Oxygen Solubility in Titanium-Containing Melts of the Ni–Co System

A. A. Aleksandrov[a], * and V. Ya. Dashevskii[a]

[a]Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, 119334 Russia
*e-mail: a.a.aleksandrov@gmail.com

Abstract—Thermodynamic analysis is performed for the oxygen solutions in titanium-containing melts of the Ni–Co system. The equilibrium constants of the reactions of titanium with oxygen, activity coefficients at infinite dilution, and interaction parameters in melts of various compositions at 1873 K are determined for the first time. The titanium contents at the equilibrium points between the oxide phases TiO_2, Ti_3O_5, and Ti_2O_3 are determined. The dependences of the oxygen solubility on the titanium content in the studied melts are calculated. The deoxidation ability of titanium decreases with an increase in the cobalt content to 40% and then increases as the cobalt content in the melt further increases. The titanium contents at the minimum points on the curves of the oxygen solubility and the corresponding minimum oxygen contents are determined.

Superalloys based on the Ni–Co system are widely used in modern engineering [1–4]. Oxygen is one of the detrimental impurities in these alloys and exists in the metal in the both diluted form and nonmetallic inclusions. The presence of oxygen deteriorates service properties of the alloys. Titanium is often used as an alloying element to provide the optimum level of mechanical characteristics for manufacturing nickel–cobalt superalloys [1, 4]. The study of the influence of titanium on the oxygen solubility in alloys is of significant interest for the practice of manufacturing alloys of the Ni–Co system. The influence of titanium on the oxygen solubility in melts of the Ni–Co system can be evaluated, since data on the thermodynamics of oxygen solutions in liquid nickel and cobalt are available [5, 6].
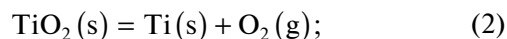
The following oxides can be formed as a result of the deoxidation of nickel–cobalt alloys with titanium depending on the titanium content in the melt: $(Ni, Co)O \cdot TiO_2$, TiO_2, Ti_3O_5, Ti_2O_3, and TiO. At 1873 K oxide $NiO \cdot TiO_2$ is formed at the titanium content in liquid nickel lower than $9.0 \times 10^{-8}\%$ [7], whereas oxide $CoO \cdot TiO_2$ is formed at the titanium content in liquid cobalt lower than $1.9 \times 10^{-6}\%$ [8]. Therefore, the formation of oxide $(Ni, Co)O \cdot TiO_2$ is not considered in this work.

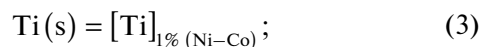The deoxidation of nickel–cobalt melts with titanium, the product of which is oxide TiO_2,

$$TiO_2(s) = [Ti] + 2[O]; \quad (1)$$
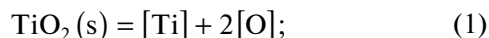
$$K_{(1)} = \frac{([Ti] f_{Ti})([O] f_O)^2}{a_{TiO_2}},$$

can be presented as the sum of the reactions

$$TiO_2(s) = Ti(s) + O_2(g); \quad (2)$$

$$\Delta G_{(2)}^\circ = 939\,535 - 175.76T, \text{ J/mol [8]};$$

$$Ti(s) = [Ti]_{1\% \, (Ni-Co)}; \quad (3)$$

$$\Delta G_{(3)}^\circ = RT \ln\left(\frac{\gamma_{Ti(Ni-Co)}^\circ M_{Ni-Co}}{100 M_{Ti}}\right);$$

$$O_2(g) = 2[O]_{1\% \, (Ni-Co)}; \quad (4)$$

$$\Delta G_{(4)}^\circ = 2RT \ln\left(\frac{\gamma_{O(Ni-Co)}^\circ M_{Ni-Co}}{100 M_O}\right),$$

where R is the gas constant, T is temperature, γ_i° is the activity coefficient of the ith element at infinite dilution, and M_i is the molecular weight of the component i.

Table 1. Equilibrium constants of reactions (1), (7), and (14), activity coefficients, and interaction parameters for the melts of the Ni–Co system at 1873 K

Parameter	Co, %					
	0	20	40	60	80	100
$M_{\text{Ni–Co}}$	58.69	58.738	58.787	58.836	58.884	58.933
X_{Ni}	1	0.801	0.601	0.401	0.201	0
X_{Co}	0	0.199	0.399	0.599	0.799	1
$\gamma_{\text{Ti}}^{\circ}$	0.00019 [5]	0.00024	0.00032	0.00045	0.00064	0.00091 [5]
$\gamma_{\text{O}}^{\circ}$	0.337 [5]	0.259	0.208	0.176	0.161	0.161 [5]
$\log K_{(1)}$	−7.581	−7.454	−7.391	−7.395	−7.472	−7.625
$\log K_{(7)}$	−19.621	−19.356	−19.262	−19.346	−19.614	−20.073
$\log K_{(14)}$	−11.597	−11.458	−11.427	−11.507	−11.699	−12.005
$e_{\text{Ti}}^{\text{Ti}}$	0.080 [7]	0.077	0.074	0.070	0.067	0.064 [8]
e_{O}^{Ti}	−0.510 [7]	−0.506	−0.503	−0.499	−0.495	−0.492 [6]
e_{Ti}^{O}	−1.535 [7]	−1.524	−1.513	−1.502	−1.490	−1.479 [6]
e_{O}^{O}	0 [5]	0	0	0	0	0 [5]
r_{O}^{Ti}	0.036 [7]	0.036	0.036	0.036	0.036	0.036

A 1% solution having the properties of an ideal dilute solution was chosen as a standard state for titanium and oxygen dissolved in a nickel–cobalt melt. The corresponding pure components were chosen as standard states for nickel and cobalt forming a concentrated solution (nickel–cobalt melt).

The Gibbs energy for reaction (1) was calculated using the equation $\Delta G_{(1)}^{\circ} = \Delta G_{(2)}^{\circ} + \Delta G_{(3)}^{\circ} + \Delta G_{(4)}^{\circ}$. The equilibrium constant of reaction (1) can be calculated using the equation $\ln K = -\Delta G_{T}^{\circ}/RT$. The molecular weight of melts of the Ni–Co system can be calculated by the equation $M_{\text{Ni–Co}} = M_{\text{Ni}}X_{\text{Ni}} + M_{\text{Co}}X_{\text{Co}}$ [9]. The activity coefficients $\gamma_{\text{Ti(Ni–Co)}}^{\circ}$ and $\gamma_{\text{O(Ni–Co)}}^{\circ}$ can be calculated by the equation [10]

$$\ln \gamma_{i(\text{Ni–Co})}^{\circ} = X_{\text{Ni}} \ln \gamma_{i(\text{Ni})}^{\circ} + X_{\text{Co}} \ln \gamma_{i(\text{Co})}^{\circ}$$
$$+ X_{\text{Ni}}X_{\text{Co}}\left[X_{\text{Co}}\left(\ln \gamma_{i(\text{Co})}^{\circ} - \ln \gamma_{i(\text{Ni})}^{\circ} + \varepsilon_{i(\text{Co})}^{\text{Ni}} \right) \right]$$
$$+ X_{\text{Ni}}\left(\ln \gamma_{i(\text{Ni})}^{\circ} - \ln \gamma_{i(\text{Co})}^{\circ} + \varepsilon_{i(\text{Ni})}^{\text{Co}} \right),$$

where X_i is the molar fraction, and ε_i^j is the interaction parameter of the first order when the contents of the components i and j are expressed in molar fractions [11].

The calculated equilibrium constants of reaction (1), the activity coefficients $\gamma_{\text{Ti}}^{\circ}$ and $\gamma_{\text{O}}^{\circ}$ for nickel and cobalt, and the activity coefficients $\gamma_{\text{Ti(Ni–Co)}}^{\circ}$ and $\gamma_{\text{O(Ni–Co)}}^{\circ}$ at 1873 K calculated for the nickel–cobalt alloys are presented in Table 1. The following values of interaction parameters were used in the calculations: $\varepsilon_{\text{Ti(Ni)}}^{\text{Co}} = 0.98$ [6], $\varepsilon_{\text{O(Ni)}}^{\text{Co}} = -1.4$ [5], $\varepsilon_{\text{Ti(Co)}}^{\text{Ni}} = -1.7$ [6], and $\varepsilon_{\text{O(Co)}}^{\text{Ni}} = -0.25$ [5].

The oxygen content in the melt equilibrium with the specified titanium content can be calculated using the equation

$$\log[\%\,\text{O}]_{\text{Ni–Co}}$$
$$= 1/2\Big\{ \log K_{(1)} + \log a_{\text{TiO}_2} - \log[\%\,\text{Ti}]$$
$$- \left(e_{\text{Ti(Ni–Co)}}^{\text{Ti}} + 2e_{\text{O(Ni–Co)}}^{\text{Ti}} \right)[\%\,\text{Ti}] \qquad (5)$$
$$- \left(2e_{\text{O(Ni–Co)}}^{\text{O}} + e_{\text{Ti(Ni–Co)}}^{\text{O}} \right)[\%\,\text{O}]$$
$$- 2r_{\text{O(Ni–Co)}}^{\text{Ti}}[\%\,\text{Ti}]^2 \Big\},$$

where $e_{i(\text{Ni–Co})}^j$ is the first-order interaction parameter when the contents of the components i and j are expressed in wt %, $r_{i(\text{Ni–Co})}^j$ is the second-order interaction parameter when the component contents are expressed in wt % [11, 12].

Oxide TiO$_2$ at 1873 K is solid ($T_{\text{m}} = 2185$ K [13]) and, hence, $a_{\text{TiO}_2} = 1$. The value of [% O] in the right hand of Eq. (5) can be expressed via the ratio $(K_{(1)}/[\%\,\text{Ti}]f_{\text{Ti}}f_{\text{O}}^2)^{1/2}$. For [% O] → 0, f_{O} → 1. Since the value of [% O] is negligible, [% O] can be accepted to be $(K_{(1)}/[\%\,\text{Ti}]f_{\text{Ti}})^{1/2}$. This replacement will not con-

tribute an appreciable inaccuracy to the calculations. Then Eq. (5) takes the form

$$\log[\%O]_{Ni-Co} = 1/2\Big\{\log K_{(1)} - \log[\%Ti] \\ - \big(e_{Ti(Ni-Co)}^{Ti} + 2e_{O(Ni-Co)}^{Ti}\big)[\%Ti] \\ - \big(2e_{O(Ni-Co)}^{O} + e_{Ti(Ni-Co)}^{O}\big)\big(K_{(1)}/[\%Ti]f_{Ti}\big)^{1/2} \\ - 2r_{O(Ni-Co)}^{Ti}[\%Ti]^2\Big\}. \tag{6}$$

The interaction parameters for the melts of various compositions used in the calculations are presented in Table 1. The interaction parameters e_{Ti}^{Ti}, e_{O}^{Ti}, e_{Ti}^{O}, and e_{O}^{O} for the melts of the Ni–Co system were determined by the equation $\varepsilon_{i(Ni-Co)}^{j} = \varepsilon_{i(Ni)}^{j}X_{Ni} + \varepsilon_{i(Co)}^{j}X_{Co}$ [9].

The second-order interaction parameter in nickel is $r_{O(Ni)}^{Ti} = 0.036$ [7], and data on the second-order interaction parameter in cobalt $r_{O(Co)}^{Ti}$ are lacking. Since the first-order interaction parameters e_{O}^{Ti} are close ($e_{O(Ni)}^{Ti} = -0.510$ [7], $e_{O(Co)}^{Ti} = -0.492$ [6]) in nickel and cobalt, we can accept that $r_{O(Co)}^{Ti} = r_{O(Ni)}^{Ti} = 0.036$.

Taking into account the values of interaction parameters at 1873 K, Eq. (6) takes the following form:

(a) for Ni,

$$\log[\%O]_{Ni} = -3.790 - 1/2\log[\%Ti] \\ + 0.470[\%Ti] + 1.244\times10^{-4}/[\%Ti]^{1/2} \\ - 0.036[\%Ti]^2;$$

(b) for Ni–20% Co

$$\log[\%O]_{Ni-20\% Co} = -3.727 - 1/2\log[\%Ti] \\ + 0.468[\%Ti] + 1.428\times10^{-4}/[\%Ti]^{1/2} \\ - 0.036[\%Ti]^2;$$

(c) for Ni–40% Co,

$$\log[\%O]_{Ni-40\% Co} = -3.696 - 1/2\log[\%Ti] \\ + 0.466[\%Ti] + 1.525\times10^{-4}/[\%Ti]^{1/2} \\ - 0.036[\%Ti]^2;$$

(d) for Ni–60% Co,

$$\log[\%O]_{Ni-60\% Co} = -3.698 - 1/2\log[\%Ti] \\ + 0.464[\%Ti] + 1.506\times10^{-4}/[\%Ti]^{1/2} \\ - 0.036[\%Ti]^2;$$

(e) for Ni–80% Co,

$$\log[\%O]_{Ni-80\% Co} = -3.736 - 1/2\log[\%Ti] \\ + 0.462[\%Ti] + 1.369\times10^{-4}/[\%Ti]^{1/2} \\ - 0.036[\%Ti]^2;$$

(f) for Co,

$$\log[\%O]_{Co} = -3.812 - 1/2\log[\%Ti] \\ + 0.460[\%Ti] + 1.139\times10^{-4}/[\%Ti]^{1/2} \\ - 0.036[\%Ti]^2.$$

The further increase in the titanium content results in the situation where the product of deoxidation of the melts of the Ni–Co system with titanium is oxide Ti_3O_5. In this case, the deoxidation reaction

$$Ti_3O_5(s) = 3[Ti] + 5[O]; \tag{7}$$
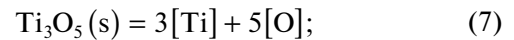
$$K_{(7)} = \frac{([Ti]f_{Ti})^3([O]f_O)^5}{a_{Ti_3O_5}},$$

can be presented as the sum of the reactions

$$Ti_3O_5(s) = 3Ti(s) + 5/2O_2(g); \tag{8}$$
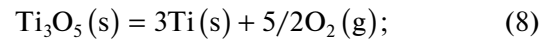
$$\Delta G_{(8)}^{\circ} = 2427004 - 414.41T, \text{ J/mol [8]};$$

$$3Ti(s) = 3[Ti]_{1\% (Ni-Co)}; \tag{9}$$

$$\Delta G_{(9)}^{\circ} = 3RT\ln\left(\frac{\gamma_{Ti(Ni-Co)}^{\circ}M_{Ni-Co}}{100M_{Ti}}\right);$$

$$5/2O_2(g) = 5[O]_{1\% (Ni-Co)}; \tag{10}$$
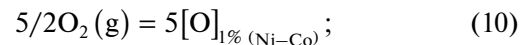
$$\Delta G_{(10)}^{\circ} = 5RT\ln\left(\frac{\gamma_{O(Ni-Co)}^{\circ}M_{Ni-Co}}{100M_O}\right).$$

The Gibbs energy for reaction (7) was calculated using the equation $\Delta G_{(7)}^{\circ} = \Delta G_{(8)}^{\circ} + \Delta G_{(9)}^{\circ} + \Delta G_{(10)}^{\circ}$. The calculated equilibrium constants for reaction (7) at 1873 K are presented in Table 1.

The oxygen content in the melt equilibrium with the specified titanium content can be calculated by the equation

$$\log[\%O]_{Ni-Co} \\ = 1/5\Big\{\log K_{(7)} + \log a_{Ti_3O_5} - 3\log[\%Ti] \\ - \big(3e_{Ti(Ni-Co)}^{Ti} + 5e_{O(Ni-Co)}^{Ti}\big)[\%Ti] \\ - \big(5e_{O(Ni-Co)}^{O} + 3e_{Ti(Ni-Co)}^{O}\big)[\%O] \\ - 5r_{O(Ni-Co)}^{Ti}[\%Ti]^2\Big\}. \tag{11}$$

Oxide Ti_3O_5 at 1873 K is solid ($T_m = 2050$ K [13]) and, hence, $a_{Ti_3O_5} = 1$. The value of [%O] in the right hand of Eq. (11) can be expressed via the ratio $\big(K_{(7)}/[\%Ti]^3 f_{Ti}^3 f_O^5\big)^{1/5}$. For [%O] → 0, f_O → 1. Since

the value of [% O] is negligible, [% O] can be accepted to be $\left(K_{(7)}/[\%\text{Ti}]^3 f_{\text{Ti}}^3\right)^{1/5}$. Then Eq. (11) takes the form

$$\log[\%O]_{\text{Ni–Co}}$$
$$= 1/5\left\{\log K_{(7)} - 3\log[\%\,\text{Ti}]\right.$$
$$- \left(3e_{\text{Ti(Ni–Co)}}^{\text{Ti}} + 5e_{\text{O(Ni–Co)}}^{\text{Ti}}\right)[\%\,\text{Ti}]$$
$$- \left(5e_{\text{O(Ni–Co)}}^{\text{O}} + 3e_{\text{Ti(Ni–Co)}}^{\text{O}}\right)\left(K_{(7)}/[\%\,\text{Ti}]^3 f_{\text{Ti}}^3\right)^{1/5}$$
$$\left. - 5r_{\text{O(Ni–Co)}}^{\text{Ti}}[\%\,\text{Ti}]^2\right\}. \tag{12}$$

Taking into account the obtained values of interaction parameters at 1873 K, Eq. (12) takes the following form:

(a) for Ni,

$$\log[\%O]_{\text{Ni}} = -3.924 - 3/5\log[\%\,\text{Ti}]$$
$$+ 0.462[\%\,\text{Ti}] + 1.096\times10^{-4}/[\%\,\text{Ti}]^{3/5}$$
$$- 0.036[\%\,\text{Ti}]^2;$$

(b) for Ni–20% Co,

$$\log[\%O]_{\text{Ni–20\% Co}} = -3.871 - 3/5\log[\%\,\text{Ti}]$$
$$+ 0.460[\%\,\text{Ti}] + 1.230\times10^{-4}/[\%\,\text{Ti}]^{3/5}$$
$$- 0.036[\%\,\text{Ti}]^2;$$

(c) for Ni–40% Co,

$$\log[\%O]_{\text{Ni–40\% Co}} = -3.852 - 3/5\log[\%\,\text{Ti}]$$
$$+ 0.459[\%\,\text{Ti}] + 1.275\times10^{-4}/[\%\,\text{Ti}]^{3/5}$$
$$- 0.036[\%\,\text{Ti}]^2;$$

(d) for Ni–60% Co,

$$\log[\%O]_{\text{Ni–60\% Co}} = -3.869 - 3/5\log[\%\,\text{Ti}]$$
$$+ 0.457[\%\,\text{Ti}] + 1.218\times10^{-4}/[\%\,\text{Ti}]^{3/5}$$
$$- 0.036[\%\,\text{Ti}]^2;$$

(e) for Ni–80% Co,

$$\log[\%O]_{\text{Ni–80\% Co}} = -3.923 - 3/5\log[\%\,\text{Ti}]$$
$$+ 0.455[\%\,\text{Ti}] + 1.068\times10^{-4}/[\%\,\text{Ti}]^{3/5}$$
$$- 0.036[\%\,\text{Ti}]^2;$$

(f) for Co,

$$\log[\%O]_{\text{Co}} = -4.015 - 3/5\log[\%\,\text{Ti}]$$
$$+ 0.453[\%\,\text{Ti}] + 0.858\times10^{-4}/[\%\,\text{Ti}]^{3/5}$$
$$- 0.036[\%\,\text{Ti}]^2.$$

The combined solution of Eqs. (6) and (12) makes it possible to determine the equilibrium point $\text{TiO}_2 \rightleftarrows \text{Ti}_3\text{O}_5$. Neglecting the terms containing the

interaction parameters because of their low values, we have

$$1/2\log K_{(1)} - 1/2\log[\text{Ti}]$$
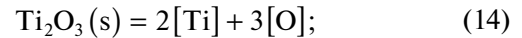$$= 1/5\log K_{(7)} - 3/5\log[\text{Ti}], \tag{13}$$

or

$$\log[\text{Ti}]^{*1} = 2\log K_{(7)} - 5\log K_{(1)}. \tag{13a}$$

The titanium contents at this point ($[\text{Ti}]^{*1}$) for the melts of various compositions at 1873 K are given below.
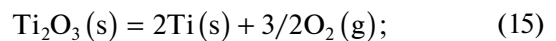
Co, %	0	20	40	60	80	100
$[\text{Ti}]^{*1}$, %	0.0458	0.0362	0.0270	0.0193	0.0135	0.0095

At higher titanium contents, the product of deoxidation of the melts of the Ni–Co system is oxide Ti_2O_3. In this case, the deoxidation reaction

$$\text{Ti}_2\text{O}_3\,(s) = 2[\text{Ti}] + 3[\text{O}]; \tag{14}$$

$$K_{(14)} = \frac{([\text{Ti}]f_{\text{Ti}})^2([\text{O}]f_{\text{O}})^3}{a_{\text{Ti}_2\text{O}_3}},$$

can be presented as the sum of the reactions

$$\text{Ti}_2\text{O}_3\,(s) = 2\text{Ti}\,(s) + 3/2\text{O}_2\,(g); \tag{15}$$

$$\Delta G_{(15)}^{\circ} = 1495106 - 251.21T,\ \text{J/mol [8]};$$

$$2\text{Ti}\,(s) = 2[\text{Ti}]_{1\%\,(\text{Ni–Co})}; \tag{16}$$

$$\Delta G_{(16)}^{\circ} = 2RT\ln\left(\frac{\gamma_{\text{Ti(Ni–Co)}}^{\circ}M_{\text{Ni–Co}}}{100M_{\text{Ti}}}\right);$$

$$3/2\text{O}_2\,(g) = 3[\text{O}]_{1\%\,(\text{Ni–Co})}; \tag{17}$$
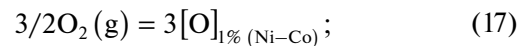
$$\Delta G_{(17)}^{\circ} = 3RT\ln\left(\frac{\gamma_{\text{O(Ni–Co)}}^{\circ}M_{\text{Ni–Co}}}{100M_{\text{O}}}\right).$$

The Gibbs energy for reaction (14) was calculated using the equation $\Delta G_{(14)}^{\circ} = \Delta G_{(15)}^{\circ} + \Delta G_{(16)}^{\circ} + \Delta G_{(17)}^{\circ}$. The calculated equilibrium constants for reaction (14) at 1873 K are presented in Table 1.

The oxygen content in the melt equilibrium with the specified titanium content can be calculated by the equation

$$\log[\%O]_{\text{Ni–Co}}$$
$$= 1/3\left\{\log K_{(14)} + \log a_{\text{Ti}_2\text{O}_3} - 2\log[\%\,\text{Ti}]\right.$$
$$- \left(2e_{\text{Ti(Ni–Co)}}^{\text{Ti}} + 3e_{\text{O(Ni–Co)}}^{\text{Ti}}\right)[\%\,\text{Ti}]$$
$$\left. - \left(3e_{\text{O(Ni–Co)}}^{\text{O}} + 2e_{\text{Ti(Ni–Co)}}^{\text{O}}\right)[\%O] - 3r_{\text{O(Ni–Co)}}^{\text{Ti}}[\%\,\text{Ti}]^2\right\}. \tag{18}$$

Oxide Ti_2O_3 at 1873 K is solid ($T_{\text{m}} = 2110$ K [13]) and, hence, $a_{\text{Ti}_2\text{O}_3} = 1$. The value of [% O] in the right hand of Eq. (18) can be expressed via the ratio

$\left(K_{(14)}\big/\left[\%\,\mathrm{Ti}\right]^2 f_{\mathrm{Ti}}^2 f_{\mathrm{O}}^3\right)^{1/3}$. For $[\%\,\mathrm{O}]\to 0, f_{\mathrm{O}}\to 1$. Since the value of $[\%\,\mathrm{O}]$ is negligible, $[\%\,\mathrm{O}]$ can be accepted to $\left(K_{(14)}\big/\left[\%\,\mathrm{Ti}\right]^2 f_{\mathrm{Ti}}^2\right)^{1/3}$. Then Eq. (18) takes the form

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Ni-Co}}$$
$$= 1/3\Big\{\log K_{(14)} - 2\log\left[\%\,\mathrm{Ti}\right]$$
$$- \left(2e_{\mathrm{Ti(Ni-Co)}}^{\mathrm{Ti}} + 3e_{\mathrm{O(Ni-Co)}}^{\mathrm{Ti}}\right)\left[\%\,\mathrm{Ti}\right] \tag{19}$$
$$- \left(3e_{\mathrm{O(Ni-Co)}}^{\mathrm{O}} + 2e_{\mathrm{Ti(Ni-Co)}}^{\mathrm{O}}\right)\left(K_{(14)}\big/\left[\%\,\mathrm{Ti}\right]^2 f_{\mathrm{Ti}}^2\right)^{1/3}$$
$$- 3r_{\mathrm{O(Ni-Co)}}^{\mathrm{Ti}}\left[\%\,\mathrm{Ti}\right]^2\Big\}.$$

Taking into account the obtained values of interaction parameters at 1873 K, Eq. (19) takes the following form:

(a) for Ni,

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Ni}} = -3.866 - 2/3\log\left[\%\,\mathrm{Ti}\right]$$
$$+ 0.457\left[\%\,\mathrm{Ti}\right] + 1.394\times 10^{-4}\big/\left[\%\,\mathrm{Ti}\right]^{2/3}$$
$$- 0.036\left[\%\,\mathrm{Ti}\right]^2;$$

(b) for Ni–20% Co,

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Ni-20\%\,Co}} = -3.819 - 2/3\log\left[\%\,\mathrm{Ti}\right]$$
$$+ 0.455\left[\%\,\mathrm{Ti}\right] + 1.540\times 10^{-4}\big/\left[\%\,\mathrm{Ti}\right]^{2/3}$$
$$- 0.036\left[\%\,\mathrm{Ti}\right]^2;$$

(c) for Ni–40% Co,

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Ni-40\%\,Co}} = -3.809 - 2/3\log\left[\%\,\mathrm{Ti}\right]$$
$$+ 0.454\left[\%\,\mathrm{Ti}\right] + 1.565\times 10^{-4}\big/\left[\%\,\mathrm{Ti}\right]^{2/3}$$
$$- 0.036\left[\%\,\mathrm{Ti}\right]^2;$$

(d) for Ni–60% Co,

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Ni-60\%\,Co}} = -3.836 - 2/3\log\left[\%\,\mathrm{Ti}\right]$$
$$+ 0.452\left[\%\,\mathrm{Ti}\right] + 1.462\times 10^{-4}\big/\left[\%\,\mathrm{Ti}\right]^{2/3}$$
$$- 0.036\left[\%\,\mathrm{Ti}\right]^2;$$

(e) for Ni–80% Co,

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Ni-80\%\,Co}} = -3.900 - 2/3\log\left[\%\,\mathrm{Ti}\right]$$
$$+ 0.450\left[\%\,\mathrm{Ti}\right] + 1.252\times 10^{-4}\big/\left[\%\,\mathrm{Ti}\right]^{2/3}$$
$$- 0.036\left[\%\,\mathrm{Ti}\right]^2;$$

(f) for Co,

$$\log\left[\%\,\mathrm{O}\right]_{\mathrm{Co}} = -4.002 - 2/3\log\left[\%\,\mathrm{Ti}\right]$$
$$+ 0.449\left[\%\,\mathrm{Ti}\right] + 0.983\times 10^{-4}\big/\left[\%\,\mathrm{Ti}\right]^{2/3}$$
$$- 0.036\left[\%\,\mathrm{Ti}\right]^2.$$

The combined solution of Eqs. (12) and (19) enables one to determine the equilibrium point

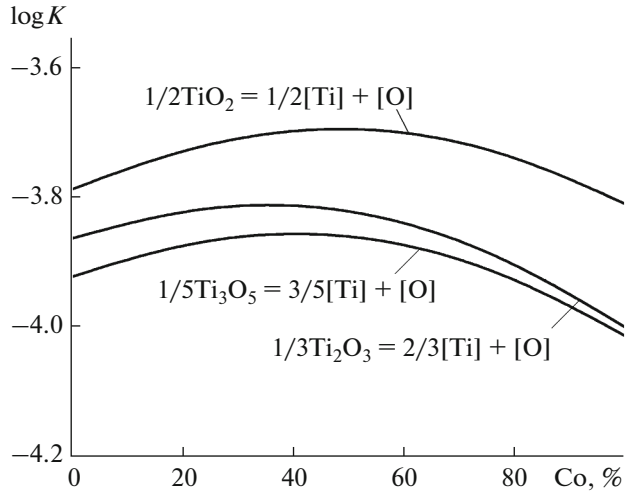**Fig. 1.** Equilibrium constants of reactions (1), (7), and (14) vs. the base composition in the Ni–Co melt at 1873 K.

$\mathrm{Ti_3O_5} \rightleftarrows \mathrm{Ti_2O_3}$. Neglecting the terms containing the interaction parameters because of their low values, we have

$$1/5\log K_{(12)} - 3/5\log\left[\mathrm{Ti}\right]$$
$$= 1/3\log K_{(19)} - 2/3\log\left[\mathrm{Ti}\right], \tag{20}$$

or

$$\log\left[\mathrm{Ti}\right]^{*2} = 5\log K_{(19)} - 3\log K_{(12)}. \tag{20a}$$

The titanium contents at this point ($\left[\mathrm{Ti}\right]^{*2}$) for the melts of various compositions at 1873 K are given below.

Co, %	0	20	40	60	80	100
$\left[\mathrm{Ti}\right]^{*2}$, %	7.563	5.984	4.452	3.181	2.231	1.570

Titanium monoxide TiO is formed in the reaction of titanium and oxygen in the Ni–Co melts at the titanium contents substantially higher than those used for alloying these melts. Therefore, this region of titanium contents is not considered in the present work.

The dependences of the equilibrium constants of reactions (1), (7), and (14) on the composition of the alloy base at 1873 K are presented in Fig. 1. For clarity of data comparison, the values of equilibrium constants for these reactions are given for the interaction of titanium with one oxygen atom dissolved in the melt. It is seen that the equilibrium constant of reaction (1) increases with the cobalt content in the melt up to 50–60%. The equilibrium constants of reactions (7) and (14) increase with the cobalt content up to 35–45%. A smooth decrease in the equilibrium constants of all reactions is observed with the further increase in the cobalt content.

The dependences of the equilibrium oxygen concentrations on the contents of titanium and cobalt in
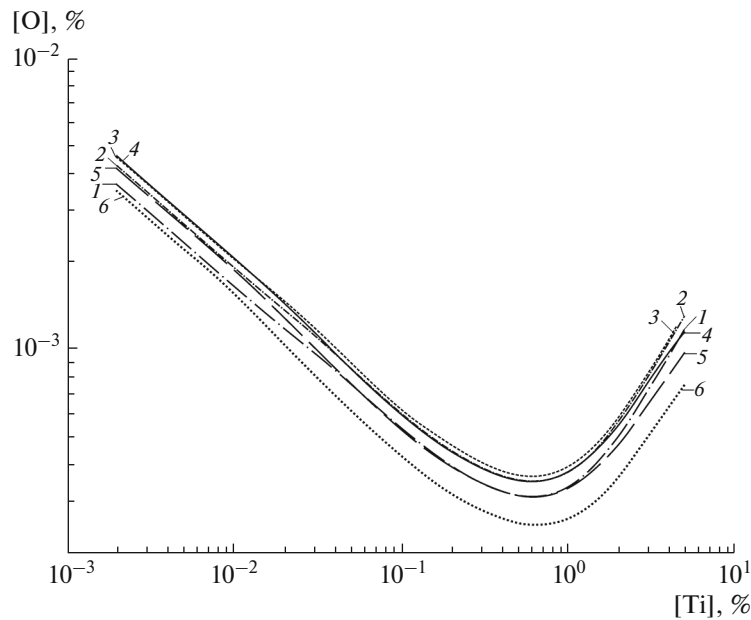
Fig. 2. Oxygen content in the melts of the Ni–Co system vs. the titanium content at 1873 K at the Co content (%): (*1*) 0, (*2*) 20, (*3*) 40, (*4*) 60, (*5*) 80, and (*6*) 100.
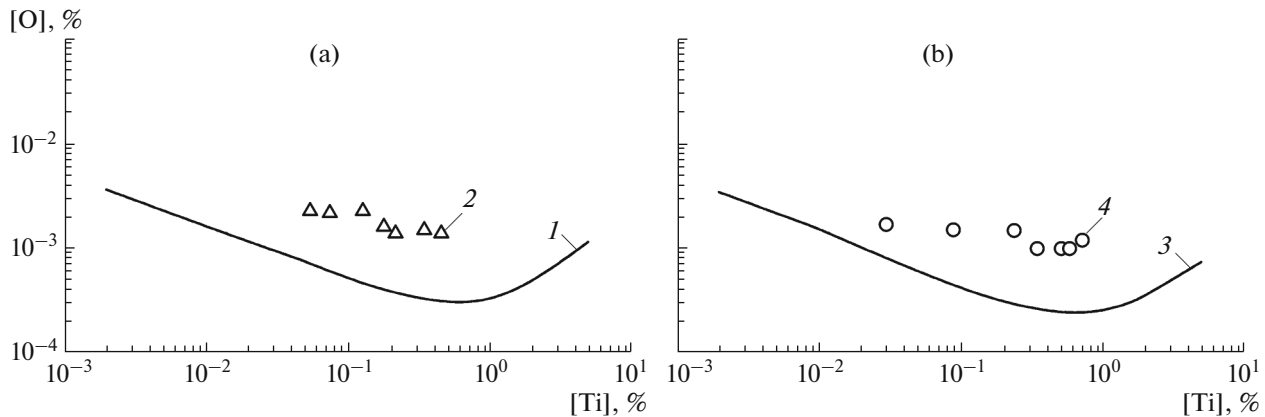

Fig. 3. Deoxidation ability of titanium in liquid (a) nickel and (b) cobalt at 1873 K: (*1, 3*) calculation and (*2, 4*) data from [14] and [15], respectively.

the melt at 1873 K are shown in Fig. 2. According to the data presented, the deoxidation ability of titanium decreases with an increase in the cobalt content to 40% and then increases as the cobalt content in the melt further increases. The deoxidation ability of titanium is almost the same in the melts containing 20, 40, and 60% of Co.

The calculated equilibrium contents of titanium and oxygen in nickel and cobalt are presented in Fig. 3 in comparison with the published data [14, 15]. It is seen that the calculation results are satisfactorily consistent with the literature data.

The curves of the oxygen solubility in the nickel–cobalt melts pass through a minimum. The titanium

contents to which the minimum oxygen contents correspond can be determined from the equation

$$[\% R]' = -\frac{m}{2.3\left(me_R^R + ne_O^R\right)}, \qquad (21)$$

where m and n are the coefficients in the formula of R_mO_n oxide.

For the melts of the Ni–Co system, the minimum falls onto the region of existence of oxide Ti_3O_5. In this case, Eq. (21) takes the form

$$[\% \, Ti]' = -\frac{3}{2.3\left(3e_{Ti}^{Ti} + 5e_O^{Ti}\right)}. \qquad (21a)$$

The titanium contents at the minimum points calculated by Eq. (21a) and the corresponding oxygen contents are presented below

Co, %	[% Ti]′	[% O]$_{min}$
0	0.565	2.98×10^{-4}
20	0.567	3.36×10^{-4}
40	0.569	3.50×10^{-4}
60	0.571	3.36×10^{-4}
80	0.573	2.96×10^{-4}
100	0.576	2.39×10^{-4}

CONCLUSIONS

(1) Titanium has a high deoxidation ability in the melts of the Ni−Co system. The deoxidation ability of titanium decreases with an increase in the cobalt content to 40% and then increases as the cobalt content in the melt further increases.

(2) The deoxidation ability of titanium is almost the same in the melts Ni−20% Co, Ni−40% Co, and Ni−60% Co.

(3) The curves of the oxygen solubility in the titanium-containing nickel−cobalt melts pass through a minimum, whose position shifts toward a little higher titanium content as the cobalt content in the melt increases. The further titanium additives result in an increase in the oxygen content in the melt.

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