereby reduces the GB energy. This assumption explains that the ΔG_{PE} can be ignored and the total segregation energy of P in the $Bcc(Fe, P)$ solid solution can be described by composition-independent ΔG_{PO} , because the negative interaction energy between Fe and P is mainly used to form Fe_3P clusters and the chemical interaction between Fe and Fe_3P is ideal.

Fig. 2. (a) The Gibbs energy of α -Fe at 500 and 1000°C described by the substitutional solution model bcc(Fe,P) and the associate model bcc(Fe,Fe₃P,P); (b) the Fe-P phase diagram with P concentration up to 50 at%.

Kaptay [36] modeled the GB segregation of P based on the GB segregation transition theory. He also attributed the large negative interaction between Fe and P to the formation of Fe₃P clusters. However, he further assumed a large miscibility gap, i.e., a strong repulsive interaction between the Fe and Fe₃P clusters. Because of this miscibility gap, the P segregation at GBs is subjected to a first order abrupt transition from a low- to a high-segregation state with increasing bulk P contents. This sudden transition was not observed in either the Erhart et al. [3] or the Matsuyama et al. [20] work, in which the P segregation increased continuously with increasing bulk P contents.

2.3 Kinetics model

The GB segregation kinetics is based on the Hofmann and Erlewein model [37], in which solute atoms move along a potential gradient with a direction perpendicular to the interface. The potential barrier is diffusion barrier ΔG_D in the bulk. The potential at GBs is lowered by the segregation energy ΔG_S , as shown in Fig. 3. To overcome difficulties with the solution of a diffusion equation in a potential gradient, this approach describes the attainment of concentration distributions by atomic fluxes based on reaction rate theory. This model assumes no concentration gradient occurring within atomic layers parallel to the GB plane, so that the model is confined to a one-dimensional problem.

Fig. 3. Assumed free energy versus depth for segregant atoms at the surface and in the bulk.

The GB segregation of P in α -Fe occurs in two steps: the P solute atoms move along the potential gradient followed by the transformation from P atom to Fe₃P clusters at GBs. The solute flux equations are described by Eqs. 18(a~d):

$$J_{12} = a_1 - 2X_1W_1\theta_1 \exp(-\Delta G_D - \Delta G_S)RT. \quad (18a)$$

$$J_{21} = a_2 - 2X_2W_2\theta_2 \exp(-\Delta G_D)RT. \quad (18b)$$

$$J_{23} = a_1 - 2X_2W_{23}\vartheta_2 \exp(-\Delta G_D/RT). \quad (18c)$$

...

$$J_{i,i+1} = a_i - 2X_iW_{i,i+1}\vartheta_i \exp(-\Delta G_D/RT). \quad (18d)$$

where a_i is the atomic jump distance, X_i is the concentration of solute atoms in layer “ i ”, ϑ_i is the solute atom oscillation frequency, and $W_{i,i+1}$ is the jump probability factors of the solute atoms. In a first order approximation, all jump frequencies are assumed to be equal, as well as the jump distances. The deviation for a_1 and ϑ_1 from this assumption will be accounted for by segregation energy. In the kinetic modeling, the segregation energy ΔG_{PO} , i.e., ΔG_S , was set to be $34469 + 22.9T$ (J/mole atoms) derived in this work. The ΔG_D is the activation energy for diffusion, and it was derived from the experimental diffusion coefficient of P in α -Fe, based on $D = D_0 \exp(-Q/RT) = a_1^2 \vartheta_1 \exp(-\Delta G_D/RT)$. The phosphorus diffusion coefficient in α -Fe has been measured experimentally, i.e., $1.38 \cdot 10^5 \exp(-3.4 \text{ eV}/kT) \text{ cm}^2/\text{s}$ in the temperature range (932–1017 K) and $8 \cdot 10^5 \exp(-3.2 \text{ eV}/kT) \text{ cm}^2/\text{s}$ in the temperature range (783–923 K) [38]. The P diffusion is much larger than the self-diffusion coefficient. Indeed, at 870 K, the self-diffusion coefficient is $10^{-20} \text{ m}^2/\text{s}$, while the diffusion coefficient of P in ferromagnetic BCC Fe is $10^{-17} \text{ m}^2/\text{s}$ [38]. This fact could be associated with diffusion involving interstitials rather than vacancies. Domain and Besquart did ab-initio calculations of the diffusion of P in α iron [39]. They found that the diffusion coefficient of P based on a vacancy mechanism, although less than the experimental measurement of P in α iron, was already larger than the self-diffusion coefficient by one to three orders of magnitude. Owing to the lack of quantitative description of the interstitial diffusion of P in α iron, we will use experimental diffusion coefficient data for P in α iron in this work. The jump probability factor was assigned using the following relationship based on Hofmann’s work:

$$w_{21} = X_{SM} - X_S, \quad (19a)$$

$$w_{12} = 1 - X_2, \quad (19b)$$

$$w_{23} = 1 - X_3, \quad (19c)$$

$$W_{i,i+1} = 1 - X_{i+1}, \quad (19d)$$

where X_S is surface composition and X_{SM} is the maximum allowable surface coverage. In this study, X_{SM} equals 0.25 because the saturated chemical state of P on surface is Fe_3P . Equation (9) denotes the maximum allowable coverage as 1. When the maximum allowable surface coverage is X_{SM} , Eq. (9) should be modified to

$$x_P \varphi_{x_S M} - x_P \varphi = x_P B_1 - x_P B \exp(-(\Delta G_{PO} + \Delta G_{PE})/RT). \quad (20)$$

Computational codes for calculating the thermodynamics and kinetics of thermal segregation were implemented using Matlab. The system was modeled by N parallel atomic planes perpendicular to the diffusion axis. The first plane corresponds to the GB plane and planes >1 get

into the bulk. The maximum plane ends at about $1\mu\text{m}$ distance from GB. The flux is set to zero between plane <1 and Plane=1 or plane $>\text{max}$ and plane=max. The ODE15 solver with variable time step algorithm in the Matlab was used to solve the differential equations.

3. Results and discussion

The calculated equilibrium P composition at GBs is plotted as a function of alloy composition and temperature in Fig. 4(a) and (b); they compare well with the experimental data from Erhart and Grabke. The results calculated from thermal segregation models suggest that the segregation of P at GBs increases with increasing bulk composition and decreasing temperature and saturates at 25 at. %, which is in good agreement with experimental observations. The thermodynamic calculation of GB segregation gives the equilibrium values after infinite long times. The following kinetics simulation will show how fast the system can reach equilibrium.

Fig. 4. The equilibrium segregation of phosphorus at the grain boundary (a) as a function of alloy composition (bulk phosphorus content) at 500°C , and (b) as a function of both alloy composition (wt %) and temperature, compared with the experimental data from Erhart and Grabke [3].

We simulated the GB composition of P as a function of time, temperature, and bulk composition. For an alloy with a high P composition of 0.33 wt % P at 723K (450°C), the calculated concentration profile of P as a function of distance from GB is plotted in Fig. 5(a). The red curve denotes the profile at 0.1 h and the blue curve at 10,000 h. The results suggest that at the earlier stage of segregation, there is a depletion regime of P at the sub-GB region. This is because the segregation energy leads to a large flux from the sub-GB region to the GB plane while, during this time, the flux into the sub-GB regime is supplied by continuous diffusion from the bulk. For longer times, the GB segregation gradually reaches equilibrium, and the depleted region gradually disappears until a steady state is established.

Fig. 5. (a) The composition of P at GBs at 450°C for Fe-0.33wt %P as a function of distance from the GBs for the 0.1 h and 10,000 h periods; (b) as a function of time for alloy Fe-0.33 wt % P and Fe-0.003 wt % P at 723 and 1073K (450 and 800°C), respectively.

In Fig. 5(b), the P composition at GBs as a function of time is calculated for Fe-0.33wt % P and Fe-0.003 wt % P alloys at 723 and 1073K (450 and 800°C), respectively. The plateau in each curve suggests the equilibrium segregation is reached. The results show that more than 90% of the equilibrium segregation at 800°C can be reached within $10^{-4} \sim 10^{-2}$ h, whereas the time to reach equilibrium at 723K(450°C) is 10 h for a high-P alloy and 10^5 h for a low-P alloy. The equilibrium segregation level predicted from the kinetic modeling is quite consistent with the thermodynamic calculations in Fig. 4 (b), indicating correct boundary conditions for an infinitely long time and the self-consistency between the thermodynamic and kinetic models. However, based on the kinetic simulation, an immediate question is whether the experimental data at 723K(450°C) obtained from Erhart and Grabke's work [3] were truly reaching equilibrium segregation values. Although they did not give the annealing time for alloys at each temperature, it is impossible for the annealing time to be more than 10^5 h. Therefore, the segregation data for low temperatures and low-P alloys in Erhart and Grabke's work are considered not to reach equilibrium, and these data should be used with caution for deriving the segregation energy. This result also supports that XSM cannot be 1, because then an even longer time would be required to reach the reported GB composition in Erhart and Grabke [3].

4. Conclusions

This work carefully evaluates experimental data for P segregation at GBs in α -Fe and provides a new formula for converting the AES peak height ratio to the composition. The newly assessed GB compositions, in combination with the XPS and AES data and the first-principles calculated results in the literature, suggest that the P segregated at the GBs of α -Fe is in a similar chemical state to crystalline Fe_3P ; and the saturated composition is no more than 25 at. %. This work proposes that the major driving force for P segregation at GBs is the formation of Fe_3P -type clusters at the GBs, because the modeling of the Gibbs energy of α -Fe using the Bcc(Fe,P) substitutional model and the Bcc(Fe, Fe_3P , P) associate model shows that the energy change due to the formation of such a cluster is very small. The newly developed associate model provides a consistent thermodynamic description that is compatible with both the Langmuir-McLean

segregation theory and the attainment of composition-independent segregation energy. The thermodynamic modeling results are in good agreement with experimental data. The kinetic modeling results suggest the thickness of the segregation layer decreases with time until it reaches equilibrium. They also suggest that the segregation data for low temperatures and low-P alloys should be used with caution in deriving the segregation energy, as they may not reach equilibrium.

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6. References

1. McMahon Jr, C. and L. Marchut, *Solute segregation in iron-based alloys*. Journal of Vacuum Science & Technology, 1978. **15**(2): p. 450-466.
2. Briant, C. and R. Mulford, *Surface segregation in austenitic stainless steel*. Metallurgical Transactions A, 1982. **13**(5): p. 745-752.
3. Erhart, H. and H. Grabke, *Equilibrium segregation of phosphorus at grain boundaries of Fe-P, Fe-C-P, Fe-Cr-P, and Fe-Cr-C-P Alloys*. Metal Science, 1981. **15**(9): p. 401-408.
4. Guttman, M., P. Dumoulin, and M. Wayman, *The thermodynamics of interactive co-segregation of phosphorus and alloying elements in iron and temper-brittle steels*. Metallurgical Transactions A, 1982. **13**(10): p. 1693-1711.
5. Hänsel, H. and H.J. Grabke, *Grain boundary segregation of phosphorus and carbon in ferritic iron*. Scripta metallurgica, 1986. **20**(11): p. 1641-1644.
6. Hondros, E. *The influence of phosphorus in dilute solid solution on the absolute surface and grain boundary energies of iron*. in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. The Royal Society. 1965. 286(1407): P. 479-498.
7. Suzuki, S., K. Abiko, and H. Kimura, *Phosphorus segregation related to the grain boundary structure in an Fe-P alloy*. Scripta Metallurgica, 1981. **15**(10): p. 1139-1143.
8. Suzuki, S., et al., *Effect of carbon on the grain boundary segregation of phosphorus in α -iron*. Scripta metallurgica, 1983. **17**(11): p. 1325-1328.
9. Viswanathan, R., *Temper embrittlement in a Ni-Cr steel containing phosphorus as impurity*. Metallurgical Transactions, 1971. **2**(3): p. 809-815.
10. Brimhall, J., D. Baer, and R. Jones, *Effect of irradiation on phosphorus segregation*. Journal of Nuclear Materials, 1983. **117**: p. 218-223.
11. Druce, S.G., et al. *The modelling of irradiation-enhanced phosphorus segregation in neutron irradiated reactor pressure vessel submerged-arc welds*. in *Effects of Radiation on Materials: 17th International Symposium*. 1996. ASTM International.
12. Faulkner, R., et al., *Grain boundary segregation under neutron irradiation in dilute alloys*. Journal of nuclear materials, 1998. **255**(2): p. 189-209.
13. Gurovich, B., et al., *Intergranular and intragranular phosphorus segregation in Russian pressure vessel steels due to neutron irradiation*. Journal of nuclear materials, 2000. **279**(2): p. 259-272.
14. Nishiyama, Y., et al., *Effects of neutron-irradiation-induced intergranular phosphorus segregation and hardening on embrittlement in reactor pressure vessel steels*. Acta Materialia, 2008. **56**(16): p. 4510-4521.

15. Song, S.-H., et al., *Grain boundary phosphorus and molybdenum segregation under irradiation and thermal conditions in a 2.25 Cr1Mo steel*. Materials Science and Engineering: A, 2000. **286**(2): p. 230-235.
16. Watanabe, H., et al., *Effects of phosphorus on defect behavior, solute segregation and void swelling in electron irradiated Fe-Cr-Ni alloys*. Journal of Nuclear Materials, 1988. **155**: p. 815-822.
17. Faulkner, R., S. Song, and P. Flewitt, *A model describing neutron irradiation-induced segregation to grain boundaries in dilute alloys*. Metallurgical and Materials Transactions A, 1996. **27**(11): p. 3381-3390.
18. Yang, Y.F., Kevin; Allen, Todd; and Busby, Jeremy, *Roles of Vacancy/Interstitial Diffusion and Segregation in the Microchemistry at Grain Boundaries of Irradiated Fe-Cr-Ni alloys* Journal of Nuclear materials, 2016. **473**: p. 35-53.
19. Inman, M. and H. Tipler, *Grain-boundary segregation of phosphorus in an iron-phosphorus alloy and the effect upon mechanical properties*. Acta Metallurgica, 1958. **6**(2): p. 73-84.
20. Matsuyama, T. and H. Suto, *Equilibrium Grain Boundary Segregation of P in Fe-P Binary Alloys*. Transactions of the Japan Institute of Metals, 1979. **20**(2): p. 44-50.
21. Oku, M., et al., *Study of chemical states at intergranular fracture planes of iron-phosphorus alloys by auger and electron energy-loss spectroscopies*. Journal of electron spectroscopy and related phenomena, 1984. **34**(1): p. 55-65.
22. Ramasubramanian, P. and D. Stein, *An investigation of grain-boundary embrittlement in Fe- P, Fe- P- S, and Fe- Sb- S alloys*. Metallurgical Transactions, 1973. **4**(7): p. 1735-1742.
23. Abiko, K., S. Suzuki, and H. Kimura, *Chemical state of phosphorus segregated at grain boundaries of iron*. Tetsu-to-Hagane(J. Iron Steel Inst. Jpn.), 1983. **69**(6): p. 625-630.
24. Egert, B. and G. Panzner, *Electron spectroscopic study of phosphorus segregated to α -iron surfaces*. Surface Science, 1982. **118**(1-2): p. 345-368.
25. Hashimoto, M., et al., *Atomistic studies of grain boundary segregation in Fe-P and Fe-B alloys—I. Atomic structure and stress distribution*. Acta Metallurgica, 1984. **32**(1): p. 1-11.
26. Hashimoto, M., et al., *Transformation of the grain boundary structure in iron by phosphorus segregation*. Scripta Metallurgica, 1982. **16**(3): p. 267-270.
27. Ishida, Y. and M. Mori, *Theoretical studies of segregated internal interfaces*. Le Journal de Physique Colloques, 1985. **46**(C4): p. C4-465-C4-474.
28. Yoshihara, K., M. Kurahashi, and K. Nii, *The Segregation Behavior of Sulfur, Oxygen and Phosphorus at the (100) Surface of Iron Single Crystal*. Transactions of the Japan Institute of Metals, 1980. **21**(7): p. 425-432.
29. Davis, L.E., et al., *Handbook of Auger electron spectroscopy*. Physical Electronics Industries, Eden Prairie, MN, 1976. **27**: p. 61-93.
30. Lejček, P., *Characterization of grain boundary segregation in an Fe-Si alloy*. Analytica chimica acta, 1994. **297**(1-2): p. 165-178.
31. Hondros, E., et al., *Physical metallurgy, vol. 2* North Holland. 1996, Amsterdam.
32. McLean, D., *Grain boundaries in metals*. 1957.
33. Lejcek, P., *Grain boundary segregation in metals*. Vol. 136. 2010: Springer Science & Business Media.
34. Du Plessis, J. and G. Van Wyk, *A model for surface segregation in multicomponent alloys—part I: Equilibrium segregation*. Journal of Physics and Chemistry of Solids, 1988. **49**(12): p. 1441-1450.
35. Miettinen, J. and G. Vassilev, *Thermodynamic Description of Ternary Fe-XP Systems. Part I: Fe-Cr-P*. Journal of Phase Equilibria and Diffusion, 2014. **35**(4): p. 458-468.
36. Kaptay, G., *Modelling equilibrium grain boundary segregation, grain boundary energy and grain boundary segregation transition by the extended Butler equation*. Journal of Materials Science, 2016. **51**(4): p. 1738-1755.

37. Hofmann, S. and J. Erlewein, *A model of the kinetics and equilibria of surface segregation in the monolayer regime*. Surface Science, 1978. **77**(3): p. 591-602.
38. Le Claire, A. and G. Neumann, *Diffusion of Impurities in Solid Metallic Elements, Chap. 3 in: Diffusion in Solid Metals and Alloys, H. Mehrer (Vol. Ed.), Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series Vol. III/26*. 1990, Springer-Verlag.
39. Domain, C. and C. Becquart, *Diffusion of phosphorus in α -Fe: An ab initio study*. Physical Review B, 2005. **71**(21): p. 214109.

Appendix I: Derivation of segregation energy according to the Langmuir-McLean equation

Using the new compositions in Fig. 1, we plotted the figure below with y axis being $\ln x_P \frac{x_P^\phi}{1-x_P^\phi} - \ln x_P \frac{x_P^B}{1-x_P^B}$, and x axis being $1/T \times 10^3$. The “T” is temperature in Kelvin. The linear relationship between x and y can be obtained, which is $y = 4.146x + 2.7551$. According to the Langmuir-McLean equation, $x_P \frac{x_P^\phi}{1-x_P^\phi} = x_P \frac{x_P^B}{1-x_P^B} \exp(-\Delta G_P / RT)$, the segregation energy is $-34469 + 22.9T$ (J/mol).

Appendix II: Derivation of the Gibbs energy of the Fe_3P cluster

$G_{\text{Fe}3\text{P}0, \text{Bcc}}$ in Eq. (12) denotes the Gibbs energy of the Fe_3P cluster. It can be described by

$$G_{\text{Fe}3\text{P}0, \text{Bcc}} = 3G_{\text{Fe}0, \text{Bcc}} + G_{\text{P}0, \text{Bcc}} + \Delta G_{\text{Fe}3\text{P}0, f}.$$

Assuming the large negative interaction between Fe and P in the substitutional model is used to form Fe_3P clusters, the excess energy at $\text{Fe}_{0.75}\text{P}_{0.25}$ can be described by

$$\Delta G_{Fe0.750.25ex} = x_{Fe}x_P w_{Fe-P} - P_{substitutional} = 0.75 \times 0.25 (-182800 + 25.6T)$$

Once a Fe_3P cluster is formed, the entropy due to random mixing at the $Fe_{0.75}P_{0.25}$ stoichiometric composition becomes zero. In addition, the excess energy and the random mixing entropy derived from the substitutional model is in terms of per mole atoms. When converted to the formation energy of the Fe_3P associate, it should be multiplied by 4 to denote the formation energy per mole formula. Therefore, the true formation energy of Fe_3P should be

$$\Delta G_{Fe3P0,f} = 4(\Delta G_{Fe0.750.25ex} + RT(0.75 \ln 0.75 + 0.25 \ln 0.25)).$$

Finally, we can obtain the Gibbs energy of the Fe_3P cluster:

$$G_{Fe3P0,Bcc} = 3G_{Fe0,Bcc} + G_{P0,Bcc} - 139692 + 0.5T.$$

Appendix III. Comparison between the regular solution model (Fe,P) and ideal associate solution model (Fe, Fe_3P ,P)

The figures below show comparison of phase diagram, integral Gibbs energy and partial Gibbs energy of P in Bcc in the full concentration range of Fe-P system. For an Fe-P bcc solid solution with a solubility less than a few atomic percent in the bulk case, and the maximum 25 at% in the GB case, the direct conversion from the mixing energy of a regular solution model at $Fe_{0.75}P_{0.25}$ to the formation energy of the Fe_3P associate resulted in good similarity between two models within experimental uncertainties. This similarity breaks up when the P composition is beyond 25 at%.