

## Theoretical investigations of mixing properties in Ni-Pd liquid alloys

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**Abstract** : A simple approach to statistical mechanical theory based on regular solution has been used to investigate possible chemical association in Ni-Pd liquid alloys at 1873K. Assuming the existence of a chemical association of the form NiPd, the model was used to deduce information on thermodynamic, structural and surface properties of the alloys. The concentration dependent of the free energy of mixing, heat of mixing, entropy of mixing, concentration fluctuation in the long wavelength limit, Warren-Cowley short range order

parameter, ratio of diffusion coefficients, activity of the components, surface tension and surface concentration of nickel-palladium alloys have got special attention to show a tendency of like atom pairing in the mixture.

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**Keywords** : Simple statistical mechanical theory; Thermodynamic properties; Surface concentration; Surface tension.

### INTRODUCTION

The liquid alloys are well-recognized as important and promising area for research in physics and chemistry because its atomic arrangements are not spatially periodic in contrast to the case of crystalline materials. Liquid alloys are disorder system with short range order and exhibit a significant variety of atomic structures. Thermodynamic, structural and surface properties of mixing of the initial melt play important role in the formation of solid alloys. Thus the properties of the alloys in the melt are helpful to understand the alloying behaviour in the solid state. They can provide enormous amount of information for understanding metallurgical process and material preparation of the metal alloys. The solubility of a homogeneous solid phase is

governed predominantly by the size factor, electrochemical effect and electron concentration. Experiences say that these factors cannot be used effectively to explain the alloying behaviour of liquid alloys in details. So, liquid alloys generate manifold interest for both the experimentalists<sup>[1-5]</sup> and the theoreticians<sup>[6-19]</sup>.

Nickel-palladium alloys were originally developed as a low cost replacement for gold. Typically contacts and connectors are plated with nickel/palladium and then flashed with gold. This reduces the cost significantly. The properties are similar to gold with excellent corrosion resistance, low porosity, low contact resistance and good solderability<sup>[19]</sup>. In the present work we intend to explain the alloying behaviour of nickel-palladium liquid alloy on the basis of simple statistical model<sup>[14]</sup>. Thermodynamic parameters give us an idea

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about the stability and bonding strength of the constituent species of the alloy, whereas structural parameters provide the idea about ordering and segregating nature of the alloy. The properties of mixing of Ni-Pd alloys are symmetrical about equiatomic composition despite the large size difference of Ni and Pd<sup>[1]</sup>.

## FORMALISM

### Thermodynamic and microscopic properties

The grand partition function for simple binary liquid alloys consisting of  $N_A (=Nc)$  number of A atoms and  $N_B (=N(1-c))$  number of B atoms can be generalized as<sup>[14]</sup>

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp\left(\frac{\mu_A N_A + \mu_B N_B - E}{k_B T}\right) \quad (1)$$

Where  $q_i^{N_i}$  are the partition functions of atoms ( $i=A$  or  $B$ ) associated with inner and vibrational degree of freedom.  $q_i$  the same whether the atom  $i$  is located in the pure state or in alloy.  $\mu_A$  and  $\mu_B$  are the chemical potentials and  $E$  is the configurational energy,  $k_B$ , the Boltzmann constant,  $c$ , the concentration of the component and  $T$ , absolute temperature. The standard thermodynamic relation for free energy of mixing is

$$\Delta G_M = \Delta G_M^{id} + \Delta G_M^{XS} \quad (2)$$

where

$$\Delta G_M^{id} = RT \{c \ln c + (1-c) \ln(1-c)\} \quad (3)$$

And

$$\Delta G_M^{XS} = \int_0^c \ln \sigma^Z dc = RT \{c \ln \gamma_A + (1-c) \ln \gamma_B\} \quad (4)$$

with

$$\sigma = (\beta + 2c - 1) \exp(-\omega / zk_B T) / 2c \quad (4a)$$

$$\gamma_A = [(\beta - 1 + 2c) / c(1 + \beta)]^{z/2} \quad (4b)$$

$$\gamma_B = [(\beta + 1 - 2c) / (1 - c)(1 + \beta)]^{z/2} \quad (4c)$$

$$\beta = \{1 + 4c(1 - c) [\exp(2\omega / zk_B T) - 1]\}^{1/2} \quad (4d)$$

For the equiatomic composition ( $c = \frac{1}{2}$ ), relation (8) reduces to

$$\frac{\Delta G_M^{XS}}{RT} = \ln 2^{z/2} [1 + \exp(-\omega / zk_B T)]^{-z/2} \quad (5)$$

Using the relations (2),(3) and (4), the free energy of mixing<sup>[15]</sup> will be

$$\begin{aligned} \Delta G_M &= RT [c \ln c + (1-c) \ln(1-c) + c \ln \gamma_A + (1-c) \ln \gamma_B] \\ &= RT [c \ln c + (1-c) \ln(1-c) + c(1-c) \frac{\omega}{k_B T}] \quad (6) \end{aligned}$$

The heat of mixing ( $\Delta H_M$ ) can be obtained from the standard thermodynamic expression as

$$\begin{aligned} \Delta H_M &= \Delta G_M - T \left( \frac{\partial \Delta G_M}{\partial T} \right)_{C,P,N} \\ &= RT \left[ c(1-c) \frac{\omega}{k_B T} - c(1-c) \frac{1}{k_B} \frac{d\omega}{dT} \right] \quad (7) \end{aligned}$$

and entropy of mixing ( $\Delta S_M$ ) is also obtained from the relation

$$\Delta S_M = (\Delta H_M - \Delta G_M) / T \quad (8)$$

The activity of binary liquid alloys,  $a_i$  ( $i=A$  or  $B$ ), can be related to the free energy of mixing by the relation

$$\begin{aligned} RT \ln a_i &= \left( \frac{\partial \Delta G_M}{\partial N_i} \right)_{T,P,N} \\ &= \Delta G_M + (1 - c_i) \left( \frac{\partial \Delta G_M}{\partial c_i} \right)_{T,P,N} \quad (9) \end{aligned}$$

Then we have<sup>[14]</sup> from Eq.(9),

$$\ln a_A = \ln c + (1-c)^2 \frac{\omega}{k_B T} \quad (10a)$$

$$\ln a_B = \ln(1-c) + c^2 \frac{\omega}{k_B T} \quad (10b)$$

Concentration fluctuations in the long-wavelength limit ( $S_{cc}(0)$ ) is an essential microscopic function which has been widely used to study the nature of atomic order in binary liquid alloys<sup>[16]</sup>.  $S_{cc}(0)$  is thermodynamically related to free energy of mixing ( $\Delta G_M$ )<sup>[16]</sup>. It is given as

$$S_{cc}(0) = RT \left( \frac{\partial^2 \Delta G_M}{\partial c^2} \right)_{T,P,N}^{-1} \quad (11)$$

The value of  $S_{cc}(0)$  can also be determined using activity data in the following thermodynamic equations:

$$S_{cc}(0) = (1-c)a_A \left( \frac{\partial a_A}{\partial c} \right)^{-1} \quad (12a)$$

$$= ca_B \left( \frac{\partial a_B}{\partial (1-c)} \right)^{-1} \quad (12b)$$

which are usually considered as the experimental values.

From equations (6) and (11), one obtains the theoretical value of  $S_{cc}(0)$  as:

$$S_{cc}(0) = c(1-c) \left[ 1 + \frac{z}{2\beta}(1-\beta) \right]^{-1} \quad (13)$$

The ideal values of concentration-concentration fluctuations  $S_{cc}^{id}(0)$ , when the ordering energy zero is usually computed from:

$$S_{cc}^{id}(0) = c(1-c) \quad (14)$$

At a given composition if  $S_{cc}(0) < S_{cc}^{id}(0)$ , ordering in liquid alloy is expected while  $S_{cc}(0) > S_{cc}^{id}(0)$  gives the indication of tendency of segregation.

The Warren-Cowley short range order parameter ( $\alpha_1$ ) gives insight into the local arrangement of the atoms in the molten alloys. Although it is difficult to obtain the experimental values of  $\alpha_1$ , theoretical values of this parameter are easily obtain via conditional probability [A/B] which defines the probability of finding an A-atom as a nearest neighbor of a given B-atom. To quantify the degree of order in the molten alloys  $\alpha_1$ <sup>[21,22]</sup> can be evaluated theoretically:

$$\frac{S_{cc}(0)}{c(1-c)} = \frac{1 + \alpha_1}{1 - (z-1)\alpha_1} \quad (15)$$

where  $z$  is the coordination number, which is taken as 10 for our purposes.  $\alpha_1$  for the first coordination shell<sup>[21,22]</sup> in term of  $\omega$  can be taken as

$$\frac{\alpha_1}{(1-\alpha_1)^2 c(1-c)} = \exp(2\omega / z k_B T) - 1 \quad (16)$$

The knowledge of  $\alpha_1$  provides an immediate insight into the nature of the local arrangement of atoms in the mixture. The minimum possible value of  $\alpha_1$  is -1 and it indicates complete ordering of unlike atom pairing at nearest atoms. On the other hand the maximum value of  $\alpha_1$  is +1, which implies complete segregation leading

to phase separation and  $\alpha_1 = 0$  corresponds to a random distribution of atoms.

The mixing behaviour of the alloy forming molten metals can also be studied at the microscopic level in terms of coefficient of diffusion. The mutual diffusion coefficient ( $D_M$ ) of binary liquid alloys can be related to self-diffusion coefficient ( $D_{id}$ ) of pure component through ordering energy ( $\omega$ ) with the help of Darken's equation<sup>[19]</sup>:

$$D_M = D_{id} \left[ 1 - c(1-c) \left( \frac{2\omega}{k_B T} \right) \right] \quad (17)$$

$$\text{With } D_M = cD_B + (1-c)D_A \quad (18)$$

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

The ratio  $D_M / D_{id}$  indicates the mixing nature of molten alloys;  $D_M / D_{id} < 1$  indicates the tendency of homo-coordination while  $D_M / D_{id} > 1$  indicates the tendency of hetero-coordination and  $D_M / D_{id}$  approaches 1 for ideal mixing.

### Surface properties

The study of surface phenomenon is necessary for understanding many properties of physical relevant such as catalytic activity of alloy catalyst, mechanical behaviour and kinetics of phase transformation<sup>[23,24]</sup>. It plays a significant role in the formation of solid alloys by solidification process of the melts. Several metallurgical phenomena such as crystal growth, welding, gas absorption, nucleation of gas bubbles are closely associated with the surface tension phenomena. Surface segregation results from the interaction among the atoms and the surface tension, is the enrichment of the surface by the atoms of a particular component element<sup>[24]</sup>. In the statistical formulation of Prasad et al.<sup>[23,24]</sup> binary liquid alloy is considered to have a layered structure near the surface with thermodynamic equilibrium existing between the species at the surface and in the bulk. The surface properties of liquid alloys are influenced by their bulk thermodynamic properties. The surface grand partition function is related to the surface tension  $\tau$  by the expression

$$\Xi^S = \exp\left( \frac{-S\tau}{k_B T} \right) = \exp\left( \frac{-N^S \tau \xi}{k_B T} \right) \quad (19)$$

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where  $S$  is the surface area and  $\xi$  is the mean area of the surface per atom and is defined as  $\xi = S/N^s$ , and  $N^s$  is the total number of atoms at the surface.  $k_B$  is the Boltzmann constant.

A pair of equations for surface tension of the binary liquid alloys in terms of activity coefficient ( $\gamma_i$ ) of the alloy components and interchange energy parameter ( $\omega$ ) proposed by Prasad et al.<sup>[23,24]</sup>, is reduced to simple form by using the zeroth approximation<sup>[15]</sup> as

$$\tau = \tau_A + \frac{k_B T}{\xi} \ln \frac{c^s}{c} + \frac{\omega}{\xi} \left[ p(1-c^s)^2 + (q-1)(1-c)^2 \right] \quad (20a)$$

$$\tau = \tau_B + \frac{k_B T}{\xi} \ln \frac{(1-c^s)}{(1-c)} + \frac{\omega}{\xi} \left[ p(c^s)^2 + (q-1)(c)^2 \right] \quad (20b)$$

where  $\tau_A$  and  $\tau_B$  are the surface tension values for the pure components A and B respectively;  $C$  and  $C^s$  are the bulk and surface concentrations of component A;  $p$  and  $q$  are the surface coordination fractions, which are defined as the fraction of the total number of nearest neighbors made by atom within its own layer and that in the adjoining layer. For  $p$  and  $q$ , the following relation is available<sup>[23-26]</sup>.

$$p + 2q = 1 \quad (21)$$

For closed packed structure,  $p = 0.5$  while  $q = 0.25$  [in view of the disordered structure and relaxation effect of the surface layer  $p$  and  $q$  should be treated as parameters<sup>[24]</sup>].

The pair of Eqs. 20(a) and 20(b) can be solved numerically to obtain  $C^s$  as a function of  $C$ . Obviously the surface concentration depends upon the surface tension of the  $i$ th component in the pure state ( $\tau_i$ ), surface area per atom ( $\xi$ ), ordering energy ( $\omega$ ) and the coordination fractions ( $p$  and  $q$ ). This approach is useful because it can be used to investigate the dependence of surface composition on ordering energy and surface coordination.

The mean atomic surface area  $\xi$  ( $=A/N^s$ ) is given as

$$\xi = \sum c_i \xi_i \quad (i = A, B) \quad (22)$$

Where the atomic area of hypothetical surface for each component is given as:

$$\xi_i = 1.102 \left( \frac{\Omega_i}{N_0} \right)^{2/3} \quad (23)$$

where  $\Omega_i$  is the molar volume of the species  $i$  and  $N_0$  stands for Avogadro number<sup>[23]</sup>.

## RESULTS AND DISCUSSION

### Thermodynamic and structural properties

The energy parameters for the calculation of the various mixing properties of Ni-Pd liquid alloys at 1873K has been estimated using experimental value of  $G_M^{xs}$  and  $\Delta H_M$  for equiatomic composition ( $C=1/2$ ), through the equations (5) and (7), which are found as

$$\omega = 0.48 k_B T \quad \text{and} \quad \frac{\partial \omega}{\partial T} = 9.076 \times 10^{-5} k_B T$$

The positive value of energy parameter ( $\omega$ ) suggests that there is higher tendency for like atoms to pair in the alloy which implies a homo-coordination system. However, the tendency of pairing is weak since energy parameter is small. We have observed that if energy parameters are supposed to be independent of temperature ( $\partial \omega / \partial T = 0$ ), then  $\Delta S_M$  and  $\Delta H_M$  so obtained are in poor agreement with experimental data. This suggests the importance of temperature dependence ordering energy,  $\omega$ .

The computed values of free energy of mixing ( $\Delta G_M / RT$ ) and entropy of mixing ( $\Delta S_M / R$ ) are plotted as a function of concentration in Figure 1 and compared with experimental values<sup>[1]</sup>. Like the experimental values,  $\Delta G_M / RT$  is negative at all concentrations. There is reasonable agreement between theory and experiment. Minimum of  $\Delta G_M / RT$  has been observed around  $C_{Ni} = 0.5$ . As regards  $\Delta S_M / R$ , theory agrees well with experiment. The existence of atomic order may be inferred from the positive values of  $\Delta S_M / R$  at all concentrations. The heat of mixing ( $\Delta H_M / RT$ ) for Ni-Pd liquid alloy at 1873K has been computed from equation (7). The plot of  $\Delta H_M / RT$  versus  $C_{Ni}$  are depicted in Figure 2. The theoretical and experimental values of  $\Delta H_M / RT$  are in good agreement in all concentrations of Ni.  $\Delta H_M / RT$  is minimum at  $C_{Ni} = 0.5$ , which shows that Ni-Pd liquid alloy is symmetric about equiatomic concentration. We have used the same values of the energy parameters for the evaluation of chemical activities of the components of the alloy. There is well agreement between experimental and theoretical values of the activities of the components

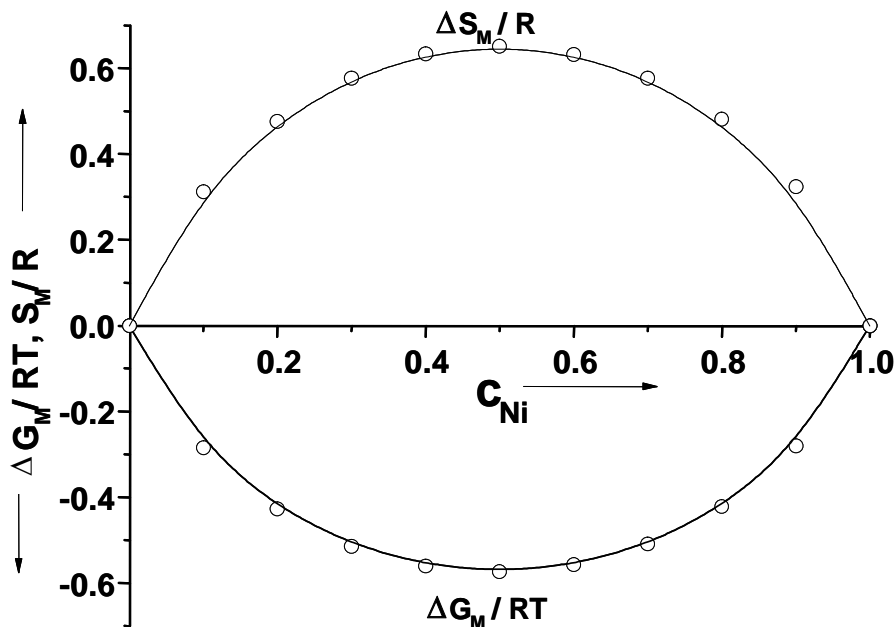


Figure 1 : Free energy of mixing ( $\Delta G_M$ ) and entropy of mixing ( $\Delta S_M$ ) Vs concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K; solid lines for calculated values and circles for experimental values<sup>[1]</sup>.

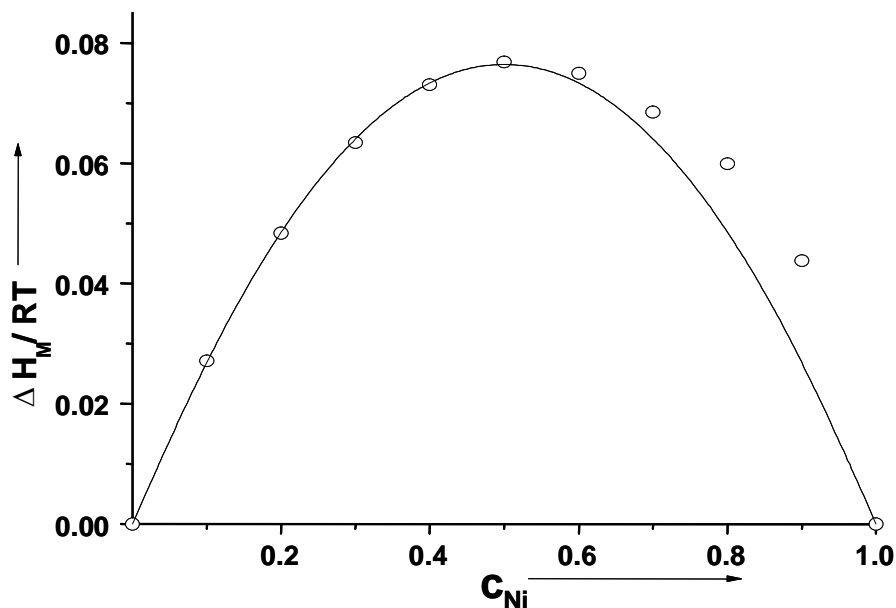


Figure 2 : Heat of mixing ( $\Delta H_M$ ) Vs concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K; solid lines for calculated values and circles for experimental values<sup>[1]</sup>.

Ni and Pd of the alloy (Figure 3).

Using the estimated energy parameter, the theoretical values of  $S_{cc}(0)$  and  $\alpha_1$  are computed from equations (13) and (17). Figure 4 shows a plot of the theoretical and experimental values of  $S_{cc}(0)$  along with the ideal values and  $\alpha_1$  against  $C_{Ni}$ . The theoretical values of  $S_{cc}(0)$  are in good agreement with the experimental values of  $S_{cc}(0)$ . The result can be used to understand the nature of atomic order in binary liquid alloys. Figure

4 shows that  $\alpha_1$  is positive, maximum at  $C_{Ni} = 0.5$  and  $S_{cc}(0) > S_{cc}^{id}(0)$  throughout whole concentration range of Ni, showing that Ni-Pd liquid alloy at 1873K is segregating.

The estimated values of  $\omega$  is used in Eq. (17) to evaluate the ratio of the mutual and intrinsic-diffusion coefficients,  $\frac{D_M}{D_{id}}$ . The plot of  $\frac{D_M}{D_{id}}$  against  $C_{Ni}$  depicted

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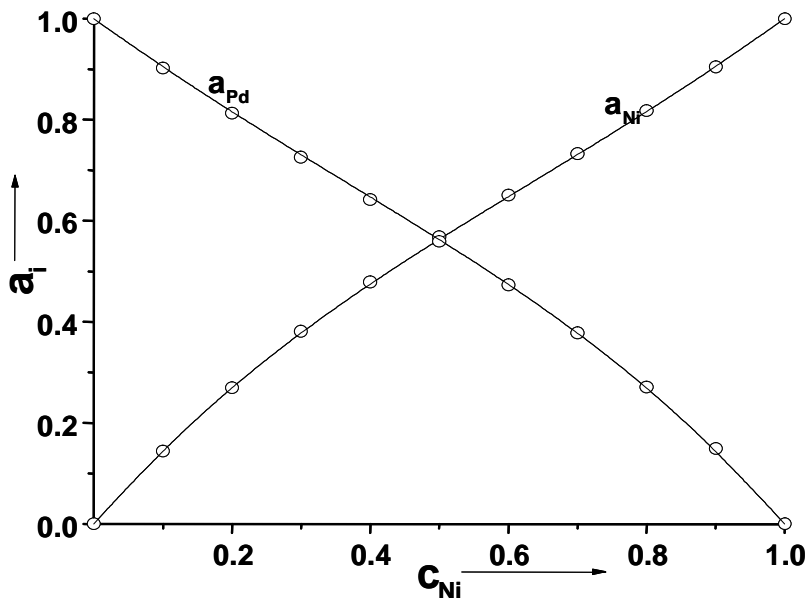


Figure 3 : Chemical activity ( $a_i$ ) Vs concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K; solid lines for calculated values and circles for experimental values<sup>[1]</sup>.

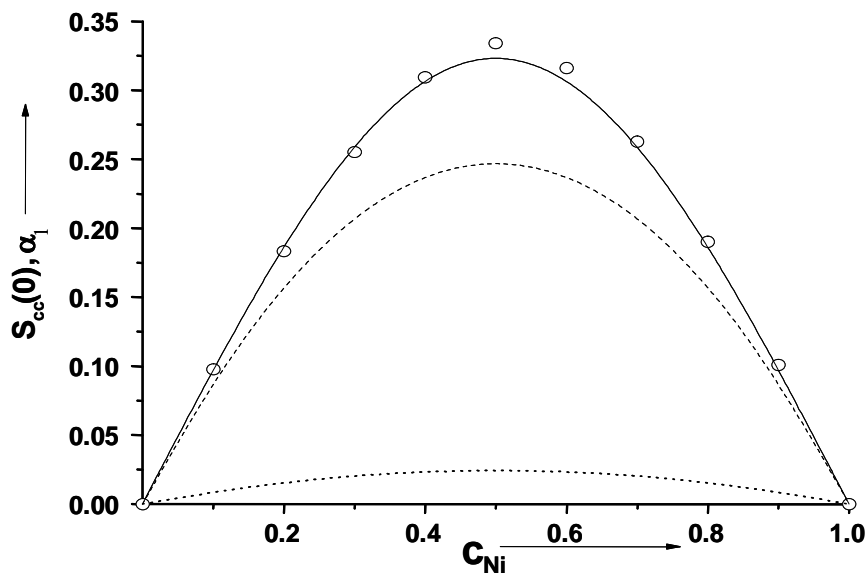


Figure 4 : Concentration fluctuation at long wavelength limit ( $S_{cc}(0)$ ) and short range order parameter ( $\alpha_1$ ) Vs concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K;  $S_{cc}(0)$ : calculated values (solid lines), experimental values (circles)<sup>[1]</sup> and ideal values (dashed lines);  $\alpha_1$ : dotted lines.

in Figure 5 shows that the value of  $\frac{D_M}{D_{id}}$  is less than 1, in the entire range of concentration of  $C_{Ni}$ , which is indicative for the phase separation in the mixture. A minimum value of  $\frac{D_M}{D_{id}} = 0.760$  for  $c_{in} = 0.5$ , confirms a weak tendency for segregation, as observed by the  $S_{cc}(0)$  and CSRO parameter.

## Surface properties

On the basis of approach of Prasad et al, the surface concentrations and surface tension of Ni-Pd were computed numerically from the expressions in Eqs. 20(a) and 20(b). For this, we need experimental data of density and surface tension of the components at the working temperature. We calculated the density and surface tension for the components Ni and Pd<sup>[5,27]</sup> at the working temperature 1873K by

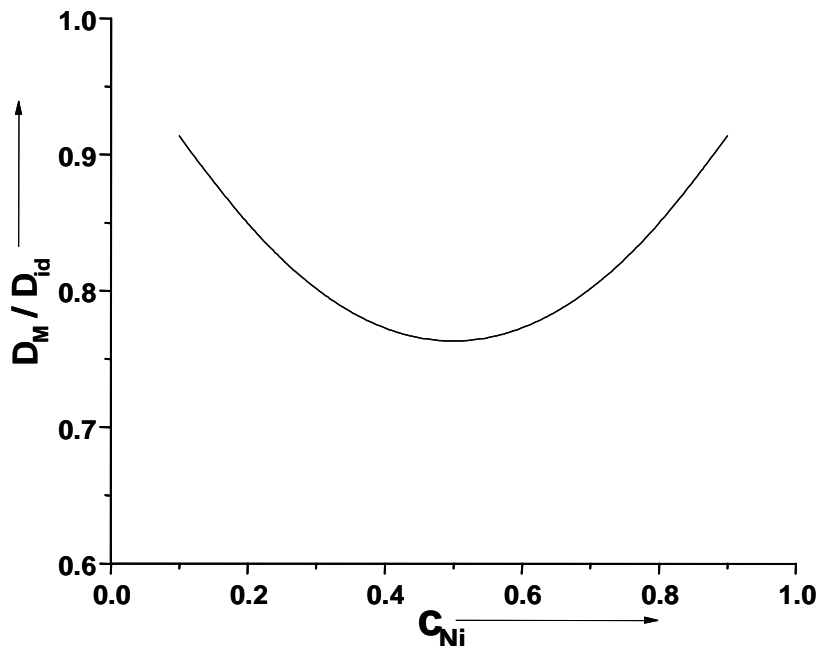


Figure 5 : Ratio of chemical and intrinsic diffusion coefficients Vs concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K.

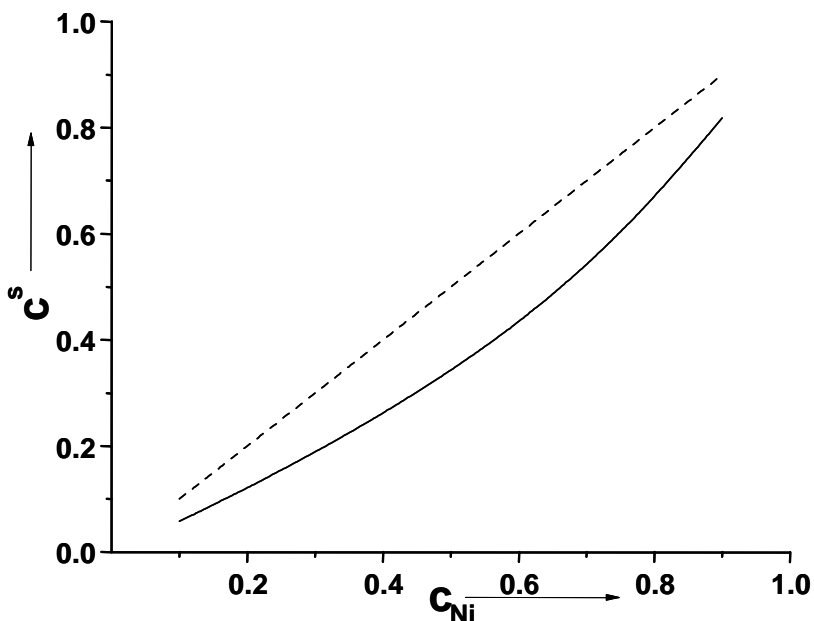


Figure 6 : Surface concentration of nickel ( $C_{Ni}^s$ ) Vs bulk concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K; solid line for values from theoretical approach, dashed line for values from additive rule.

using the equations as

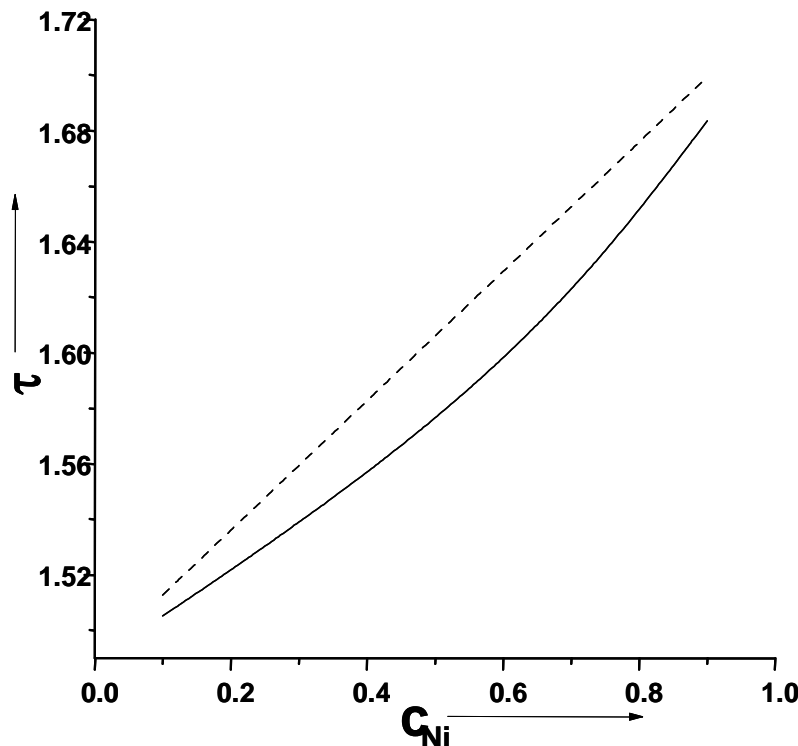
$$\rho(T) = \rho_0 + (T - T_0) \frac{d\rho}{dT} \quad (24)$$

$$\tau(T) = \tau_0 + (T - T_0) \frac{d\tau}{dT} \quad (25)$$

Where  $T$  and  $T_0$  are respectively the temperature of

investigation and melting temperature;  $\frac{d\rho}{dT}$  and  $\frac{d\tau}{dT}$  represent the temperature coefficient of density and surface tension respectively for component metal of the alloys. The mean atomic surface area  $\xi$  was calculated by using Eqs.(22) and (23). For calculating surface tension we used same estimated energy parameter,  $\omega$ . At first, surface concentrations of nickel in alloy Ni-Pd have

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**Figure 7 :** Surface tension ( $\tau$ ) Vs concentration of nickel ( $C_{Ni}$ ) in liquid Ni-Pd alloy at 1873K; solid line for values from theoretical approach and dotted line for ideal values.

been obtained as a function of bulk concentration by concurrently solving the equations 20(a) and 20(b). Using the obtained values of surface concentrations we computed the surface tension of Ni-Pd liquid alloys at temperature 1873K for whole concentration range. The analysis gives that the computed surface tension for Ni-Pd alloys at 1873K is less than ideal values at all concentration of nickel; i.e. there is negative departure of surface tension from ideality. Theoretical approach predicts that there is linear relation between the surface tension and bulk concentration of nickel part in Ni-Pd alloy [Figure 7]. It is also noticed that the surface concentration of nickel in Ni-Pd alloys is found to increase with the increase of bulk concentration of Ni [Figure 6]. This is an indication that in the alloys there are more atoms of component with bigger atom at the surface. Hence, at the surface of liquid Ni-Pd, Pd-atoms segregate at the surface in preference to Ni-atoms throughout the entire composition.

### CONCLUSION

The analysis reveals that there is a tendency of like atom pairing or homo-coordination (Ni-Ni, Pd-Pd) in

liquid Ni-Pd alloys at all concentrations. The thermodynamical analysis suggests that this alloy is of a weakly interacting nature. The ordering energy is found to be temperature dependent. Theoretical study shows that metal with lower surface tension tends to segregate on the surface of molten alloys. In Ni-Pd system at 1873K, the surface tension of Ni-Pd alloys always smaller than ideal values, increases with the increase of bulk concentrations of nickel, Pd atoms segregate to the surface at all bulk concentrations of nickel.

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