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

L.-S. Chang¹, C.-H. Yeh¹ and B.B. Straumal²

¹Department of Materials Science and Engineering, National Chung Hsing University, 40227, Taichung, Taiwan, ROC
²Institute 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

\[
\frac{c^e}{1-c^e} = \frac{c^e}{1-c^e} \exp\left(\frac{-\Delta G_{\text{seg}}}{RT}\right) = \frac{c^e}{1-c^e} \exp\left(\frac{\Delta H_{\text{seg}}}{RT}\right) \exp\left(\frac{\Delta S_{\text{seg}}}{R}\right)
\]

(1)
where \(c^b\) and \(c^\Phi\) are the impurity concentrations in GBs and in bulk, \(\Delta G_{seg}\) is the Gibb's segregation free energy or the segregation energy, \(\Delta H_{seg}\) and \(\Delta S_{seg}\) 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 \(\Delta G_{seg}\) 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 \(\Delta G_{seg}\) 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

\[
\Delta G^* = \Omega^* (c^* - c^b)^2
\]

(2)

for a binary system, where \(\Omega^*\) 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 \(B\), \(\Phi\) and \(S\) indicate the bulk, GBs and plane between bulk and GB phases, respectively. The total Gibbs free energy of the alloy is

\[
G' = N^B G^B_m + N^\Phi G^\Phi_m + n^B (G^B_m - G^B_0) + n^\Phi (G^\Phi_m - G^\Phi_0) + N^B \Delta G^B_{mix} + N^\Phi \Delta G^\Phi_{mix} + 2N^K \Delta G^S_{c}
\]

(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 \(n^b\), one can get

\[\text{Fig. 1. Schemes of segregation types: (a) Langmuir-McLean type, (b) Fowler-Guggenheim type.}\]
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Fig. 2. Impurity concentration in GBs in various binary alloys in terms of annealing temperature.

\[ \frac{c^a}{1 - c^a} = \frac{c^b}{1 - c^b} \exp \left[ - \frac{(\Delta G^a - \Omega^a + \Omega^b)}{RT} \right] \]

\[ \frac{2(\Omega^a - 2\Omega^b)c^a}{RT} \]

The interchange energy on the plane \( \Omega^s \) is defined as \( N^s Z^s \nu (\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2) \), where \( Z^s \nu \) is the coordination number toward the atoms in the adjacent plane and \( \varepsilon \) is the binding energy. In general, \( Z \) is about a quarter of the total coordination number in the bulk and \( \Omega^s = \Omega^B/4 \). For the interchange energy in GBs \( \Omega^s \), 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) \( Z_{\nu} \) and that toward the atoms outside the GB region (outside) \( Z_{out} \). When the GB region is composed of \( N_i \) atoms, the enthalpy is

\[ H^i = \frac{NZ}{2} \varepsilon_s + 2 \frac{N}{h} Z_{\nu} \varepsilon_{\nu} - \frac{N}{h} Z_l \varepsilon_s. \] (5)

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

\[ H^B = \frac{N_A N_B}{N} Z_{AB} \varepsilon_{AB} + \frac{N_A N_A}{2N} Z_{AA} \varepsilon_{AA} + \frac{N_B N_B}{2N} Z_{BB} \varepsilon_{BB} + \]

\[ 2 \frac{N_A}{h} Z_{\nu} \varepsilon_{\nu} + 2 \frac{N_B}{h} Z_{\nu} \varepsilon_{\nu} - \frac{N_A N_A}{hN} Z_A \varepsilon_{AB} - \]

\[ \frac{N_B N_B}{hN} Z_B \varepsilon_{BB} \]

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

\[ \Delta H_{mix} = \frac{H_{mix}^B - H_{mix}^A - H_{mix}}{N} \]

\[ c_A^2 c_B \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \]

(7)

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

\[ \Delta H_{mix} = \frac{1}{2} c_A^2 c_B^2 \varepsilon_{AB} = c_A^2 c_B^2 \varepsilon_{AB}. \] (8)

That means \( \Omega^s = \Omega^B/2 \). Finally, one can get \( \Omega^s = \Omega^B/2 \). The general segregation isotherm Eq. (4) is simplified accordingly.
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Table 1. Segregation enthalpies and entropies experimentally determined and elastic energy in various binary alloys.

<table>
<thead>
<tr>
<th>System</th>
<th>Cu–Bi</th>
<th>Ni–Bi</th>
<th>Ni–In</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{seg}$ [kJ/mol]</td>
<td>-65</td>
<td>-58</td>
<td>-34</td>
</tr>
<tr>
<td>$\Delta S_{seg}$ [J/mol·K]</td>
<td>30</td>
<td>50</td>
<td>-0.7</td>
</tr>
<tr>
<td>$E_{el}$ [kJ/mol]</td>
<td>85</td>
<td>112</td>
<td>22</td>
</tr>
</tbody>
</table>

$E_{el} = \frac{24\pi N_A K_G r_1 (r - r_s)^2}{3K_r + 4G r_s}$,  \hspace{1cm} (10)

where $r_1$ and $r_s$ 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...
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energy in this system has been determined. According to the isotherm of FG type

\[
\frac{c^c}{1 - c^c} = \frac{c^g}{1 - c^g} \exp \left( - \frac{\Delta G^g}{RT} \right)
\]

(11)

where \(\Delta G\) is the concentration independent item. Eq. (10) can be rewritten as

\[
T = -\frac{\Delta G^g - 2\Omega^g c^g}{R\left[\ln c^g - \ln(1 - c^g) - \ln c^c\right]}
\]

(12)

By differentiating \(T\) to \(c^g\) and assuming \(c^g >> c^c\), one gets the criterion for the existence of a sudden jump in the \(c^g-T\) diagram as a following inequality

\[
0 > \frac{\Delta G^g}{\Omega^g} > 1 + \frac{\ln c^g}{2}
\]

(13.1)

And the temperature of occurrence is

\[
T = \frac{\Delta G^g - \Omega^g}{R\ln c^g}
\]

(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. \(\Delta G^g\) is accordingly about \(60\) kJ/mol. The fraction \(\Delta G^g/\Omega^g\) 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 \(900\)K. While this jump is not occur at \(900\) K due to the high segregation amount even above \(1000\)K, 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