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THE INFLUENCE OF INTERFACIAL COHERENT ENERGY ON THE THEORY OF GRAIN BOUNDARY SEGREGATION

L.-S. Chang[1], C.-H. Yeh[1] and B.B. Straumal[2]

[1]Department of Materials Science and Engineering, National Chung Hsing University, 40227, Taichung, Taiwan, ROC

[2]Institute of Solid State Physics, Russian Academy of Science, Chernogolovka, Russia

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Abstract. Grain boundary (GB) segregation in binary systems was traditionally classified into two types: the Langmuir-McLean (LM) and Fowler-Guggenheim (FG) types which differ in the continuity of temperature- or concentration-dependence of impurity amount at GBs. In the LM type, the segregation energy changes with concentration so radically that a sudden jump in enrichment with temperature or concentration can be seen. The concentration-dependent segregation energy is derived from nonzero interchange energy in GBs. In this aspect, a system with high tendency of de-mixing is believed to possess the LM type of GB segregation. However, the FG type had also been observed in some systems with high tendency of de-mixing and sometimes even both types can be found in a single binary system. In this work, a new energetic term, the interfacial coherent energy, which has not been considered previously in the literature, was introduced into the theory of GB segregation and a more general isotherm was obtained. It was suggested from this new isotherm that a binary system with solute segregation less than one monolayer at general GBs obey the LM type, no matter how high the interchange energy is. That means, the introduction of the interfacial coherent energy eliminates the contribution of interchange energy in grains with that in GBs. In this paper, it was shown that this theoretical prediction agrees well with published data in the GB segregation in some Cu alloys. It must be mentioned that this work is not aimed at the overthrow of the application of the FG type which is beneficial in its simplicity.

1. INTRODUCTION

Grain boundary segregation discovered more than a century ago plays an important role in the modern materials engineering and become a key issue in the so-called grain boundary engineering [1]. For example, the well control of grain boundary segregation strongly enhances the fracture strength and toughness of traditional steel tools [2] and improves the carrier lifetime in solar cells [3]. The equilibrium thermodynamics offers a quantitative fundamental for describing the temperature- and concentration-dependence of impurity enrichment at grain boundaries (GBs). There are two different approaches to derive the isotherm for grain boundary segregation [4,5]. Both approaches start from the equalization of chemical potential, but Hondros and Seah took the equilibrium criterion for bulk phase and du Plessis proposed an equation via the position exchange of a host atom and an impurity atom in grains and GBs. The general segregation isotherm from both approaches is

$$\frac{c^{\Phi}}{1-c^{\Phi}} = \frac{c^{B}}{1-c^{B}} \exp\left(-\frac{\Delta G_{seg}}{RT}\right) = \frac{c^{B}}{1-c^{B}} \exp\left(-\frac{\Delta H_{seg}}{RT}\right) \exp\left(\frac{\Delta S_{seg}}{R}\right), \quad (1)$$

Corresponding author: L.-S. Chang, e-mail: lschang@dragon.nchu.edu.tw

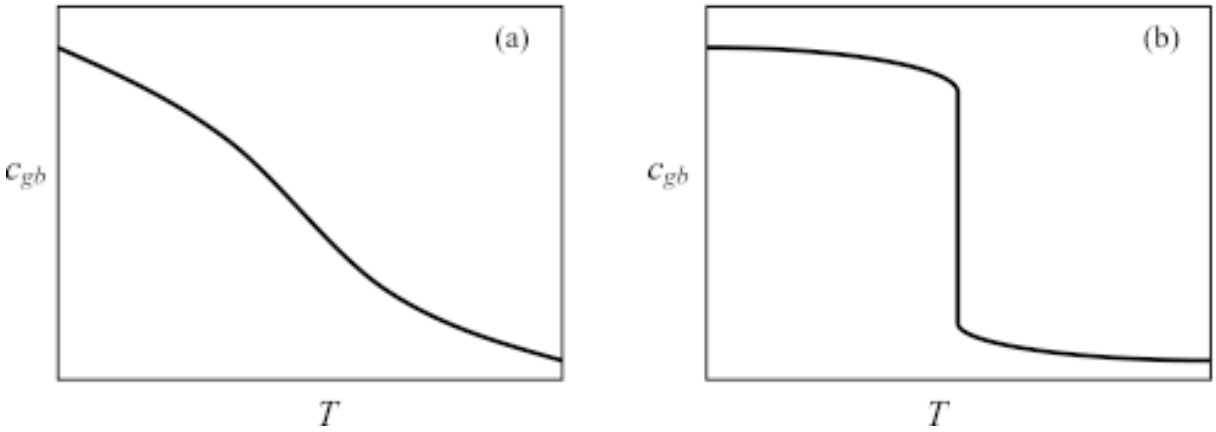

Fig. 1. Schemes of segregation types: (a) Langmuir-McLean type, (b) Fowler-Guggenheim type.

where c^{Φ} and c^{B} are the impurity concentrations in GBs and in bulk, ΔG_{seg} is the Gibbs segregation free energy or the segregation energy, ΔH_{seg} and ΔS_{seg} are the segregation enthalpy and entropy respectively. R and T have their usual meanings.

According to Eq.(1), GB segregation in binary systems was traditionally classified into two types: the Langmuir-McLean (LM) and Fowler-Guggenheim (FG) types which differ in the continuity of temperature- or concentration-dependence of impurity amount at GBs. The schemes of both types are plotted as Fig. 1. In the FG type, the segregation energy ΔG_{seg} changes with the impurity concentration in GBs c_{gb} so radically that a sudden jump in enrichment with temperature or concentration can be seen. Normally, a linear relation between ΔG_{seg} and c_{gb} is applied. The concentration-dependent segregation energy is derived from non-zero interchange energy in GBs. In this aspect, a system with high tendency of de-mixing is believed to possess the FM type of GB segregation. However, both the LM and FG types had been observed in the Cu–Bi and Ni–Bi binary systems which show high tendency of de-mixing [6,7]. Besides, since the discovery of the abrupt change of GB segregation in the Cu–Bi system, no other binary system except the Ni–Bi system has found showing the FG type. Both facts reveal that the FG type possesses merely a mathematic description of GB segregation.

In this work, a new energetic term, the interfacial coherent energy, which has not been considered previously in the literature, was introduced into the theory of GB segregation and a modified isotherm was obtained with which the vagueness between the LM and FG type could be rid.

2. THEORETICAL DERIVATION

As mentioned previously, the segregation isotherm, Eq. (1), can be derived from two different approaches in which the bulk and GB phases are considered independent, i.e. the thermodynamic properties of these phases depend only on their own variables. However, if one takes the plane between the bulk and GB phases into consideration, there is an essential energetic contingent which relies on the concentrations of both phases. This energetic term is the interfacial coherent energy [8] which can be written as

$$\Delta G_c^S = \Omega^S \left(c^{\Phi} - c^{B}\right)^2 \tag{2}$$

for a binary system, where Ω^S is the interchange energy on the plane. Now let us consider a polycrystalline binary alloy containing totally N atoms and n impurity atoms. The subscript symbols i and m refer to the impurity and matrix atoms, while the superscript symbols B, Φ and S indicate the bulk, GBs and plane between bulk and GB phases, respectively. The total Gibbs free energy of the alloy is

$$G' = N^B G_m^{B0} + N^{\Phi} G_m^{\Phi 0} + n^B \left(G_i^{B0} - G_m^{B0}\right) + n^{\Phi}\left(G_i^{\Phi 0} - G_m^{\Phi 0}\right) + N^B \Delta G_{mix}^B + N^{\Phi} \Delta G_{mix}^{\Phi} + 2N^S \Delta G_c^S. \tag{3}$$

All symbols have their usual thermodynamic meanings. Both the grain and GB phases are taken as regular solutions. From the total differential of G to n^{Φ}, one can get

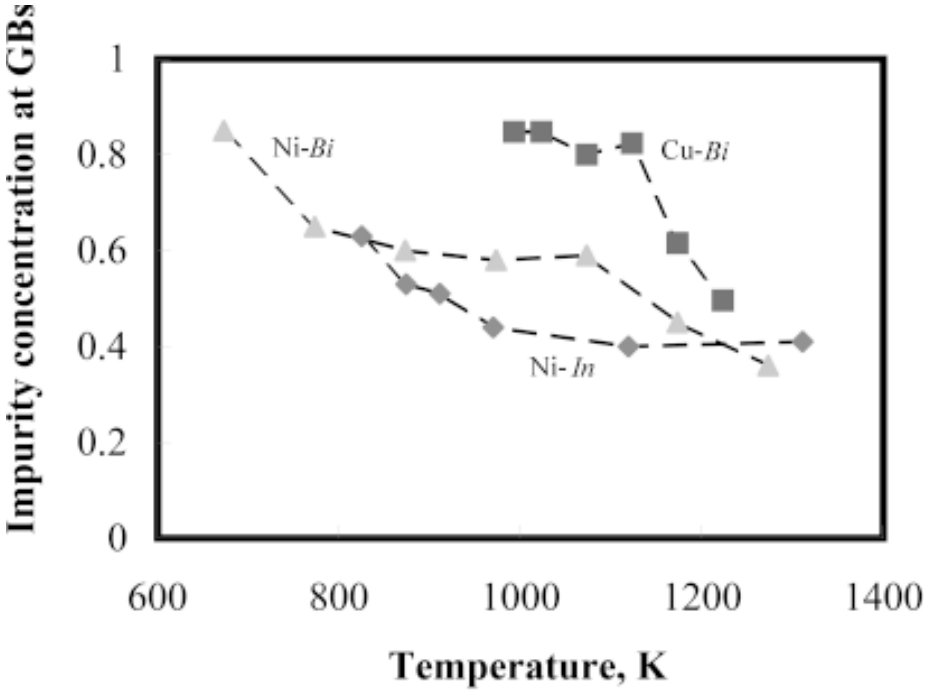

Fig. 2. Impurity concentration in GBs in various binary alloys in terms of annealing temperature.

$$\frac{c^{\Phi}}{1-c^{\Phi}} = \frac{c^{B}}{1-c^{B}} \exp\left[-\frac{\left(\Delta G^{0} - \Omega^{B} + \Omega^{\Phi}\right)}{RT} + \frac{2\left(\Omega^{\Phi} - 2\Omega^{S}\right)c^{\Phi}}{RT} \right]. \quad (4)$$

The interchange energy on the plane Ω^S is defined as $N^S Z_v(\varepsilon_{AB} - (\varepsilon_{AA}+\varepsilon_{BB})/2)$, where Z_v is the coordination number toward the atoms in the adjacent plane and ε is the binding energy. In general, Z_j is about a quarter of the total coordination number in the bulk and $\Omega^S = \Omega^B/4$. For the interchange energy in GBs Ω^{Φ}, an estimation is done as following.

The GB phase is assumed as a homogeneous thin region with a thickness of h monolayers. All atoms in this region have the same coordination number Z which can be divided into three parts: that between atoms inside the same layer (lateral) Z_l, that toward the atoms in the adjacent layer in the GB region (vertical) Z_v and that toward the atoms outside the GB region (outside) Z_{out}. When the GB region is composed of N_i i atoms, the enthalpy is

$$H_i^{\Phi} = \frac{N_i Z}{2}\varepsilon_{ii} + 2\frac{N_i}{h}Z_{out}\varepsilon_{io} - \frac{N_i}{h}Z_v\varepsilon_{ii}. \quad (5)$$

The enthalpy for a binary GB containing N_A A atoms and N_B B atoms ($N_A + N_B = N$) is

$$H_{AB}^{\Phi} = \frac{N_A N_B}{N}Z\varepsilon_{AB} + \frac{N_A N_A}{2N}Z\varepsilon_{AA} + \frac{N_B N_B}{2N}Z\varepsilon_{BB} + 2\frac{N_A}{h}Z_{out}\varepsilon_{Ao} + 2\frac{N_B}{h}Z_{out}\varepsilon_{Bo} - \frac{N_A N_B}{hN}Z_v\varepsilon_{AB} - \frac{N_B N_A}{hN}Z_v\varepsilon_{AB} - \frac{N_A N_A}{hN}Z_v\varepsilon_{AA} - \frac{N_B N_B}{hN}Z_v\varepsilon_{BB}. \quad (6)$$

The enthalpy of mixing can be written from Eqs. (5) and (6) as

$$\Delta H_{mix}^{\Phi} = \frac{H_{AB}^{\Phi} - H_A^{\Phi} - H_B^{\Phi}}{N} = c_A^{\Phi}c_B^{\Phi}\left(Z - \frac{2Z_v}{h}\right)\left(\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right). \quad (7)$$

For a single monolayer GB region, i.e $h = 1$, and $Z_v/Z = 1/4$, the enthalpy of mixing is

$$\Delta H_{mix}^{\Phi} = \frac{1}{2}c_A^{\Phi}c_B^{\Phi}\Omega^{B} = c_A^{\Phi}c_B^{\Phi}\Omega^{\Phi}. \quad (8)$$

That means $\Omega^{\Phi} = \Omega^B/2$. Finally, one can get $\Omega^S = \Omega^{\Phi}/2$. The general segregation isotherm Eq. (4) is simplified accordingly

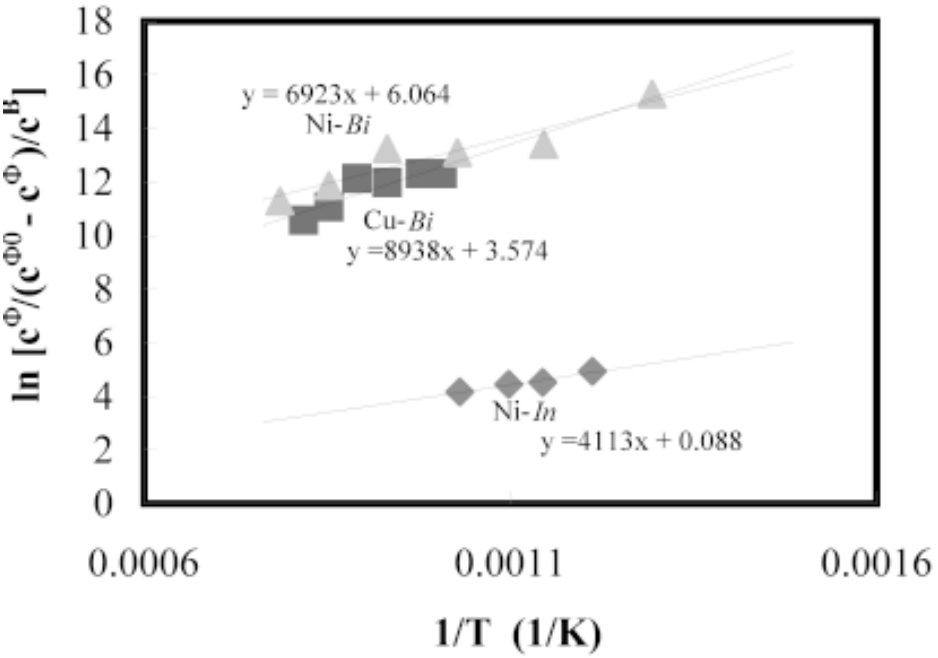

Fig. 3. The diagram of $\ln[c^{\Phi}/(c^{\Phi 0}-c^{\Phi})/c^{B}]$ vs. $1/T$.

$$\frac{c^{\Phi}}{1-c^{\Phi}} = \frac{c^{B}}{1-c^{B}} \exp\left(-\frac{\Delta G^{0} - \Omega^{B} + \Omega^{\Phi}}{RT}\right). \qquad (9)$$

where ΔG^0, Ω^B and Ω^Φ are all concentration independent. This reveals an important speculation that the behavior of GB segregation in all binary elemental systems is LM type, no matter how strong is the de-mixing tendency, as long as the segregation layer is one monolayer thick.

3. EXPERIMENTAL EVIDENCE

To verify this speculation, some binary systems with potentially high de-mixing tendency were examined. Fig. 2 shows the impurity enrichment at GBs in terms of annealing temperature in various binary systems including Cu–Bi [6], Ni–Bi [7], Ni–In [9] where the italic symbols are impurities and the solute concentrations in bulk are 25 at.ppm, 15 at.ppm, and 1.2% respectively. While the differences between atomic volumes of the matrix and impurity atoms exceed 25% of the host atomic volume, a certain de-mixing tendency is expected in these systems. The segregation enthalpies and entropies experimentally determined and elastic energies calculated about these systems are listed in Table 1. The elastic energies associated with one mole of solute were calculated according to the equation proposed by Wynblatt and Ku [10]

Table 1. Segregation enthalpies and entropies experimentally determined and elastic energy in various binary alloys.

System	Cu–Bi	Ni–Bi	Ni–In
ΔH_{seg} [kJ/mol]	–65	–58	–34
ΔS_{seg} [J/mol·K]	30	50	–0.7
E_{el} [kJ/mol]	85	112	22

$$E_{el} = \frac{24\pi N_A K G r_0 r_1 (r_1 - r_0)^2}{3Kr_1 + 4Gr_0}, \qquad (10)$$

where r_0 and r_1 are the radii of solvent and solute atoms respectively, K is the solute bulk modulus, G is the solvent or matrix shear modulus and N_A is the Avogadro's number.

The high values of the elastic energy in these three binary systems in Table 1 indicate that strong de-mixing tendencies may occur and positive large interchange energies in these systems are expected. However, in Fig. 2 no obvious abnormal change of the impurity enrichment at GBs is to observe. To verify the existence of the sudden jump in the temperature range of investigation, the Cu–Bi system is taken because that the interchange

energy in this system has been determined. According to the isotherm of FG type

$$\frac{c^{\Phi}}{1-c^{\Phi}} = \frac{c^{B}}{1-c^{B}} \exp\left(-\frac{\Delta G^{0} - 2\Omega^{\Phi} c^{\Phi}}{RT}\right), \qquad (11)$$

where ΔG is the concentration independent item. Eq. (10) can be rewritten as

$$T = -\frac{\Delta G^{0} - 2\Omega^{\Phi} c^{\Phi}}{R\left[\ln c^{\Phi} - \ln\left(1-c^{\Phi}\right) - \ln c^{B}\right]}. \qquad (12)$$

By differentiating T to c^{Φ} and assuming $c^{\Phi} >> c^{B}$, one gets the criterion for the existence of a sudden jump in the c^{Φ}–T diagram as a following inequality

$$0 > \frac{\Delta G^{0}}{\Omega^{\Phi}} > 1 + \frac{\ln c^{B}}{2}. \qquad (13.1)$$

And the temperature of occurrence is

$$T = \frac{\Delta G^{0} - \Omega^{\Phi}}{R \ln c^{B}}. \qquad (13.2)$$

The segregation energy of the Cu–Bi system is about –100 kJ/mol and the interchange energy at GBs reported in literature is 20 kJ/mol. ΔG^{0} is accordingly about –60 kJ/mol. The fraction $\Delta G^{0}/\Omega^{\Phi}$ is –3. Based on Eq. (13), this value lies within the range of criterion (0, –4.3) and the temperature of a possible jump at concentration is 900K. While this jump is not occur at 900 K due to the high segregation amount even above 1000K, one may conclude that the influence of interchange energy vanishes at the case of a single layer segregation and this may be taken as an evidence of the influence of interfacial coherent energy in the segregation isotherm.

4. SUMMARY

The introduction of the interfacial coherent energy into the energetic consideration about the GB segregation isotherm results in a concentration-independent segregation energy no matter how strong the de-mixing tendency of a binary system may be. In this paper, this hypothesis was indirectly proven by investigating some alloys which show Langmuir-McLean type of GB segregation but, however, possess a high level of elastic energy. It is suggested that the Fowler-Guggenheim equation may have merely a mathematic representation for the GB segregation.

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REFERENCES

[1] P. E. J. Flewitt and R. K. Wild, *Grain Boundaries: Their Microstructure and Chemistry* (Wiley, NY 2001).
[2] R.D.K. Misra // *Surface and Interface Analysis* **31** (2001) 509.
[3] K.-I. Kurobe, M. Miura, K. Hirano and H. Matsunami // *Solar Energy Materials and Solar Cells* **74** (2002) 183.
[4] E.D. Hondros and D. McLean // *Phil. Mag.* **31** (1974) 711.
[5] J. du Plessis // *Defect and Diffusion Data* **11** (1990) 1.
[6] L.-S. Chang, E. Rabkin, B. Straumal, P. Lejceck, S. Hofmann and W. Gust // *Scripta Mater.* **37** (1997) 729.
[7] L.-S. Chang and K.-B. Huang // *Scripta Mater.* **51** (2004) 551.
[8] R. Becker // *Ann. Phys.* **32** (1938) 128.
[9] T. Muschik, W. Gust, S. Hofmann and B. Predel // *Acta metall.* **37** (1989) 2917.
[10] P. Wynblatt and R.C. Ku, In: *Interfacial Segregation*, ed. by W.C. Johnson and J.M. Blakely (ASM, Metal Park, OH, 1979), p. 115.