Size-dependent continuous binary solution phase diagram

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Size-dependent continuous binary solution phase diagram

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Abstract
Size-dependent solution phase diagrams for binary systems are established based on models of size-dependent melting temperature and melting enthalpy of components and a newly developed model for the size-dependent interaction energy. The results show that as the size of the components decreases, the temperatures of solidus and liquidus curves drop and the two-phase zone becomes small. As the size of the components decreases to a critical size, the two-phase zone deteriorates into a curve where the liquid phase and the solid phase are indistinguishable in structure and thus the phase numbers transform from two to one.

1. Introduction

It is well known that the phase transition properties of metallic, semiconductors and organic nanocrystals differ from those of the corresponding bulks; their melting temperature and melting enthalpy decrease with reduction in size when the nanocrystals have free surfaces or are deposited on inert matrices [1–4]. Based on Lindemann’s criterion, a model to interpret these phenomena has recently been developed [5–7]. However, the above work relates to a single component (elements or compounds) and systematic studies of phase equilibria among nanometre-sized components related to phase diagrams are scarce [8, 9]. Study of the nanophase diagram may deepen phase transition theory and extend possible industrial applications. Since the nanophase equilibrium is metastable in nature and is difficult to measure, theoretical work may be an alternative.

To calculate nanophase diagrams, the size dependences of melting temperature and melting enthalpy of components, and that of atomic interaction energy among components, are basic thermodynamic quantities. One consideration of the size effect is to separate the thermodynamic quantities into bulk item and surface items, related to the contribution of the surface/volume ratio [8, 9]. However, when the size of the nanophase decreases to the mesoscopic size range, the size effect becomes stronger than the surface/volume ratio [10]. Moreover, the known studies of the nanophase diagram have neglected the size effect of the atomic interaction energy [8, 9]. Thus, the nanophase diagram needs to be studied further.

Recently, a model without any adjustable parameters for size-dependent melting temperature $T_m(D)$ and size-dependent melting enthalpy $H_m(D)$, based on Lindemann’s melting criterion, was developed where $D$ is the particle diameter [10]. The model predicts an exponential relation between $T_m(D)$ and $1/D$, and the predictions are in agreement with experimental results for metals, semiconductors and organic crystals over the full nanometre size range [5–7, 10]. In this contribution, as well as the introduction of $T_m(D)$ and $H_m(D)$ functions, a model for the size-dependent atomic interaction energy $\Omega(D)$ among components is established. Using the above-mentioned models, the size effects on the solidus and the liquidus curves of some typical binary continuous solution phase diagrams are obtained. The results show that as $D$ decreases, both solidus and liquidus curves drop and the area of the two-phase zone decreases.

2. Model

To make this work more systematic, we first introduce a general thermodynamic frame for a binary regular solution system consisting of components $A$ and $B$. When the liquid and solid of the binary system are in equilibrium, the chemical potentials $\mu$ of component $A$ in both phases are equal, or

$$\mu_A^L = \mu_A^S,$$

where the superscripts $L$ and $S$ denote the liquid and solid phases respectively, and the subscripts $A$ and $B$ denote the

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components (for component B we have the same equation but with subscript B). It is known that

$$
\mu_A^L = G_A^L + RT \ln \alpha_A^L, \quad (2a) \\
\mu_A^S = G_A^S + RT \ln \alpha_A^S, \quad (2b)
$$

where \( \alpha \) is activity, \( R \) denotes the ideal gas constant, \( T \) is temperature and \( G \) shows the molar Gibbs free energies. In equations (2),

$$
G_A^L - G_A^S = G_{mA} = H_{mA} - T S_{mA} = H_{mA} - T H_{mA}/T_{mA} \quad (3)
$$

with \( G_{mA}, H_{mA}, S_{mA} \) and \( T_{mA} \) being the melting Gibbs free energy, melting enthalpy, melting entropy and melting temperature respectively. Combining equations (1)–(3),

$$
\ln(\alpha_A^L/\alpha_A^S) = H_{mA}(T_{mA} - T)/(T_{mA} RT). \quad (4)
$$

Similarly, for component B,

$$
\ln(\alpha_B^L/\alpha_B^S) = H_{mB}(T_{mB} - T)/(T_{mB} RT). \quad (5)
$$

Let \( a_A = f_A x_A \) and \( a_B = f_B x_B \) with activity coefficient \( f \) and atomic percentage \( x \) of a component where \( x_A + x_B = 1 \). For a regular solution, \( \ln a_A = (\Omega / RT) x_A^2 \) and \( \ln a_B = (\Omega / RT) x_B^2 \) in a quasichemical approach where \( \Omega \) is the atomic interaction energy [11]. Substituting the above relations into equations (4) and (5),

$$
H_{mA}(T_{mA} - T)/T_{mA} = \Omega^S (1 - x_A^2) \\
- \Omega^L (1 - x_A^2) + RT \ln(\alpha_A^S/\alpha_A^L), \quad (6)
$$

$$
H_{mB}(T_{mB} - T)/T_{mB} = \Omega^S (x_B^2) \\
- \Omega^L (x_B^2) + RT \ln(1 - x_B^2)/(1 - x_B^2). \quad (7)
$$

When \( T \) is certain, \( x_A^L \) and \( x_A^S \) in a bulk phase diagram are both unique and can be determined through equations (6) and (7) when other quantities are known. Equations (6) and (7) can in return be utilized to determine \( \Omega^S \) and \( \Omega^L \) when \( T \), \( x_A^L \) and \( x_A^S \) are known besides \( H_{mA} \) and \( T_{mA} \). Thus, through taking values of \( T \), \( x_A^L \) and \( x_A^S \) from the corresponding bulk phase diagrams, bulk \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) can be determined through equations (6) and (7). Since \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) are weak functions of composition, to a first-order approximation, \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) will be determined at \( T \approx (T_{mA} + T_{mB})/2 \) in this work with the corresponding \( x_A^L \) and \( x_A^S \) in the bulk phase diagrams. With the determined \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) values (for detailed results see section 3), the bulk phase diagrams are replotted in terms of equations (6) and (7) which are shown in figures 1–5. It can be seen from the figures that the bulk solidus and liquidus curves in the binary regular solution phase diagrams are in agreement with the experimental results. This agreement in return confirms that the fitted \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) values have only minor errors.

The above discussion has introduced how to determine the solidus and liquidus curves in a binary regular solution phase diagram and the method to determine \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) through the known bulk phase diagrams. If \( T_m(D) \) and \( H_m(D) \) of each component and \( \Omega^S(D) \) and \( \Omega^L(D) \) may be determined and substituted for the corresponding bulk values \( T_m(\infty), \ H_m(\infty), \ \Omega^S(\infty) \) and \( \Omega^L(\infty) \) based on equations (6) and (7), nanophase diagrams could be given. The function \( T_m(D) \) has been deduced as [5–7],

$$
T_m(D) = T_m(\infty) \exp \left[ -\frac{2S_{ vib}(\infty)}{3R} \frac{1}{D/D_0 - 1} \right] \quad (8)
$$

where \( S_{ vib}(\infty) \) shows the vibrational part of the overall bulk melting entropy \( S_m(\infty) \) (except for semiconductors, \( S_{ vib}(\infty) \approx S_m(\infty) \)) since the other contributions on \( S_m(\infty) \) are small [6]. \( D_0 \) denotes a critical size where almost all of atoms or molecules are located on the surface. For particles, \( D_0 \) is calculated by [5–7],

$$
D_0 = 6h \quad (9)
$$

where \( h \) is atomic/molecular diameter. For the \( H_m(D) \) function [7],

$$
H_m(D) = H_m(\infty) \left( 1 - \frac{1}{D/D_0 - 1} \right) \times \exp \left[ -\frac{2S_{ vib}(\infty)}{3R} \frac{1}{D/D_0 - 1} \right]. \quad (10)
$$

When \( D = 2D_0, \ H_m(2D_0) = 0 \), which implies that as \( D \to 2D_0 \) where half of the atoms (molecules) of the particles are located on the surface, the solid and the liquid have similar structure [5–7].

It is well known that \( \Delta \Omega = N_v Z[\epsilon_{ AB} - (\epsilon_{ AA} + \epsilon_{ BB})]/2 \) with \( \epsilon \) being interaction bond energy where the subscripts have the same meaning as above. \( N_v \) is Avogadro’s number and \( Z \) the coordinate number of an atom. The values of all \( \epsilon \), which are negative, decrease with reducing \( D \) [15–17]. If rates of decrease of \( \epsilon \) are different, \( \Delta \Omega \) is size dependent. According to general quantum chemistry considerations [17], all thermodynamic quantities are roughly linear functions of \( 1/D \) that corresponds to the surface/volume ratio of particles. It is assumed that \( \Delta \Omega \) has the same relationship. Because \( H_m(2D_0) = 0 \) in terms of equation (10), \( \Delta \Omega \) should have the same limit and is thus assumed to have the following form,

$$
\Delta \Omega(D)/\Delta \Omega(\infty) = 1 - 2D_0/D. \quad (11)
$$

Since \( 2D_0 = 12h \) in terms of equation (9) where \( h \) is component dependent, different components have different \( D_0 \) values and a larger \( h \) value for two components will be taken to calculate \( 2D_0 \), which avoids a physically unreasonable negative \( H_m(D) \) in terms of equation (10) without evident error. In light of equation (11), \( \Omega^S(D) \) and \( \Omega^L(D) \) have the same size dependence and are composition independent to a first-order approximation.

Taking \( T_m(D), \ H_m(D) \) and \( \Delta \Omega(D) \) functions into equations (6) and (7), binary continuous solution nanophase diagrams can be calculated.

3. Results and discussion

Figures 1–5 show continuous solution phase diagrams of different binary systems of metals Cu–Ni, semiconductors Ge–Si, ceramics Al₂O₃–Cr₂O₃ and V₂O₃–Cr₂O₃ and organic crystals p-chlorobromobenzene–p-dibromobenzene in terms of equations (6) and (7). Note that \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) are firstly determined by equations (6) and (7) through introducing the corresponding known bulk phase diagrams [12–14].
Figure 1. Cu–Ni nano and bulk phase diagram where the full curves show the theoretical calculation for a regular solution in terms of equations (6) and (7) and the symbols denote the bulk experimental results [12]. For the necessary parameters see table 1.

Figure 2. Ge–Si nano and bulk phase diagram where the full curves show the theoretical calculation for a regular solution in terms of equations (6) and (7) and the symbols denote the bulk experimental results [12]. For the necessary parameters see table 1.

determine $\Omega_1^L(\infty)$ and $\Omega_1^S(\infty)$. $T = 1573.15$ K, $x_{Ni}^L = 0.45$ and $x_{Ni}^S = 0.57$ are used in calculation in figure 1; $T = 1506.5$ K, $x_{Si}^L = 0.40$ and $x_{Si}^S = 0.73$ in figure 2; $T = 2430$ K, $x_{Cr_2O_3}^L = 0.44$ and $x_{Cr_2O_3}^S = 0.67$ in figure 3; $T = 2357.73$ K, $x_{Cr_2O_3}^L = 0.36$ and $x_{Cr_2O_3}^S = 0.59$ in figure 4 and $T = 347.39$ K, $x_{p-dbb}^L = 0.50$ and $x_{p-dbb}^S = 0.57$ in figure 5. For nanophase diagrams based on equations (6) and (7), $T_m(D)$, $H_m(D)$ and $\Omega(D)$ functions are calculated respectively in terms of equations (8), (10) and (11). Except for figure 2, where $S_{vib}(\infty)$ is cited from [20], $S_{vib}(\infty) \approx S_{m}(\infty) = H_m(\infty)/(n T_m(\infty))$ where $n$ is the number of atoms in a molecule since the unit of $S_{vib}(\infty)$ is J g K$^{-1}$/atom [6]. $n = 1$ in figures 1 and 2; $n = 5$ in figures 3 and 4 and $n = 12$ in figure 5. To determine $2D_0$ in equation (11), larger $h$ values between two component counterparts are always taken in all figures as illustrated above. For molecules, $h = \sqrt{V_c}$ where $V_c$ is volume of the cell [6]. For organic molecules, there is no direct value of $V_c$. $V_c$ is determined by $V_c = M/\rho N_a$ with molecular mass $M$ and density $\rho$. Other necessary parameters during the calculations and the calculated results are shown in tables 1 and 2.

Although the chemical bonds between components in the above phase diagrams are different in nature, our model can be utilized in a unified form. However, the assumption that $\Omega_1$ is composition independent is only valid for the continuous solution phase diagram where the electronegativity difference between two components is small.

As $D$ decreases, solidus and liquidus curves drop since $T_m(D)$ of each component decreases. When $D \rightarrow 2D_0$, $T_m(2D_0) = T_m(\infty) \exp[-2S_{vib}(\infty)/(3R)]$ in terms
Size-dependent continuous binary solution phase diagram

Table 1. Related parameters and data used in figures 1 and 2.

<table>
<thead>
<tr>
<th>$D$ [nm]</th>
<th>$T_m$ [K][18]</th>
<th>$H_m$ [Jmol$^{-1}$][18]</th>
<th>$\Omega^0$ [Jmol$^{-1}$]</th>
<th>$\Omega^+$ [Jmol$^{-1}$]</th>
<th>$\rho_{vib}$ [Jg-atom$^{-1}$K$^{-1}$]</th>
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<td>1959.7</td>
<td>1731.46</td>
<td>1859.8</td>
<td>597.1</td>
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</table>

Table 2. Related parameters and data used in figures 3–5 where $p$-chlorobromobenzene and $p$-dibromobenzene are respectively abbreviated as $p$-cbb and $p$-dbb. To determine the $h$ value, the related data are $V_{cA_2O_3} = 0.2548$ nm$^3$ [21], $V_{cCr_2O_3} = 0.2898$ nm$^3$ and $V_{cV_2O_3} = 0.2974$ nm$^3$ [21], $M_{p-cbb} = 191.46$ g and $\rho_{p-cbb} = 1.576$ g cm$^{-3}$ [23], $M_{p-dbb} = 235.92$ g and $\rho_{p-dbb} = 1.841$ g cm$^{-3}$ [23].

<table>
<thead>
<tr>
<th>$D$ [nm]</th>
<th>$T_m$ [K]</th>
<th>$H_m$ [Jmol$^{-1}$]</th>
<th>$\Omega^0$ [Jmol$^{-1}$]</th>
<th>$\Omega^+$ [Jmol$^{-1}$]</th>
<th>$\rho_{vib}$ [Jg-atom$^{-1}$K$^{-1}$]</th>
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<td>165.96</td>
<td>6.344</td>
</tr>
</tbody>
</table>

of equation (8), which implies that $T_m(2D_0)$ is determined by $T_m(\infty)$ and $S_{vib}(\infty)$. The latter reflects the size of the structural difference between the liquid and the solid. Because $S_{vib}(\infty)$ of semiconductors and organic crystals are small, their drops of $T_m$ are also small.

Another evident change compared with the bulk phase diagram is that the two-phase zone of the nanophase diagram becomes small. As $D \rightarrow 2D_0$, which is about several nanometres, the zone even approaches zero. This is a direct result of $\Omega(2D_0) = 0$ where the regular solution deteriorates into the ideal solution and the structures of the liquid and the solid become similar due to the short-range order.

Note that although a separate surface energy contribution to nanophase equilibrium is not directly considered in our model, the nonlinear relation between $T_m(D)$ and $1/D$ in terms of equation (8) implies that energy change comes not
only from the surface but also from the interior contributions of nanoparticles [10]. Furthermore, since $H_m(D)$ and $\Omega(D)$ functions are size dependent, our model predicts a stronger drop of the solidus and liquidus curves and decrease of the two-phase zone area than other models do [8, 9]. Certainly, some assumptions in our model may lead to minor errors. However, the minor errors do not affect the above two tendencies.

Some experimental studies have given evidence that when the size of components decreases to the nanometre size range, their phase formations, such as eutectic composition and transition temperature, differ from those of the bulk [24, 25]. These experimental results are expected according to the above model and will be considered in our further work.

Since the second-phase strengthening is one of the strengthening methods for all structural materials, the model established in this work could be extended to deal with this kind of problem where only the size of one component decreases and another remains the bulk. In this case, only one component has size-dependent thermodynamic quantities.

4. Conclusion

In summary, a model for the size dependence of the atomic interaction energy between two components in binary systems is presented. Using our model, together with models for the size-dependent melting temperature and size-dependent melting enthalpy, the size dependence of binary regular solution phase diagrams of metals, semiconductors, ceramics and organic crystals are studied and predicted. As the size of the components decreases, the temperatures of the solidus and liquidus curves drop and the area of the two-phase zone decreases.

Acknowledgments

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