Segregation in Fe-Pd melt at 1873 K

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Abstract

The thermodynamic and structural properties of Fe-Pd liquid alloys at 1873 K have been computed using regular associated solution model. To compute these functions we have estimated the mole fractions of the complex assuming the existence of $FePd_3$ complex in the melt. The thermodynamic properties such as free energy of mixing (G_M), heat of mixing (H_M), entropy of mixing (S_M) and activity (a) of the melt have been estimated. To understand the microscopic structural properties, we have estimated the concentration fluctuation in long wavelength limit $(S_{cc}(0))$ and the Warren-Cowley short range parameter (α_1). The free energy of mixing was found to be negative at all compositions. But the heat of mixing and the entropy of mixing are found to be positive at all compositions. The equilibrium constant (K) is found be less than negative. The interaction energy parameters $(w_{12}, w_{13}$ and $w_{23})$ are all found to be positive and temperature dependent. The theoretical estimation of the concentration fluctuation in long wavelength limit $(S_{CC}(0))$ is found to be greater than the ideal values throughout the whole range. The theoretical analysis suggests that the Fe-Pd liquid alloy at 1873 K near the melting point is segregating (homo-coordinating) system. The Warren-Cowley short range order parameter is found to be positive which too suggest the homo-coordinating (segregating) nature of the system at all compositions. The theoretical analysis also suggests that the Fe-Pd liquid alloy near melting point is weakly interacting system.

Keywords: Fe-Pd alloy; Thermodynamic properties; Interaction energy parameters; Equilibrium constant; Segregation.

1. Introduction

A number of researchers of present day are concentrated on developing and devising new alloys to meet the demands of today. The alloys comprises of dynamical properties which leads them to multidisciplinary uses. There also appears keen interest in investigating and developing Fe-Pd alloys as they can be used in shape memory alloys, computational chips, medical purposes and their nanopartiples are used as electro-catalyst for oxygen reduction. The alloys are generally grown from the liquid state at temperatures nearer to their melting points. Thus, the thermodynamic and structural properties of initial melt plays important role in understanding the properties of the solid alloys. Different theories have long been proposed to explain the thermodynamic and microscopic structural properties of binary liquid alloys. In present work we intend to investigate and to understand the thermodynamic and microscopic structural features of Fe-Pd liquid alloys at 1873 K on the basis of regular associated solution model [1-4].

According to the regular associated solution model, the existence of chemical complex in the binary solution of the alloy near to their melting point is assumed. According to this model, binary solution is considered to be the ternary mixture of complexes and unassociated atoms. It is assumed that there appears unequal interaction between the complexes and the unassociated atoms and the equations of the thermodynamic and microscopic structural functions are derived on this basis. It can be seen from the

phase diagram of Fe-Pd [5] the appearance of different phases such as FePd, $FePd_3$, Fe_3Pd. Among the different phases, in this work we have computed the thermodynamic behavior and microscopic structural properties such as concentration fluctuation in long wavelength limit ($S_{CC}(0)$) and Warren-Cowley short-range order parameter (α_1) [6,7] assuming the presence of $FePd_3$ complex in the binary solution of Fe-Pd at 1873 K. We have also computed the activities of the unassociated atoms [8] to investigate the strength of complex in the liquid state and ratio of diffusion coefficients for the greater insight of local ordering in the liquid state. In this model the interaction energy parameters are considered to be temperature dependent.

The formulations used for the calculations are presented in section 2, the results and discussions are presented in section 3 and the conclusions are presented in section 4.

2. Theory

Consider one mole of a liquid binary alloys of the form A-B (A=Pd, B=Fe) which consists of n_1 atoms of species A and n_2 atoms of species B. According to Lele and Ramchandrarao [8], it is assumed that the chemical complexes A_pB ($A_pB <=> pA + B$) exists in the melt, where p is a small integer whose value is determined from the compound forming concentration ($= p/ (p +1)$) in the solid state. Hence, the liquid alloy can be considered to be the ternary mixtures of unassociated atoms A (=Pd), B (=Fe) and the complex A_pB ($= Pd_3Fe$) in tranquility, where p =3. Let n_A, n_B and n_{A_pB} moles are the concentrations of A, B and A_pB in the melt. Then according to the conservation of mass, in the partially associated solution the formation of the complex A_pB requires $n_1 = n_A + pn_{A_pB}$ and $n_2 = n_B + n_{A_pB}$. But the thermodynamic and microscopic structural behaviours of the complexes in the melt are ruled by their true mole fractions X_A, X_B and X_{A_pB} in spite of their gross mole fractions x_1 and x_2, where

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \tag{1}$$

$$x_A = \frac{n_A}{n_A + n_B + n_{A_pB}}, \quad x_B = \frac{n_B}{n_A + n_B + n_{A_pB}} \text{ and } x_{A_pB} = \frac{n_{A_pB}}{n_A + n_B + n_{A_pB}} \tag{2}$$

Then the relation between the two sets of true mole fractions can be derived using the eqns. (1) and (2) as

$$x_A = x_1 - px_2x_{A_pB} \quad \text{and} \quad x_B = x_2 - (1 - px_2)x_{A_pB} \tag{3}$$

Following Jordan [3], the activity coefficients of monomers γ_A, γ_B and γ_{A_pB} and complex can be represented in terms of pairwise interaction energies as

$$\text{RT} \ln\gamma_A = x_B^2 \omega_{12} + x_{A_pB}^2 \omega_{13} + x_B x_{A_pB} (\omega_{12} - \omega_{23} + \omega_{13}) \tag{4}$$

$$\text{RT} \ln\gamma_B = x_{A_pB}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{A_pB}(\omega_{23} - \omega_{13} + \omega_{12}) \tag{5}$$

$$\text{RT} \ln\gamma_{A_pB} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_A x_B(\omega_{13} - \omega_{12} + \omega_{23}) \tag{6}$$

where ω_{12}, ω_{13} and ω_{23} represents the pairwise interaction energies for the species A, B; A, A_pB and B, A_pB respectively. Temperature and universal gas constant are represented by T and R respectively.

Following Lele and Ramchandrarao [8], the equilibrium constant for the reaction $A_pB <=> pA + B$ is given by following equation

$$k = \frac{x_A^p x_B \gamma_A^p \gamma_B}{x_{A_pB} \gamma_{A_pB}} \tag{7}$$

Using Eqs. (3) , (4) and (5), the relation for the equilibrium constant can be obtained as

$$lnk = \ln\left(\frac{x_A^p\, x_B}{x_{A_pB}}\right) + \frac{\omega_{12}}{RT} + \frac{\omega_{12}}{RT}\left[\,px_B\,(1-x_A) + x_A\,\right] + \frac{\omega_{13}}{RT}\left[\,px_{A_pB}\,(1-x_A) - x_A\,\right] +$$
$$\frac{\omega_{23}}{RT}\left[\,x_{A_pB}\,(1-\,px_B) - x_B\right] \tag{8}$$

and the free energy of mixing (G_M) is given as

$$G_M = \frac{1}{1+Px_{A_pB}}\,RT\left[\left(x_Ax_B\frac{\omega_{12}}{RT} + x_Ax_{A_pB}\frac{\omega_{13}}{RT} + x_Bx_{A_pB}\frac{\omega_{23}}{RT}\right) + \left(x_A\ln X_A + x_B\ln X_B + x_{A_pB}\ln X_{A_pB}\right) +$$
$$x_{A_pB}lnk\right] \tag{9}$$

In a regular associated solution model $x_1\gamma_1 = x_A\gamma_A$ and $x_2\gamma_2 = x_B\gamma_B$ where γ_1 and γ_2 are the gross activity coefficients of components 1 and 2 respectively. Hence it follows

$$ln\gamma_1 = ln\gamma_A + \ln\left(\frac{x_A}{x_1}\right) \tag{10a}$$
$$\text{and, } ln\gamma_2 = ln\gamma_B + \ln\left(\frac{x_B}{x_2}\right) \tag{10b}$$

On solving equations (4) and (5), we get

$$\frac{\omega_{13}}{RT} = \frac{x_B\,ln\left(\frac{\alpha_2}{x_B}\right) + (1-x_B)\ln\left(\frac{\alpha_1}{x_A}\right) - x_B\,(1-x_B)\frac{\omega_{12}}{RT}}{x_{A_pB}^2} \tag{11}$$

$$\frac{\omega_{23}}{RT} = \frac{x_A\,\ln\left(\frac{\alpha_1}{x_A}\right) + (1-x_A)\ln\left(\frac{\alpha_2}{x_B}\right) - x_A(1-x_A)\frac{\omega_{12}}{RT}}{x_{A_pB}^2} \tag{12}$$

where α_1 and α_2 are activities of components 1 and 2 respectively.

The pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be written as [2]

$$\ln\gamma_1^0 = \frac{\omega_{12}}{RT} \tag{13a}$$
$$k\,\exp\left(\frac{\omega_{13}}{RT}\right) = \left(\frac{\gamma_1^0\,\gamma_2^0}{\gamma_1^0 - \gamma_2^0}\right) \tag{13b}$$

On solving equations (8) and (13), we obtain

$$lnk + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{A_pB}}\right)\ln\left(\frac{\alpha_1}{x_A}\right) + \frac{x_B}{x_{A_pB}}\left[\ln\left(\frac{\alpha_1}{x_A}\right) - \frac{\omega_{12}}{RT}\right] + \ln\left(\frac{a_1^p a_2}{x_{A_pB}}\right) \tag{14}$$

The other thermodynamic functions such as heat of mixing (H_M), entropy of mixing (S_M) and concentration fluctuation in the long wavelength limit ($S_{CC}(0)$) are corelated with free energy of mixing (G_M) by the following standard thermodynamic relations

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_P \tag{15a}$$
$$S_M = \frac{H_M - G_M}{T} \tag{15b}$$
$$S_{CC}(0) = RT\left(\frac{\partial^2 G_M}{\partial x_1^2}\right)_{T,P}^{-1} \tag{15c}$$
$$S_{CC}(0) = x_2\,\alpha_1\left(\frac{\partial \alpha_1}{\partial x_1}\right)_{T,P}^{-1} = x_1\,\alpha_2\left(\frac{\partial \alpha_2}{\partial x_2}\right)_{T,P}^{-1} \tag{15d}$$

Using equation (9) in equation (15a), the expression for the enthalpy of mixing can be obtained as

$$H_M = \frac{1}{1+px_{A_pB}} \left[\left(x_A x_B \frac{\omega_{12}}{RT} + x_A x_{A_pB} \frac{\omega_{13}}{RT} + x_B x_{A_pB} \frac{\omega_{23}}{RT} \right) - T \left(x_A x_B \frac{\partial \omega_{12}}{\partial T} + x_A x_{A_pB} \frac{\partial \omega_{13}}{\partial T} + x_B x_{A_pB} \frac{\partial \omega_{23}}{\partial T} \right) - RT^2 \frac{dlnk}{dT} \right]$$

(16)

The expression for the concentration fluction in the long-wavelength limit $(S_{CC}(0))$ can be obtained as using equation (9) in equations (15c) and (15d) as

$$S_{CC}(0) = \left[\left(\frac{1}{1+px_{A_pB}} \right) \left\{ \frac{2}{RT} \left(x_A' \ x_B' W_{12} + x_A' x_{A_pB}' W_{13} + x_B' \ x_{A_pB}' W_{23} \right) + \left(\frac{x_A'^2}{x_A} + \frac{x_B'^2}{x_B} + \frac{x_{A_pB}'^2}{x_{A_pB}} \right) \right\} \right]^{-1}$$

(17)

Here, $\frac{\partial^2 G_M}{\partial x_1^2} > 0$ for $\frac{\partial G_M}{\partial x_1} = 0$. The prime denotes the differentiations with respect to concentrations, and x_A' and x_B' are obtained by using Eqn. (3). x_{A_pB}' is obtained using Eqn. (8) by using the condition $\frac{dlnk}{dx_1} = 0$ [10-11]. The factor $(1+ px_{A_pB})^{-1}$, which appears as a coefficient of all terms containing x_A, x_B and x_{A_pB} in Eqn. (9), (16) and (17), is a result of change in the basis for expressing mole fractions of species A, B and A_pB from that used for x_1 and x_2.

The concentration fluctuation in long wavelength limit $(S_{CC}(0))$ helps to understand the nature of atomic order in the binary liquid alloys. At a given concentration, if $S_{CC}(0) < S_{CC}^{id}(0)$ then ordering (unlike atoms pairing) is expected and if $S_{CC}(0) > S_{CC}^{id}(0)$, then segregation (like atoms pairing) is expected, where $S_{CC}^{id}(0) = x_1 x_2$. The experimental values of $S_{CC}(0)$ can be obtained from Eqn. (15d) [12].

Further, the degree of local ordering in the liquid alloys can be studied by estimating Warren-Cowley short range order parameter (α_1) with the knowledge of $(S_{CC}(0))$ [13-14]. The expression for α_1 in terms of $S_{CC}(0)$ is

$$\alpha_1 = \frac{S-1}{S(Z-1)+1} \quad \text{where,} \quad S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)} \quad \text{and } S_{CC}^{id}(0) = x_1 x_2$$

(18)

where Z is the coordination number and Z= 10 is taken for our calculation.

The greater insight of microscopic structural properties can be done by evaluating diffusion coefficient which is expressed in terms of $S_{CC}(0)$ by using Darken thermodynamic equation [15, 16] as

$$\frac{D_M}{D_{id}} = \frac{x_1 x_2}{S_{CC}(0)}$$

(19)

where D_M stands for the chemical or mutual diffusion coefficient and D_{id} stands for the intrinsic diffusion coefficient for an ideal mixture which are related as

$$D_M = D_{id} \frac{\partial ln a_A}{\partial x_1}, \text{ with } D_M = x_1 D_B + x_2 D_A$$

(20)

where D_A and D_B are the self-diffusion coefficient of pure components A and B respectively.

3. Results and Discussion

In the present work, we have used regular associated solution model to compute the thermodynamic and microscopic structural behavior of Fe-Pd liquid binary alloys at 1873 K. We have assumed the existance of $FePd_3$ complex in the initial melt at 1873 K. At first, the model parameters $\frac{\omega_{12}}{RT}$ and k exp $\left(\frac{\omega_{13}}{RT}\right)$ were estimated using equations (13a) and (13b) with the help of experimental datas of activities coefficients [5]. With the knowledge of these parameter, the mole fractions of the complexes (x_{A_pB}) and unassociated

atoms of(x_A and x_B) were calculated using the eqations (14) and (3) respectively. The graph between the mole fraction of Pd (x_{Pd}) vs the mole fractions of the complex ($FePd_3$) and the unassociated monomers (x_{Pd} and x_{Fe}) is shown in Fig. 1. It is found that the computed value of $FePd_3$ as a function of concentration shows maximum association at $x_{Pd} = 0.7$, which at 8.1 percentage of Pd. This is close to the complex forming composition.
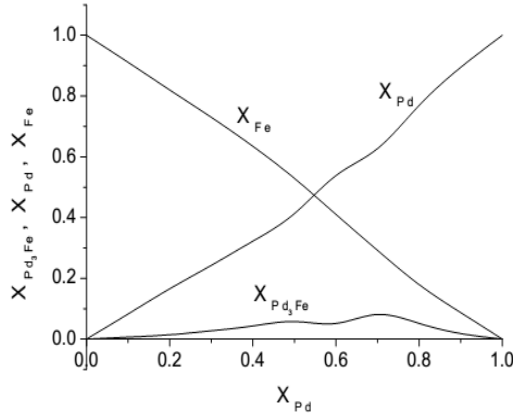

Then the other interaction energy parameters such as $\frac{\omega_{13}}{RT}$ and $\frac{\omega_{23}}{RT}$ were estimated using the equations (11) and (12) with the help of the values of determined complexes. These values of the interaction energy parameters and the complexes were substituted in equation (8) to estimate the value of the equilibrium constant k. The estimated values of the interaction energy parameters and equilibrium constant have been slightly adjusted to explain the experimental values of the free energy of mixing G_M [5], using equation (9). The best fit values of the equilibrium constant and the   interaction energies for Fe-Pd   liquid binary alloys at 1873 K were found to be

Figure 1: Mole fractions Fe, Pd, Fe-Pd vs conc. of Pd in Fe-Pd liquid alloys at1873 K.

$$k = 0.192, \quad \frac{\omega_{12}}{RT} = +1.03, \quad \frac{\omega_{13}}{RT} = +4.21 \text{ and } \quad \frac{\omega_{13}}{RT} = +2.06$$

The theoretical values of the free energy of mixing (G_M) were computed using the equation (9) and the best fit model parameters shown above. The theoretical calculations shows that the minimum value of G_M is found to be at $x_{Pd} = 0.50$ (the theoretical value of $\frac{G_M}{RT} = -0.48878$ and the experimental value of $\frac{G_M}{RT} = -0.48263$ [5]). Hence the theoretical analysis suggests that the tendency of complex formation in the Fe-Pd liquid alloys at 1873 K is weaker. The plot of x_{Pd} vs free energies of mixing (G_M/RT) is shown in Fig. 2. It is found that both the estimated values and the experimental values of the free energies of mixing are in a good agreement.
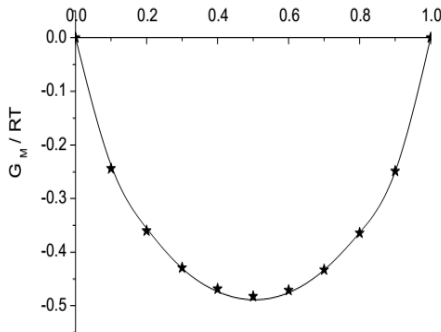
The other model parameters were estimated by successive approximation by using equation (16) and the experimental values of the enthalpy of mixing (H_M) [5]. The best fit values of the parameters $\partial\omega_{12}/\partial T$, $\partial\omega_{13}/\partial T$, $\partial\omega_{23}/\partial T$ and $RT^2\partial lnk/\partial T$ were found to be

$$\frac{\partial\omega_{12}}{\partial T} = 1.20 \text{Jmol}^{-1}\text{K}^{-1}, \quad \frac{\partial\omega_{13}}{\partial T} = 13.21 \text{ J mol}^{-1}\text{ K}^{-1},$$
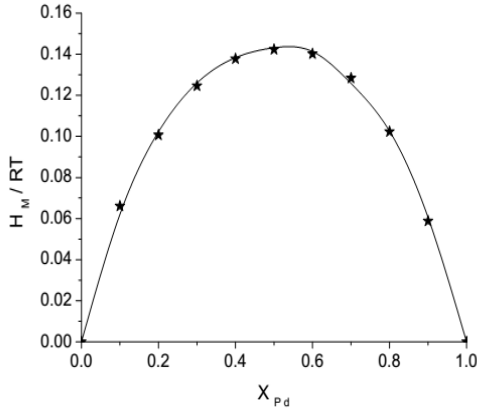
$$\frac{\partial\omega_{23}}{\partial T} = 3.79 \text{J mol}^{-1}\text{ K}^{-1}$$

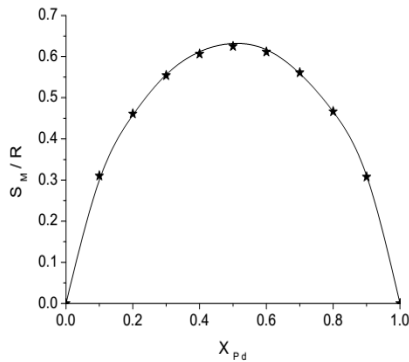and $RT^2 \frac{dlnk}{dT} = 39500 \pm 3500 \text{ J mol}^{-1}$

Using the best fit values of the above parameters and equation (16), the theoretical values of the enthalpy of mixing (H_M/RT) were computed.

Figure 2: Free energy of mixing (G_M/RT) vs concentration of Pd in Fe-Pd liquid alloy at 1873 K. The solid line is for the theoretical values and stars in black are for the experimental values.

The enthalpy of mixing is found to be positive throughout the concentration of Pd. The H_M/RT is found to be maximum at $x_{Pd} = 0.50$ (the theoretical value of H_M/RT =+ 0.143121 and the experimental value of H_M/RT = +0.142287 [5]). The positive values of the enthalpy of mixing suggest that the Fe-Pd melt at 1873 K is segregating in nature. It can be observed that both the theoretical and the experimental values are in a good agreement. The theoretical analysis also suggests that the Fe-Pd liquid alloy at 1873 K is weakly interacting system. The plot of H_M/RT vs concentration of Pd is shown in the Fig. 3.

Using the computed values of the free energy of mixing (G_M/RT) and the heat of mixing (H_M/RT), the entropy of mixing (S_M/R) can be calculated from equation (15b). The calculated and the observed values for the Fe-Pd liquid alloy at 1873 K are found to be positive at all concentrations. It can be observed that both the theoretical and the experimental values [5] of the entropy of mixing (S_M/R) are in a good agreement (Fig. 4).

The activity is an important parameter for the liquid alloys as most of the thermodynamic as well as the microscopic functions depend on it. It can be measured in terms of the alloy composition and the temperature. The deviations of the behaviour determining parameter

Figure 3: Heat of mixing (H_M/RT) vs concentration of Pd in liquid Fe-Pd alloy at 1873 K; the solid line is for the theoretical values and the stars in black are for the experimental values.

from the ideal behavior can be incorporated into the activity. The activities of both the monomers a_A and a_B (A = Pd and B = Fe) are estimated using equations (10a) and (10b). Both the theoretical and the observed values [5] of the activities are in a good agreement throughout the whole concentrations (Fig. 5).

To understand the microscopic structural behavior of the liquid alloy, the theoretical values of the concentration fluctuation in long- wavelength limit ($S_{CC}(0)$) were computed using equation (17) and the ideal values of $S_{CC}(0)$ were computed using equation (18). The computed and the

Figure 4: Entropy of mixing (S_M/R) vs concentration of Pd in Fe-Pd liquid alloy at 1873 K; the solid line is for the theoretical values and the stars in black are for the experimental values.

observed values [5] of the $S_{CC}(0)$ are reasonably in a good agreement. Both the theoretical and the observed values [5] of the concentration fluctuation in long-wavelength limit are found to be greater than the ideal values throughout the whole concentrations of Pd (Fig. 6).

Hence, the theoretical analysis suggest that the Fe-Pd liquid alloy at 1873 K is segregating in nature i. e. the associations of like atoms (Pd-Pd and Fe-Fe) are favoured in the the liquid state. As a result of which there must be separation of phase in the solid state.
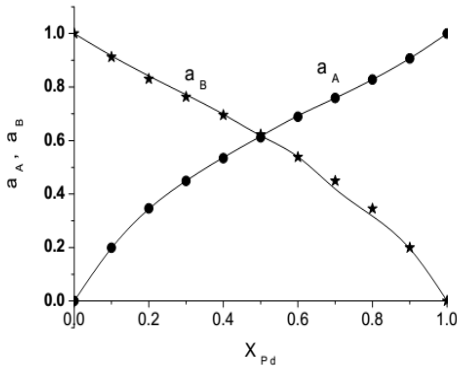
For the better insight of the local ordering and the complex forming behavior of the liquid alloy we have computed the Warren–Cowley short range order parameter (α_1) from the equation (18). The normalized value of α_1 lies between -1 to +1. If the computed values of $\alpha_1 = -1$ indicates complete ordering (unlike atoms pairing), if $\alpha_1 = +1$ indicates complete segregating (like atoms pairing) and if $\alpha_1 = 0$ indicates a randomness of atoms in the liquid state. It has been found that the values of short range parameter (α_1) are found to be positive and less than 1 for the entire concentrations of Pd (Fig. 7) which suggest that the

Figure 5: Activities of the monomers A(=Pd) and B(=Fe) vs concentrations of Pd in Fe-Pd liquid alloys at 1873 K; the solid lines are for the theoretical values and the experimental values are represented by circles in black (for Pd) and stars in black (for Fe) respectively.
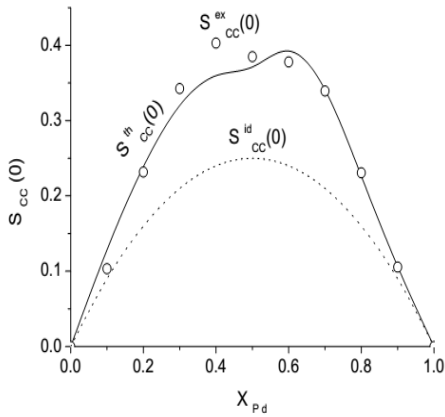
Figure 6: Concentration fluctuation in long-wavelength limit ($S_{CC}(0)$) vs concentration of Pd in Fe-Pd liquid alloy at 1873 K; the solid lines are for the theoretical values, the circles are for the experimental values and the dotted lines are for the ideal values.
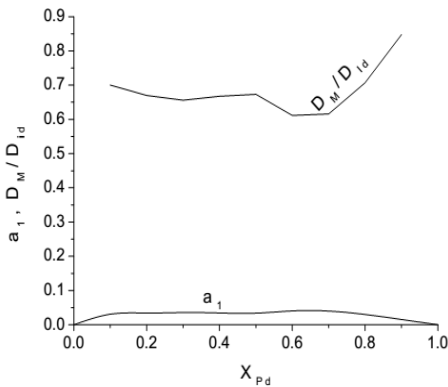
Figure 7: The ratio of mutual and intrinsic diffusion coefficients (D_M/D_{id}) and Warren – Cowley short range order parameter (α_1) vs concentrations of Pd in Fe-Pd liquid alloy at 1873 K.

Fe-Pd liquid alloy at 1873 K is complete segregating system. Also, the ratio of the mutual and intrinsic-diffusion coefficients (D_M/D_{id}) were evaluated using equation (19). The theoretical values of D_M/D_{id} are found to be positive and less than one (figure 7) which further verifies the segregating (homo-coordinating) nature of Fe-Pd liquid alloy at 1873 K.

4. Conclusion

The theoretical analysis suggests that the Fe-Pd liquid alloy at 1873 K is weakly interacting system. It also suggests that Fe-Pd system at 1873 K is segregating (homo-coordinating) system. The interaction energy parameters are found to be positive at all concentrations of Pd and are found to be temperature dependent.

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