Paper

Excess Volume in Grain Boundary Segregation

Pavel Lejček,[1]* Lei Zheng[2] and Ye Meng[2]

1Laboratory of Nanostructures and Nanomaterials, Institute of Physics, AS CR, Na Slovance 2,
182 21 Prague 8, Czech Republic
2School of Mater. Sci. Eng., University of Science and Technology Beijing, 100083, Beijing, China

*lejcekp@fzu.cz

Segregation volume is an important quantity controlling the pressure effect on grain boundary chemistry. In the present paper, we define molar segregation volume on basis of fundamental thermodynamics and evaluate it for example of phosphorus and sulfur grain boundary segregation in low-alloy ferritic steels including its development during non-equilibrium segregation under tensile and compressive deformations. We also show expected effect of anisotropy on equilibrium segregation under pressure.

Dedicated to Prof. Siegfried Hofmann on occasion of his 75th birthday

1. Introduction

Grain boundary segregation is a phenomenon affecting many materials properties e.g. cohesion and recrystallization [1]. For its theoretical representation, mainly the Langmuir–McLean segregation isotherm has been used as it operates with thermodynamic quantities like Gibbs energy, enthalpy and entropy [1,2]. Unfortunately, no sufficient information has been published about *segregation volume*, ΔV_I, although it controls the grain boundary segregation under pressure or deformation [1]. Lojkowski *et al.* [3,4] mentioning this quantity in connection to the grain boundary diffusion and wetting under pressure, correctly define ΔV_I as the difference of the crystal volume with the solute segregated at the grain boundary and that without segregation,

$$\Delta V_I = \alpha(V_I^{GB} - V_M^{GB} + V_M - V_I + V_r),\qquad(1)$$

where V_j^{ξ} is the molar volume of component j ($j = I$, M) at state ξ (ξ=grain boundary (GB) or bulk), V_r is the contribution of changed grain boundary structure due to segregation, and α is the relaxation factor [3,4]. Zhang and Ren [5] define ΔV_I as the difference of partial molar volumes of solute I at the grain boundary and in bulk that is not completely correct as they omit

the effect of the host component, M.

Here, we define the segregation volume, evaluate it for real systems and analyze various effects on this quantity.

2. Segregation Volume: Definition

The Langmuir–McLean segregation isotherm relates the grain boundary concentration of solute I, X_I^{GB}, to its bulk concentration, X_I^B, [1]

$$\frac{X_I^{GB}}{X^0 - \sum_{j=1}^{M-1} X_j^{GB}} = \frac{X_I^B}{1 - \sum_{j=1}^{M-1} X_j^B}\exp\left(-\frac{\Delta G_I}{RT}\right)\qquad(2)$$

where ΔG_I is the molar Gibbs energy of segregation of I, X^0 is the grain boundary saturation. ΔG_I is principally composed of two terms, the *standard* molar Gibbs energy of segregation [1,2], ΔG_I^0, representing the segregation in an ideal system, and the partial molar *excess* Gibbs energy of segregation, $\Delta \overline{G}_I^E$, controlled by the difference between the real and ideal behavior, $\Delta G_I = \Delta G_I^0 + \Delta \overline{G}_I^E$. ΔG_I^0 is combination of the standard chemical potentials, $\mu_j^{0,\zeta}$,

$$\Delta G_I^0 = \left(\mu_{I(M)}^{0,GB} - \mu_{I(M)}^{0,B}\right) - \left(\mu_M^{0,GB} - \mu_M^{0,B}\right)\qquad(3)$$

The standard state is chosen to be pure substance (*M,I*) at temperature, normal pressure and *structure of the host M, both in the bulk and at the grain boundary.* $\Delta \overline{G}_I^{\,E}$ is defined as

$$\Delta \overline{G}_I^{\,E} = RT \ln \frac{\gamma_I^{GB} \gamma_M^B}{\gamma_I^B \gamma_M^{GB}} \qquad (4)$$

where γ_i^{ζ} are the activity coefficients.

Application of fundamental thermodynamic relationship to the grain boundary segregation provides us with

$$d\Delta G_I = -\Delta S_I \, dT + \Delta V_I \, dP + \sum_{j,\xi} \mu_j^{\xi} dX_i^{\xi} + \sigma dA \quad (5)$$

where σ is the grain boundary energy, *A* is the grain boundary molar area, ΔS_I is the molar segregation entropy involving all contributions except the configuration one [1,2]. According to Eq. (5) the *molar segregation volume, ΔV_I,* is defined as

$$\Delta V_I = \left(\frac{\partial \Delta G_I}{\partial P} \right)_{T,A,X_i^{\xi}} \qquad (6)$$

ΔV_I is constructed in the same way as other segregation quantities,

$$\Delta V_I = \left(V_I^{GB} - V_I^B \right) - \left(V_M^{GB} - V_M^B \right) \qquad (7)$$

Equation (7) is very similar to Eq. (1) in [3], if α and V_r are inherently incorporated in the terms of Eq. (7).

Similarly to ΔG_I, ΔV_I consists of two parts, the standard molar segregation volume, ΔV_I^0, and the partial molar excess segregation volume, $\Delta \overline{V}_I^{\,E}$, $\Delta V_I = \Delta V_I^0 + \Delta \overline{V}_I^{\,E}$. Accepting the chosen standard state,

$$\Delta V_I^0 = \left(V_{I(M)}^{0,GB} - V_{I(M)}^{0,B} \right) - \left(V_M^{0,GB} - V_M^{0,B} \right) \equiv 0$$

as $V_{I(M)}^{0,GB} \equiv V_M^{0,GB}$ and $V_{I(M)}^{0,B} \equiv V_M^{0,B}$ Therefore, all contributions to ΔV_I originate from the real behavior of the system, i.e. $\Delta V_I = \Delta \overline{V}_I^{\,E}$,

$$\Delta V_I = \Delta \overline{V}_I^{\,E} = \left(\overline{V}_I^{GB} - \overline{V}_I^B \right) - \left(\overline{V}_M^{GB} - \overline{V}_M^B \right) \qquad (8)$$

where $\overline{V}_j^{\xi}$ are the partial molar volumes of components *j* at states ξ. The pressure effect on grain boundary segregation can be expressed as

$$\frac{X_I^{GB}(P)}{X^0 - \sum_{j=1}^{M-1} X_j^{GB}(P)} =$$

$$\frac{X_I^{GB}(P = P_0)}{X^0 - \sum_{j=1}^{M-1} X_j^{GB}(P = P_0)} \exp\left[-\frac{(P - P_0)\Delta \overline{V}_I^{\,E}}{RT} \right] \qquad (9)$$

which is principally similar to Eq. (4) in [5].

3. Segregation Volume: Evaluation

The relationship between $\Delta \overline{V}_I^{\,E}$ and pressure dependence of X_I^{GB} for binary *M–I* system is obtained from Eqs. (2) and (6) as

$$\Delta \overline{V}_I^{\,E} = -\frac{RTX^0}{X_I^{GB}(X^0 - X_I^{GB})} \frac{dX_I^{GB}}{dP} \qquad (10)$$

Equation (10) may be simplified by $X^0 = 1$ which is often used in quantification of grain boundary segregation [1]. According to Eq. (10), $\Delta \overline{V}_I^{\,E}$ can be obtained from experimental data on pressure/stress dependence of X_I^{GB}. For example, Shinoda and Nakamura [6] studied the effect of applied elastic stress of 30 MPa on P grain boundary segregation at 773 K in a 0.05 wt% P-doped low-alloy steel by AES. From the Auger peak-to-peak ratios [6] X_P^{GB} was determined according to [7,8] as 30.3 at% under normal pressure and 30.8 at.% in stressed sample after equilibration supposing simplification of the alloy to binary Fe–P system (Fig. 1). According to Eq. (10), $\Delta \overline{V}_P^{\,E} \approx -5.1$ ml/mol. On the other hand, no change of X_P^{GB} was
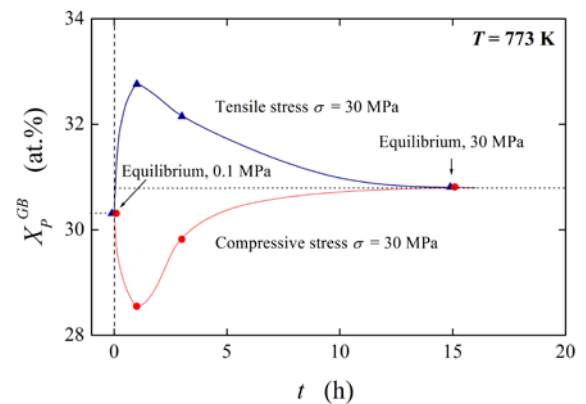

Fig. 1   Time dependence of X_P^{GB} in a 0.05 wt% P-doped low alloy steel at 773 K under tensile (▲) or compressive (●) stress of 30 MPa (cf. [6]).

observed in 2.25Cr1Mo steel [9] under the stress of 40 MPa at 793 K which implies ideal behavior, $\Delta \overline{V}_P^E = 0$. Surprisingly, the same conclusion results for this system loaded by 100, 200 and 350 MPa which all cause plastic deformation of the material. An increase of X_S^{GB} by 0.3 at.% was observed by Misra [10] in S-doped low-alloy steel stressed plastically at 883 K by 343 MPa, providing the value $\Delta \overline{V}_S^E \approx -5.5$ ml/mol.

The value of $\Delta \overline{V}_I^E$ can also be estimated in other ways. First, for Eq. (7), $V_{Fe}^B = 7.1 \times 10^{-6}$ m³/mol if pure Fe substitutes the 2.6NiCrMoV steel. As the average boundary density is of about 50% of the bulk density [11], $V_{Fe}^{GB} = 1.42 \times 10^{-5}$ m³/mol. Based on the density of FeS (4.82 g/cm³ [12]), $V_S^{GB} = 1.76 \times 10^{-5}$ m³/mol if GB is regarded as a Fe–48at%S since the atomic fraction of S in 2.6NiCrMoV is 48at% after stress-aging for 20 h [13]. Then $V_S^B = 0.002 \times V_{Fe}^B = 1.4 \times 10^{-9}$ m³/mol, and $\Delta \overline{V}_S^E = 1.0 \times 10^{-5}$ m³/mol. On the other hand, the values of $\Delta \overline{V}_S^E = -8.1 \times 10^{-6}$ m³/mol, $\Delta \overline{V}_P^E = -3.0 \times 10^{-6}$ m³/mol and $\Delta \overline{V}_{Se}^E = -3.0 \times 10^{-6}$ m³/mol were calculated using the density functional theory technique for segregation of S, P and Se, respectively, at {012} grain boundary in Ni [14]. The values of $\Delta \overline{V}_I^E$ of the order of 10^{-6} to 10^{-5} m³/mol are low. It suggests that the pressure dependence of ΔG_I and therefore, of X_I^{GB} is weak (cf. Eq. (9)). Even the value $\Delta \overline{V}_I^E \approx -1 \times 10^{-5}$ m³/mol under pressure/stress of 100 MPa causes reduction of ΔG_I by −1 kJ/mol, representing a change of X_I^{GB} by units of percents. This explains why X_I^{GB} measured under pressure differs only slightly from that detected under normal pressure [6,15,16].
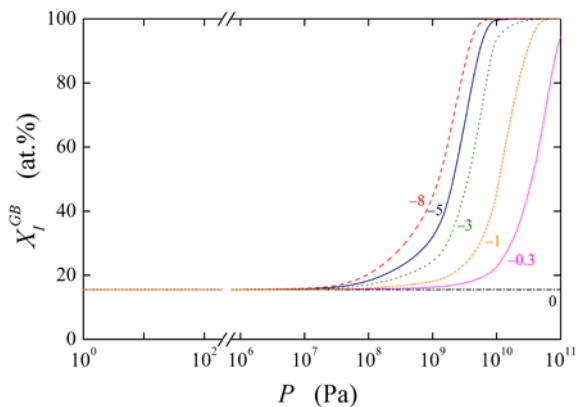

Fig. 2   Dependence of X_I^{GB} in a model *M–I*(0.01 at%) alloy at 800 K under hydrostatic pressure for various values of $\Delta \overline{V}_I^E$ (in ml/mol) as indicated.

The effect of $\Delta \overline{V}_I^E$ on X_I^{GB} can be demonstrated on a model example. Supposing the values of the standard enthalpy, entropy of segregation of *I*, and bulk concentration to be $\Delta H_I^0 = -30$ kJ/mol, $\Delta S_I^0 = +25$ J/(mol.K) (representing e.g. P segregation in b.c.c. Fe [1]), and $X_I = 0.0001$ (i.e. 0.01 at.%), respectively, $X_I^{GB}(0) = 0.1554$ (i.e. 15.54 at.%) under normal pressure at $T = 800$ K, accepting $X^0 = 1$ in Eq. (9). The pressure dependence of calculated grain boundary concentration is plotted in Fig. 2 for the values of $\Delta \overline{V}_I^E$ ranging from −8 ml/mol to 0. Figure 2 clearly documents that the changes of X_I^{GB} appear when the pressure is higher than 10 MPa: at much higher pressures the increase of X_I^{GB} becomes steep. It confirms that the effect of elastic deformation on grain boundary segregation is small but shows clearly that X_I^{GB} significantly changes with increasing pressure beyond the elastic limit. During high hydrostatic pressure this effect is rather large: In this case, X_I^{GB} should reach the values up to 1 (i.e. 100 at.%, cf. Fig. 2).
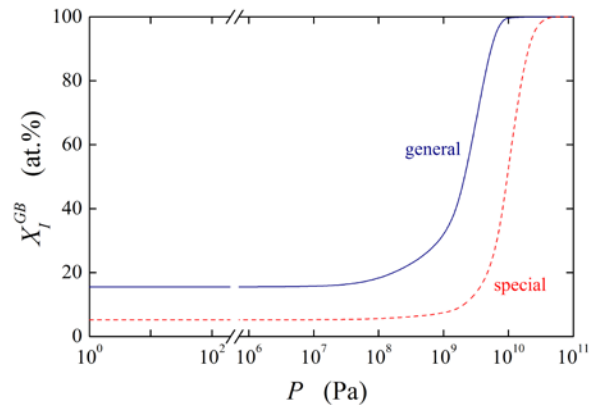

Fig. 3   Dependence of X_I^{GB} at special (red, dashed line) and general (blue, full line) grain boundaries in a model *M–I*(0.01 at%) alloy under hydrostatic pressure at 800 K. See text for details.

Similarly to other thermodynamic quantities of segregation [1] we may suppose existence of anisotropy of $\Delta \overline{V}_I^E$. We may rationally expect that brittle fracture of polycrystals, which has been used for determination of X_I^{GB} by means of AES, opens predominantly general boundaries with high tendency to embrittlement. Therefore, we may ascribe the above mentioned value $\Delta \overline{V}_P^E = -5.1 \times 10^{-6}$ m³/mol, determined for P grain boundary segregation in a 0.05 wt% P-doped low alloy steel at 773 K under tensile or

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P. Lejček et al.   Excess Volume in Grain Boundary Segregation

compressive stress of 30 MPa [6] to general grain boundaries. As its value is negative, the values of $\Delta \overline{V}_P^E$ for special grain boundaries must be higher (i.e. of lower absolute values). In our model calculation we assumed the values of the thermodynamic parameters of segregation of I to be $\Delta H_I^0 = -30$ kJ/mol, $\Delta S_I^0 = +25$ J/(mol.K) and $\Delta \overline{V}_P^E = -5 \times 10^{-6}$ m^3/mol for general grain boundary, and $\Delta H_I^0 = -10$ kJ/mol, $\Delta S_I^0 = +40$ J/(mol.K) and $\Delta \overline{V}_P^E = -2 \times 10^{-6}$ m^3/mol for special grain boundary. For $X_I = 0.0001$, the pressure dependence of X_I^{GB} for both types of the grain boundaries at 800 K is shown in Fig. 3. As expected, the segregation is lower at the special boundary compared to the general one. The concentration change at the special grain boundary requires higher pressure. In both cases, however, complete saturation of the grain boundary is reached under ultimate pressures.

4. Conclusions

For the first time, the segregation volume, ΔV_I, was thermodynamically defined in this paper. It is shown that the standard molar segregation volume, $\Delta V_I^0 \equiv 0$ at any temperature while the other component of ΔV_I, the excess molar volume of segregation $\Delta \overline{V}_I^E \neq 0$ in real systems. It implies that the grain boundary concentration, X_I^{GB}, in real systems is affected by pressure. A fundamental relationship between $\Delta \overline{V}_I^E$ and the pressure change of X_I^{GB} was derived. The values of $\Delta \overline{V}_I^E$ were determined for example of P and S grain boundary segregation under stress in bcc-Fe based systems. It was shown that $\Delta \overline{V}_I^E$ plays an important role in this kind of studies. The effect of anisotropy of $\Delta \overline{V}_I^E$ is also proposed.

6. References

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