Deoxidation Equilibrium of Manganese and Silicon in Liquid Iron–Nickel Alloys

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The thermodynamic analysis of oxygen solutions in Fe–Ni melts containing manganese and silicon has been carried out. The deoxidation power of manganese essentially increases with the nickel content in melt. The solubility curves pass through a minimum, which shifts to lower manganese contents, as nickel content in melt increases. For alloys containing more than 50–60 % nickel, the minimal oxygen concentrations are obtained at manganese content equal to 1–1.5 %, the further increase of manganese concentration results in an increase of oxygen content. Silicon deoxidation power also increases with the increase of nickel content in melt, but not so sharply as in the case of manganese. In the range of silicon contents considered, no minimum was observed in oxygen solubility curves. Thermodynamics of oxygen, manganese and silicon solutions in the Fe–40%Ni melts has been studied experimentally in a temperature range of 1823–1923 K. With temperature drop, deoxidation power of both manganese and silicon increases. In the Fe–40%Ni melts in both cases it is higher than in iron but lower than in nickel. Dependence of oxygen concentration on manganese and silicon contents is expressed by empirical equations. Upon combined deoxidation with manganese and silicon, it is possible to obtain lower oxygen concentrations in metal, in comparison with separate deoxidation due to decreased activities of manganese oxide and silica.

KEY WORDS: deoxidation equilibrium; manganese; silicon; iron–nickel melts; thermodynamic analysis; experimental study.

1. Introduction

The Fe–Ni alloys are widely used in modern engineering and are, in particular, the basis of a large group of special alloys. It is known that oxygen is a harmful impurity in these alloys. Deoxidizing elements used upon alloy production allow one to obtain the final metal with low oxygen content and small amount of nonmetallic inclusions. Manganese and silicon are most often used as deoxidizing elements. Available thermodynamic data on the oxygen solutions in liquid iron^{1,2)} and nickel^{1,3)} are useful to estimate the oxygen solubility in the Fe–Ni melts⁴⁾ as well as effect of manganese and silicon on the oxygen solubility.

This study presents analytical and experimental investigations on the thermodynamics of oxygen solutions in the Fe–Ni melts containing manganese and silicon.

2. Thermodynamic Consideration

Reaction of deoxidizing elements R with oxygen in the Fe–Ni melt:

$$K_R = \frac{([\%R] \cdot f_R)^m ([\%O] \cdot f_O)^n}{X_{R_mO_n} \gamma_{R_mO_n}} \quad \text{.....(1a)}$$

where X_i is mole fraction, f_i and γ_i is the activity coefficient

of element i in mass percent base and mole fraction base, respectively, can be written as the sum of reactions:

$$\Delta G_{(3)}^\circ = RT \ln(\gamma_{R(\text{Fe-Ni})}^\circ M_{\text{Fe-Ni}} / M_R \cdot 100)$$

$$\Delta G_{(4)}^\circ = RT \ln(\gamma_{O(\text{Fe-Ni})}^\circ M_{\text{Fe-Ni}} / M_O \cdot 100)$$

where γ_i° denotes the activity coefficient of element i in infinite dilution, and M_i denotes the molecular mass of element i .

From Gibbs energy of reaction (1):

$$\Delta G_{(1)}^\circ = \Delta G_{(2)}^\circ + m\Delta G_{(3)}^\circ + n\Delta G_{(4)}^\circ \quad \text{.....(5)}$$

it is possible to calculate the equilibrium constant of reaction (1):

$$\ln K_R = -\Delta G_{(1)}^\circ / RT \quad \text{.....(6)}$$

The concentration of oxygen, which is in equilibrium with R, at a given R content can be calculated by the equation:

Table 1. Equilibrium constants for reaction (1), activity coefficients and interaction parameters for in the Fe–Ni melts at 1 873 K.

Parameter	Ni, %					
	0	25	40	50	75	100
$\log K_{\text{Mn}}$	-1.274 ²⁾	-1.622	-1.807	-1.974	-2.495	-3.104
$\log K_{\text{Si}}$	-4.676 ²⁾	-4.899	-5.049	-5.174	-5.654	-6.542 ⁶⁾
$\gamma_{\text{O}}^{\circ}$	0.0105 ⁹⁾	0.0168	0.0254	0.0355	0.0984	0.357 ⁹⁾
$\gamma_{\text{Mn}}^{\circ}$	1.44 ²⁾	1.132	1.130	1.175	1.372	1.50 ¹⁰⁾
$\gamma_{\text{Si}}^{\circ}$	0.0013 ²⁾	0.00091	0.00055	0.00037	0.00014	0.00009 ⁶⁾
e_{O}^{O}	-0.17 ²⁾	-0.132	-0.110	-0.092	-0.052	0 ³⁾
$e_{\text{Mn}}^{\text{Mn}}$	0 ²⁾	0.00139	0.00226	0.00285	0.00439	0.006 ¹⁾
e_{O}^{Mn}	-0.021 ²⁾	-0.121	-0.182	-0.226	-0.318	-0.45 ³⁾
e_{Mn}^{O}	-0.083 ²⁾	-0.426	-0.637	-0.787	-1.103	-1.53 ³⁾
$e_{\text{Si}}^{\text{Si}}$	0.103 ²⁾	0.123	0.136	0.144	0.167	0.19 ⁶⁾
e_{O}^{Si}	-0.066 ²⁾	-0.066	-0.066	-0.065	-0.065	-0.065 ⁶⁾
e_{Si}^{O}	-0.119 ²⁾	-0.117	-0.116	-0.115	-0.112	-0.110 ⁶⁾

$$\log[\%O]_{\text{Fe-Ni}} = (1/n) \{ \log K_{\text{R}} + \log X_{\text{R}_m\text{O}_n} + \log \gamma_{\text{R}_m\text{O}_n} - m \log[\%R]_{\text{(Fe-Ni)}} - [me_{\text{R(Fe-Ni)}}^{\text{R}} + ne_{\text{O(Fe-Ni)}}^{\text{R}}][\%R]_{\text{(Fe-Ni)}} - [ne_{\text{O(Fe-Ni)}}^{\text{O}} + me_{\text{R(Fe-Ni)}}^{\text{O}}][\%O]_{\text{(Fe-Ni)}} \} \dots\dots\dots(7)$$

where e_i^j denotes the interaction parameters when the component concentrations are expressed as mass percents.

The value $[\%O]_{\text{(Fe-Ni)}}$ in the right-hand part of Eq. (7) can be expressed through the ratio $(K_{\text{R}}/[\%R]^m)^{1/n}$, assuming that $X_{\text{R}_m\text{O}_n} \approx 1$, $\gamma_{\text{R}_m\text{O}_n} \approx 1$, $f_{\text{R}} \approx 1$, and $f_{\text{O}} \approx 1$ in Eq. (1a). This substitution does not result in appreciable error because of small value $[\%O]_{\text{(Fe-Ni)}}$. This Eq. (7) takes the form:

$$\log[\%O]_{\text{Fe-Ni}} = (1/n) \{ \log K_{\text{R}} + \log X_{\text{R}_m\text{O}_n} + \gamma_{\text{R}_m\text{O}_n} - m \log[\%R]_{\text{(Fe-Ni)}} - [me_{\text{R(Fe-Ni)}}^{\text{R}} + ne_{\text{O(Fe-Ni)}}^{\text{R}}][\%R]_{\text{(Fe-Ni)}} - [ne_{\text{O(Fe-Ni)}}^{\text{O}} + me_{\text{R(Fe-Ni)}}^{\text{O}}](K_{\text{R}}/[\%R]^m)^{1/n} \} \dots\dots\dots(7a)$$

The Gibbs energies, J/mol, for reaction (2) are quoted from the published data⁵⁾:

$$\Delta G_{(2)}^{\circ}(\text{MnO}) = 401\,263 - 84.32T;$$

$$\Delta G_{(2)}^{\circ}(\text{SiO}_2) = 906\,442 - 175.85T$$

For iron the reference literature²⁾ gives the values of the equilibrium constants of reaction (1) for the deoxidation of this melt with manganese and silicon:

$$\log K_{\text{Mn(Fe)}} = -14\,880/T + 6.67;$$

$$\log K_{\text{Si(Fe)}} = -30\,110/T + 11.40$$

For nickel the equilibrium constant of reaction (1) is given for the melts deoxidized with silicon as follows:

$$\log K_{\text{Si(Ni)}} = -15\,680/T + 1.83^{6)}$$

In other cases the values of the equilibrium constant of reaction (1) for Fe–Ni melts are calculated according to the

scheme described above (Eqs. (2)–(6)).

The molecular mass for the Fe–Ni melts was calculated by the formula:

$$M_{\text{Fe-Ni}} = M_{\text{Fe}}X_{\text{Fe}} + M_{\text{Ni}}X_{\text{Ni}} \dots\dots\dots(8)$$

Based on a subregular model, the activity coefficients in dilute solution range $\gamma_{\text{R(Fe-Ni)}}^{\circ}$ and $\gamma_{\text{O(Fe-Ni)}}^{\circ}$ are represented by the following equation⁷⁾:

$$\begin{aligned} \ln \gamma_{i(\text{Fe-Ni})}^{\circ} &= X_{\text{Fe}} \ln \gamma_{i(\text{Fe})}^{\circ} + X_{\text{Ni}} \ln \gamma_{i(\text{Ni})}^{\circ} \\ &+ X_{\text{Fe}}X_{\text{Ni}}[X_{\text{Ni}}(\ln \gamma_{i(\text{Ni})}^{\circ} - \ln \gamma_{i(\text{Fe})}^{\circ} + \varepsilon_{i(\text{Ni})}^{\text{Fe}}) \\ &+ X_{\text{Fe}}(\ln \gamma_{i(\text{Fe})}^{\circ} - \ln \gamma_{i(\text{Ni})}^{\circ} + \varepsilon_{i(\text{Fe})}^{\text{Ni}})] \dots\dots\dots(9) \end{aligned}$$

where ε_i denotes the interaction parameters in mole fraction base.

The activity coefficients for iron and nickel are given in **Table 1**. Interaction parameters used in calculations were the following: $e_{\text{Mn(Fe)}}^{\text{Ni}} = -0.0072^{2)}$; $e_{\text{Si(Fe)}}^{\text{Ni}} = 0.001^{6)}$; $e_{\text{Si(Ni)}}^{\text{Ni}} = 0^{6)}$; $e_{\text{O(Fe)}}^{\text{Ni}} = 0.006^{8)}$; $e_{\text{O(Ni)}}^{\text{Fe}} = 0.025^{8)}$. The $e_{\text{Mn(Ni)}}^{\text{Fe}}$ parameter was assumed to be zero similar to $e_{\text{Si(Ni)}}^{\text{Fe}}$ because of absence of experimental data. The results of calculations are listed in Table 1.

Dependence of calculated values of the equilibrium constant for reaction (1) on the content of deoxidizing agent and nickel in the Fe–Ni melt deoxidized with manganese and silicon at 1 873 K is represented in Table 1 and **Fig. 1**. The equilibrium constants are given for the reaction of deoxidizer with one atom of oxygen dissolved in melt, this allows one to more conveniently compare the above relationships. As is seen from the given data, the equilibrium constant of reaction (1) in both cases decreases with an increase in the nickel content in melt, which indicates an increase in the deoxidation power of both silicon and manganese. With manganese, the degree of this increase is much larger than that with silicon.

Fig. 1. Dependence of the equilibrium constant of reaction (1) on Ni content for deoxidation of Fe-Ni melts at 1873 K.

The interaction parameters for different melts (Table 1) are estimated from the following assumption:

$$\varepsilon_{i(\text{Fe-Ni})}^j = \varepsilon_{i(\text{Fe})}^j X_{\text{Fe}} + \varepsilon_{i(\text{Ni})}^j X_{\text{Ni}} \quad \text{.....(10)}$$

In case of the deoxidation of iron-based melt with silicon and the residual silicon content in melt above 0.0022%, an oxide phase contains only SiO_2 ,¹⁾ and $a_{\text{SiO}_2} = X_{\text{SiO}_2} = 1$. In the nickel-based melt, the silicon content in the presence of only SiO_2 is quite low, since nickel is characterized by the less affinity to oxygen in comparison with iron.

When iron-nickel melts are deoxidized with manganese, the oxide phase, in addition to MnO, also contains FeO and NiO. Therefore, it is necessary to consider the following reactions¹⁰⁾:

$$\Delta G_{(11)}^\circ = -91\,614 \text{ J/mol}, \quad K_{(11)} = 357.81 \text{ at } 1873 \text{ K};$$

$$\Delta G_{(12)}^\circ = -168\,751 \text{ J/mol}, \quad K_{(12)} = 50\,682.9 \text{ at } 1873 \text{ K}$$

In the FeO-MnO system, the continuous series of solutions is observed both in the liquid and solid states¹¹⁾; however, there are no published data on the NiO-MnO phase diagram. Therefore, based on the FeO-MnO phase diagram, as the first approximation, we assume that the oxide phase formed upon deoxidation of iron-nickel melts with manganese is the perfect solution ($\gamma_{\text{MnO}} = 1$, $\gamma_{\text{FeO}} = 1$, $\gamma_{\text{NiO}} = 1$). The manganese solutions in the iron-nickel melts are characterized by slight positive deviations from the ideality (Table 1) and the dependence of the manganese activity coefficient on its concentration in liquid iron at 1843 K can be described¹²⁾ by the expression $\lg \gamma_{\text{Mn}} = \lg \gamma_{\text{Mn}}^\circ (1 - X_{\text{Mn}})^2$; therefore, it can be assumed that, at the low manganese contents ($X_{\text{Mn}} \leq 0.03$), $\gamma_{\text{Fe}} \approx 1$, $\gamma_{\text{Ni}} \approx 1$, $\gamma_{\text{Mn}} \approx \gamma_{\text{Mn}}^\circ$ for the iron-nickel melt. In this case, the following equations may be written:

$$\frac{X_{\text{MnO}}}{X_{\text{FeO}}} = \frac{K_{(11)} \gamma_{\text{Mn(Fe-Ni)}}^\circ X_{\text{Mn}}}{X_{\text{Fe}}}$$

Fig. 2. Dependence of MnO mole fraction in oxide phase on Mn and Ni contents in melt at 1873 K.

$$\frac{X_{\text{MnO}}}{X_{\text{NiO}}} = \frac{K_{(12)} \gamma_{\text{Mn(Fe-Ni)}}^\circ X_{\text{Mn}}}{X_{\text{Fe}}} \quad \text{.....(13)}$$

$$X_{\text{MnO}} + X_{\text{FeO}} + X_{\text{NiO}} = 1$$

A mole fraction of MnO in the oxide phase can be calculated by these three equations. The dependence of MnO mole fraction in the oxide phase on the contents of manganese and nickel in a melt¹⁰⁾ is shown in Fig. 2. In iron-based melt, the MnO mole fraction in the oxide phase reaches to 0.3–0.5 at the low manganese content ($< 0.2\%$). With increasing nickel and manganese contents in melt, the mole fraction of MnO in oxide phase increases also. For pure nickel, it approaches unity, *i.e.* practically the oxide phase consists of manganese oxide.

The dependence of equilibrium oxygen concentration estimated by Eq. (7a) on the contents of manganese and silicon in the Fe-Ni melts at 1873 K is given in Fig. 3. From the given data one can see that the manganese deoxidation power considerably increases with the increase of nickel content in melt (Fig. 3(a)). The oxygen solubility curves pass through the minimum, which shifts to the lower manganese content with increase of nickel content in melt. For alloys containing more than 50% of nickel, the minimum oxygen concentrations are observed at the manganese content equal to 1–1.5%. The deoxidation power of silicon also increases with the increase of nickel content in melt (Fig. 3(b)). In considered range of silicon content no minimum was observed as seen from the oxygen solubility curves.

3. Experimental

Deoxidation of Fe-Ni melts with manganese and silicon (separately or together) has been studied experimentally by using Fe-40%Ni alloy in a wide range of temperatures and concentrations of deoxidizing agent. The experiments have been carried out in an induction furnace fed by an 10 kV·A HF generator. Carbonyl iron (99.99%), electrolytic nickel (99.99%), electrolytic manganese (99.99%) and crystalline silicon (99.999%) were used as a charge. The metal was melted in the Ar-H₂ atmosphere at temperatures of 1823–

Fig. 3. Dependence of oxygen content in the Fe-Ni melts on the content of Mn (a), Si (b), and Ni at 1873 K.

1923 K in an alumina crucible in the case of manganese or manganese-silicon deoxidation and in a quartz crucible in the case of silicon deoxidation. Deoxidizing agents (Mn, Si) were introduced into the melt without breaking the furnace air-tightness; then this melt was held at a given temperature until equilibrium in Ar atmosphere. The temperature was measured by Pt-6%Ph/Pt-30%Ph thermocouple. Equilibrium being achieved, a sample was taken from the melt and analyzed for nickel, manganese and silicon. The oxygen concentration was determined by inert gas fusion-infrared absorptiometry.

4. Results and Discussion

4.1. Deoxidation with Manganese

The experimental results are shown in Fig. 4(a) as compared to the calculated lines. As is seen from the experimental data points, the manganese deoxidation power considerably increases with the temperature drop. Oxygen solubility curves pass through a minimum, which shifts to the lower manganese contents when temperature drops. Experimental values of the equilibrium oxygen concentration for the Fe-40%Ni alloy at 1873 K are lie below the calculated lines. The distinctions between experimental and calculated data may be attributed to the fact that oxide phase contained small amounts of Al_2O_3 along with MnO , FeO , and NiO , owing to reactions of oxide phase with alumina crucible used in these experiments.

Dependence of oxygen concentration and value of $\log K'_{Mn}$ ($K'_{Mn} = [\%Mn][\%O]$) on the manganese content and temperature can be described by the following empirical equations:

$$1873 \text{ K; } 0.21\text{--}2.50\% \text{ Mn}$$

$$\log[\%O] = -2.49 + 0.18[\%Mn] - 0.68 \log[\%Mn] \dots(14)$$

Fig. 4. Dependence of oxygen content in Fe-40% melts on the contents of Mn (a) and Si (b).

$$\log K'_{Mn} = -2.25 + 0.68 \log[\%Mn] \dots(15)$$

$$1873 \text{ K; } 0.05\text{--}1.47\% \text{ Mn}$$

$$\log[\%O] = -2.26 + 0.14[\%Mn] - 0.76 \log[\%Mn] \dots(16)$$

$$\log K'_{Mn} = -2.13 + 0.35 \log[\%Mn] \dots(17)$$

$$1923 \text{ K; } 0.07\text{--}1.99\% \text{ Mn}$$

$$\log[\%O] = -1.18 - 0.26[\%Mn] - 0.18 \log[\%Mn] \dots(18)$$

$$\log K'_{Mn} = -1.59 + 0.48 \log[\%Mn] \dots(19)$$

4.2. Deoxidation with Silicon

The experimental results are given in Fig. 4(b) as compared to the estimated data. As is seen from the given data, the silicon deoxidation power considerably increases with the temperature drop. Dependence of oxygen concentration and value of $\log K'_{Si}$ ($K'_{Si} = [\%Si][\%O]$) on the silicon content in melt and the temperature within the range of silicon concentrations considered can be described by the following empirical equations:

$$1823 \text{ K; } 0.08\text{--}4.30\% \text{ Si}$$

$$\log[\%O] = -2.67 - 0.50 \log[\%Si] \dots(20)$$

$$\log K'_{Si} = -5.32 + 0.037 \log[\%Si] \dots(21)$$

$$1873 \text{ K; } 0.08\text{--}4.30\% \text{ Si}$$

$$\log[\%O] = -2.53 - 0.51 \log[\%Si] \dots(22)$$

$$\log K'_{Si} = -5.03 + 0.026 \log[\%Si] \dots(23)$$

1 923 K; 0.08–1.90% Si

$$\log[\%O] = -2.35 - 0.52 \log[\%Si] \quad \dots\dots\dots(24)$$

$$\log K'_{Si} = -4.65 + 0.075 \log[\%Si] \quad \dots\dots\dots(25)$$

The experiments have been carried out to study the deoxidation of the Fe–40%Ni with silicon at its low contents (0.009–0.08%) at 1 873 K. Data obtained are plotted in Fig. 4(b). The experimental finding that relationship between oxygen and silicon contents is not linear at $[Si] < 0.05\%$ suggests the presence of iron–nickel silicates $(Fe, Ni)O \cdot SiO_2$ as reaction products at such silicon concentrations.¹⁾

Extrapolation of the relations $\log K'_{Si} - [\%Si]$ obtained for the Fe–40%Ni alloy to zero silicon content allowed one to determine the equilibrium constant K_{Si} for the temperatures considered:

$$(SiO_2) = [Si] + 2[O] \quad \dots\dots\dots(26)$$

$$K_{Si} = \frac{a_{[Si]} a_{[O]}^2}{a_{(SiO_2)}} \quad \dots\dots\dots(26a)$$

and to obtain equation for the temperature dependence of the equilibrium constant:

$$\log K_{Si} = -\frac{23\,607}{T} + 7.610 \quad \dots\dots\dots(27)$$

The K_{Si} equilibrium constant determined by Eq. (27) at 1 873 K is in good agreement with the data above estimated (Fig. 1).

4.3. Complex Deoxidation with Manganese and Silicon

Complex deoxidation with manganese and silicon gives lower concentrations of oxygen in metal due to a decrease in the activities of silica and manganese oxides. The deoxidation of the Fe–40%Ni alloy with silicon has been studied experimentally at the manganese content in melt equal to 0.05–0.06, 0.10–0.12, 0.20–0.22, and 0.48–0.51% at 1 873 K. The results obtained are given in Fig. 5. As is seen from these data, the manganese–silicon complex deoxidation enables one to obtain the lower oxygen concentrations than silicon deoxidation and the considerably less contents than manganese deoxidation. Dependence of oxygen concentrations in melt on the silicon content for each manganese concentrations range can be described by the following empirical equations:

0.05–0.06% Mn and 0.02–0.19% Si

$$\log[\%O] = -2.77 + 1.05[\%Si] - 0.61 \log[\%Si] \quad \dots\dots(28)$$

0.10–0.12% Mn and 0.01–0.22% Si

$$\log[\%O] = -2.77 + 0.94[\%Si] - 0.57 \log[\%Si] \quad \dots\dots(29)$$

0.20–0.22% Mn and 0.02–0.50% Si

$$\log[\%O] = -2.75 + 0.51[\%Si] - 0.52 \log[\%Si] \quad \dots\dots(30)$$

0.48–0.51% Mn and 0.05–1.41% Si

$$\log[\%O] = -2.67 + 0.04[\%Si] - 0.43 \log[\%Si] \quad \dots\dots(31)$$

The region of silica-saturated silicates ($a_{SiO_2} = 1$) is bound by curve 1 (Fig. 5), which corresponds to Eq. (22). These results agree with those of combined deoxidation of iron-based melts with manganese and silicon.¹³⁾ Solving Eqs.

Fig. 5. Dependence of oxygen content in the Fe–40%Ni melt on the contents of Mn and Si at 1 873 K.

(28) to (31) and (22) together, one can determine the content of silicon ($[Si]^*$) corresponding to the deoxidation products saturated with silica at 1 873 K for the given manganese content in the Fe–40%Ni melt:

[Mn], %	0.05–0.06	0.10–0.12	0.20–0.22	0.48–0.51
$[Si]^*$, %	0.15	0.20	0.43	2.63

The results obtained can be described by the following equation:

$$\log[\%Si]^* = -0.96 + 2.78[\%Mn] \quad \dots\dots\dots(32)$$

Solving this equation for $[Mn] = 0$, we obtain $[\%Si]^* = 0.11\%$, which agrees with the above given results of deoxidation of the Fe–40%Ni melt only with silicon. When deoxidized with couple of manganese and silicon, they are in the equilibrium with the deoxidation products:

$$K_{(33)} = \frac{a_{MnO}^2 a_{[Si]}}{a_{SiO_2} a_{Mn}^2} \quad \dots\dots\dots(34)$$

The activities of manganese oxide and silica in the deoxidation products can be calculated by the following formulas¹⁴⁾:

$$a_{MnO} = [\%O]_{MnSi} / [\%O]_{Mn} \quad \text{at the same } [\%Mn] \quad \dots\dots(35)$$

$$a_{SiO_2} = [\%O]_{MnSi}^2 / [\%O]_{Si}^2 \quad \text{at the same } [\%Si] \quad \dots\dots(36)$$

These activities estimated by Eqs. (35) and (36), are given in Table 2. This calculation performed for 0.20% Mn and 0.01–0.43% Si in melt. Oxygen concentrations for the melts deoxidized with manganese ($[O]_{Mn}$) were estimated by Eq. (16), for the melts deoxidized with silicon ($[O]_{Si}$) by Eq. (22), and for the melts deoxidized with manganese and silicon ($[O]_{MnSi}$) by Eq. (30).

Dependencies of MnO and SiO_2 activities in the MnO– SiO_2 melt on their mole fractions reported by Abraham *et al.*¹⁵⁾ are given in Fig. 6. If it is assumed that MnO and SiO_2 were only present in the oxide phase during our experiments on manganese and silicon deoxidation, then, by plotting the estimated values of the SiO_2 activity (Table 2) on the line obtained in previous work,¹⁵⁾ it is possible to determine the MnO and SiO_2 mole fractions in the oxide phase (Table 3). The obtained dependence of the MnO activity on

Table 2. Calculated activities of silica and manganese oxide for the combined deoxidation of the Fe-40%Ni alloy with manganese and silicon at 1 873 K.

[Si], %	[O] _{Si} , % Eq. (22)	[Mn], %	[O] _{Mn} , % Eq. (16)	[O] _{MnSi} , % Eq. (30)	a_{SiO_2} Eq.(36)	a_{MnO} Eq.(35)	$K'_{(33)}$
0.01	0.0700	0.20	0.0192	0.0197	0.079	0.990	3.102
0.02	0.0320	0.20	0.0192	0.0140	0.191	0.704	0.704
0.05	0.01348	0.20	0.0192	0.00895	0.441	0.449	0.572
0.07	0.01136	0.20	0.0192	0.00770	0.459	0.387	0.569
0.10	0.00948	0.20	0.0192	0.00662	0.488	0.332	0.566
0.20	0.00667	0.20	0.0192	0.00519	0.606	0.261	0.560
0.30	0.00543	0.20	0.0192	0.00473	0.759	0.237	0.557
0.43	0.00458	0.20	0.0192	0.00458	1.0	0.230	0.555

Table 3. Calculated values of SiO₂ and MnO mole fractions in oxide phase.

a_{SiO_2}	a_{MnO}	X_{SiO_2}	X_{MnO}	(SiO ₂), %	(MnO), %
0.079	0.990	0.740	0.260	22.89	77.11
0.191	0.704	0.670	0.330	29.39	70.61
0.441	0.449	0.588	0.412	37.19	62.81
0.459	0.387	0.583	0.417	37.67	62.33
0.488	0.332	0.578	0.422	38.16	61.84
0.606	0.261	0.550	0.450	40.88	59.12
0.758	0.237	0.521	0.479	43.72	56.28
1.0	0.230	0.490	0.510	46.80	53.20

Fig. 6. Activities of MnO and SiO₂ in the MnO-SiO₂ melt.

the mole fraction (Table 3) is shown in **Fig. 6** by dotted curve. As is seen from Fig. 6, the dependence obtained in the present study agrees satisfactorily with the reported one.¹⁵⁾ Small discrepancy seems to be caused by small amounts of Al₂O₃ dissolved from Al₂O₃ crucibles at the experiment.

The values of $K'_{(33)}$ given in Table 2 were calculated by the following equation:

$$K'_{(33)} = \frac{a_{\text{MnO}}^2 [\% \text{Si}]}{a_{\text{SiO}_2} [\% \text{Mn}]^2} \dots\dots\dots (37)$$

Calculating $K'_{(33)}$ and assuming that activity coefficients of manganese oxide and silica calculated at [Mn]=0.2% are available at different manganese and silicon contents in melt, it is possible to evaluate the silicon content by Eq. (37) and the oxygen concentration in the melts deoxidized with silicon and a couple of silicon and manganese by Eqs. (22) and (36), respectively. Calculation has been performed for manganese concentrations of 0.1, 0.3, 0.4 and 0.5%. Dependence of the oxygen concentration on contents of silicon and manganese in melt at 1 873 K can be written in the form of the following empirical equations:

at [Mn]=0.1 %

$$\log [\% \text{O}] = -2.75 + 2.33 [\% \text{Si}] - 0.52 \log [\% \text{Si}] \dots (38)$$

at [Mn]=0.3 %

$$\log [\% \text{O}] = -2.75 + 0.23 [\% \text{Si}] - 0.52 \log [\% \text{Si}] \dots (39)$$

at [Mn]=0.4 %

$$\log [\% \text{O}] = -2.75 + 0.13 [\% \text{Si}] - 0.52 \log [\% \text{Si}] \dots (40)$$

at $[\text{Mn}] = 0.5\%$

$$\log[\%O] = -2.75 + 0.082[\%Si] - 0.52 \log[\%Si] \dots (41)$$

The obtained dependencies are in good agreement with similar results calculated on the basis of experimental data (Eqs. (29) and (31)). **Figure 7** shows the dependence of oxygen concentration on the contents of silicon and manganese in melt at 1873 K. The joint solution of Eqs. (30), (38)–(41) and (22) allowed one to evaluate the content of silicon ($[\text{Si}]^*$) when deoxidation products are saturated with silica:

$[\text{Mn}], \%$	0.1	0.2	0.3	0.4	0.5
$[\text{Si}]^*, \%$	0.105	0.430	0.945	1.680	2.625

The obtained data can be empirically written as:

$$\log[\%Si]^* = -1.167 + 3.398[\%Mn] \dots (42)$$

If $[\text{Mn}] = 0$, then $[\text{Si}] = 0.07\%$, which agrees with that calculated by Eq. (32).

It is also possible to calculate the corresponding manganese contents for a given silicon contents by Eq. (37) when silica saturated oxide phase ($a_{\text{SiO}_2} = 1$) is formed. In this case, Eq. (37) can be revised to Eq. (43)

$$[\%Mn] = a_{\text{MnO}}^o ([\%Si] / 0.555)^{1/2} \dots (43)$$

where a_{MnO}^o represents the activity of manganese monoxide in the silica-saturated oxide phase at 1873 K, which equals to 0.230 (Table 2). The relations of residual manganese and silicon contents for the boundary of immiscibility region in the $\text{MnO}-\text{SiO}_2$ system at 1873 K are represented below and in **Fig. 8**:

$[\text{Si}], \%$	0.05	0.1	0.2	0.5	1.0	2.0	3.0	5.0
$[\text{Mn}], \%$	0.069	0.098	0.138	0.218	0.309	0.436	0.535	0.690
$[\%Mn]/[\%Si]$	1.380	0.976	0.690	0.436	0.309	0.218	0.178	0.138

It is seen from the data shown that the high $[\%Mn]/[\%Si]$ ratios are necessary when silicon residual contents are rather low, namely, not above 0.05%, *i.e.* when the loss of deoxidizers is high. At low losses (low degree of oxidation in melt), it is not necessary to have the high $[\%Mn]/[\%Si]$ ratio. The oxide phase containing a large amount of manganese oxide is inexpedient because of the high melting point of manganese oxide (2058 K); at $\text{MnO} > 80\%$ the solid phase is formed in the $\text{MnO}-\text{SiO}_2$ system.¹⁴⁾ Super high $[\%Mn]/[\%Si]$ ratio can be calculated by Eq. (37), above these ratios the deoxidation product contains solid manganese oxide. As shown above, in the case of $a_{\text{MnO}} = 0.99$, $a_{\text{SiO}_2} = 0.079$, and $K'_{(32)} = 3.102$ (Table 2), Eq. (37) is revised as follows:

$$[\%Mn] = 2.00([\%Si])^{1/2} \dots (44)$$

The results calculated by this equation at 1873 K are shown below:

$[\text{Si}], \%$	0.01	0.02	0.05	0.1	0.2	0.5	1.0	2.0	3.0	5.0
$[\text{Mn}], \%$	0.200	0.283	0.447	0.632	0.894	1.414	2.000	2.828	3.464	4.472
$[\%Mn]/[\%Si]$	20.00	14.14	8.944	6.324	4.472	2.828	2.000	1.414	1.155	0.894

On condition that the liquid products of deoxidation should be obtained as a result of deoxidation of the Fe–40% Ni melt and summarizing the data given above, the region

Fig. 7. Oxygen content in the Fe–40%Ni melt deoxidized with Mn and Si at 1873 K.

Fig. 8. Boundary of immiscibility region in the $\text{MnO}-\text{SiO}_2$ system between solid SiO_2 and liquid silicates at 1873 K.

Fig. 9. Regions of solid and liquid products of deoxidation with Mn and Si in the Fe–40%Ni melt at 1873 K.

of solid and liquid products of deoxidation with manganese and silicon at 1873 K can be determined from the dependence given in **Fig. 9**. Curve 1 separates manganese sili-

cates saturated with silica from the silica solid solutions. Curve 2 is a boundary between liquid manganese silicates and the solid solutions based on manganese oxide in the MnO–SiO₂ system. The region between these curves corresponds to liquid manganese silicates in equilibrium with manganese and silicon in metal.

In the left-hand portion of this plot (Fig. 9) the zone (up to 0.05% Si) of liquid silicates (iron silicates mainly) is shown, as the equilibrium oxide phase above the Fe–40%Ni melt contains >99% FeO and <1% NiO.⁴⁾ In addition, two straight lines in parallel to X-axis are drawn in the region of liquid silicates, which divide this region into three portions. These lines are drawn from the viewpoint of deoxidation kinetics. When the complex deoxidizer was used, for example, silico-manganese, processes of dissolution and oxidation proceed simultaneously. Thus, it is most probable to assume that deoxidation rate is controlled by the dissolution and diffusion of deoxidizing agent in a melt. Therefore, manganese and silicon react in amounts directly proportional to their contents in the deoxidizer. So, it is as optimum to assume $[\%Mn]/[\%Si]=1.4-8$. Based on the reasons indicated, despite of the amount of manganese alloys added as a deoxidizing agent, the solid reaction products can be in the form of solid inclusions due to low diffusion rates.

Shaded zone (Fig. 9) represents liquid silicates formed after deoxidation with manganese and silicon. Within the region A deoxidation products should be in the liquid state under equilibrium conditions. However, if to consider the deoxidation process from viewpoint of kinetics or choice of deoxidizer composition through the ratio $[\%Mn]/[\%Si]$, then, the liquid–solid products will be obtained after deoxidation using alloys with $[\%Mn]/[\%Si]$ ratio <1.4. To form liquid manganese silicates, manganese should be consumed in amounts than those of silicon by a factor 1.4. Therefore, silicon is first oxidized, being precipitated in the form of solid inclusions and, when $[\%Mn]/[\%Si]$ ratio increases, liquid silicates are formed. Formation of solid manganese oxide in the region B is possible due to the reasons similar to those indicated in the case of A region. With temperature drop, the range of the optimum manganese to silicon ratios in the deoxidizer narrows.

5. Conclusions

The thermodynamic analysis of oxygen, manganese and silicon dissolved in Fe–Ni melts has been carried out. The deoxidation power of manganese essentially increases with an increase in the nickel content in melt. The solubility curves pass through the minimum, which shifts to the lower manganese contents with an increase in the nickel con-

centration in melt. For alloys containing more than 50–60% nickel, the minimum oxygen concentrations are reached at the manganese content in melt equal to 1–1.5%. The further increase in the manganese content causes the increase of oxygen concentration.

The silicon deoxidation power also increases with an increase in the nickel content in melt, but not so sharply, as in the case of manganese. In the considered range of silicon contents, no minimum was observed in the oxygen solubility curves.

Thermodynamics of oxygen solutions in the Fe–40%Ni melts containing manganese and silicon has been studied experimentally within a temperature range of 1823–1923 K. With temperature drop, the deoxidation power of both manganese and silicon increases. In the Fe–40%Ni melts, the deoxidation power of manganese and that of silicon are higher than in iron but lower than in nickel. Dependence of oxygen concentration on manganese and silicon contents is described by empirical equations. When complexly deoxidized with manganese and silicon, it is possible to obtain the lower oxygen concentrations in metal, in comparison with the individual deoxidation, due to the decrease in the activities of manganese oxide and silica in the oxide phase.

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