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Thermodynamics of Oxygen Solutions in Niobium-Containing Fe–Co Melts

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Abstract—Thermodynamic analysis of oxygen solutions in niobium-containing Fe–Co melts performed for the first time showed that the deoxidizing ability of niobium increases with cobalt content in the melt. Oxygen solubility curves for niobium-containing iron–cobalt melts pass through a minimum which is shifted to higher niobium concentration with an increase in cobalt content in the melt.

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Iron–cobalt melts are widely used in modern engineering, in particular, in soft magnetic materials. Oxygen is one of the detrimental impurities in these alloys, which is present in the metal both in dissolved state and as nonmetallic inclusions. The presence of oxygen in these melts leads to a decrease in magnetic permeability and an increase in coercive force.

Niobium is used in alloy manufacture as an alloying constituent. It is of practical interest for the manufacture of Fe–Co alloys to study the niobium effect on the oxygen solubility therein. The data on thermodynamics of niobium and oxygen solutions in molten iron [1, 2] and cobalt [2, 3] allows one to assess the niobium effect on the oxygen solubility in Fe–Co melts.

In this work, we performed thermodynamic analysis of oxygen solutions in niobium-containing Fe–Co melts. We determined for the first time the equilibrium constants of deoxidation reactions of iron–cobalt melts with niobium, activity coefficients at infinite dilution, and parameters of interaction in the melts of different composition. The dependences of oxygen solubility in the studied melts on cobalt and niobium content were calculated. The niobium content at the minima on oxygen solubility curves and the corresponding oxygen concentrations were determined.

The reaction of niobium with oxygen in Fe–Co melts can be described by the following reaction

$$\mathrm{NbO_2(s)} = [\mathrm{Nb}]_{\mathrm{Fe-Co}} + 2[\mathrm{O}]_{\mathrm{Fe-Co}}, \qquad (1)$$

$$K_{(1)} = \frac{([\%\mathrm{Nb}]\cdot f_{\mathrm{Nb}})\,([\%\mathrm{O}]\cdot f_{\mathrm{O}})^2}{a_{\mathrm{NbO_2}}}, \qquad (1a)$$

where f_i is activity coefficient when the component concentration is expressed in weight percent; $\log f_{\mathrm{Nb}} = e_{\mathrm{Nb}}^{\mathrm{Nb}}[\%\mathrm{Nb}] + e_{\mathrm{Nb}}^{\mathrm{O}}[\%\mathrm{O}]$, $\log f_{\mathrm{O}} = e_{\mathrm{O}}^{\mathrm{O}}[\%\mathrm{O}] + e_{\mathrm{O}}^{\mathrm{Nb}}[\%\mathrm{Nb}]$, e_i^j is a first-order interaction parameter when the component concentration is expressed in weight percent [4].

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

$$\mathrm{NbO_2(s)} = \mathrm{Nb(s)} + \mathrm{O_2(g)}, \qquad (2)$$

$$\Delta G^{\circ}_{(2)} = 773\,302 - 160.15\,T,\ \text{J/mol [2]};$$

$$\mathrm{Nb(s)} = [\mathrm{Nb}]_{1\%\,(\mathrm{Fe-Co})}, \qquad (3)$$

$$\Delta G^{\circ}_{(3)} = RT\ln\left(\frac{\gamma^{\circ}_{\mathrm{Nb(Fe-Co)}}M_{\mathrm{Fe-Co}}}{M_{\mathrm{Nb}}\cdot 100}\right);$$

$$\mathrm{O_2(g)} = 2[\mathrm{O}]_{1\%\,(\mathrm{Fe-Co})}, \qquad (4)$$

$$\Delta G^{\circ}_{(4)} = 2RT\ln\left(\frac{\gamma^{\circ}_{\mathrm{O(Fe-Co)}}M_{\mathrm{Fe-Co}}}{M_{\mathrm{O}}\cdot 100}\right),$$

where $\gamma^{\circ}_{i(\mathrm{Fe-Co})}$ is the activity coefficient of the ith component at infinite dilution, M_i is the molecular weight of the ith component, X is the molar fraction of the ith component.

The molecular weight of Fe–Co melts was calculated by the formula $M_{\mathrm{Fe-Co}} = M_{\mathrm{Fe}}X_{\mathrm{Fe}} + M_{\mathrm{Co}}X_{\mathrm{Co}}$ [5], while activity coefficients $\gamma^{\circ}_{\mathrm{Nb(Fe-Co)}}$ and $\gamma^{\circ}_{\mathrm{O(Fe-Co)}}$ were calculated by the equation [6]

$$\begin{aligned}\ln\gamma^{\circ}_{i\,(\mathrm{Fe-Co})} &= X_{\mathrm{Fe}}\ln\gamma^{\circ}_{i(\mathrm{Fe})} + X_{\mathrm{Co}}\ln\gamma^{\circ}_{i(\mathrm{Co})} + X_{\mathrm{Fe}}X_{\mathrm{Co}}\\ &\times[X_{\mathrm{Co}}(\ln\gamma^{\circ}_{i(\mathrm{Co})} - \ln\gamma^{\circ}_{i(\mathrm{Fe})} + \varepsilon^{\mathrm{Fe}}_{i(\mathrm{Co})})\\ &+ X_{\mathrm{Fe}}(\ln\gamma^{\circ}_{i(\mathrm{Fe})} - \ln\gamma^{\circ}_{i(\mathrm{Co})} + \varepsilon^{\mathrm{Co}}_{i(\mathrm{Fe})})].\end{aligned}$$

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Equilibrium constant of reaction (1), activity coefficients, and interaction parameters for Fe–Co melts at 1873 K

Parameter	Co, %					
	0	20	40	60	80	100
$M_{\mathrm{Fe-Co}}$	55.847	56.438	57.042	57.659	58.289	58.933
X_{Fe}	1	0.808	0.613	0.413	0.209	0
X_{Co}	0	0.192	0.387	0.587	0.791	1
$\gamma^{\circ}_{\mathrm{Nb}}$	0.174 [2]	0.0984	0.0477	0.0209	0.0089	0.0039 [2]
$\gamma^{\circ}_{\mathrm{O}}$	0.0103 [1]	0.0151	0.0233	0.0392	0.0738	0.161 [3]
$\log K_{(1)}$	−3.335	−3.432	−3.510	−3.618	−3.809	−4.145
$e^{\mathrm{Nb}}_{\mathrm{Nb}}$	0 [1]	0.0053	0.0109	0.0167	0.0227	0.029 [2]
$e^{\mathrm{Nb}}_{\mathrm{O}}$	−0.12 [1]	−0.1042	−0.0878	−0.0706	−0.0526	−0.0338 [2]
$e^{\mathrm{O}}_{\mathrm{Nb}}$	−0.71 [1]	−0.6199	−0.5257	−0.4274	−0.3245	−0.217 [2]
$e^{\mathrm{O}}_{\mathrm{O}}$	−0.17 [1]	−0.139	−0.106	−0.073	−0.037	0 [3]

The calculated values of the equilibrium constant of reaction (1), the activity coefficients $\gamma^{\circ}_{\mathrm{Nb}}$ and $\gamma^{\circ}_{\mathrm{O}}$ for iron and cobalt and activity coefficients calculated for iron–cobalt alloys at 1873 K are given in table. The following values of interaction parameters were used in the calculations: $\varepsilon^{\mathrm{Co}}_{\mathrm{Nb(Fe)}} = -2.51$ [7], $\varepsilon^{\mathrm{Fe}}_{\mathrm{Nb(Co)}} = 3.68$ [8], $\varepsilon^{\mathrm{Co}}_{\mathrm{O(Fe)}} = 1.9$ [1], $\varepsilon^{\mathrm{Fe}}_{\mathrm{O(Co)}} = -4.1$ [3].

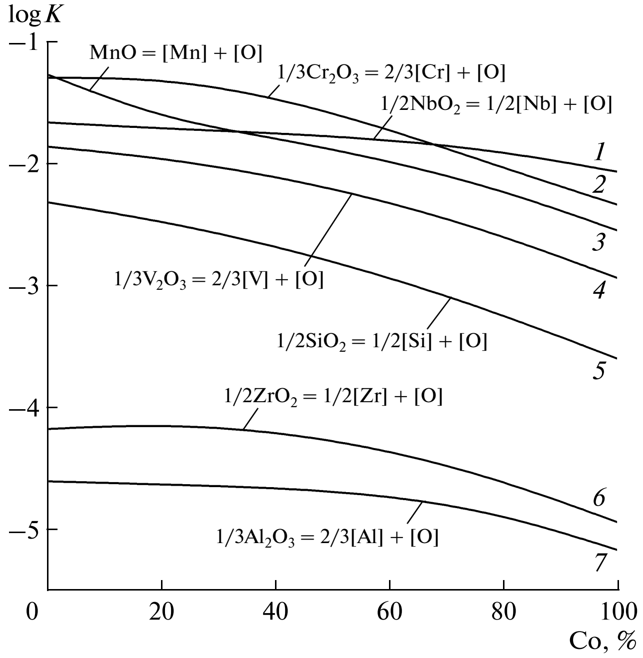

Fig. 1. Dependence of equilibrium constants for the reactions of Fe–Co melt deoxidation with (*1*) niobium, (*2*) chromium, (*3*) manganese, (*4*) vanadium, (*5*) silicon, (*6*) zirconium, and (*7*) aluminum on the melt composition at 1873 K.

The dependence of the equilibrium constant on the cobalt content in the melt at 1873 K for reaction (1) is shown in Fig. 1, which also displays similar data for the deoxidation reaction of Fe–Co melts with chromium [9], manganese [10], vanadium [11], silicon [12], zirconium [13], and aluminum [14] at 1873 K. The equilibrium constants are given for the reactions of the deoxidizing agent with one oxygen atom dissolved in the melt, which provides more evident comparison of the given dependences. The equilibrium constant of reaction (1) slightly decreases as the cobalt content in the melt increases, which indicates the growth of the deoxidizing ability of niobium. This is explained by the fact that, on the one hand, the binding strength of oxygen in liquid cobalt is much weaker than in liquid iron ($\gamma^{\circ}_{\mathrm{O(Fe)}} = 0.0103$ [1], $\gamma^{\circ}_{\mathrm{O(Co)}} = 0.161$ [3]), and on the other hand, the binding strength of niobium in cobalt is considerably higher than in iron ($\gamma^{\circ}_{\mathrm{Nb(Fe)}} = 0.174$ [2], $\gamma^{\circ}_{\mathrm{Nb(Co)}} = 0.0039$ [2]). The deoxidizing ability of chromium, manganese, vanadium, silicon, zirconium, and aluminum in Fe–Co melts also increases with an increase in cobalt content for all alloys (Fig. 1).

The oxygen concentration in the melt that is in equilibrium with the given niobium content can be calculated on the basis of equation (1a) using the following formula

$$\log[\%\mathrm{O}]_{\text{Fe–Co}} = \frac{1}{2}\{\log K_{(1)} + \log a_{\mathrm{NbO_2}} - \log[\%\mathrm{Nb}] - [e^{\mathrm{Nb}}_{\mathrm{Nb(Fe–Co)}} + 2e^{\mathrm{Nb}}_{\mathrm{O(Fe–Co)}}][\%\mathrm{Nb}] - [2e^{\mathrm{O}}_{\mathrm{O(Fe–Co)}} + e^{\mathrm{O}}_{\mathrm{Nb(Fe–Co)}}][\%\mathrm{O}]\}. \quad (5)$$

Niobium dioxide at 1873 K is solid ($T_m = 2270$ K); therefore, $a_{\mathrm{NbO_2}} = 1$. The value of [%O] on the right-hand side of Eq. (5) due to its insignificance can be expressed via relationship $(K_{(1)}/[\%\mathrm{Nb}])^{1/2}$ if one takes in Eq. (1a) that $f_{\mathrm{Nb}} \approx 1$, $f_{\mathrm{O}} \approx 1$. This replacement causes no marked error and is used in thermodynamic calculations of such a kind [2]. Then, Eq. (5) takes the form

$$\log[\%\mathrm{O}]_{\text{Fe–Co}} = \frac{1}{2}\{\log K_{(1)} - \log[\%\mathrm{Nb}] - [e^{\mathrm{Nb}}_{\mathrm{Nb(Fe–Co)}} + 2e^{\mathrm{Nb}}_{\mathrm{O(Fe–Co)}}][\%\mathrm{Nb}] - [2e^{\mathrm{O}}_{\mathrm{O(Fe–Co)}} + e^{\mathrm{O}}_{\mathrm{Nb(Fe–Co)}}](K_{(1)}/[\%\mathrm{Nb}])^{1/2}\}. \quad (5a)$$

Equilibrium oxygen concentrations in Fe–Co melts are calculated from equation (5a). The values of interaction parameters used in calculations for the melts of different compositions are presented in the table. The values of interaction parameters $e^{\mathrm{Nb}}_{\mathrm{Nb(Fe–Co)}}$, $e^{\mathrm{Nb}}_{\mathrm{O(Fe–Co)}}$, $e^{\mathrm{O}}_{\mathrm{Nb(Fe–Co)}}$, and $e^{\mathrm{O}}_{\mathrm{O(Fe–Co)}}$ for Fe–Co melts were determined by equation $\varepsilon^{j}_{i(\text{Fe–Co})} = \varepsilon^{j}_{i(\mathrm{Fe})}X_{\mathrm{Fe}} + \varepsilon^{j}_{i(\mathrm{Co})}X_{\mathrm{Co}}$ [5], where ε^{j}_{i} is first-order interaction parameter when component concentration is expressed as molar fraction.

The calculated dependences of equilibrium oxygen concentration on the niobium content in Fe–Co melts are given below.

Fe:

$$\log[\%\mathrm{O}]_{\mathrm{Fe}} = -1.668 - 1/2\log[\%\mathrm{Nb}] + 0.120[\%\mathrm{Nb}] + 1.129 \times 10^{-2}/[\%\mathrm{Nb}]^{1/2}.$$

Fe–20% Co:

$$\log[\%\mathrm{O}]_{\text{Fe–20\% Co}} = -1.716 - 1/2\log[\%\mathrm{Nb}] + 0.102[\%\mathrm{Nb}] + 0.864 \times 10^{-2}/[\%\mathrm{Nb}]^{1/2}.$$

Fe–40% Co:

$$\log[\%\mathrm{O}]_{\text{Fe–40\% Co}} = -1.755 - 1/2\log[\%\mathrm{Nb}] + 0.082[\%\mathrm{Nb}] + 0.649 \times 10^{-2}/[\%\mathrm{Nb}]^{1/2}.$$

Fe–60% Co:

$$\log[\%\mathrm{O}]_{\text{Fe–60\% Co}} = -1.809 - 1/2\log[\%\mathrm{Nb}] + 0.062[\%\mathrm{Nb}] + 0.444 \times 10^{-2}/[\%\mathrm{Nb}]^{1/2}.$$

Fe–80% Co:

$$\log[\%\mathrm{O}]_{\text{Fe–80\% Co}} = -1.905 - 1/2\log[\%\mathrm{Nb}] + 0.041[\%\mathrm{Nb}] + 0.248 \times 10^{-2}/[\%\mathrm{Nb}]^{1/2}.$$

Co:

$$\log[\%\mathrm{O}]_{\mathrm{Co}} = -2.072 - 1/2\log[\%\mathrm{Nb}] + 0.019[\%\mathrm{Nb}] + 0.919 \times 10^{-3}/[\%\mathrm{Nb}]^{1/2}.$$

The dependences of equilibrium oxygen concentration on the niobium and cobalt content in the melt at 1873 K are shown in Fig. 2. It is seen from the presented data that the deoxidizing ability of niobium increases with an increase in the cobalt content in the melt.

The curves of oxygen solubility in iron–cobalt melts pass through a minimum. The niobium content corresponding to the minimal oxygen concentration can be determined [15] by the equation

$$[\%\mathrm{R}]' = -\frac{m}{2.3(me^{\mathrm{R}}_{\mathrm{R}} + ne^{\mathrm{R}}_{\mathrm{O}})}, \quad (6)$$

where m and n are indices in the formula of $\mathrm{R}_m\mathrm{O}_n$ oxide.

In the case of $\mathrm{NbO_2}$, Eq. (6) adopts the following form

$$[\%\mathrm{Nb}]' = -\frac{1}{2.3(e^{\mathrm{Nb}}_{\mathrm{Nb}} + 2e^{\mathrm{Nb}}_{\mathrm{O}})}. \quad (6a)$$

The niobium content at minimum points calculated by Eq. (6a) and the corresponding oxygen concentrations are listed below.

Co, %	0	20	40	60	80	100
[%Nb]'	1.81	2.14	2.64	3.49	5.27	11.26
$[\%\mathrm{O}]_{\min}$	0.0269	0.0220	0.0180	0.0138	0.0090	0.0042

Thus, the thermodynamic analysis of oxygen solutions in niobium-containing Fe–Co melts performed for the first time showed that the deoxidizing ability of niobium increases with increasing

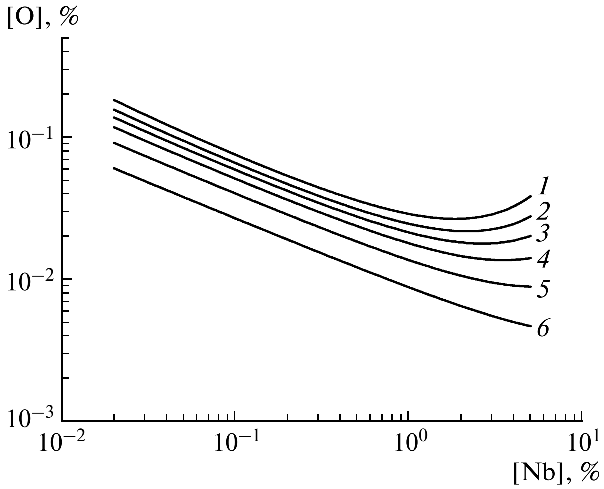

Fig. 2. Dependences of oxygen concentrations in Fe–Co melts on the niobium content at 1873 K.
Co, %: (*1*) 0, (*2*) 20, (*3*) 40, (*4*) 60, (*5*) 80, and (*6*) 100.

cobalt content in the melt. The curves of oxygen solubility in niobium-containing iron–cobalt melts pass through a minimum which is shifted to higher niobium concentrations as the cobalt content in the melt increases.

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