

Thermodynamics of liquid Fe-Ni alloys: calculations at different temperatures

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Abstract. For the description of the ion-ion interaction in a transition metal the method of pair potential calculation introduced by Wills and Harrison is used. The potential is represented as a sum of the *s*-electron and *d*-electron contributions. The first is calculated in the framework of the Bretonnet and Silbert local model pseudopotential. On the basis of this approximation the thermodynamic properties are calculated by using the variational method of the thermodynamic perturbation theory. The formalism is applied to calculate the free energy of mixing for the Fe-Ni liquid system at different compositions and temperatures. An agreement with the available experimental data is quite satisfactory.

1. Introduction

The Fe-Ni system is a basis of many amorphous alloys. From this point of view, it is interesting to investigate this system in a liquid state. Unfortunately, theoretical investigations are not sufficiently developed in this area up to now. It is connected with difficulties in the description of liquid transition metals and, especially, their alloys on the microscopic level.

One of the most successful approximations for the description of the effective pair ion-ion interactions in transition metals has been developed by Wills and Harrison (WH) [1] on the basis of separate consideration of the *d*- and *s*-electron states. The first are considered as a fully localized and are treated by using the muffin-tin potential within the atomic-sphere approximation [2]. The second are determined as a free-electron-like and are described in the framework of the nearly-free-electron (NFE) approximation (starting from [1], the Ashcroft empty-core model pseudopotential [3] was used earlier for this purpose).

Recently, we represented the WH calculations with the Oli local model pseudopotential [4] in the Bretonnet-Silbert modification [5] (OBS) instead of the Ashcroft one and extended this approach to the framework of the variational method of the thermodynamic perturbation theory in the binary liquid transition-metal alloys thermodynamics [6].

Here, we apply it to study the liquid state thermodynamics of Fe-Ni system.

2. Theory

The Wills-Harrison partial effective pair potentials may be expressed as follows (hereafter in a.u.):

$$\varphi_{ij\text{WH}}(r) = \varphi_{ij\text{NFE}}(r) + \varphi_{dij}(r), \quad (1)$$

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where $\varphi_{ij\text{NFE}}(r)$ and $\varphi_{dij}(r)$ are the pair interactions due to the s - and d -electron states, respectively.

$$\varphi_{ij\text{NFE}}(r) = \frac{z_i z_j}{r} + \frac{1}{8\pi^2 \rho} \int_0^\infty F_{ij}(q) \frac{\sin(qr)}{qr} q^2 dq, \quad (2)$$

where ρ is the mean number density of the alloy; z_i - the effective number of valence s electrons per ion in the pure metal of the i -th kind (following [7] we take z_i equal to 1.4 for both metals under consideration); $F_{ij}(q)$ - the partial energy-wavenumber characteristics:

$$F_{ij}(q) = -\frac{q^2 \omega_i(q) \omega_j(q)}{\pi \rho [(\varepsilon(q) - 1)^{-1} + 1 - f(q)]}. \quad (3)$$

Here $\varepsilon(q)$ is the Hartree dielectric function; $f(q)$ - the exchange-correlation function taken here in the approximation of Vashishta and Singwi [8]; $\omega_i(q)$ - the form factor of the ion-electron potential for the bare ion of the i -th kind. We use here the OBS pseudopotential, $\omega_{i\text{OBS}}(r)$:

$$\omega_{i\text{OBS}}(r) = \begin{cases} \sum_{n=1}^2 B_{ni} \exp\left(\frac{r}{na_i}\right), & r \leq R_{Ci} \\ -z_i / r, & r \geq R_{Ci} \end{cases}, \quad (4)$$

$$B_{1i} = (z_i / R_{Ci}) [1 - 2a_i / R_{Ci}] \exp(R_{Ci} / a_i),$$

$$B_{2i} = (2z_i / R_{Ci}) [a_i / R_{Ci} - 1] \exp(0.5R_{Ci} / a_i)$$

for $i = 1, 2$. R_{Ci} and a_i - parameters.

The last term in the right side of (1) consists of two parts: the first, $\varphi_{bij}(r)$, is due to the finite d -band width, and second, $\varphi_{cij}(r)$, arises from the shift of the d -band center:

$$\varphi_{dij}(r) = \varphi_{bij}(r) + \varphi_{cij}(r), \quad (5)$$

$$\varphi_{bij}(r) = -\bar{z}_d \left(\frac{10 - \bar{z}_d}{10} \right) \left(\frac{12}{\nu} \right)^{1/2} V_{dij}(r), \quad (6)$$

where $\bar{z}_d = c_1 z_{d1} + c_2 z_{d2}$; z_{di} - the effective number of valence d electrons per ion in the pure metal of the i -th kind; c_i - the concentration of the i -th kind's component; ν - the coordination number;

$$V_{dij}(r) = \frac{(r_{di} r_{dj})^{3/2}}{r^5} \left(\sum_{m=2}^2 \frac{y_m^2}{2l+1} \right)^{1/2}, \quad (7)$$

where r_{di} is the d -state radius of the free atom of the i -th kind; l - the orbital quantum number (equal to 2 for the d state); m - the magnet quantum number; y_m and x_m - combinatoric coefficients. At $l=2$: $y_0 = -45/\pi$; $y_1 = 30/\pi$; $y_2 = -7.5/\pi$.

$$\varphi_{cij}(r) = -\bar{z}_d \frac{2}{5} \frac{(r_{di}r_{dj})^3}{r^8} \sum_{m=-2}^2 y_m x_m, \quad (8)$$

where

$$x_m = -\frac{1}{8} \left(1 + \frac{4m^2 - 1}{9} \right) y_m.$$

Summation in (7) and (8) is performed without the account of the exchange effects between d states.

Further, we use the variational method with the additive hard-sphere (HS) reference system [9]. The Gibbs-Bogoliubov inequality for the free energy, F , of the liquid metal alloy looks as follows:

$$F \leq F_{\text{HS}} + U_s + \langle U_1 \rangle_{\text{HS}} - TS_e, \quad (9)$$

where U_s is the s -electron contribution to the potential energy; U_1 - the structure-depended perturbation of the potential energy; S_e - the electron contribution to the entropy; $F_{\text{HS}} = 3k_B T / 2 - TS_{\text{HS}}$ (per atom); S_{HS} - the HS entropy in the analytical form [10].

For the binary transition-metal alloy

$$\langle U_1 \rangle_{\text{HS}} = 2\pi\rho \sum_{i,j=1}^2 c_i c_j \int_{\sigma_{ij}}^{\infty} g_{ij\text{HS}}(r) \varphi_{ij\text{WH}}(r) r^2 dr \quad (10)$$

per atom, where σ_{ij} are the partial HS diameters; $g_{ij}(r)$ - partial pair distribution functions.

The using of the HS reference system gives the opportunity to write the right side of inequality (10), F_v , in the wave-number space:

$$F_v = F_{\text{HS}} + E_s + E_1 + E_2 + E_M + E_d - TS_e, \quad (11)$$

where E_s is the energy of the free-electron gas including the Nozieres-Pains exchange-correlation contribution [11]; E_1, E_2 - the terms arising from the first and second order pseudopotential perturbation theory, respectively; E_M - the Madelung energy; E_d - d -electron contribution to internal energy (per atom):

$$E_d = 2\pi\rho \sum_{i,j=1}^2 c_i c_j \int_{\sigma_{ij}}^{\infty} \varphi_{dij}(r) g_{ij\text{HS}}(r) r^2 dr. \quad (12)$$

Detail expressions of all named above terms can be found in [10] and [6].

The minimization of F_v is performed with respect to the mean number density and HS diameters.

3. Results and Discussion

In Figure 1, we present the concentration dependences of the free energy of mixing, ΔF , for the Fe-Ni liquid system at different temperatures near the melting point in comparison with the available experimental data [12]. The coincidence is rather satisfactory. It should be mentioned that a weak tendency to some phase separation occurs at 1823 K (a weak kink at 1 % of Ni content). It may be caused by a local structure transformation in liquid Fe with the rise of Ni content, but such a suggestion needs experimental and detailed analytical justification.

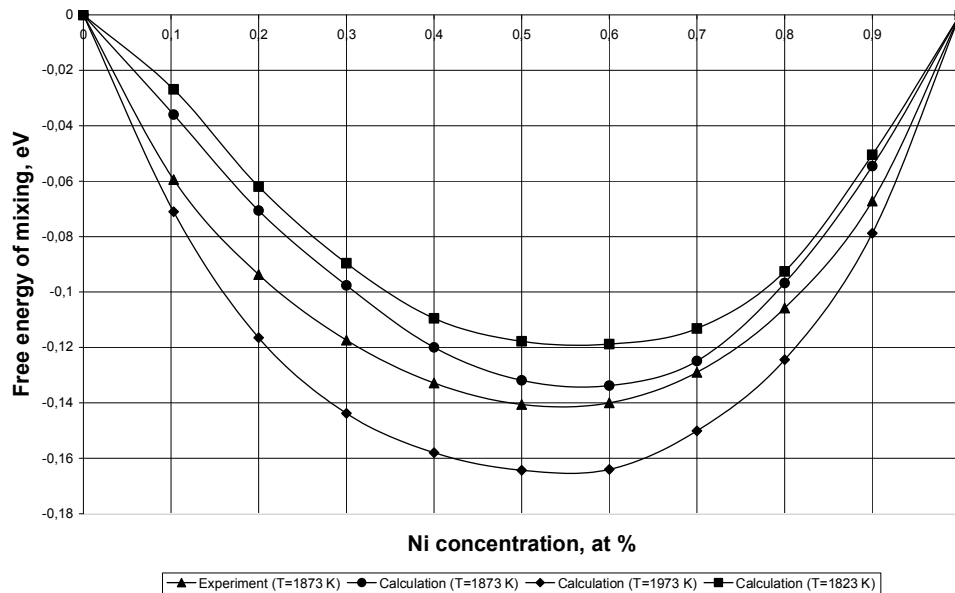


Figure 1. Calculated free energy of mixing for Fe-Ni system at different temperatures together with available experimental data [12]

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