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Solubility of Oxygen in Titanium-Containing Iron–Nickel Melts

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Abstract—The solubility of oxygen in titanium-containing iron–nickel melts is studied experimentally for the example of Fe–40% Ni alloy at 1873 K. The experiments yield values for the equilibrium constant of the reaction of titanium and oxygen dissolved in Fe–40% Ni melt ($\log K_{(1)(\mathrm{Fe-40\%\,Ni})} = -15.17$), the Gibbs energy of that reaction ($\Delta G^{\circ}_{(1)(\mathrm{Fe-40\%\,Ni})} = 543\,360$ J/mol), and the interaction parameters for those solutions ($e^{\mathrm{O}}_{\mathrm{Ti(Fe-40\%\,Ni)}} = -1.420$; $e^{\mathrm{Ti}}_{\mathrm{O(Fe-40\%\,Ni)}} = -0.472$; $e^{\mathrm{Ti}}_{\mathrm{Ti(Fe-40\%\,Ni)}} = 0.116$). For a broad range of alloy compositions in the Fe–Ni system, the equilibrium constant of the reaction of titanium and oxygen dissolved in the melt, the Gibbs energy of that reaction, and the interaction parameters for those solutions are calculated at 1873 K. The solubility of oxygen in titanium-containing iron–nickel melts is determined at 1873 K. The reducing properties of titanium fall with increase in the Ni content to 40% and then increase sharply with further increase in the melt's Ni content. This may be explained in that increase in the Ni content is associated, on the one hand, with significant decrease in the bond strength of oxygen atoms in the melt ($\gamma^{\circ}_{\mathrm{O(Fe)}} = 0.0103$; $\gamma^{\circ}_{\mathrm{O(Ni)}} = 0.337$) and, on the other, with considerable increase in the bond strength of titanium atoms ($\gamma^{\circ}_{\mathrm{Ti(s)(Fe)}} = 0.0083$; $\gamma^{\circ}_{\mathrm{Ti(s)(Ni)}} = 0.000083$). The solubility curves of oxygen in iron–nickel melts pass through a minimum. As the Ni content increases, the minimum is shifted to lower Ti content.

Keywords: iron–nickel melts, solubility of oxygen, titanium, experiments, thermodynamic analysis, interaction parameters

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Iron–Nickel alloys are widely used in engineering today. We know that the presence of oxygen in such alloys impairs their performance. The physicochemical properties of oxygen solutions in iron and nickel melts have been studied in some detail. The thermodynamic parameters of such solutions may be found in handbooks [1, 2]. However, in order to optimize the production of iron–nickel alloys, we need to study the thermodynamic parameters of oxygen solutions in Fe–Ni melts, since they cannot be derived by adding the properties of solutions in pure iron and nickel.

In the production of iron–nickel alloys, titanium is used as an alloying element. It has greater oxygen affinity than iron and nickel. If titanium is added to the unreduced melt, much of it will be oxidized and lost. Hence, it is of both theoretical and practical interest to investigate the thermodynamics of solutions of oxygen in Fe–Ni melts.

THERMODYNAMIC ANALYSIS

In iron–nickel melts, the reaction product of titanium and dissolved oxygen is the oxide Ti_3O_5. The reaction of titanium and dissolved oxygen

$$\mathrm{Ti_3O_5(s)} = 3[\mathrm{Ti}]_{\mathrm{(Fe-Ni)}} + 5[\mathrm{O}]_{\mathrm{(Fe-Ni)}}, \qquad (1)$$

$$K_{(1)} = \frac{([\%\mathrm{Ti}]f_{\mathrm{Ti}})^3([\%\mathrm{O}]f_{\mathrm{O}})^5}{a_{\mathrm{Ti_3O_5}}} \qquad (1\mathrm{a})$$

may be expressed as the sum of the reactions

$$\begin{gathered}\mathrm{Ti_2O_3(s)} = 3\mathrm{Ti(s)} + 5/2\mathrm{O_2(g)},\\ \Delta G^{\circ}_{(2)} = 2427\,004 - 414.41\,T, \text{ J/mol [3]};\end{gathered} \qquad (2)$$

$$\begin{gathered}3\mathrm{Ti(s)} = 3[\mathrm{Ti}]_{1\%\mathrm{(Fe-Ni)}},\\ \Delta G^{\circ}_{(3)} = 3RT\ln\left(\frac{\gamma^{\circ}_{\mathrm{Ti(s)(Fe-Ni)}}M_{\mathrm{Fe-Ni}}}{M_{\mathrm{Ti}} \times 100}\right);\end{gathered} \qquad (3)$$

$$\begin{gathered}5/2\mathrm{O_2(g)} = 5[\mathrm{O}]_{1\%\mathrm{(Fe-Ni)}},\\ \Delta G^{\circ}_{(4)} = 5RT\ln\left(\frac{\gamma^{\circ}_{\mathrm{O(Fe-Ni)}}M_{\mathrm{Fe-Ni}}}{M_{\mathrm{O}} \times 100}\right).\end{gathered} \qquad (4)$$

For Eq. (1), the Gibbs energy is calculated as

$$\Delta G^{\circ}_{(1)} = \Delta G^{\circ}_{(2)} + \Delta G^{\circ}_{(3)} + \Delta G^{\circ}_{(4)}.$$

Since the thermodynamic calculations in the present work correspond to a temperature of 1873 K,

Table 1. Equilibrium concentrations of titanium and oxygen in Fe–40% Ni alloy at 1873 K, % (experimental values)

[Ni]	[Ti]	[O]	[Ni]	[Ti]	[O]
42.3	0.01	0.0145	41.2	0.487	0.0019
42.0	0.015	0.0133	40.4	0.6	0.0025
40.4	0.038	0.0065	40.4	0.72	0.0031
42.1	0.107	0.0050	41.3	0.882	0.0028
41.6	0.153	0.0045	40.9	1.03	0.0027
42.1	0.158	0.0017	40.4	1.11	0.0018
41.6	0.249	0.0025	40.4	1.12	0.0020

where titanium is solid ($T_m = 1944$ K [4]), $\gamma^{\circ}_{\text{Ti(s)(Fe)}}$ is calculated.

The solution of solid titanium in iron

$$\text{Ti(s)} = [\text{Ti}]_{1\%(\text{Fe})},$$
$$\Delta G^{\circ}_{(5)} = RT\ln\left(\frac{\gamma^{\circ}_{\text{Ti(s)(Fe)}}M_{\text{Fe}}}{M_{\text{Ti}} \times 100}\right) \tag{5}$$

may be expressed as the sum of the reactions

$$\text{Ti(s)} = \text{Ti(l)},$$
$$\Delta G^{\circ}_{(6)} = 2093, \text{ J/mol [5]}; \tag{6}$$

$$\text{Ti(l)} = [\text{Ti}]_{1\%(\text{Fe})},$$
$$\Delta G^{\circ}_{(7)} = RT\ln\left(\frac{\gamma^{\circ}_{\text{Ti(l)(Fe)}}M_{\text{Fe}}}{M_{\text{Ti}} \times 100}\right). \tag{7}$$

For solutions of liquid titanium in iron, the temperature dependence of $\gamma^{\circ}_{\text{Ti(l)(Fe)}}$ was presented in [6]

$$\ln\gamma^{\circ}_{\text{Ti(l)(Fe)}} = -20890/T + 6.228.$$

The Gibbs energy for Eq. (5) at 1873 K is $\Delta G^{\circ}_{(5)} = -143930$ J/mol. That permits the calculation of $\gamma^{\circ}_{\text{Ti(s)(Fe)}}$ from the equation

$$\ln\gamma^{\circ}_{\text{Ti(s)(Fe)}} = \frac{\Delta G^{\circ}_{(5)}}{RT} + \ln\left(\frac{M_{\text{Ti}} \times 100}{M_{\text{Fe}}}\right).$$

Thus, $\gamma^{\circ}_{\text{Ti(s)(Fe)}} = 0.0083$ at 1873 K.

The oxygen concentration in the melt in equilibrium with the specified titanium content for Eq. (1) may be calculated from the formula

$$\begin{aligned}\log[\%\,\text{O}]_{\text{Fe–Ni}} = {} & \frac{1}{5}\{\log K_{(1)} + \log a_{\text{Ti}_3\text{O}_5} - 3\log[\%\,\text{Ti}] \\ & - [3e^{\text{Ti}}_{\text{Ti(Fe–Ni)}} + 5e^{\text{Ti}}_{\text{O(Fe–Ni)}}][\%\,\text{Ti}] \\ & - [5e^{\text{O}}_{\text{O(Fe–Ni)}} + 3e^{\text{O}}_{\text{Ti(Fe–Ni)}}][\%\,\text{O}]\}.\end{aligned} \tag{8}$$

The oxide Ti_3O_5 ($T_m = 2050$ K [7]) is solid at 1873 K. Therefore, $a_{\text{Ti}_3\text{O}_5} = 1$. On the right side of Eq. (8), [% O] is small and may be expressed in terms of the ratio $(K_{(1)}/[\%\,\text{Ti}]^3)^{1/5}$ if we assume in Eq. (1a) that $f_{\text{Ti}} \approx 1$ and $f_{\text{O}} \approx 1$. This does not introduce much error in the calculations [3]. Then Eq. (8) takes the form

$$\begin{aligned}\log[\%\,\text{O}]_{\text{Fe–Ni}} = {} & \frac{1}{5}\Bigg\{\log K_{(1)} - 3\log[\%\,\text{Ti}] \\ & - [3e^{\text{Ti}}_{\text{Ti(Fe–Ni)}} + 5e^{\text{Ti}}_{\text{O(Fe–Ni)}}][\%\,\text{Ti}] \\ & - [5e^{\text{O}}_{\text{O(Fe–Ni)}} + 3e^{\text{O}}_{\text{Ti(Fe–Ni)}}]\left(\frac{K_{(1)}}{[\%\,\text{Ti}]^3}\right)^{1/5}\Bigg\}\end{aligned} \tag{8a}$$

or in general form

$$\begin{aligned}\log[\%\,\text{O}]_{\text{Fe–Ni}} = {} & A - \frac{3}{5}\log[\%\,\text{Ti}] \\ & + B[\%\,\text{Ti}] + \frac{C}{[\%\,\text{Ti}]^{3/5}}.\end{aligned} \tag{9}$$

EXPERIMENTAL

In the present work, we investigate the solubility of oxygen in titanium-containing iron–nickel melts. In particular, we select the Fe–40% Ni alloy, which is widely used in engineering.

The experimental method and procedure were described in [8]. The batch consists of carbonyl iron (99.99% purity), electrolytic nickel (99.99% purity), and iodide titanium (99.8% purity). A LECO TC-600 gas analyzer (precision $\pm 5 \times 10^{-5}$%) is used for analysis of the oxygen content in the metal samples; the titanium and nickel content is determined on a Horiba Jobin Yvon Ultima-2 atomic-emission spectrometer with inductive plasma (precision ±0.001%).

RESULTS AND DISCUSSION

The experimental results are presented in Table 1 and in Fig. 1. The dashed line in Fig. 1 corresponds to the solubility of oxygen in Fe–40% Ni melt at 1873 K: $[\text{O}]_{(\text{Fe–40\% Ni})} = 0.17\%$ [9].

Quattro Pro software is used for regression analysis of the experimental data on the basis of Eq. (9). We obtain the following values of the coefficients in Eq. (8) (determination coefficient $R^2 = 0.70$)

$$\begin{aligned}\log[\%\,\text{O}]^{\text{exp}}_{(\text{Fe–40\% Ni})} = {} & -3.034 - \frac{3}{5}\log[\%\,\text{Ti}] \\ & + 0.402[\%\,\text{Ti}] + \frac{8.860 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}.\end{aligned} \tag{10}$$

In Eq. (9)

$$A = \frac{1}{5}\log K_{(1)};$$

$$B = -\frac{1}{5}[3e^{\mathrm{Ti}}_{\mathrm{Ti(Fe-40\%\,Ni)}} + 5e^{\mathrm{Ti}}_{\mathrm{O(Fe-40\%\,Ni)}}];$$

$$C = -\frac{1}{5}[5e^{\mathrm{O}}_{\mathrm{O(Fe-40\%\,Ni)}} + 3e^{\mathrm{O}}_{\mathrm{Ti(Fe-40\%\,Ni)}}](K_{(1)})^{1/5}.$$

That permits calculation of the interaction parameters and equilibrium constants in Eq. (1) on the basis of experimental data.

Iron–Nickel melts are characterized by slight deviation from ideal behavior [10]. That permits the calculation of the interaction parameters $\varepsilon^{j}_{i(\mathrm{Fe-Ni})}$ (and correspondingly $e^{j}_{i(\mathrm{Fe-Ni})}$) from the following formula, in the first approximation [11]

$$\varepsilon^{j}_{i(\mathrm{Fe-Ni})} = \varepsilon^{j}_{i(\mathrm{Fe})}X_{\mathrm{Fe}} + \varepsilon^{j}_{i(\mathrm{Ni})}X_{\mathrm{Ni}}. \qquad (11)$$

Knowing $e^{\mathrm{O}}_{\mathrm{O(Fe)}} = -0.17$ [1] and $e^{\mathrm{O}}_{\mathrm{O(Ni)}} = 0$ [2] at 1873 K (Table 2), we find from Eq. (11) that $e^{\mathrm{O}}_{\mathrm{O(Fe-40\%\,Ni)}} = -0.106$. Taking account of the numerical values in Eq. (10) and the value of $e^{\mathrm{O}}_{\mathrm{O(Fe-40\%\,Ni)}}$ for Fe–40% Ni alloy at 1873 K, we obtain

$$e^{\mathrm{O}}_{\mathrm{Ti(Fe-40\%\,Ni)}} = -1.420;\ e^{\mathrm{Ti}}_{\mathrm{O(Fe-40\%\,Ni)}} = -0.472;$$

$$e^{\mathrm{Ti}}_{\mathrm{Ti(Fe-40\%\,Ni)}} = 0.116;\ \log K_{(1)(\mathrm{Fe-40\%\,Ni})} = -15.17;$$

$$K_{(1)(\mathrm{Fe-40\%\,Ni})} = 6.761 \times 10^{-16};$$

$$\Delta G^{\circ}_{(1)(\mathrm{Fe-40\%\,Ni})} = 543360\ \mathrm{J/mol}.$$

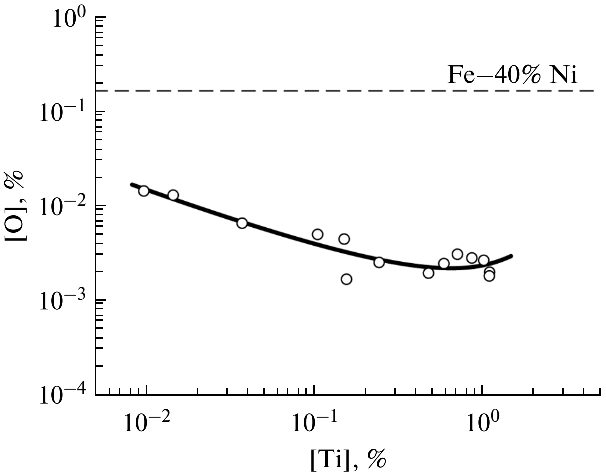

Fig. 1. Dependence of the oxygen concentration in Fe–40% Ni melt on the Ti content at 1873 K.

On that basis, we may calculate the interaction parameters for Fe–Ni alloys of different composition (Table 2).

For Eq. (4) at 1873 K, we find that $\Delta G^{\circ}_{(4)(\mathrm{Fe-40\%\,Ni})} = -559136$ J/mol. The molecular mass for Fe–Ni melts is calculated from the equation [11]

$$M_{\mathrm{Fe-Ni}} = M_{\mathrm{Fe}}X_{\mathrm{Fe}} + M_{\mathrm{Ni}}X_{\mathrm{Ni}}$$

and the activity coefficient $\gamma^{\circ}_{i(\mathrm{Fe-Ni})}$ from the equation [12]

$$\ln\gamma^{\circ}_{i(\mathrm{Fe-Ni})} = X_{\mathrm{Fe}}\ln\gamma^{\circ}_{i(\mathrm{Fe})} + X_{\mathrm{Ni}}\ln\gamma^{\circ}_{i(\mathrm{Ni})}$$
$$+ X_{\mathrm{Fe}}X_{\mathrm{Ni}}[X_{\mathrm{Ni}}(\ln\gamma^{\circ}_{i(\mathrm{Ni})} - \ln\gamma^{\circ}_{i(\mathrm{Fe})} + \varepsilon^{\mathrm{Fe}}_{i(\mathrm{Ni})}) \qquad (12)$$
$$+ X_{\mathrm{Fe}}(\ln\gamma^{\circ}_{i(\mathrm{Fe})} - \ln\gamma^{\circ}_{i(\mathrm{Ni})} + \varepsilon^{\mathrm{Ni}}_{i(\mathrm{Fe})})].$$

Table 2. Equilibrium constants of Eq. (1) and the activity coefficients and interaction parameters in Fe–Ni melts at 1873 K

Parameter	Ni, %					
	0	20	40	60	80	100
$\Delta G^{\circ}_{(1)}$, J/mol	601471	559428	543360	554108	593874	664140
$\log K_{(1)}$	–16.792	–15.619	–15.170	–15.470	–16.580	–18.542
X_{Fe}	1.0	0.808	0.612	0.412	0.208	0
X_{Ni}	0	0.192	0.388	0.588	0.792	1.0
$M_{\mathrm{Fe-Ni}}$	55.847	56.393	56.950	57.519	58.098	58.69
$\gamma^{\circ}_{\mathrm{Ti(s)}}$	0.0083	0.00229	0.00067	0.00023	0.00011	0.000083
$\gamma^{\circ}_{\mathrm{O}}$	0.0103 [1]	0.0128	0.0214	0.0457	0.1171	0.337 [2]
$e^{\mathrm{O}}_{\mathrm{O}}$	–0.17 [1]	–0.139	–0.106	–0.072	–0.037	0 [2]
$e^{\mathrm{Ti}}_{\mathrm{Ti}}$	0.041 [1]	0.078	0.116	0.156	0.197	0.240
$e^{\mathrm{Ti}}_{\mathrm{O}}$	–0.34 [6]	–0.405	–0.472	–0.542	–0.615	–0.690
$e^{\mathrm{O}}_{\mathrm{Ti}}$	–1.026 [6]	–1.219	–1.420	–1.629	–1.845	–2.071

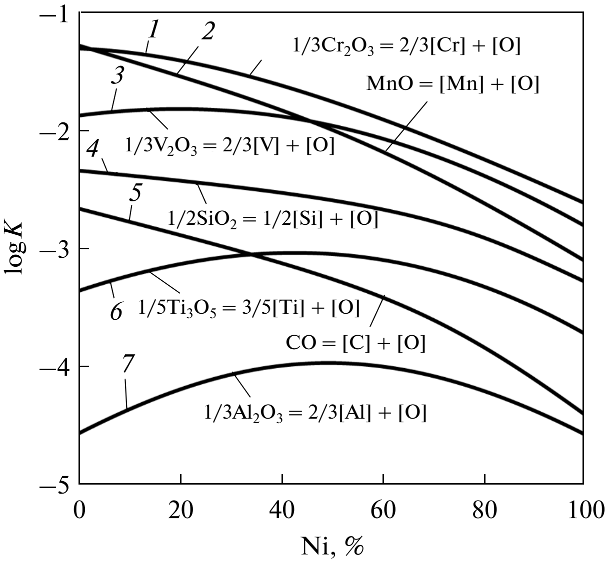

Fig. 2. Dependence of the equilibrium constants for the reduction of Fe–Ni melts by chromium (*1*), manganese (*2*), vanadium (*3*), silicon (*4*), carbon (*5*), titanium (*6*), and aluminum (*7*) on the Ni content at 1873 K.

In calculating the activity coefficient $\gamma^\circ_{\text{O(Fe–Ni)}}$, we use the values $\gamma^\circ_{\text{O(Fe)}} = 0.0103$ [1] and $\gamma^\circ_{\text{O(Ni)}} = 0.337$ [2] (Table 2) and also the interaction parameters $\varepsilon^{\text{Ni}}_{\text{O(Fe)}} = 0.270$ [13] and $\varepsilon^{\text{Fe}}_{\text{O(Ni)}} = -5.179$ [13]. Table 2 presents the results.

Knowing $\Delta G^\circ_{(1)(\text{Fe–40\% Ni})}$ and $\Delta G^\circ_{(4)(\text{Fe–40\% Ni})}$ and calculating $\Delta G^\circ_{(2)(\text{Fe–40\% Ni})} = 1650814$ J/mol at 1873 K, we may determine the Gibbs energy for Eq. (3): $\Delta G^\circ_{(3)(\text{Fe–40\% Ni})} = -548318$ J/mol. That permits the calculation of $\gamma^\circ_{\text{Ti(s)(Fe–40\% Ni)}}$ from the equation

$$\ln\gamma^\circ_{\text{Ti(s)(Fe–40\% Ni)}} = \frac{\Delta G^\circ_{(3)}}{3RT} + \ln\left(\frac{M_{\text{Ti}} \times 100}{M_{\text{Fe–40\% Ni}}}\right).$$

At 1873 K, $\gamma^\circ_{\text{Ti(s)(Fe–40\% Ni)}} = 0.00067$. Knowing $\gamma^\circ_{\text{Ti(s)(Fe)}} = 0.0083$ (Table 2) and $\gamma^\circ_{\text{Ti(s)(Fe – 40\% Ni)}}$, we may determine the activity coefficient $\gamma^\circ_{\text{Ti(s)(Ni)}} = 0.000083$ from Eq. (12) and then the activity coefficient $\gamma^\circ_{\text{Ti(s)(Fe–Ni)}}$ for Fe–Ni alloys of different composition (Table 2). In the calculations, we use the value $\varepsilon^{\text{Ni}}_{\text{Ti(Fe)}} = -6.17$ [14]. The handbooks do not give a value for $\varepsilon^{\text{Fe}}_{\text{Ti(Ni)}}$. It is assumed to be zero, by analogy with aluminum [15].

On the basis of the results, we may calculate the Gibbs energy $\Delta G^\circ_{(1)}$ and equilibrium constant $K_{(1)}$ for Fe–Ni alloys of different composition (Table 2). The dependence of the equilibrium constants for Eq. (1) on the Ni content is shown in Fig. 2 in comparison with data for the reduction of Fe–Ni melts by chromium [16], manganese [17], vanadium [18], silicon [17], carbon [19], and aluminum [20]. The equilibrium constants are presented for the reaction of the reducing agent with a single oxygen atom dissolved in melt. That clarifies the comparison of the results. As we see for the example of titanium, the equilibrium constant for Eq. (1) at first increases with increase in Ni content to ~40% and then declines at higher Ni contents. This may be explained in that increase in the Ni content significantly lowers the bond strength of the oxygen atoms in the melt ($\gamma^\circ_{\text{O(Fe)}} = 0.0103$; $\gamma^\circ_{\text{O(Ni)}} = 0.337$), on the one hand; and considerably increases the bond strength of the titanium atoms ($\gamma^\circ_{\text{Ti(s)(Fe)}} = 0.0083$; $\gamma^\circ_{\text{Ti(s)(Ni)}} = 0.000083$), on the other.

Given the values of the equilibrium constants for Eq. (1) and the interaction parameters for alloys of different composition at 1873 K (Table 2), we may write Eq. (8a) in the form

$$\log[\%\,\text{O}]_{\text{Fe}} = -3.359 - \frac{3}{5}\log[\%\,\text{Ti}] + 0.315[\%\,\text{Ti}] + \frac{3.441 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}; \tag{13a}$$

$$\log[\%\,\text{O}]_{(\text{Fe–20\% Ni})} = -3.124 - \frac{3}{5}\log[\%\,\text{Ti}] + 0.358[\%\,\text{Ti}] + \frac{6.545 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}; \tag{13b}$$

$$\log[\%\,\text{O}]_{(\text{Fe–40\% Ni})} = -3.034 - \frac{3}{5}\log[\%\,\text{Ti}] + 0.402[\%\,\text{Ti}] + \frac{8.860 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}; \tag{13c}$$

$$\log[\%\,\text{O}]_{(\text{Fe–60\% Ni})} = -3.094 - \frac{3}{5}\log[\%\,\text{Ti}] + 0.448[\%\,\text{Ti}] + \frac{8.450 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}; \tag{13d}$$

$$\log[\%\,\text{O}]_{(\text{Fe–80\% Ni})} = -3.316 - \frac{3}{5}\log[\%\,\text{Ti}] + 0.496[\%\,\text{Ti}] + \frac{5.525 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}; \tag{13e}$$

$$\log[\%\,\text{O}]_{\text{Ni}} = -3.708 - \frac{3}{5}\log[\%\,\text{Ti}] + 0.546[\%\,\text{Ti}] + \frac{2.431 \times 10^{-4}}{[\%\,\text{Ti}]^{3/5}}. \tag{13f}$$

The dependence of the equilibrium oxygen concentration on the Ti and Ni content in Fe–Ni melts at

Table 3. Equilibrium concentrations of titanium and oxygen in Fe–Ni melts at 1873 K, % (calculated values)

[Ti]	[O]					
	Fe	Fe–20% Ni	Fe–40% Ni	Fe–60% Ni	Fe–80% Ni	Ni
0.01	0.00708	0.01231	0.01532	0.01330	0.00790	0.00317
0.02	0.00469	0.00812	0.01009	0.00877	0.00524	0.00211
0.05	0.00275	0.00477	0.00593	0.00518	0.00311	0.00126
0.1	0.00188	0.00327	0.00408	0.00358	0.00217	0.00089
0.2	0.00133	0.00234	0.00295	0.00261	0.00160	0.00066
0.5	0.00096	0.00173	0.00224	0.00205	0.00130	0.00056
1.0	0.00091	0.00172	0.00235	0.00227	0.00152	0.00069
2.0	0.00124	0.00258	0.00391	0.00420	0.00313	0.00160

1873 K according to Eqs. (13a)–(13f) is shown in Table 3 and in Fig. 3. As follows from the results, the reducing properties of titanium at first decline with increase in Ni content to 40% and then rise sharply at higher Ni contents. The solubility curves of oxygen in iron–nickel melts pass through a minimum, which is shifted to lower Ti content with increase in the Ni content.

The titanium content corresponding to the minimum oxygen concentration may be determined from the equation [21]

$$[\%\ \mathrm{R}]' = -\frac{m}{2.3[me_{\mathrm{R}}^{\mathrm{R}} + ne_{\mathrm{O}}^{\mathrm{R}}]}, \qquad (14)$$

where m and n are the subscripts in the formula for the oxide $\mathrm{R}_m\mathrm{O}_n$. In the case of $\mathrm{Ti_3O_5}$, Eq. (14) takes the form

$$[\%\ \mathrm{Ti}]' = -\frac{3}{2.3[3e_{\mathrm{Ti}}^{\mathrm{Ti}} + 5e_{\mathrm{O}}^{\mathrm{Ti}}]}. \qquad (14a)$$

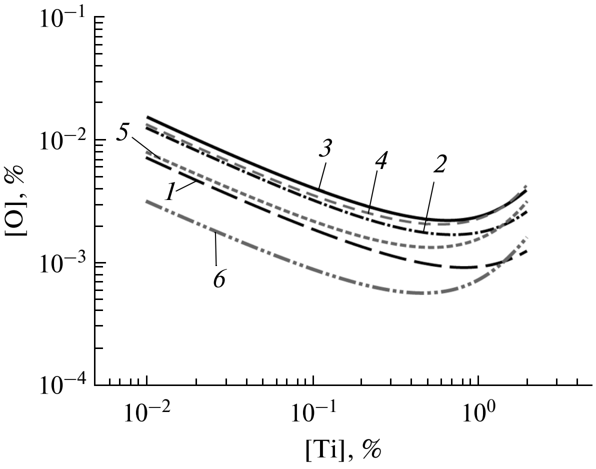

Fig. 3. Dependence of the oxygen concentration in Fe–Ni melts on the titanium content at 1873 K, with 0% (*1*), 20% (*2*), 40% (*3*), 60% (*4*), 80% (*5*), and 100% (*6*) Ni.

The titanium content at the minima and the corresponding oxygen concentrations according to Eq. (14a) are as follows:

Ni, %	0	20	40	60	80	100
[% Ti]'	0.827	0.729	0.648	0.582	0.526	0.478
$[\%\ \mathrm{O}]_{\min}$	8.96×10^{-4}	16.6×10^{-4}	22.0×10^{-4}	20.4×10^{-4}	13.0×10^{-4}	5.56×10^{-4}

CONCLUSIONS

The solubility of oxygen in titanium-containing iron–nickel melts has been investigated experimentally for the example of Fe–40% Ni melt at 1873 K. We have determined the equilibrium constant for the reaction of titanium and oxygen dissolved in Fe–40% Ni melt ($\log K_{(1)(\mathrm{Fe-40\%\,Ni})} = -15.17$), the Gibbs energy of this reaction ($\Delta G^{\circ}_{(1)(\mathrm{Fe-40\%\,Ni})} = 543\,360$ J/mol), and the interaction parameters characterizing the solutions ($e^{\mathrm{O}}_{\mathrm{Ti(Fe-40\%\,Ni)}} = -1.420$; $e^{\mathrm{Ti}}_{\mathrm{O(Fe-40\%\,Ni)}} = -0.472$; $e^{\mathrm{Ti}}_{\mathrm{Ti(Fe-40\%\,Ni)}} = 0.116$).

Over a broad concentration range at 1873 K, we have calculated the Gibbs energy of the reaction of titanium and oxygen dissolved in Fe–Ni melts, the equilibrium constant of this reaction, and the interaction parameters characterizing the solutions. We have determined the solubility of oxygen in titanium-containing iron–nickel melts of different composition at 1873 K.

The reducing properties of titanium fall with increase in the Ni content of the melt to 40% and then increase sharply with further increase in the Ni content. This may be explained in that increase in the Ni content is associated, on the one hand, with significant decrease in the bond strength of oxygen atoms in the melt ($\gamma^{\circ}_{\mathrm{O(Fe)}} = 0.0103$; $\gamma^{\circ}_{\mathrm{O(Ni)}} = 0.337$) and, on the other, with considerable increase in the bond strength of titanium atoms ($\gamma^{\circ}_{\text{Ti(s)(Fe)}} = 0.0083$; $\gamma^{\circ}_{\text{Ti(s)(Ni)}} = 0.000083$).

The solubility curves of oxygen in Fe–Ni melts pass through a minimum. As the Ni content increases, the minimum is shifted to lower Ti content.

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