Deoxidation Equilibrium of Vanadium in the Iron–Nickel Melts

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Thermodynamic analysis of oxygen solutions in the Fe–Ni melts with vanadium has been carried out. The deoxidizing ability of vanadium decreases slightly with the nickel content up to 20% but it considerably rises with a further increase in its concentration. The oxygen solubility curves pass through a minimum, which shifts to the lower vanadium concentrations with a rise in the nickel content, i.e., from 2.32% for pure iron to 0.77% for pure nickel. The further vanadium addition causes an increase in the oxygen concentration in melt. For pure nickel or alloys with the nickel concentration higher than 60%, the deoxidizing ability of vanadium is lower in comparison with that of manganese and is close to the deoxidizing ability of chromium. This can be explained by the fact that although the bond strength of oxygen with nickel is appreciably weaker as compared to that with iron (\(\gamma_{O(Fe)}^{\text{O}}=0.0105; \gamma_{O(Ni)}^{\text{O}}=0.357\)), but the vanadium bond strength with nickel is much stronger than that with iron (\(\gamma_{V(Fe)}^{\text{O}}=0.1; \gamma_{V(Ni)}^{\text{O}}=0.0111\)). The deoxidation of iron–nickel melts with vanadium was experimentally studied by the example of the Fe–40%Ni alloy.

KEY WORDS: deoxidation equilibrium; V; Fe–Ni melts; thermodynamic analysis; experimental study.

1. Introduction

The Fe–Ni alloys are widely used in modern technologies. Deoxidation of these alloys with chromium, manganese, silicon, and aluminium was studied earlier.2–3 Vanadium is a component of many iron–nickel alloys. The study of vanadium effect on the oxygen solubility in these alloys is of interest of their commercial production.

The oxygen solutions in liquid iron and nickel containing vanadium are currently studied in detail.4–21 The deoxidizing ability of vanadium was studied using different techniques, namely, the method of equilibrium between liquid iron and steam-hydrogen mixture,4,5,7,11,14) the emf method,8–10,15,16) and also the method of levitation melting (Fig. 1). Unlike the well-studied Fe–V–O system, only several studies were devoted to the deoxidizing ability of vanadium in the Ni–V–O system, which were performed by the method of equilibrium between liquid iron and the steam-hydrogen mixture10,20) and by the emf method.11) There are contradictory opinions of different researchers on the dependence of region of existence of oxide phases on the vanadium content in melt where one or another deoxidation product is in equilibrium (Fig. 1).

There are no experimental data on the oxygen solubility in the Fe–Ni alloys with vanadium. The thermodynamic data on the oxygen solutions in the iron and nickel melts that contain vanadium22,23) allow us to estimate the vanadium effect on the oxygen solubility in the Fe–Ni melts.

This paper represents the thermodynamic analysis of oxygen solutions in the Fe–Ni melts deoxidized with vanadium and the experimental data on the vanadium deoxidation of the Fe–40%Ni melt.

2. Thermodynamic Consideration

At low contents of vanadium, because of its relatively low deoxidizing ability in the iron–nickel melts, the products of deoxidation are FeV2O4 and NiV2O4 spinels; at the higher vanadium concentrations, the product is V2O5.

The deoxidation of the Fe–Ni melts with vanadium at its low concentrations can be described as:

\[(\text{Fe}, \text{Ni})\text{V}_2\text{O}_4(s)\Rightarrow(\text{Fe}, \text{Ni})\text{O}(l)+2\text{V}+4\text{[O]}\] (1)

where \(C_{\text{Fe}+\text{Ni}}\text{O}=(100-\%\text{V}\%\text{O})/100\) is the total concentration of iron and nickel in melt;3) since the oxygen content is considerably lower than the vanadium concentration, one can assume \(C_{\text{Fe}+\text{Ni}}\text{O}=(100-\%\text{V})/100; f_i\) denotes the activity coefficient.

Reaction (1) can be represented as a sum of reactions

\[\text{FeV}_2\text{O}_4(s)\Rightarrow\text{FeO}(l)+\text{V}_2\text{O}_3(s)\] (2)
\[\Delta G_{\text{G}_{\text{Fe}}^{\text{O}}}^0=22190, \text{J/mol}^{(3)}\]

\[\text{FeO}(l)\Rightarrow\text{Fe}(l)+\frac{1}{2}\text{O}_2(g)\] (3)
\[\Delta G_{\text{G}_{\text{Fe}}^{\text{O}}}^0=239987-49.577, \text{J/mol}^{(3)}\]

\[\text{V}_2\text{O}_3(s)\Rightarrow2\text{V}(s)+\frac{1}{2}\text{O}_2(g)\] (4)
\[\Delta G_{\text{G}_{\text{Fe}}^{\text{O}}}^0=1231128-239.617, \text{J/mol}^{(3)}\]
\[
\text{NiV}_2\text{O}_4(s) = \text{NiO}(s) + V_2\text{O}_3(s) \quad \Delta G^\circ_{(5)} = 16,747 \text{ J/mol}^{13} 
\]
\[
\text{NiO}(s) = \text{Ni}(l) + \frac{1}{2}\text{O}_2(g) \quad \Delta G^\circ_{(6)} = 253,929 - 95.29T \text{ J/mol}^{13} 
\]
\[
2\text{V}(s) = 2\text{[V]}_{\text{mass}(\text{Fe–Ni})} \quad \Delta G^\circ_{(7)} = 2\RT\ln\left(\frac{\gamma_{\text{V}}^\circ}{X_{\text{Fe}}\gamma_{\text{Fe}}^\circ}\right)^{24} 
\]
\[
2\text{O}_2(g) = 4\text{[O]}_{\text{mass}(\text{Fe–Ni})} \quad \Delta G^\circ_{(8)} = 4\RT\ln\left(\frac{\gamma_{\text{O}}^\circ}{X_{\text{Ni}}\gamma_{\text{Ni}}^\circ}\right)^{24} 
\]

where \(\gamma_i^\circ\) denotes the activity coefficient of an \(i\) element at infinite dilution; \(\gamma_i\) denotes the activity coefficient; \(M_i\) denotes the molecular mass; \(X_i\) denotes the mole fraction.

As a standard state for vanadium and oxygen dissolved in the iron–nickel melt, an 1 mass% solution with the properties of ideal dilute solution was chosen, which is indicated in indexes \([\text{V}]_{\text{mass}(\text{Fe–Ni})}\) and \([\text{O}]_{\text{mass}(\text{Fe–Ni})}\). As a standard state for iron and nickel, the Fe–Ni mixture melt was chosen; in this case \(\alpha_{\text{Fe–Ni}} = 1\); \(\alpha_{\text{Fe–Ni}} = 1\). The Gibbs energy for the transition of these elements into the melt can be calculated by the equation

\[
\Delta G^\circ_{i} = \Delta G^\circ_{(5)} + \alpha_{\text{Fe–Ni}}\Delta G^\circ_{(6)} + \alpha_{\text{Fe–Ni}}\Delta G^\circ_{(7)} + \alpha_{\text{Fe–Ni}}\Delta G^\circ_{(8)} 
\]

where \(m\) denotes the FeO mole fraction and \((1-m)\) is the NiO mole fraction in the oxide phase above the Fe–Ni melts.\(^{25}\) When the iron–nickel melts are deoxidized with vanadium at its low concentrations, the FeV\(_2\)O\(_4\) and NiV\(_2\)O\(_4\) contents in the oxide phase is most likely proportional to the FeO and NiO in the same phase above the Fe–Ni melts, since the affinity of vanadium oxide to iron and nickel oxides are numerically similar, i.e., \(\Delta G^\circ_{(5)} = 22,190 \text{ J/mol}^{13}\) \(\Delta G^\circ_{(6)} = 16,747 \text{ J/mol}^{13}\). The \(m\) values are given in Table 1.

The equilibrium constant of reaction (1) was calculated using Eq. (12)

\[
\ln K = -\frac{\Delta G^\circ_{(1)}}{RT} \quad \text{(12)} 
\]

The molecular mass of the Fe–Ni melts was calculated as

\[
M_{\text{Fe–Ni}} = M_{\text{Fe}}X_{\text{Fe}} + M_{\text{Ni}}X_{\text{Ni}} \quad \text{(13)} 
\]

and the \(\gamma_{\text{Fe–Ni}}\) and \(\gamma_{\text{Fe–Ni}}\) activity coefficients were estimated according to the following equation\(^{26}\)

\[
\ln \gamma_{\text{Fe–Ni}} = X_{\text{Fe}}\ln \gamma_{\text{Fe}} + X_{\text{Ni}}\ln \gamma_{\text{Ni}} - (\ln \gamma_{\text{Fe}} + \ln \gamma_{\text{Ni}}) + \frac{X_{\text{Fe}}}{X_{\text{Ni}}}\ln \gamma_{\text{Ni}} - \ln \gamma_{\text{Fe}} 
\]

where \(\gamma_i^\circ\) denotes the activity coefficient of an \(i\) element at infinite dilution; \(\gamma_i\) denotes the activity coefficient; \(M_i\) denotes the molecular mass; \(X_i\) denotes the mole fraction.

As a standard state for vanadium and oxygen dissolved in the iron–nickel melt, an 1 mass% solution with the properties of ideal dilute solution was chosen, which is indicated in indexes \([\text{V}]_{\text{mass}(\text{Fe–Ni})}\) and \([\text{O}]_{\text{mass}(\text{Fe–Ni})}\). As a standard state for iron and nickel, the Fe–Ni mixture melt was chosen; in this case \(\alpha_{\text{Fe–Ni}} = 1\); \(\alpha_{\text{Fe–Ni}} = 1\). The Gibbs energy for the transition of these elements into the melt can be calculated by the equation \(\Delta G^\circ_{i} = RT\ln(X_i\gamma_i^\circ)\).

For reaction (1), the Gibbs energy was calculated using Eq. (11)

\[
\Delta G^\circ_{(1)} = m\Delta G^\circ_{(2)} + m\Delta G^\circ_{(3)} + m\Delta G^\circ_{(4)} + (1-m)\Delta G^\circ_{(5)} + (1-m)\Delta G^\circ_{(6)} + m\Delta G^\circ_{(7)} + m\Delta G^\circ_{(8)} + (1-m)\Delta G^\circ_{(10)} \quad \text{(11)} 
\]

where \(m\) denotes the FeO mole fraction and \((1-m)\) is the NiO mole fraction in the oxide phase above the Fe–Ni melts.\(^{25}\) When the iron–nickel melts are deoxidized with vanadium at its low concentrations, the FeV\(_2\)O\(_4\) and NiV\(_2\)O\(_4\) contents in the oxide phase is most likely proportional to the FeO and NiO in the same phase above the Fe–Ni melts, since the affinity of vanadium oxide to iron and nickel oxides are numerically similar, i.e., \(\Delta G^\circ_{(5)} = 22,190 \text{ J/mol}^{13}\) \(\Delta G^\circ_{(6)} = 16,747 \text{ J/mol}^{13}\). The \(m\) values are given in Table 1.

The equilibrium constant of reaction (1) was calculated using Eq. (12)

\[
\ln K = -\frac{\Delta G^\circ_{(1)}}{RT} \quad \text{(12)} 
\]

The molecular mass of the Fe–Ni melts was calculated as

\[
M_{\text{Fe–Ni}} = M_{\text{Fe}}X_{\text{Fe}} + M_{\text{Ni}}X_{\text{Ni}} \quad \text{(13)} 
\]

and the \(\gamma_{\text{Fe–Ni}}\) and \(\gamma_{\text{Fe–Ni}}\) activity coefficients were estimated according to the following equation\(^{26}\)

\[
\ln \gamma_{\text{Fe–Ni}} = X_{\text{Fe}}\ln \gamma_{\text{Fe}} + X_{\text{Ni}}\ln \gamma_{\text{Ni}} - (\ln \gamma_{\text{Fe}} + \ln \gamma_{\text{Ni}}) + \frac{X_{\text{Fe}}}{X_{\text{Ni}}}\ln \gamma_{\text{Ni}} - \ln \gamma_{\text{Fe}} \quad \text{(14)} 
\]
where $\epsilon_i$ denotes the first-order interaction parameter when component concentrations are expressed in mole fractions.

The $\gamma_\text{Fe}$ and $\gamma_\text{Ni}$ activity coefficients in molten iron and nickel, which were calculated for the iron–nickel melts are given in Table 1. The interaction parameters $e_{\text{NiO(Fe)}}^{\text{V}}(H_{11005}) = 0.27027); \quad e_{\text{FeO(Ni)}}^{\text{V}}(H_{11005}/H_{11002}) = 5.17927); \quad e_{\text{NiV(Fe)}}^{\text{O}}(H_{11005}/H_{11002}) = 2.8128$ were used for these calculations. There are no published data on the $e_{\text{FeV(Ni)}}^{\text{O}}$ interaction parameter; it is assumed as zero similar to the case of manganese. The $\gamma_\text{Fe}$ and $\gamma_\text{Ni}$ activity coefficients were taken from the published data.29) The calculated equilibrium constants of reaction (1) for different nickel contents in melt at 1873 K are shown in Table 1. The dependence of the equilibrium constant of this reaction on the nickel concentration is given in Fig. 2 in comparison with similar data on the deoxidation of the Fe–Ni melts with chromium,3) manganese,1) silicon,1) and aluminium.2) The equilibrium constants are given for the deoxidizer interaction with one atom of oxygen dissolved in melt.

The oxygen concentration in equilibrium with a given vanadium content can be calculated according to the equation

$$\log[\%O]_{\text{Fe–Ni}} = \frac{1}{4} \left( \log K_1 + \log a_{\text{FeNOV}} - \log C_{\text{Fe+Ni}} - 2 \log[\%V] \right) - [2e_{\text{FeV–Ni}}^\text{O} + 4e_{\text{FeO–Ni}}^\text{O}][\%V] - [4(1)^2 + 2e_{\text{FeV–Ni}}^\text{O}][\%O]$$ ..........................(15)

The Fe$_3$O$_4$ and NiV$_2$O$_4$ spinels are solid at 1873 K,30) therefore we can assume $a_{\text{FeNOV}} = 1$. The $[\%O]$ term in the right side of Eq. (15) can be expressed by the ratio $(K_1/C_{\text{Fe+Ni}})^{1/4}$ because of smallness of the [\%O] term one can assume$^{21}$ that

\[
(K_1/C_{\text{Fe+Ni}})^{1/4} = (\log[\%V])^{3/4} \quad \text{for} \quad \log K_1 < 0
\]

Such a substitution does not cause an appreciable error in the calculations and Eq. (15) takes the form

$$\log[\%O]_{\text{Fe–Ni}} = \frac{1}{4} \left( \log K_1 - \log C_{\text{Fe+Ni}} \right) - 2 \log[\%V] - [2e_{\text{FeV–Ni}}^\text{O} + 4e_{\text{FeO–Ni}}^\text{O}][\%V] - [4e_{\text{FeO–Ni}}^\text{O} + 2e_{\text{FeV–Ni}}^\text{O}][\%O]$$ ..........................(15a)

The reaction of deoxidation of the Fe–Ni melts with vanadium at its higher concentrations

$$V_2O_3(s) = 2[V] + 3[O]$$ ..........................(16)
can be represented as a sum of reactions (4), (7) and the reaction
\[ \frac{1}{2}O_2(g) = 3[O]_{\text{mas}[Fe-Ni]} \]
\[ \Delta G_{f}^{0}(7) = 3RT \ln(\gamma_{O}(Fe-Ni)M_{Fe-Ni}/M_{O}) - 100 \]

For reaction (16), the Gibbs energy and equilibrium constant were calculated using the equation

\[ \Delta G_{f}^{0}(16) = \Delta G_{f}^{0}(4) + \Delta G_{f}^{0}(7) + \Delta G_{f}^{0}(17) \]

and Eq. (12), respectively. The results obtained are shown in Table 1. The dependence of the equilibrium constant of the V₂O₃ formation at 1873 K on the nickel content in melt is considerably stronger in comparison with iron (\( \gamma_{O}(Fe) = 0.122 \)); the deoxidizing ability of vanadium is lower than that of manganese and is close to the deoxidizing ability of chromium. This can be explained by the fact that the bond strength of oxygen with liquid nickel is appreciably weaker than that with liquid iron (\( \gamma_{O}(Fe) = 0.0105 \)); \( \gamma_{O}(Ni) = 0.357 \)), but the bond strength of vanadium with nickel is considerably stronger in comparison with iron (\( \gamma_{O}(Fe) = 0.122 \); \( \gamma_{O}(Ni) = 0.011 \)).

The oxygen concentration in melt that is in equilibrium with a given vanadium content at its higher concentrations can be calculated according to Eq. (15a); when it was higher than this melt was taken from reference books. There are no published data on the vanadium concentration in this point (\([%V]^*\)) for different melts at 1873 K is the following:

| Ni, % | 0 | 20 | 40 | 60 | 80 | 100 |
|-------|---|----|----|----|----|-----|
| [%V]^* | 0.137 | 0.165 | 0.200 | 0.142 | 0.038 | 7.027 \cdot 10^{-4} |

With increasing nickel content, [%V]^* initially rises but, then, decreases sharply (Fig. 3). In all likelihood, a change in the reaction mechanism occurs not in the point but in a narrow concentration range. Figure 1 demonstrates a comparison of the [%V]^* values obtained for iron and nickel with the published data.

The equilibrium oxygen concentrations in the Fe–Ni melts at the vanadium content lower than [%V]^* were calculated according to Eq. (15a); when it was higher than this value, Eq. (19a) was used. The \( e_{i}^{V(Ni)} \) interaction parameters used in these calculations for different melts are given in Table 1. The interaction parameters for iron and nickel melts were taken from reference books. There are no published numerical data on the \( e_{i}^{V(Ni)} \) interaction parameter; for this reason, it was calculated using the formula

\[ e_{i}^{V(Ni)} = -2\Delta H_{i}^{e}/RT \]

According to the published data, \( \Delta H_{i}^{e} = -52.126 \). Therefore, \( e_{i}^{V(Ni)} = 6.693 \) and \( e_{i}^{V(Ni)} = 0.0329 \).

The Fe–Ni melts are characterized by a slight deviation from the ideality (\( \gamma_{Fe}^{Ni} \) and \( \gamma_{Ni}^{Fe} \) activity coefficients that characterize the behavior of iron and nickel in these melts are given in Table 1), which allows one (as a first approximation) to use the relationship

\[ e_{i}^{Fe-Ni} = e_{i}^{Fe-Ni} + e_{i}^{Ni}X_{Ni} \]

for the calculation of the \( e_{i}^{Fe-Ni} \), \( e_{i}^{Ni} \), and \( e_{i}^{O} \) interaction parameters as applied to the Fe–Ni melts.

The calculated dependences of the oxygen concentration on the vanadium content in the Fe–Ni melts are given below:

\[ [V] < 0.137\%: \]
\[ \log[\%O]_{Fe} = -1.721 - 0.129[\%V] + 7.606 \cdot 10^{-3}[\%V]^{2}; \]

\[ [V] > 0.137\%: \]
\[ \log[\%O]_{Fe} = \frac{1}{3} \log K_{i}^{(16)} - \frac{1}{2} \log [\%V] + \frac{1}{3} \log K_{i}^{(16)} - \frac{1}{2} \log [\%O] \]

or

\[ K_{i}^{(16)} = \frac{([%V] - \alpha_{v(Fe_{Ni})})^{2}}{([%O] - \alpha_{v(Fe_{Ni})})^{2}} \] (16a)

1/2 log \([%V]\) - 1/2 log \([%O]\) = 1/3 log \([%V]\) - 2/3 log \([%O]\) .... (20a)

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The obtained dependences of the equilibrium oxygen concentration on the contents of vanadium and nickel in melt at 1873 K are shown in Fig. 4. As is seen, the deoxidizing ability of vanadium slightly decreases when the nickel content in melt rises to 20% but then it increases considerably with nickel. The oxygen solubility curves for the iron–nickel melts with vanadium have minima whose positions shift to the lower vanadium concentrations as the nickel content rises. The more addition of vanadium causes the increase in the oxygen concentration in melt; in this case, the higher the nickel content, the sharper the increase in the oxygen concentration after the minimum when vanadium is added into the melt.

The curves of oxygen solubility in the Fe–Ni melts pass through a minimum. To determine the vanadium concentrations corresponding to the minimum oxygen contents ([%O]_{min}), the equation\(^{(21)}\)

\[
\%R = \frac{1}{2.3} \cdot \frac{x}{(x \cdot e_x^R + y \cdot e_y^R)}
\]

was used, where \(x\) and \(y\) are the indexes in the formula of \(R \cdot O\) oxide.

In the given case, this equation for \(V_2O_3\) oxide takes form

\[
\%V = \frac{1}{2.3} \cdot \frac{2}{(2 \cdot e_x^V + 3 \cdot e_y^V)}
\]

The vanadium concentrations calculated by Eq. (23a) and the oxygen contents corresponding to these concentrations are shown below:

\[
\begin{array}{ccccccc}
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} & \text{Ni} \\
\end{array}
\]

3. Experimental

The deoxidation of iron–nickel melts with vanadium was experimentally studied by the example of the Fe–40%Ni alloy. These experiments have been carried out in an induction furnace fed by a 10 kV · A high-frequency (400 kHz) generator. The scheme of experimental apparatus is shown in Fig. 6. As initial materials, carbonyl iron (99.99%), electrolytic nickel (99.99%), and aluminothermic vanadium (98%) were used. Total charge was 200 g. This charge containing iron and nickel in the ratio corresponding to the Fe–40%Ni alloy was placed into an Al₂O₃ crucible (outer diameter: 43 mm, inner diameter: 39 mm, height: 54 mm), which, in turn, was located in an external protective crucible. The charge was melted under Ar–H₂ atmosphere. Hydrogen and argon were preliminarily purified from oxygen impurities, water vapor, sulphides, organic compounds, and mechanical and other impurities. We used high-pure argon
(99.992%), where the volume percent of oxygen was ≤0.0007% according to the Russian Standard GOST 10157-79. After a gas purification system of experimental unit, the volume fraction of oxygen in argon was less than 10⁻⁵%. Argon and hydrogen consumptions were 150 and 50 mL/min, respectively. When metal was completely melted, the supply of hydrogen was stopped and the melt was held under argon atmosphere (150 mL/min, 1873 K). Vanadium was introduced into the melt without breaking the furnace air-tightness; then this melt was held at the given temperature under Ar atmosphere until the equilibrium was stated. The temperature was measured by the Pt-6%Rh/Pt-30%Rh thermocouple. On reaching the equilibrium, the melt was sampled to determine the nickel, vanadium, and oxygen contents. The time of equilibrium attainment was 30 min (determined according to the results of previous experiments). The oxygen concentration was analyzed using a TC-600 gas analyzer (Leco Instruments). Vanadium and nickel contents were determined by an ULTIMA 2 ICP optical emission spectrometer (Horiba Jobin Yvon).

4. Results and Discussion

The experimental data on the deoxidation of Fe–Ni alloys with vanadium are shown in Table 2 and Fig. 7 in comparison with the data calculated by Eqs. (25a) and (25b). The vanadium concentration in melt was changed from 0.014 to 3.19%. With increasing vanadium content the oxygen concentration decreases.

![Fig. 5. Oxygen concentration in liquid (a) iron and (b) nickel depending on the content of vanadium at 1873 K.](image)
![Fig. 6. Schematic diagram of the experimental apparatus.](image)

![Fig. 7. Oxygen concentration in the Fe–40%Ni melt depending on the vanadium content at 1873 K.](image)

| [Ni] | [V] | [O] | [Ni] | [V] | [O] |
|------|-----|-----|------|-----|-----|
| 40.1 | 0.014 | 0.0458 | 41.2 | 0.46 | 0.0138 |
| 40.0 | 0.014 | 0.0748 | 40.0 | 0.66 | 0.0166 |
| 41.2 | 0.016 | 0.0666 | 38.2 | 0.68 | 0.0248 |
| 40.1 | 0.058 | 0.0350 | 40.6 | 0.70 | 0.0105 |
| 41.2 | 0.076 | 0.0234 | 39.9 | 0.79 | 0.0151 |
| 40.0 | 0.12 | 0.0209 | 40.6 | 0.89 | 0.0097 |
| 40.1 | 0.13 | 0.0278 | 38.2 | 1.03 | 0.0152 |
| 39.9 | 0.14 | 0.0133 | 39.9 | 1.15 | 0.0256 |
| 40.0 | 0.22 | 0.0263 | 39.9 | 1.23 | 0.0247 |
| 40.1 | 0.23 | 0.0271 | 38.2 | 1.43 | 0.0144 |
| 40.6 | 0.27 | 0.0166 | 38.2 | 1.84 | 0.0094 |
| 41.2 | 0.27 | 0.0101 | 41.2 | 1.87 | 0.0148 |
| 40.1 | 0.32 | 0.0291 | 38.2 | 2.28 | 0.0168 |
| 40.0 | 0.34 | 0.0163 | 38.2 | 2.69 | 0.0085 |
| 39.9 | 0.35 | 0.0158 | 38.2 | 3.19 | 0.0117 |
log[%O] = A + 1/2 log[%V] + B · [%V] + C [%V]^{1/2}

and in a range of 0.2–3.19%, the form of equation was assumed as

log[%O] = A + 2/3 log[%V] + B · [%V] - C [%V]^{2/3}

This program using the methods of regression analysis allowed us to determine the coefficients for each term of the equation. The following dependences were obtained:

0.014% < [%V] < 0.2%

log[%O]_{FE-40%Ni} = -2.091 - 1/2 log[%V] + 0.273 [%V] - 4.803 \cdot 10^{-3} [%V]^{1/2} \ldots \ldots \ldots (30)

0.2% < [%V] < 3.19%

log[%O]_{FE-40%Ni} = -2.091 - 2/3 log[%V] + 0.252 [%V] - 4.133 \cdot 10^{-3} [%V]^{2/3} \ldots \ldots \ldots (31)

As is seen in Fig. 7, the deoxidation ability of vanadium in the Fe–Ni melts determined experimentally somewhat exceeds that obtained by calculations.

5. Conclusions

The thermodynamic analysis of oxygen solutions in the Fe–Ni melts with vanadium has been carried out. When the nickel concentration in these melts increases to 20%, the deoxidizing ability of vanadium slightly decreases but, then, it rises appreciably as the nickel content increases. The oxygen solubility curves pass through the minima whose positions shift to the lower vanadium concentrations as the nickel content rises, i.e., from 2.32% V for pure iron to 0.77% for pure nickel. The further addition of vanadium causes an increase in the oxygen concentration in melts. In pure nickel and alloys containing more than 60% Ni, the deoxidization ability of vanadium is lower than that of manganese and is close to the deoxidizing ability of chromium. This can be explained by the fact that, although the bond strength of oxygen with nickel is considerably weaker in comparison with that with iron ($\gamma^{0}_{OFe}$ = 0.0105; $\gamma^{0}_{O Ni}$ = 0.357), the bond strength of vanadium with nickel is appreciably stronger as compared to iron ($\gamma^{0}_{OFe}$ = 0.1; $\gamma^{0}_{VN i}$ = 0.011). The deoxidation of iron–nickel melts with vanadium was experimentally studied by the example of the Fe–40%Ni alloy.

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