Thermodynamic study of grain boundary segregation

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Abstract: A simple physical grain boundary model is often employed in discussing the segregation behaviour in Fe, where the grain boundary has a constant thickness and the Gibbs energy can be assigned to the boundary material. The Gibbs energy of the grain boundary is sometimes expressed as a liquid or amorphous state. It seems unusual to apply the Gibbs energy of the liquid state to the grain boundary; however, this could be reasonable when considering the structural analogy between an amorphous state and a grain boundary composed of simple structural units. Based on this background, the present study used molecular dynamics simulation to construct grain boundary structures. The Fe polyhedral structures were extracted from the grain boundary layers. The segregation energies for alloying elements were calculated with some regions around a polyhedral structure being truncated into spherical shapes and the energies between the cases where a solute atom is inside and outside the polyhedral structures were compared using the first-principles calculation. Based on these results, the origin of the grain boundary segregation behaviour in Fe is discussed.

1. INTRODUCTION

Grain boundaries play the most important role among steel defects in determining the mechanical properties of steels. A simple physical grain boundary model shows that the grain boundary has a finite thickness, while the bulk phase is infinite in size. Under this assumption, the common tangent law does not denote the equilibrium between the grain boundary and the bulk phase, but the grain boundary concentration is defined by the tangent to the Gibbs energy of the grain boundary parallel to that for the bulk phase at the matrix concentration [1]. A question arises: how can the free energy of the grain boundary phase be expressed when applying a parallel tangent scheme? Sometimes the Gibbs energy of the grain boundary is expressed using the thermodynamic properties of the liquid phase. In the present study, the validity of such a treatment is discussed from a thermodynamic perspective.

2. PRIOR SEGREGATION MODEL

2.1. Langmuir–McLean type of segregation isotherm

The empirical approach taken to analyze grain boundary segregation is based on the equality of the chemical potentials of the components in equilibrium; this model has often been applied when considering experimental data on grain boundary segregation [2]. For a binary system, the model leads to the expression of the grain boundary solute concentration x_X^{gb} as

$$x_X^{gb} = \frac{x_X^{\varphi} \cdot \exp\left(\dfrac{\Delta E_X^{gb}}{RT}\right)}{1 + x_X^{\varphi} \cdot \exp\left(\dfrac{\Delta E_X^{gb}}{RT}\right)} \tag{1}$$

where x_X^{φ} is the bulk solute concentration and ΔE_X^{gb} is the molar energy of segregation. The segregation coefficient k_X^{gb} is defined in terms of ΔE_X^{gb} as

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$$k_X^{gb} = \exp\left(\frac{\Delta E_X^{gb}}{RT}\right). \tag{2}$$

2.2. Parallel tangent scheme

Let us consider a closed system containing the grain boundary (gb) inside the crystalline grains (φ). The grain boundary has a finite thickness, while the bulk phase of the crystal is infinite in size. Grain boundary segregation is then defined as a redistribution of solute atoms between the crystal and grain boundary. In an equilibrium state, the total Gibbs free energy of the whole system $\Delta G^{\varphi+gb}$ must be minimized. The variation in $\Delta G^{\varphi+gb}$ when small amounts of matrix atoms A and segregated atoms X, dm_A and dm_X, are moved from φ to the grain boundary is given by

$$d\Delta G^{\varphi+gb} = \left(\mu_A^{gb} - \mu_A^{\varphi}\right)dm_A + \left(\mu_X^{gb} - \mu_X^{\varphi}\right)dm_X = 0. \tag{3}$$

As dm_A and dm_X vary arbitrarily in a typical two-phase equilibrium, the condition to fulfil Eq. 3 is the so-called common tangent for finding the equilibrium:

$$\mu_A^{gb} = \mu_A^{\varphi}, \ \ \mu_X^{gb} = \mu_X^{\varphi}. \tag{4}$$

However, if the total number of atoms in the finite grain boundary region, $m_A + m_X$, remains constant, the value of $dm_A + dm_X$ should be zero. Inserting this condition into Eq. 3, we obtain the equilibrium condition for the grain boundary and matrix phase as

$$\mu_A^{gb} - \mu_A^{\varphi} = \mu_X^{gb} - \mu_X^{\varphi}. \tag{5}$$

The equilibrium concentration at the boundary x_X^{gb} is then found by parallel tangent construction based on the composition of the matrix [1].

3. THERMODYNAMIC EXPRESSION OF SEGREGATION ENERGY
3.1. Using regular solution approximation

Simple physical grain boundary models for metals have been used many times in the discussion of grain boundary segregation. If the grain boundary has a constant thickness and the material in the boundary can be regarded as a separate phase, the regular solution model can be applied to the grain boundary region in the A–X binary system. In this model, the chemical potentials for each component are expressed as

$$\mu_A^{\varphi} = {}^oG_A^{\varphi} + RT\ln\left(1-x_X^{\varphi}\right) + \left(x_X^{\varphi}\right)^2 L_{A,X}^{\varphi} \tag{6}$$

$$\mu_X^{\varphi} = {}^oG_X^{\varphi} + RT\ln x_X^{\varphi} + \left(1-x_X^{\varphi}\right)^2 L_{A,X}^{\varphi} \tag{7}$$

$$\mu_A^{gb} = {}^oG_A^{gb} + RT\ln\left(1-x_X^{gb}\right) + \left(x_X^{gb}\right)^2 L_{A,X}^{gb} \tag{8}$$

$$\mu_X^{gb} = {}^oG_X^{gb} + RT\ln x_X^{gb} + \left(1-x_X^{gb}\right)^2 L_{A,X}^{gb} \tag{9}$$

where ${}^oG_i^{\varphi}$ and ${}^oG_i^{gb}$ denote the molar Gibbs energies of element i (= A, X) in the matrix φ and grain boundary, respectively. The parameters $L_{A,X}^{\varphi}$ and $L_{A,X}^{gb}$ represent the interaction energies between atoms A and X in the matrix phase and grain boundary region. For low X content, the equilibrium condition of Eq. 5 thus yields

$$\frac{x_X^{gb}}{1-x_X^{gb}} \simeq \frac{x_X^{\varphi}}{1-x_X^{\varphi}} \cdot \exp\left\{\frac{\left({}^oG_A^{gb} - {}^oG_A^{\varphi}\right) - \left({}^oG_X^{gb} - {}^oG_X^{\varphi}\right) - \left(L_{A,X}^{gb} - L_{A,X}^{\varphi}\right)}{RT}\right\}. \tag{10}$$

This equation has the same form as the McLean segregation isotherm. Consequently, we obtain an expression for the grain boundary solute concentration with the regular solution approximation:

$$x_X^{gb} = \frac{x_X^{\varphi} \cdot \exp\left(\frac{\Delta G_X^{\varphi seg}}{RT}\right)}{1 + x_X^{\varphi} \cdot \exp\left(\frac{\Delta G_X^{\varphi seg}}{RT}\right)} \tag{11}$$

where.

$$\Delta G_X^{\varphi seg} = \left({}^oG_A^{gb} - {}^oG_A^{\alpha}\right) - \left({}^oG_X^{gb} - {}^oG_X^{\alpha}\right) - \left(L_{A,X}^{gb} - L_{A,X}^{\alpha}\right). \tag{12}$$

Comparison of Eq. 11 with Eq. 1 gives $\Delta E_X^{gb} = \Delta G_X^{\varphi seg}$.

3.2. Using compound energy approximation

The same consideration can be applied to the system in which a solution phase is described by the compound energy approximation [3]. The Gibbs free energy for the solution in which two sublattices exist and the lattice ratio is $a:c$, i.e., $A_a(X,Va)_c$ is expressed as

$$G_m^{\varphi} = y_X^{\varphi}\,{}^oG_{A:X}^{\varphi} + y_{Va}^{\varphi}\,{}^oG_{A:Va}^{\varphi} + RTc\left(y_X^{\varphi}\ln y_X^{\varphi} + y_{Va}^{\varphi}\ln y_{Va}^{\varphi}\right) + y_X^{\varphi}y_{Va}^{\varphi}L_{A:X,Va}^{\varphi} \tag{13}$$

where ${}^oG_{A:X}^{\varphi}$ represents the Gibbs energy when A atoms occupy the first sublattice and X atoms occupy the second sublattice. ${}^oG_{A:Va}^{\varphi}$ denotes the Gibbs energy when the second sublattice is vacant; therefore, this parameter substantially represents the value for pure A element. $L_{A:X,Va}^{\varphi}$ is the interaction parameter between the X atoms and vacancy in the second sublattice. y_X^{φ} is the site fraction of X atoms in the second sublattice. If the X atoms behave interstitially in the crystal lattice, this model is described as the interstitial solution model. The chemical potentials for each component in the matrix φ and grain boundary region are derived as Eqs. 15 through 18 following Eq. 14.

$$\mu_{A_aX_c}^{\varphi} = a\mu_A^{\varphi} + c\mu_X^{\varphi} = {}^oG_m^{\varphi} - \sum_j y_j^{\varphi}\frac{\partial {}^oG_m^{\varphi}}{\partial y_j^{\varphi}} + \frac{\partial {}^oG_m^{\varphi}}{\partial y_A^{\varphi}} + \frac{\partial {}^oG_m^{\varphi}}{\partial y_X^{\varphi}} \tag{14}$$

$$\mu_A^{\varphi} = \left(1/a\right)^{\varphi}{}^oG_{A:Va}^{\varphi} + \left(c/a\right)^{\varphi}RT\ln\left(1-y_X^{\varphi}\right) + \left(1/a\right)^{\varphi}\left(y_X^{\varphi}\right)^2 L_{A:X,Va}^{\varphi} \tag{15}$$

$$\mu_X^{\varphi} = \left(1/c\right)^{\varphi}\left({}^oG_{A:X}^{\varphi} - {}^oG_{A:Va}^{\varphi} + L_{A:X,Va}^{\varphi}\right) + RT\ln\frac{y_X^{\varphi}}{1-y_X^{\varphi}} - 2\left(1/c\right)^{\varphi}y_X^{\varphi}L_{A:X,Va}^{\varphi} \tag{16}$$

$$\mu_A^{gb} = \left(1/a\right)^{gb}{}^oG_{A:Va}^{gb} + \left(c/a\right)^{gb}RT\ln\left(1-y_X^{gb}\right) + \left(1/a\right)^{gb}\left(y_X^{gb}\right)^2 L_{A:X,Va}^{gb} \tag{17}$$

$$\mu_X^{gb} = \left(1/c\right)^{gb}\left({}^oG_{A:X}^{gb} - {}^oG_{A:Va}^{gb} + L_{A:X,Va}^{gb}\right) + RT\ln\frac{y_X^{gb}}{1-y_X^{gb}} - 2\left(1/c\right)^{gb}y_X^{gb}L_{A:X,Va}^{gb}. \tag{18}$$

Considering that both y_X^{φ} and y_X^{gb} are quite small, Eq. 5 may be rearranged as

$$\frac{y_X^{gb}}{1-y_X^{gb}} \simeq \frac{y_X^{\varphi}}{1-y_X^{\varphi}} \cdot \exp\left\{\frac{\left(\Delta G_X^{\varphi A} - \Delta G_X^{gbA}\right) + \left({}^\circ G_{A:Va}^{gb} - {}^\circ G_{A:Va}^{\varphi}\right)}{RT}\right\} \tag{19}$$

where

$$\Delta G_X^{\varphi A} = \left(1/c\right)^{\varphi}\left({}^\circ G_{A:X}^{\varphi} - {}^\circ G_{A:Va}^{\varphi} + L_{A:X,Va}^{\varphi}\right) \tag{20}$$

$$\Delta G_X^{gbA} = \left(1/c\right)^{gb}\left({}^\circ G_{A:X}^{gb} - {}^\circ G_{A:Va}^{gb} + L_{A:X,Va}^{gb}\right). \tag{21}$$

When y_X^{α} and y_X^{gb} possess very small values, $y_X^{\varphi} \simeq x_X^{\varphi}$ and $y_X^{gb} \simeq x_X^{gb}$ hold; therefore, the grain boundary solute concentration x_X^{gb} and the segregation energy are given as Eqs. 22 and 23, respectively.

$$x_X^{gb} = \frac{x_X^{\varphi} \cdot \exp\left(\dfrac{\Delta G_X^{\varphi seg}}{RT}\right)}{1 + x_X^{\varphi} \cdot \exp\left(\dfrac{\Delta G_X^{\varphi seg}}{RT}\right)} \tag{22}$$

$$\Delta G_X^{\varphi seg} \equiv \left(\Delta G_X^{\varphi A} - \Delta G_X^{gbA}\right) + \left({}^\circ G_{A:Va}^{gb} - {}^\circ G_{A:Va}^{\varphi}\right) \tag{23}$$

3.3. Calculation of segregation energy

Using Eqs. 12 and 23, $\Delta G_X^{\varphi seg}$ was calculated based on the available thermodynamic parameters of the binary systems [4-14]. The experimental measurements of the segregation energy ΔE_X^{gb} are compared with these results in Table 1, where the thermodynamic parameters of the liquid phase are substituted for those of the grain boundary. Although the models employed in sections 3.1 and 3.2 are rather simplified, a good agreement was observed between the calculated $\Delta G_X^{\varphi seg}$ and the published segregation energy ΔE_X^{gb}.

Table 1. Comparison of experimental segregation energy ΔE_X^{gb} with calculated $\Delta G_X^{\varphi seg}$.
The ΔE_X^{gb} values in this table were summarized by Lejček [15].

Elements	Temp. (K)	ΔE_X^{gb} (kJ/mol)	$\Delta G_X^{\alpha seg}$ (kJ/mol) at 800 K / $\Delta G_X^{\gamma seg}$ (kJ/mol) at 1200 K	Elements	Temp. (K)	ΔE_X^{gb} (kJ/mol)	$\Delta G_X^{\alpha seg}$ (kJ/mol) at 800 K / $\Delta G_X^{\gamma seg}$ (kJ/mol) at 1200 K
P	853	50	44	Mn	823	8	5
	773	44 to 33.5			723–923	5.4	2
	873	53.1		Mo	773	11.8 to 8.8	15
	973	55.2			823	0	
	–	55.5	50		–	50	11
	873	43.1			1073	28	
	823	46.6		Cr	823	0	15
	723–1173	47			853	20	10
Si	1073	17	17	Nb	1073	38	52
							42
	823	15.1	49	B	673	39	76
	823	17			673	44	
S	823	51.5	63		673	30 to 34	

	873	141.1			673	49	101
	973	163.9	63		1073	100	
	1143	75			873	75	62
Sn	823	44	19	C	–	92.4	
	823	45.3			873	76	19
	1693	103	11	Cu	–	–	5
Ni	823	14.4	17		–	–	8
	823	3	2				

4. CONSTRUCTION OF GRAIN BOUNDARY STRUCTURE USING MOLECULAR DYNAMICS SIMULATION

From the above discussion, the grain boundary energy and the energy of the liquid phase were shown to have approximately equivalent values. It is well known that the structures of liquid metals can be generally described by dense random packing of arrays of rigid spheres. According to the X-ray structural analysis, polyhedral structures composed of solvent atoms are observed in liquid alloys; these polyhedra show several vacancies or holes [16]. The solute atoms with appropriate atomic sizes will occupy these holes and the thermodynamic stability of the polyhedral cluster is accounted for by the formation of a local ordered structure between solvent and solute atoms. Considering its structural similarity between its amorphous phase and grain boundary, the same stabilization mechanism could be applied to grain boundary segregation. We then attempted to construct grain boundary structures using molecular dynamics (MD) simulation and used the first-principles method to calculate the thermodynamic stability of the polyhedral structure.

In the present study, our target was the random grain boundary of bcc Fe. First, two α-Fe cells were pasted at the grain boundary: one grain was tilted by 15 degrees clockwise, while the other was tilted by 15 degrees anticlockwise where the rotation axis is parallel to the boundary plane. Furthermore, the right-hand cell was twisted by 14 degrees where the rotation axis is perpendicular to the boundary plane in order to produce randomness in the atomic configuration at the grain boundary. The structure was then annealed to relax the distortion accumulated in the boundary. The Ackland potential [17] was used in the MD simulation with several variations of the annealing temperatures. Figure 1 visualizes

Fig. 1 Grain boundary structures were constructed by
(a) annealing at 300K
(b) annealing at 1000K after melting at 3000K
(c) annealing at 300K after following the method (b).

the grain boundary layer by counting the coordination numbers around vacancies; i.e., the brighter the colour, the higher the coordination number. Specifically, the blue atoms have 8 coordination numbers, which are equivalent to bcc; however, atoms with higher coordination numbers exist in the grain boundary layer.

The Fe polyhedral structures extracted from the grain boundary layers show typical polyhedral structures, i.e., hexahedron, octahedron, and decahedron. These types of polyhedral structures can often be observed in bcc structure. However, tetra dodecahedron was also found in the structure, which is the same as the structure found by Bernal [18] in amorphous alloys. This structure is rare in crystal structures and peculiar to amorphous alloys. According to the results, we supposed that an amorphous-like random structure was created for grain boundary layers in the present study. We then attempted to calculate segregation energies when a solute atom is located in the centre of the polyhedral structure. The procedure is as follows: some regions around a polyhedral structure were truncated into spherical shapes and the energies between the two states where a solute atom is inside and outside the polyhedral structure were compared based on the first-principles calculation. In the comparison, only atoms next to the vacancy site were relaxed and the other atoms were fixed to their

original positions. In this calculation, three different diameters for vacancies in polyhedra were considered, i.e., 2.095, 1.837, and 1.609 Å. The number of surfaces for each polyhedral structure is 12. The segregation energies depending on vacancy diameter were calculated for C, B, P, Ni, Cu, and Mo. The segregation energies vary with the size of vacancies; therefore, the observed segregation energies are supposed to be determined by a product of the frequency factor of formation for vacancies and their segregation energies. Irrespective of the absolute values for segregation energies, a good agreement was observed between the calculation and experiments. Therefore, we concluded that grain boundary segregation could be understood as a process for alloying elements located in a properly sized vacancy in the grain boundary of a polyhedral structure, which forms a local ordered structure with the surrounding atoms.

5. CONCLUSIONS

In the present study, the regular solution approximation was applied to calculate grain boundary segregation in iron. The Gibbs energy of the liquid phase in a system was adopted to that for the grain boundary, considering the structural analogy between the amorphous state and a grain boundary composed of simple structural units. A good agreement in segregation behaviour between our calculations and experiments was found. In addition, MD simulation was used to construct a grain boundary structure and the properties of polyhedral structures were analyzed. According to the present analysis, the grain boundary segregation in iron could be understood as a process for alloying elements located in a properly sized vacancy in the grain boundary of a polyhedral, which forms a local ordered structure with the surrounding iron atoms.

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