

Thermodynamics of Oxygen Solutions in Fe–Ni, Fe–Co, and Co–Ni Melts

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Abstract—By thermodynamic analysis of oxygen solutions in Fe–Ni–O, Fe–Co–O, and Co–Ni–O melts, the composition of the oxide phase is established for the first time. In addition, the equilibrium oxygen concentrations in these melts are determined over the whole range of alloy compositions. In Fe–Ni–O and Fe–Co–O melts, the oxide phase mainly contains FeO over a relatively broad of alloy compositions. Sharp increase in NiO content is only observed when the molar fraction of nickel exceeds one; sharp increase in CoO content is only observed when the molar fraction of cobalt exceeds 0.8. In the Co–Ni–O system, the oxide phase contains both CoO and NiO over the whole range of alloy compositions. In the Fe–Ni system, adding nickel to the melt reduces the solubility of oxygen as a result of weakening of the oxygen bonds in the melt by nickel and consequent increase in oxygen's activity. With further increase in nickel content in the melt, the oxygen content rises at first slowly and then very sharply. In the Fe–Co system, analogously, adding cobalt to the melt reduces the solubility of oxygen as a result of weakening of the oxygen bonds in the melt and consequent increase in oxygen's activity. With further increase in cobalt content, the oxygen content rises at first slowly and then relatively rapidly. In the Co–Ni system, adding nickel to cobalt increases the solubility of oxygen over the whole range of alloy compositions, on account of the significantly greater solubility of oxygen in nickel than in cobalt.

Keywords: iron, nickel, cobalt, oxygen, thermodynamic analysis, oxide phase, solubility of oxygen

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Iron, cobalt, and nickel (the iron triad) belong to the same group (VIII B) and same period (IV) of the periodic table. However, their physical and chemical properties are very different, and they form very different compounds.

Fe–Ni, Fe–Co, and Co–Ni alloys are widely used in engineering. Adding oxygen to these alloys impairs their performance. By studying the physicochemical properties of solutions of oxygen in Fe–Ni, Fe–Co, and Co–Ni melts, we may optimize the production of these alloys. There are literature data regarding the composition of the oxide phase in equilibrium with Fe–Ni–O, Fe–Co–O, and Co–Ni–O or regarding the solubility of oxygen in such alloys over a wide range of alloy compositions. By thermodynamic analysis on the basis of data regarding solutions of oxygen in liquid iron, nickel, and cobalt [1–4] and the Fe–Ni, Fe–Co, and Co–Ni systems [5], we may determine the composition of the oxide phase and assess the solubility of oxygen in such melts.

Solutions of oxygen in iron, nickel, and cobalt melts must be regarded as real; their formation is accompanied by thermal effects and changes in entropy. The equations describing the behavior of

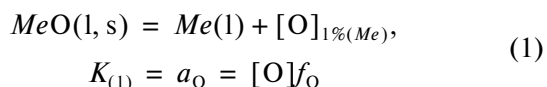
components in real solutions may be derived from the equations for ideal solutions by replacing the concentrations with the corresponding activities $a = \gamma X$, where γ is the activity coefficient and X is the mole fraction. To take account of the influence of the solution components on the thermodynamic characteristics, we use interaction parameters [6]

$$\varepsilon_i^j = \frac{\partial \ln \gamma_i}{\partial X_j}$$

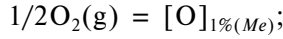
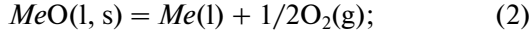
Basically, the corresponding excess thermodynamic function (ΔG_i , ΔH_i , ΔS_i) is expanded in Taylor series. In most cases, the required precision may be ensured by retaining terms of zero and first order

$$\ln \gamma_i = \ln \gamma_i^\circ + \sum \frac{\partial \ln \gamma_i}{\partial X_j} X_j = \ln \gamma_i^\circ + \sum \varepsilon_i^j X_j$$

In the case of iron, nickel, and cobalt melts, the metal–oxide equilibrium



may be expressed as the sum of the following reactions



$$\Delta G_{(3)}^\circ = RT \ln \left(\frac{\gamma_{O(Me)}^\circ M_{Me}}{M_O \times 100} \right). \quad (3)$$

Here $\gamma_{O(Me)}^\circ$ is the oxygen activity coefficient in the melt at infinite dilution; M_i is the molecular mass. The standard state of the oxygen dissolved in the melt is assumed to be 1% solution, with the properties of an ideal dilute solution.

The solubility of oxygen in the liquid metal may be calculated from the equation

$$\begin{aligned} \log [\% O]_{Me} &= \log K_{(1)} - \log f_O \\ &= \log K_{(1)} - e_{O(Me)}^\circ [\% O]_{Me}, \end{aligned} \quad (4)$$

where $e_{O(Me)}^\circ$ is the first-order interaction parameter (when the concentrations of the components are expressed in wt %).

On the right side of Eq. (4), [% O] may be expressed in terms of $K_{(1)}/f_O$. Note that $f_O \rightarrow 1$ as [% O] $\rightarrow 0$. Since [% O] is small, we may set $K_{(1)}/f_O \approx K_{(1)}$. This does not introduce much error in the calculations [4]. Then Eq. (4) takes the form

$$\log [\% O]_{Me} = \log K_{(1)} - e_{O(Me)}^\circ K_{(1)}. \quad (4a)$$

At 1873 K, iron oxide is liquid: $T_m(\text{FeO}) = 1651$ K [7]. By contrast, nickel and cobalt oxides are solid: $T_m(\text{NiO}) = 2228$ K, $T_m(\text{CoO}) = 2088$ K [7]. The temperature dependence of the Gibbs energy is as follows: for the formation of iron oxide [4]

$$\Delta G_{(2)}^\circ(\text{FeO}_{(l)}) = 239987 - 49.57T, \text{ J/mol};$$

for the formation of nickel oxide [4]

$$\Delta G_{(2)}^\circ(\text{NiO}_{(s)}) = 253929 - 95.29T, \text{ J/mol};$$

for the formation of cobalt oxide [4]

$$\Delta G_{(2)}^\circ(\text{CoO}_{(s)}) = 261884 - 85.83T, \text{ J/mol}.$$

For solutions of iron in liquid iron, nickel, and cobalt at 1873 K

$$\gamma_{O(\text{Fe})}^\circ = 0.0103 [1], \quad \gamma_{O(\text{Ni})}^\circ = 0.337 [2],$$

$$\gamma_{O(\text{Co})}^\circ = 0.161 [3].$$

Hence, we may calculate the Gibbs energy for Eq. (3) and then the Gibbs energy and equilibrium constant for Eq. (1). At 1873 K, $\Delta G_{(1)}^\circ = 23637$ J/mol and $\log K_{(1)} = -0.6599$ for iron, $\Delta G_{(1)}^\circ = 7042$ J/mol and $\log K_{(1)} = -0.1966$ for nickel, and $\Delta G_{(1)}^\circ =$

21271 J/mol and $\log K_{(1)} = -0.5939$ for cobalt. At 1873 K

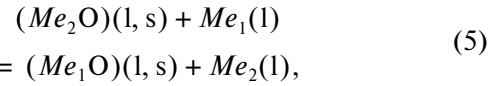
$$e_{O(\text{Fe})}^\circ = -0.17 [1], \quad e_{O(\text{Ni})}^\circ = 0 [2], \quad e_{O(\text{Co})}^\circ = 0 [3].$$

According to Eq. (4), the solubility of oxygen is $[O]_{\text{Fe}} = 0.240\%$ in iron; $[O]_{\text{Ni}} = 0.636\%$ in nickel; and $[O]_{\text{Co}} = 0.255\%$ in cobalt. The results are in good agreement with literature data

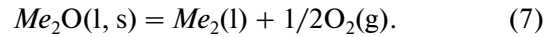
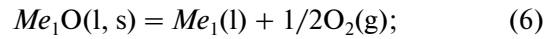
$$[O]_{\text{Fe}} = 0.23\% [8, 9], \quad [O]_{\text{Ni}} = 0.64\% [8],$$

$$[O]_{\text{Co}} = 0.23\% [9].$$

The oxide phase for Fe–Ni–O, Fe–Co–O, and Co–Ni–O melts contains the corresponding two of the oxides FeO, NiO, and CoO. The metal–oxide equilibrium may be described by the reaction



which is effectively the sum of two reactions



In the approximation of perfect solutions, for solutions of oxygen in Fe–Ni, Fe–Co, and Co–Ni melts, we may write the following formula for the oxide phase

$$K_{(5)} = \frac{X_{Me_1O} X_{Me_2} \gamma_{Me_2}}{X_{Me_2O} X_{Me_1} \gamma_{Me_1}}.$$

Since $X_{Me_1O} + X_{Me_2O} = 1$, we find that

$$X_{Me_1O} = \frac{K_{(5)} X_{Me_1} \gamma_{Me_1}}{K_{(5)} X_{Me_1} \gamma_{Me_1} + X_{Me_2} \gamma_{Me_2}}. \quad (8)$$

In calculating the Gibbs energy for Eq. (5), we take account of the Gibbs energy for the formation of the corresponding oxides, as discussed earlier. At 1873 K, $\Delta G_{(5)}^\circ = -71692$ J/mol and $K_{(5)} = 100.357$ for the Fe–Ni system; $\Delta G_{(5)}^\circ = -46018$ J/mol and $K_{(5)} = 19.265$ for the Fe–Co system; and $\Delta G_{(5)}^\circ = 25674$ J/mol and $K_{(5)} = 0.1920$ for the Co–Ni system.

We present the composition of the oxide phase in the Fe–Ni, Fe–Co, and Co–Ni systems, according to Eq. (8), in Tables 1–3 and in Fig. 1. As we see, the oxide phase in the Fe–Ni–O system consists mainly of FeO; the NiO content increases sharply only when the mole fraction of nickel is close to one. This is because the oxygen affinity of iron is significantly greater than that of nickel. The oxide phase in the Fe–Co–O system also consists mainly of FeO; the CoO content increases sharply only when the mole fraction of cobalt exceeds 0.8. Once again, this is because the oxygen affinity of iron is significantly greater than that of cobalt. The oxide phase in the Co–Ni–O system contains both CoO and NiO. However, for all alloy compositions, the mole fraction of CoO in the oxide

Table 1. Composition of the oxide phase in Fe–Ni–O melt at 1873 K

X_{Fe}	γ_{Fe} [5]	X_{Ni}	γ_{Ni} [5]	X_{FeO}	X_{NiO}
1.0	1.000	0	0.617	1.0000	0
0.9	0.996	0.1	0.675	0.9993	0.0007
0.8	0.992	0.2	0.692	0.9983	0.0017
0.7	0.990	0.3	0.697	0.9970	0.0030
0.6	0.978	0.4	0.712	0.9952	0.0048
0.5	0.941	0.5	0.745	0.9922	0.0078
0.4	0.858	0.6	0.802	0.9862	0.0138
0.3	0.726	0.7	0.877	0.9727	0.0273
0.2	0.581	0.8	0.945	0.9391	0.0609
0.1	0.454	0.9	0.987	0.8368	0.1632
0	0.355	1.0	1.000	0	1.0000

Table 2. Composition of the oxide phase in Fe–Co–O melt at 1873 K

X_{Fe}	γ_{Fe} [5]	X_{Co}	γ_{Co} [5]	X_{FeO}	X_{CoO}
1.0	1.000	0	1.051	1.0000	0
0.9	0.996	0.1	1.136	0.9935	0.0065
0.8	0.987	0.2	1.199	0.9845	0.0155
0.7	0.979	0.3	1.230	0.9728	0.0272
0.6	0.981	0.4	1.226	0.9585	0.0415
0.5	1.035	0.5	1.151	0.9454	0.0546
0.4	1.095	0.6	1.097	0.9276	0.0724
0.3	1.183	0.7	1.051	0.9029	0.0971
0.2	1.282	0.8	1.024	0.8577	0.1423
0.1	1.416	0.9	1.006	0.7508	0.2492
0	1.590	1.0	1.000	0	1.0000

phase is greater than that of cobalt in the melt, whereas the mole fraction of NiO in the oxide phase is less than that of nickel in the melt. This is because the oxygen affinity of cobalt is significantly greater than that of nickel.

The oxygen affinity of Fe, Ni, and Co may be characterized both by the Gibbs energy of formation of the corresponding oxides

$$\Delta G_{1873\text{ K}}^{\circ}(\text{FeO}) = -147\,142 \text{ J/mol [4];}$$

$$\Delta G_{1873\text{ K}}^{\circ}(\text{NiO}) = -75\,451 \text{ J/mol [4];}$$

$$\Delta G_{1873\text{ K}}^{\circ}(\text{CoO}) = -101\,124 \text{ J/mol [4],}$$

and by the oxygen activity coefficient in those melts at infinite dilution: $\gamma_{\text{O(Fe)}}^{\circ} = 0.0103$ [1]; $\gamma_{\text{O(Ni)}}^{\circ} = 0.337$

[2]; $\gamma_{\text{O(Co)}}^{\circ} = 0.161$ [3]. Larger $\gamma_{\text{O}}^{\circ}$ corresponds to lower oxygen affinity.

For melts in the Me_1 – Me_2 system, Eq. (1) takes the form

$$(Me_1O)(l, s) = [Me_1]_{Me_1-Me_2} + [O]_{1\%(Me_1-Me_2)}; \quad (9)$$

$$K_{(9)} = \frac{X_{Me_1} \gamma_{Me_1} [O] f_{\text{O}}}{X_{Me_1O}}$$

and may be expressed as the sum of the reaction in Eq. (6) and the reaction

$$1/2\text{O}_2(\text{g}) = [O]_{1\%(Me_1-Me_2)}; \quad (10)$$

$$\Delta G_{(10)}^{\circ} = RT \ln \left(\frac{\gamma_{\text{O}(Me_1-Me_2)}^{\circ} M_{Me_1-Me_2}}{M_{\text{O}} \times 100} \right).$$

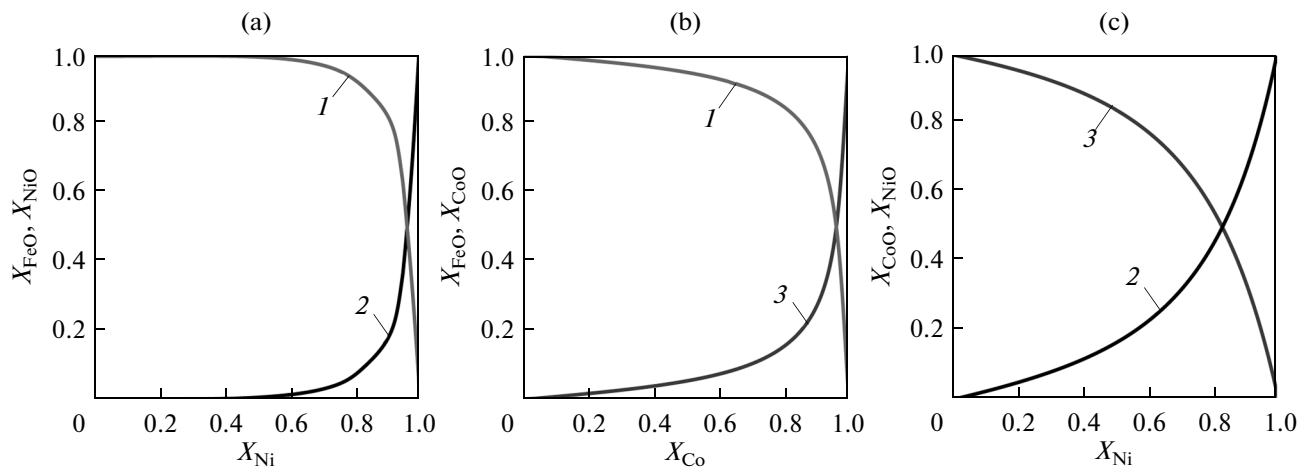


Fig. 1. Composition of the oxide phases in Fe–Ni–O (a), Fe–Co–O (b), and Co–Ni–O (c) melts at 1873 K: (1) X_{FeO} ; (2) X_{NiO} ; (3) X_{CoO} .

Table 3. Composition of the oxide phase in Co–Ni–O melt at 1873 K

X_{Co}	γ_{Co} [6]	X_{Ni}	γ_{Ni} [6]	X_{CoO}	X_{NiO}
1.0	1.0	0	1.0	1.0000	0
0.9	1.0	0.1	1.0	0.9791	0.0209
0.8	1.0	0.2	1.0	0.9541	0.0459
0.7	1.0	0.3	1.0	0.9238	0.0762
0.6	1.0	0.4	1.0	0.8863	0.1137
0.5	1.0	0.5	1.0	0.8386	0.1614
0.4	1.0	0.6	1.0	0.7760	0.2240
0.3	1.0	0.7	1.0	0.6902	0.3098
0.2	1.0	0.8	1.0	0.5651	0.4349
0.1	1.0	0.9	1.0	0.3661	0.6339
0	1.0	1.0	1.0	0	1.0000

For the melts in all systems, the molecular mass of the alloy is calculated from the equation [10]

$$M_{Me_1+Me_2} = M_{Me_1}X_{Me_1} + M_{Me_2}X_{Me_2},$$

and the activity coefficient $\gamma_{O(Me_1+Me_2)}^{\circ}$ is calculated from the equation [11]

$$\begin{aligned} \ln \gamma_{i(Me_1+Me_2)}^{\circ} &= X_{Me_1} \ln \gamma_{i(Me_1)}^{\circ} + X_{Me_2} \ln \gamma_{i(Me_2)}^{\circ} \\ &+ X_{Me_1} X_{Me_2} [X_{Me_2} (\ln \gamma_{i(Me_2)}^{\circ} - \ln \gamma_{i(Me_1)}^{\circ} + \varepsilon_{i(Me_2)}^{Me_1}) \\ &+ X_{Me_1} (\ln \gamma_{i(Me_1)}^{\circ} - \ln \gamma_{i(Me_2)}^{\circ} + \varepsilon_{i(Me_1)}^{Me_2})]. \end{aligned}$$

Table 4. Solubility of oxygen in Fe–Ni melts at 1873 K

X_{Ni}	$M_{\text{Fe-Ni}}$	$\gamma_{O(\text{Fe-Ni})}^{\circ}$	$\Delta G_{(9)}^{\circ}$, J/mol	$\log K_{(9)}$	$e_{O(\text{Fe-Ni})}^{\circ}$	[O], %
0	55.874	0.0103	23637	-0.6599	-0.1700	0.240
0.1	56.133	0.0111	24852	-0.6938	-0.1538	0.240
0.2	56.420	0.0130	27402	-0.7650	-0.1374	0.231
0.3	56.706	0.0164	31144	-0.8695	-0.1208	0.205
0.4	56.992	0.0222	35936	-1.0033	-0.1041	0.175
0.5	57.279	0.0319	41634	-1.1624	-0.0872	0.149
0.6	57.565	0.0481	48096	-1.3428	-0.0701	0.133
0.7	57.851	0.0754	55180	-1.5406	-0.0528	0.131
0.8	58.137	0.1219	62743	-1.7517	-0.0354	0.145
0.9	58.424	0.2014	70641	-1.9722	-0.0178	0.198
1.0	58.710	0.3370	7042*	-0.1966*	0	0.636

* Calculation for the reaction $\text{NiO}(s) = \text{Ni}(l) + [\text{O}]_{1\%}(\text{Ni})$.

For solutions of oxygen in liquid iron, nickel, and cobalt

$$\gamma_{O(\text{Fe})}^{\circ} = 0.0103 [1]; \quad \gamma_{O(\text{Ni})}^{\circ} = 0.337 [2];$$

$$\gamma_{O(\text{Co})}^{\circ} = 0.161 [3]; \quad \varepsilon_{O(\text{Co})}^{\text{Ni}} = 0.270 [12];$$

$$\varepsilon_{O(\text{Ni})}^{\text{Fe}} = -5.179 [12]; \quad \varepsilon_{O(\text{Fe})}^{\text{Co}} = 1.9 [1];$$

$$\varepsilon_{O(\text{Co})}^{\text{Fe}} = -4.1 [3]; \quad \varepsilon_{O(\text{Ni})}^{\text{Co}} = -1.4 [13]; \quad \varepsilon_{O(\text{Co})}^{\text{Ni}} = 0.16 [3].$$

Tables 4–6 present calculated values of $M_{Me_1+Me_2}$, $\gamma_{O(Me_1+Me_2)}^{\circ}$, the Gibbs energy, and the equilibrium constant of the reaction in Eq. (9) for the Fe–Ni, Fe–Co, and Co–Ni systems. The solubility of oxygen in Me_1 – Me_2 melts may be calculated from the equation

$$\begin{aligned} \log [\% \text{O}]_{Me_1-Me_2} &= \log K_{(9)} + \log X_{Me_1O} - \log X_{Me_1} \\ &- \log \gamma_{Me_1} - e_{O(Me_1-Me_2)}^{\circ} [\% \text{O}]_{Me_1-Me_2}. \end{aligned} \quad (11)$$

On the right side of Eq. (11), [% O] may be expressed in terms of $K_{(9)}X_{Me_1O}/X_{Me_1}\gamma_{Me_1}f_{\text{O}}$. Note that $f_{\text{O}} \rightarrow 1$ as [% O] $\rightarrow 0$. Since [% O] is small, we may set

$$\frac{K_{(9)}X_{Me_1O}}{X_{Me_1}\gamma_{Me_1}f_{\text{O}}} \approx \frac{K_{(9)}X_{Me_1O}}{X_{Me_1}\gamma_{Me_1}}.$$

This does not introduce much error in the calculations [4]. Then Eq. (11) takes the form

$$\begin{aligned} \log [\% \text{O}]_{Me_1-Me_2} &= \log K_{(9)} + \log X_{Me_1O} - \log X_{Me_1} \\ &- \log \gamma_{Me_1} - e_{O(Me_1-Me_2)}^{\circ} \frac{K_{(9)}X_{Me_1O}}{X_{Me_1}\gamma_{Me_1}}. \end{aligned} \quad (11a)$$

Table 5. Solubility of oxygen in Fe–Co melts at 1873 K

X_{Co}	$M_{\text{Fe-Co}}$	$\gamma_{\text{O(Fe-Co)}}^{\circ}$	$\Delta G_{(9)}^{\circ}$, J/mol	$\log K_{(9)}$	$e_{\text{O(Fe-Co)}}^{\circ}$	[O], %
0	55.847	0.0103	23637	-0.6599	-0.1700	0.240
0.1	56.156	0.0125	26743	-0.7467	-0.1539	0.213
0.2	56.464	0.0153	30005	-0.8377	-0.1375	0.192
0.3	56.773	0.0190	33468	-0.9344	-0.1210	0.173
0.4	57.081	0.0240	37179	-1.0380	-0.1043	0.155
0.5	57.390	0.0309	41186	-1.1497	-0.0874	0.133
0.6	57.699	0.0407	45535	-1.2713	-0.0703	0.116
0.7	58.007	0.0548	50273	-1.4036	-0.0530	0.102
0.8	58.316	0.0761	55446	-1.5480	-0.0355	0.095
0.9	58.625	0.1088	61103	-1.7059	-0.0179	0.105
1.0	58.933	0.1610	21271*	-0.5939*	0	0.255

* Calculation for the reaction $\text{CoO(s)} = \text{Co(l)} + [\text{O}]_{1\%(\text{Co})}$.

Table 6. Solubility of oxygen in Co–Ni melts at 1873 K

X_{Ni}	$M_{\text{Co-Ni}}$	$\gamma_{\text{O(Co-Ni)}}^{\circ}$	$\Delta G_{(9)}^{\circ}$, J/mol	$\log K_{(9)}$	[O], %
0	58.933	0.161	21271	-0.5939	0.255
0.1	58.911	0.164	21593	-0.6028	0.272
0.2	58.889	0.170	22077	-0.6164	0.289
0.3	58.866	0.177	22731	-0.6346	0.307
0.4	58.844	0.187	23562	-0.6578	0.324
0.5	58.822	0.199	24579	-0.6862	0.346
0.6	58.799	0.216	25789	-0.7200	0.371
0.7	58.777	0.236	27200	-0.7594	0.401
0.8	58.755	0.262	28820	-0.8046	0.444
0.9	58.732	0.295	30656	-0.8559	0.511
1.0	58.710	0.337	7042*	-0.1966*	0.636

* Calculation for the reaction $\text{NiO(s)} = \text{Ni(l)} + [\text{O}]_{1\%(\text{Ni})}$.

Fe–Ni, Fe–Co, and Co–Ni melts resemble an ideal solution [5]. Hence, we may calculate $\varepsilon_{\text{O}(Me_1-Me_2)}^{\circ}$ (and then $e_{\text{O}(Me_1-Me_2)}^{\circ}$) from the formula [10]

$$\varepsilon_{\text{O}(Me_1-Me_2)}^{\circ} = \varepsilon_{\text{O}(Me_1)}^{\circ} X_{Me_1} + \varepsilon_{\text{O}(Me_2)}^{\circ} X_{Me_2}.$$

At 1873 K, $e_{\text{O(Fe)}}^{\circ} = -0.17$ [1]; $e_{\text{O(Ni)}}^{\circ} = 0$ [2]; $e_{\text{O(Co)}}^{\circ} = 0$ [3]. Tables 4 and 5 present the calculated values of $e_{\text{O}(Me_1-Me_2)}^{\circ}$ for the Fe–Ni and Fe–Co systems. For the Co–Ni system, $e_{\text{O}(Me_1-Me_2)}^{\circ}$ is zero over the whole range of alloy compositions.

The equilibrium oxygen concentrations in the Fe–Ni, Fe–Co, and Co–Ni systems according to Eq. (11a) are shown in Tables 4–6 and in Fig 2. In the Fe–Ni system, as we see, small additions of nickel to iron (corresponding to a nickel mole fraction less than 0.15) do not markedly affect the solubility of oxygen in the melt, since low concentrations of nickel have little effect on the oxygen activity in iron (Table 4). Further additions of nickel (to a mole fraction of ~0.7) reduce the solubility of oxygen, because the nickel weakens the oxygen bonds in the melt and thereby increases its activity ($\varepsilon_{\text{O(Fe)}}^{\text{Ni}} = 0.270$). At higher Ni concentrations, the oxygen concentration in the melt increases at first slowly and then (beyond a mole fraction of 0.9) very sharply, because the solubility of oxygen in nickel is

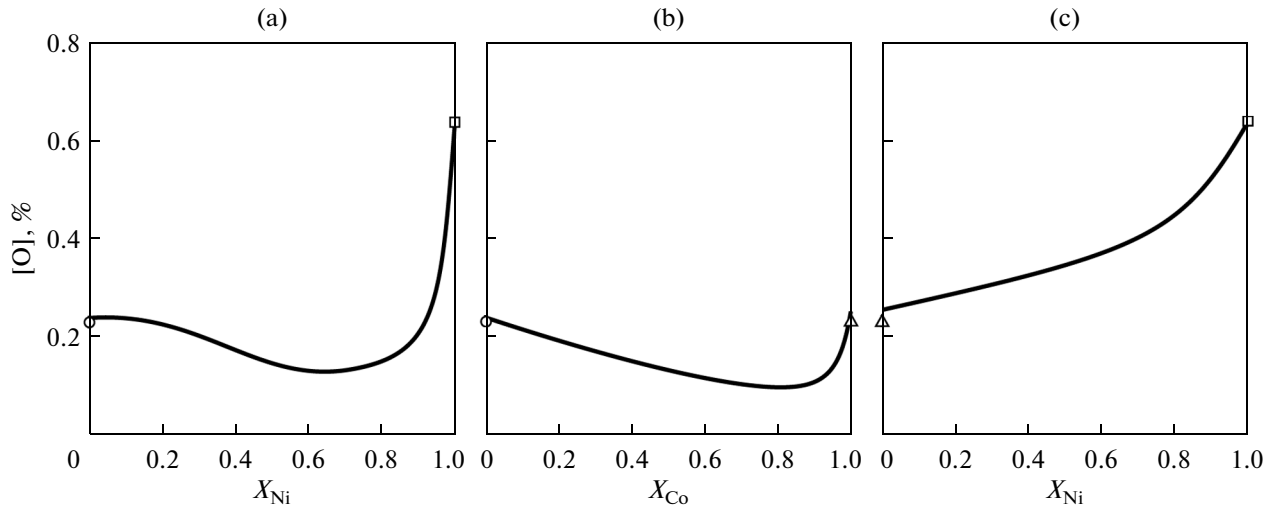


Fig. 2. Solubility of oxygen in Fe–Ni (a), Fe–Co (b), and Co–Ni (c) melts at 1873 K: (○) $[O]_{Fe}$ [8, 9]; (□) $[O]_{Ni}$ [8]; (△) $[O]_{Co}$ [9].

considerably higher than its solubility in iron. In the Fe–Co system, adding cobalt to iron markedly reduces the solubility of oxygen. Like nickel, the cobalt increases the activity coefficient of oxygen in iron ($\varepsilon_{O(Fe)}^{Co} = 1.9$), thereby reducing its solubility. When the cobalt mole fraction in the melt reaches ~ 0.8 , the oxygen concentration in the melt increases at first slowly and then relatively rapidly. Over the whole range of alloy compositions, the solubility of oxygen in Fe–Co melts is less than in Fe–Ni melts, since the solubility of oxygen in cobalt is less than its solubility in nickel. In the Co–Ni system, adding nickel to the cobalt increases the solubility of oxygen over the whole range of alloy compositions, on account of the significantly greater solubility of oxygen in nickel than in cobalt.

We note a minimum on curves showing the solubility of oxygen in Fe–Ni and Fe–Co melts (Fig. 2). With increase in the nickel and cobalt content in iron-based melts, the associated oxide phase consists mainly of iron oxide FeO, over a broad range of alloy compositions. The solubility of oxygen in the melt is determined by its activity, which increases with increase in the nickel and cobalt content (Tables 4 and 5). That leads to decrease in solubility of oxygen in the melt. When the nickel and cobalt content in the melts is considerable, the solubility of oxygen in these elements is the determining factor. The oxygen concentration begins to rise, passing through a minimum. Iron is a reducing agent for liquid nickel and cobalt, on account of its higher oxygen affinity. The iron content $[\% Fe]'$ corresponding to minimum oxygen concentration may be determined from the equation [14]

$$[\% R]' = -\frac{m}{2, 3(m e_R^R + n e_O^R)}, \quad (12)$$

where m and n are the coefficients in the formula for the oxide $R_m O_n$. In the case of FeO, Eq. (12) takes the form

$$[\% Fe]' = -\frac{1}{2, 3(e_{Fe}^{Fe} + e_O^{Fe})}. \quad (12a)$$

The iron content at the minimum and the corresponding minimum oxygen concentration for Fe–Ni and Fe–Co melts are as follows:

Melt	e_{Fe}^{Fe}	e_O^{Fe}	$[\% Fe]'$	$[\% O]_{min}$
Fe–Ni	0.013 [2]	–0.029 [2]	27.174	0.131
Fe–Co	–0.0062 [3]	–0.019 [3]	17.253	0.095

In the case of the Co–Ni system, no minimum is seen on the plot of oxygen solubility. In fact, since the activity coefficient of oxygen is equal to its concentration in cobalt, nickel, and Co–Ni melts of any composition ($e_{O(Co)}^O = 0$, $e_{O(Ni)}^O = 0$, $e_{O(Co-Ni)}^O = 0$), the oxygen concentration in the melt is determined by the nickel and cobalt content and also by the solubility of oxygen in nickel and cobalt, as well as the composition of the oxide phase.

Thus, thermodynamic analysis permits identification of the composition of the oxide phase and the equilibrium content of oxygen in Fe–Ni, Fe–Co, and Co–Ni melts over the whole range of alloy compositions.

CONCLUSIONS

In Fe–Ni–O and Fe–Co–O melts, the oxide phase mainly contains FeO over a relatively broad of nickel and cobalt content. Sharp increase in NiO content is only observed when the molar fraction of nickel

exceeds one; sharp increase in CoO content is only observed when the molar fraction of cobalt exceeds 0.8. In the Co–Ni–O system, the oxide phase contains both CoO and NiO over the whole range of alloy compositions.

In the Fe–Ni system, adding nickel to the melt (to a mole fraction of ~0.7) reduces the solubility of oxygen as a result of weakening of the oxygen bonds in the melt by nickel ($\varepsilon_{\text{O(Fe)}}^{\text{Ni}} = 0.270$) and consequent increase in oxygen's activity. With further increase in nickel content in the melt, the oxygen content rises at first slowly and then (above a Ni mole content of 0.9) very sharply, on account of the significantly greater solubility of oxygen in nickel than in iron.

In the Fe–Co system, adding cobalt to the melt markedly reduces the solubility of oxygen, because cobalt, like nickel, increases the activity of oxygen in iron ($\varepsilon_{\text{O(Fe)}}^{\text{Co}} = 1.9$) and thereby reduces its solubility. On reaching a cobalt mole fraction of ~0.8 in the melt, the oxygen content rises at first slowly and then relatively rapidly.

In the Co–Ni system, adding nickel to cobalt increases the solubility of oxygen over the whole range of alloy compositions, on account of the significantly greater solubility of oxygen in nickel than in cobalt.

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