

# THERMODYNAMICAL ASPECTS OF DECARBURIZATION OF MANGANESE MELTS

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## ABSTRACT

Oxygen solutions in the Mn-Fe melts have been thermodynamically analyzed. The equilibrium concentrations of oxygen in these melts were determined for different compositions. Iron added into manganese results in a considerable decrease in the oxygen solubility. Minimum was observed in the oxygen solubility curve at 19.32% Mn, which corresponds to  $5.136 \cdot 10^{-3}\%$  [O] at 1873 K. The further rise in the iron content causes an increase in the oxygen concentration in melt. In liquid manganese, the saturated oxygen concentration at 1873 K is 0.0472%. The interaction parameter  $e_{O(Mn)}^O = -0.207$  and activity coefficient  $\gamma_{O(Mn)}^O = 1.131 \cdot 10^{-4}$  were calculated. Compositions of the oxide phase in equilibrium with the Mn-Fe melts were determined. This phase contains mainly MnO, i.e., at the mole fraction of manganese in the melt of 0.02, that of manganese oxide in the slag is larger than 0.9. This is connected with the fact that manganese has a higher affinity to oxygen in comparison with iron. The carbon solutions in manganese melts were also thermodynamically analyzed. The temperature dependence of the carbon activity coefficient in liquid manganese  $\gamma_{C(Mn)}^O = -1.5966 + 1.0735 \cdot 10^{-3}T$  was determined. The interaction of carbon dissolved in liquid manganese with oxygen at manganese oxide saturation has been studied. Temperature dependence of its Gibbs energy change can be described as  $\Delta G_T^\circ = 375\,264 - 184.66T$  (J/mole). It was shown that, depending on carbon content, this process can develop appreciably in a temperature range of 1973–2073 K.

## 1 INTRODUCTION

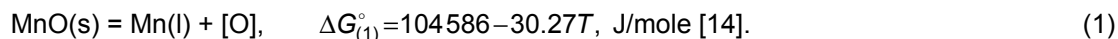
Manganese is widely used in steelmaking mainly as ferromanganese and ferrosilicomanganese for deoxidation and alloying. It is also used as a base of a number of alloys [1]. Ferromanganese is mainly produced by the carbothermic method, reducing manganese from manganese oxides with the help of carbon. Therefore, in this alloy called “high-carbon ferromanganese”, the carbon content as a rule is close to the solubility limit. To make many steels and alloys medium- and low-carbon ferromanganese are necessary. At present, these grades are produced reducing manganese oxides of manganese ores with silicon by ferrosilicomanganese [1].

Ferromanganese with a decreased carbon content can be produced by refining high-carbon ferromanganese with oxygen of manganese oxides present in manganese ores. This process has been studied earlier [2, 3] but has no commercial use. The thermodynamical investigation of this process aimed at the determination of the optimum parameters of its realization is of great interest.

The thermodynamics of oxygen solutions in Mn-Fe melts has been studied in detail. In a paper [4], the results obtained in more than forty studies dealing with the interaction of manganese and oxygen in the iron-based melts were analyzed and summarized. However, there is no sufficient information on high-manganese alloys except for [5, 6]. The thermodynamics of carbon solutions in liquid manganese have been also studied in detail [7–13], but the published information on the interactions of carbon and oxygen in manganese melts are not enough [3]. For this reason, the study of physicochemical properties of oxygen and carbon solutions in manganese-based melts is not only of scientific but also of commercial interest.

## 2 THERMODYNAMICAL ANALYSIS OF OXYGEN SOLUTIONS IN MANGANESE-IRON MELTS

The available information on the thermodynamics of oxygen solutions in liquid iron [4, 14] and manganese [14-17] and on the Mn-Fe melts [18, 19] allows us to estimate the oxygen solubility in these melts and to determine the composition of oxide phase in a wide range of alloy compositions. For manganese, the metal-oxide phase equilibrium can be described as



The oxygen solubility in liquid manganese was studied in [15–17]. However, temperature dependences of the saturated oxygen concentration in molten manganese obtained differ considerably from each other. A previous analysis showed that the results obtained in [15] are most reliable. At 1515 K,  $[\text{O}]_{\text{Mn}}^{\text{sat}} = 0.0095\%$  [15], which allows one to calculate the interaction parameter  $e_{\text{O(Mn)}}^\circ$ . At this temperature  $\Delta G_{(1)}^\circ = 58727 \text{ J/mole}$ ,  $K_{(1)} = 9.457 \cdot 10^{-3}$ . It follows that

$$e_{\text{O(Mn)}}^\circ = (\lg K_{(1)} - \lg [\% \text{O}]) / [\% \text{O}] = -0.207.$$

Hereinafter compositions are given as mass percents.

Since the interaction parameter  $e_{\text{O(Mn)}}^\circ$  depends weakly on temperature, we can calculate the saturated oxygen concentration in liquid manganese at 1873 K according to the equation

$$\lg [\% \text{O}]_{\text{Mn}}^{\text{sat}} = \lg K_{(1)} - e_{\text{O(Mn)}}^\circ K_{(1)}.$$

At 1873 K  $\Delta G_{(1)}^\circ = 47890 \text{ J/mole}$ ;  $K_{(1)} = 0.0462$ ; it follows that  $[\text{O}]_{\text{Mn}}^{\text{sat}} = 0.0472\%$ , which is in good agreement with the published data at 1873 K, namely:  $[\text{O}]_{\text{Mn}}^{\text{sat}} = 0.0462\%$  [14];  $[\text{O}]_{\text{Mn}}^{\text{sat}} = 0.045\%$  [6, 20].

For the solution of oxygen in liquid manganese, the temperature dependence of its Gibbs energy is described by equation

$$\frac{1}{2} \text{O}_2(\text{g}) = [\text{O}]_{1\%(\text{Mn})}, \quad \Delta G_{(2)}^\circ = -302287 + 57.78T, \text{ J/mole [14].} \quad (2)$$

The  $\gamma_{\text{O}}^\circ$  oxygen activity coefficient is calculated as the value that is reciprocal to the oxygen solubility.

$$\gamma_{\text{O}}^\circ = N_{\text{O}}^{\text{lim}} \rightarrow 0 \left( \frac{\sqrt{p_{\text{O}_2}}}{N_{\text{O}}} \right).$$

It can be also obtained from the Gibbs energy of oxygen dissolution in manganese melt with the formation of 1%-solution, which is calculated using the formula [21]

$$\Delta G_{(2)}^\circ = RT \ln \left( \gamma_{\text{O(Mn)}}^\circ M_{\text{Mn}} / M_{\text{O}} \cdot 100 \right).$$

Since the Gibbs energy of Eq. (2) is known one can estimate the oxygen activity coefficient  $\gamma_{\text{O(Mn)}}^\circ$ .

At 1873 K  $\Delta G_{(2)}^\circ = -194065 \text{ J/mole}$ . It follows that

$$\ln \left( \gamma_{\text{O(Mn)}}^\circ M_{\text{Mn}} / M_{\text{O}} \cdot 100 \right) = \Delta G_{(2)}^\circ / RT = -12.458$$

and

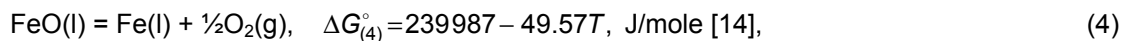
$$\gamma_{\text{O(Mn)}}^\circ = 1.131 \cdot 10^{-4}.$$

For iron, the metal-oxide phase equilibrium



$$K_{(3)} = a_{\text{O}} = [\text{O}] \cdot f_{\text{O}} \quad (3a)$$

can be described as a sum of reactions



where:  $\gamma_i^\circ$  is the activity coefficient at infinite dilution;

$M_i$  is the molecular mass.

For the oxygen solutions in liquid iron at 1873 K  $\gamma_{\text{O}(\text{Fe})}^\circ = 0.0105$  [22]. Therefore, at 1873 K  $\Delta G_{(3)}^\circ = 23\,905 \text{ J/mole}$ ,  $K_{(3)} = 0.2155$ . The oxygen solubility in iron can be described according to equation

$$\lg[\% \text{O}]_{\text{Fe}} = \lg K_{(3)} - e_{\text{O}(\text{Fe})}^\circ [\% \text{O}]. \quad (6)$$

The  $[\% \text{O}]$  concentration in the right-hand term of Eq. (3a) can be expressed as  $(K_{(3)} / f_{\text{O}})$ . At  $[\% \text{O}] \rightarrow 0$   $f_{\text{O}} \rightarrow 1$ . Because of the small oxygen solubility we can assume:  $(K_{(3)} / f_{\text{O}}) \approx K_{(3)}$ . Such a substitution gives no appreciable error in the calculation [14]. Then

$$\lg[\% \text{O}]_{\text{Fe}} = \lg K_{(3)} - e_{\text{O}(\text{Fe})}^\circ K_{(3)}. \quad (6a)$$

At 1873 K first order self interaction parameter  $e_{\text{O}(\text{Fe})}^\circ = -0.17$  [4], and the oxygen solubility is 0.235%, which is in good agreement with the reference data [4]. The oxide phase in equilibrium with Mn-Fe melts at 1873 K is liquid up to 0.2% Mn and solid above this concentration [23]. The reaction describing this equilibrium is



Depending on the manganese content of the melt, we can be presented it as a sum of reactions (2) and (8a) at a manganese concentration of up to 0.2%



$$\Delta G_{(8a)}^\circ = 352\,654 - 61.71T, \text{ J/mole [14]},$$

and as a sum of reactions (2) and (8b) at a manganese contents of 0.2% and above



$$\Delta G_{(8b)}^\circ = 406\,873 - 88.05T, \text{ J/mole [14]}.$$

It follows that  $\Delta G_{(7a)}^\circ = 112\,667 - 12.14T$ , J/mole,  $\Delta G_{(7b)}^\circ = 166\,886 - 38.48T$ , J/mole. At 1873 K  $\Delta G_{(7a)}^\circ = 89\,929 \text{ J/mole}$ ,  $K_{(7a)} = 3.110 \cdot 10^{-3}$ ,  $\Delta G_{(7b)}^\circ = 94\,813 \text{ J/mole}$ ,  $K_{(7b)} = 2.273 \cdot 10^{-3}$ .

### 3 COMPOSITION OF OXIDE PHASE

As an approximation of ideal solutions, in the case of oxygen solutions in the Mn-Fe melts, we can write for the oxide phase based on Eq. (7):

$$K_{(7)} = \frac{X_{\text{FeO}} X_{\text{Mn}} \gamma_{\text{Mn}}}{X_{\text{MnO}} X_{\text{Fe}} \gamma_{\text{Fe}}}.$$

Since  $X_{\text{FeO}} + X_{\text{MnO}} = 1$ , then

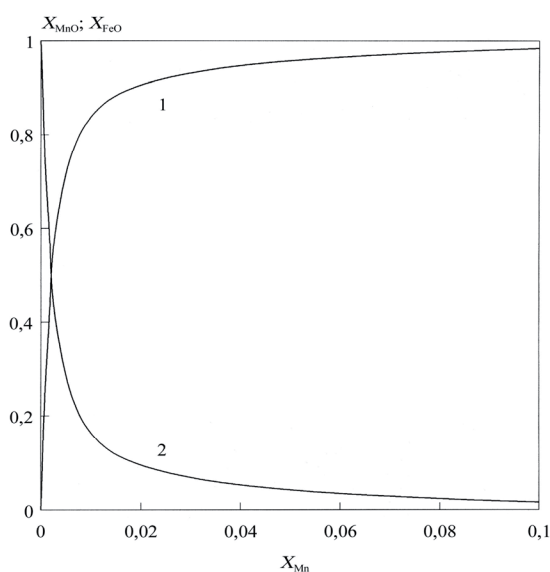
$$X_{\text{FeO}} = \frac{K_{(7)} X_{\text{Fe}} \gamma_{\text{Fe}}}{K_{(7)} X_{\text{Fe}} \gamma_{\text{Fe}} + X_{\text{Mn}} \gamma_{\text{Mn}}}. \quad (9)$$

The handbook [18] contains data on the  $\gamma_{\text{Fe}}$  and  $\gamma_{\text{Mn}}$  for the melts where the mole fraction of manganese changes from zero to one with a step of 0.1. For the melts with a low manganese concentration in a range of  $X = 0-0.1$ ,  $\gamma_{\text{Fe}}$  and  $\gamma_{\text{Mn}}$  were determined by interpolation. Compositions of the oxide phase of the Mn-Fe-O system calculated by Eq. (9) are shown in Table 1 and Fig. 1. As is seen from these data, the oxide phase represents mainly MnO; i.e., at a mole fraction of manganese of 0.02 (melt), the mole fraction of manganese oxide (slag) is 0.9. This connected with the fact that the affinity of manganese to oxygen is appreciably higher than the affinity of iron ( $\Delta G_{1873 \text{ K}}^\circ (\text{MnO}) = -241\,955 \text{ J/mole}$ ;  $\Delta G_{1873 \text{ K}}^\circ (\text{FeO}) = -147\,142 \text{ J/mole [14]}$ ).

**Table 1:** Composition of the oxide phase for the Mn-Fe-O melts at 1873 K

| $X_{Fe}$ | $\gamma_{Fe}$ [18] | $X_{Mn}$ | $\gamma_{Mn}$ [18] | $X_{FeO}$ | $X_{MnO}$ |
|----------|--------------------|----------|--------------------|-----------|-----------|
| 1.0      | 1.00               | 0        | 1.33               | 1.0       | 0         |
| 0.9995   | (1.00)             | 0.0005   | (1.32965)          | 0.8238    | 0.1762    |
| 0.999    | (1.00)             | 0.001    | (1.3293)           | 0.7004    | 0.2996    |
| 0.998    | (1.00)             | 0.002    | (1.3286)           | 0.5388    | 0.4612    |
| 0.998    | (1.00)             | 0.002    | (1.3286)           | 0.4605    | 0.5395    |
| 0.995    | (1.00)             | 0.005    | (1.3265)           | 0.2543    | 0.7457    |
| 0.99     | (1.00)             | 0.01     | (1.323)            | 0.1454    | 0.8546    |
| 0.98     | (1.00)             | 0.02     | (1.316)            | 0.0780    | 0.9220    |
| 0.95     | (1.00)             | 0.05     | (1.295)            | 0.0323    | 0.9677    |
| 0.90     | 1.00               | 0.1      | 1.26               | 0.0160    | 0.9840    |
| 0.8      | 1.01               | 0.2      | 1.20               | 0.0076    | 0.9924    |
| 0.7      | 1.03               | 0.3      | 1.15               | 0.0047    | 0.9953    |
| 0.6      | 1.05               | 0.4      | 1.11               | 0.0032    | 0.9968    |
| 0.5      | 1.07               | 0.5      | 1.07               | 0.0023    | 0.9977    |
| 0.4      | 1.11               | 0.6      | 1.05               | 0.0016    | 0.9984    |
| 0.3      | 1.15               | 0.7      | 1.03               | 0.0011    | 0.0089    |
| 0.2      | 1.20               | 0.8      | 1.01               | 0.0007    | 0.9993    |
| 0.1      | 1.26               | 0.9      | 1.00               | 0.0003    | 0.9997    |
| 0        | 1.33               | 1.0      | 1.00               | 0         | 1.0       |

Note: The  $\gamma_{Fe}$  and  $\gamma_{Mn}$  values obtained by interpolation are bracketed. The solid line separates the results obtained for the liquid ( $X_{Mn} < 0.002$ ) and solid ( $X_{Mn} > 0.002$ ) oxide phases.



**Figure 1:** Composition of oxide phase in equilibrium with melts Mn-Fe-O depending on the alloy composition at 1873 K (1 –  $X_{MnO}$ ; 2 –  $X_{FeO}$ )

#### 4 OXYGEN SOLUBILITY

The oxygen concentrations in the Fe-Mn melts were calculated by the method described earlier [24].

Reaction (3) for the Mn-Fe melts



$$K_{(10)} = \frac{X_{\text{Fe}} \gamma_{\text{Fe}} [\text{O}] f_{\text{O}}}{X_{\text{FeO}}}$$

can be represented as a sum of reactions (4) and (11)

$$\frac{1}{2}\text{O}_2(\text{g}) = [\text{O}]_{1\%(\text{Mn-Fe})}, \quad (11)$$

$$\Delta G_{(11)}^\circ = RT \ln(\gamma_{\text{O}(\text{Mn-Fe})}^\circ M_{\text{Mn-Fe}} / M_{\text{O}} \cdot 100),$$

It follows that  $\Delta G_{(10)}^\circ = \Delta G_{(2)}^\circ + \Delta G_{(11)}^\circ$  and  $\ln K_{(10)} = -\Delta G_{(10)}^\circ / RT$ .

The molecular masses of different compositions of the Mn-Fe melts were calculated by formula [24]

$$M_{\text{Mn-Fe}} = M_{\text{Mn}} X_{\text{Mn}} + M_{\text{Fe}} X_{\text{Fe}},$$

and the activity coefficients ( $\gamma_{\text{O}(\text{Mn-Fe})}^\circ$ ) by formula [25]

$$\begin{aligned} \ln \gamma_{\text{O}(\text{Mn-Fe})}^\circ &= X_{\text{Mn}} \ln \gamma_{\text{O}(\text{Mn})}^\circ + X_{\text{Fe}} \ln \gamma_{\text{O}(\text{Fe})}^\circ + \\ &+ X_{\text{Mn}} X_{\text{Fe}} \left[ X_{\text{Mn}} (\ln \gamma_{\text{O}(\text{Mn})}^\circ - \ln \gamma_{\text{O}(\text{Fe})}^\circ + \varepsilon_{\text{O}(\text{Mn})}^{\text{Fe}}) + \right. \\ &\left. + X_{\text{Fe}} (\ln \gamma_{\text{O}(\text{Fe})}^\circ - \ln \gamma_{\text{O}(\text{Mn})}^\circ + \varepsilon_{\text{O}(\text{Fe})}^{\text{Mn}}) \right]. \end{aligned}$$

For the oxygen solutions in liquid manganese and iron  $\gamma_{\text{O}(\text{Fe})}^\circ = 0.0105$  [21],  $\gamma_{\text{O}(\text{Mn})}^\circ = 1.131 \cdot 10^{-4}$  (see above), and  $\varepsilon_{\text{O}(\text{Fe})}^{\text{Mn}} = -4.735$  [4]. It was shown [26] that  $\varepsilon_{\text{C}(\text{Mn})}^{\text{Fe}} = -\varepsilon_{\text{C}(\text{Fe})}^{\text{Mn}}$  and  $\varepsilon_{\text{C}(\text{Co})}^{\text{Fe}} = -\varepsilon_{\text{C}(\text{Fe})}^{\text{Co}}$ . At the same time  $\varepsilon_{\text{O}(\text{Co})}^{\text{Fe}} = -3.01$  [22] and  $\varepsilon_{\text{O}(\text{Fe})}^{\text{Co}} = 1.9$  [22], i.e.,  $\varepsilon_{\text{O}(\text{Co})}^{\text{Fe}} \approx -\varepsilon_{\text{O}(\text{Fe})}^{\text{Co}}$ , which allows one as a first approximation to assume that  $\varepsilon_{\text{O}(\text{Mn})}^{\text{Fe}} \approx -\varepsilon_{\text{O}(\text{Fe})}^{\text{Mn}}$ . Then  $\varepsilon_{\text{O}(\text{Mn})}^{\text{Fe}} = 4.735$ . The calculated  $M_{\text{Mn-Fe}}$  and  $\gamma_{\text{O}(\text{Mn-Fe})}^\circ$  values and the equilibrium constants of reaction (10) are given in Table 2.

**Table 2:** Calculated oxygen solubility in Mn-Fe melts at 1873 K

| $X_{\text{Mn}}$ | Mn, %   | $M_{\text{Mn-Fe}}$ | $\gamma_{\text{O}}^\circ$ | $\Delta G_{(10)}^\circ$ ,<br>J/mole | $\lg K_{(10)}$ | $e_{\text{O}}^\circ$ | [O], % |
|-----------------|---------|--------------------|---------------------------|-------------------------------------|----------------|----------------------|--------|
| 0               | 0       | 55.847             | 0.01050                   | 23 905                              | -0.6665        | -0.170               | 0.235  |
| 0.0005          | 0.0492  | 55.8466            | 0.01048                   | 23 877                              | -0.6657        | -0.17002             | 0.1908 |
| 0.001           | 0.0984  | 55.8461            | 0.01045                   | 23 840                              | -0.6647        | -0.17004             | 0.1610 |
| 0.002           | 0.1968  | 55.8452            | 0.01040                   | 23 766                              | -0.6626        | -0.17008             | 0.1229 |
| 0.002           | 0.1968  | 55.8452            | 0.01040                   | 23 766                              | -0.6626        | -0.17008             | 0.1044 |
| 0.005           | 0.4919  | 55.8425            | 0.01025                   | 23 544                              | -0.6564        | -0.17019             | 0.0576 |
| 0.01            | 0.9839  | 55.8379            | 0.01002                   | 23 175                              | -0.6461        | -0.17038             | 0.0336 |
| 0.02            | 1.9681  | 55.8288            | 0.00955                   | 22 438                              | -0.6256        | -0.17075             | 0.0190 |
| 0.05            | 4.9226  | 55.8016            | 0.00830                   | 20 237                              | -0.5642        | -0.17188             | 0.0093 |
| 0.1             | 9.8533  | 55.7561            | 0.00658                   | 16 603                              | -0.4629        | -0.17376             | 0.0061 |
| 0.2             | 19.7387 | 55.6652            | 0.00523                   | 9444                                | -0.2633        | -0.17751             | 0.0051 |
| 0.3             | 29.6565 | 55.5743            | 0.00265                   | 2399                                | -0.0669        | -0.18124             | 0.0056 |
| 0.4             | 39.6068 | 55.4834            | 0.00170                   | -4569                               | 0.1274         | -0.18496             | 0.0069 |
| 0.5             | 49.5898 | 55.3925            | 0.00109                   | -11 499                             | 0.3206         | -0.18866             | 0.0089 |
| 0.6             | 59.6055 | 55.3016            | $6.99 \cdot 10^{-4}$      | -18 429                             | 0.5138         | -0.19236             | 0.0118 |
| 0.7             | 69.6543 | 55.2107            | $4.479 \cdot 10^{-4}$     | -25 398                             | 0.7081         | -0.19604             | 0.0162 |
| 0.8             | 79.7362 | 55.1198            | $2.854 \cdot 10^{-4}$     | -32 442                             | 0.9045         | -0.19971             | 0.0228 |
| 0.9             | 89.8513 | 55.0289            | $1.806 \cdot 10^{-4}$     | -39 602                             | 1.1041         | -0.20336             | 0.0326 |
| 1.0             | 100.0   | 54.938             | $1.131 \cdot 10^{-4}$     | 47 890*                             | -1.3352**      | -0.207               | 0.0472 |

Note: \*  $\Delta G_{(1)}^\circ$ ; \*\*  $\lg K_{(1)}$ ; solid line separates the results obtained for the liquid ( $X_{\text{Mn}} < 0.002$ ) and solid ( $X_{\text{Mn}} > 0.002$ ) oxide phases.

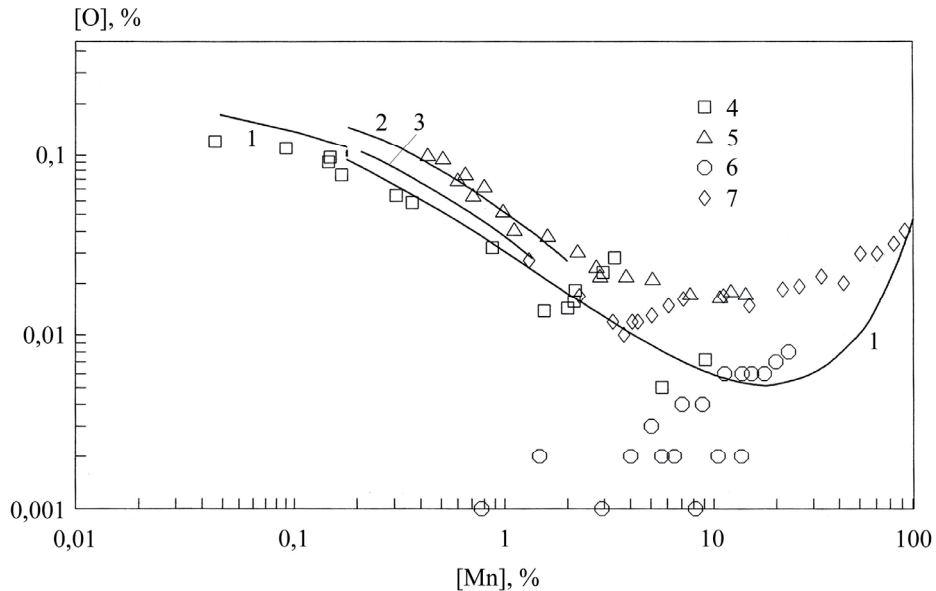
The oxygen solubility in the Mn-Fe melts can be estimated by the equation

$$\begin{aligned} \lg [\%O]_{\text{Mn-Fe}} &= \lg K_{(10)} + \lg X_{\text{FeO}} - \lg X_{\text{Fe}} - \lg \gamma_{\text{Fe}} - e_{\text{O(Mn-Fe)}}^{\text{O}} [\%O] = \\ &= \lg K_{(10)} + \lg X_{\text{FeO}} - \lg X_{\text{Fe}} - \lg \gamma_{\text{Fe}} - e_{\text{O(Mn-Fe)}}^{\text{O}} K_{(10)} X_{\text{FeO}} / X_{\text{Fe}} \gamma_{\text{Fe}} . \end{aligned} \quad (12)$$

The interaction parameter  $e_{\text{O(Mn-Fe)}}^{\text{O}}$  was calculated by formula [24]

$$e_{\text{O(Mn-Fe)}}^{\text{O}} = e_{\text{O(Mn)}}^{\text{O}} X_{\text{Mn}} + e_{\text{O(Fe)}}^{\text{O}} X_{\text{Fe}} .$$

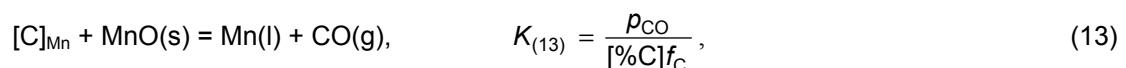
The oxygen concentrations calculated by Eq. (12) are shown in Table 2 and Fig. 2. As can be seen, the addition of manganese to iron causes a slight decrease in the oxygen solubility. At 19.32% Mn, a minimum is observed in the oxygen solubility curve, which corresponds to the oxygen concentration of  $5.136 \cdot 10^{-3}\%$  at 1873 K. At 0.2% Mn, two oxygen concentrations take place in the calculated curve 1, which is connected with the fact that, as was indicated above, the oxide phase passes from the liquid state to solid at this manganese content in melt. Probably, under real conditions, this transition is not discontinuous but occurs in a narrow range of manganese concentrations. Fig. 2 also shows the published experimental data [5, 6, 23, 27–29]. The calculated and experimental data are in good agreement.



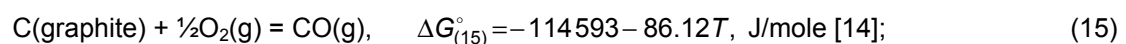
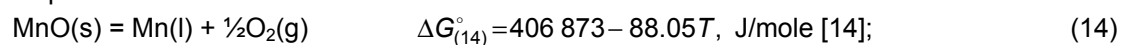
**Figure 2:** Oxygen solubility in the Mn-Fe melts depending on alloy composition at 1873 K (1 – calculation; 2 – [27]; 3 – [23]; 4 – [5]; 5 – [28]; 6 – [29]; 7 – [6])

## 5 THERMODYNAMICAL ANALYSIS OF CARBON SOLUTIONS IN MANGANESE

The interaction of carbon dissolved in liquid manganese in equilibrium with manganese oxide



can be expressed as the sum of reactions



$$C(\text{graphite}) = [C]_{1\%(\text{Mn})}, \quad \Delta G_{(16)}^{\circ} = RT \ln \left( \frac{\gamma_{C(\text{Mn})}^{\circ} M_{\text{Mn}}}{M_C \cdot 100} \right), \text{ J/mole.} \quad (16)$$

The  $\gamma_{C(\text{Mn})}^{\circ}$  coefficients determined experimentally in a number of studies are the following:

|                                 |       |       |       |       |             |
|---------------------------------|-------|-------|-------|-------|-------------|
| $T, K$                          | 1673  | 1873  | 1628  | 1628  | 1628–1773   |
| $\gamma_{C(\text{Mn})}^{\circ}$ | 0.384 | 0.414 | 0.151 | 0.749 | 0.266–0.304 |
| Issue                           | [7]   | [8]   | [10]  | [11]  | [13]        |

Based on the above data, the following temperature dependence of the  $\gamma_{C(\text{Mn})}^{\circ}$  activity coefficient was obtained:

$$\gamma_{C(\text{Mn})}^{\circ} = -1.5966 + 1.0735 \cdot 10^{-3} T. \quad (17)$$

Using the  $\gamma_{C(\text{Mn})}^{\circ}$  values calculated from Eq. (17), the Gibbs energies of reactions (13) and (16) were estimated in a wide temperature range (1673–2073 K). These temperature dependences can be described as

$$\Delta G_{(13)}^{\circ} = 375\,264 - 184.66T, \text{ J/mole;}$$

$$\Delta G_{(16)}^{\circ} = -82\,984 + 10.52T, \text{ J/mole.}$$

Therefore, reaction (13) proceeds appreciably ( $\Delta G_{(13)}^{\circ} < 0$ ) at temperatures of above 2033 K. This relates to the case when carbon content in the manganese melt is higher than 1%. The high-carbon ferromanganese contains 7–8% C; therefore, the interaction of carbon dissolved in this ferromanganese with manganese oxide can occur at the lower temperatures (1773–1873 K). The carbon content equal to 2% can be produced at a temperature of about 2023 K. The results obtained are in good agreement with the data of theoretical and experimental studies of decarburization of high-carbon ferromanganese with the help of manganese ore (manganese oxides) [2, 3].

The interaction of carbon and oxygen dissolved in liquid manganese

$$CO(g) = [C]_{\text{Mn}} + [O]_{\text{Mn}} \quad K_{(18)} = \frac{([ \%C ] f_C)([ \%O ] f_O)}{p_{CO}} \quad (18)$$

can be represented as a sum of reactions (15) and (16) and also the reaction

$$\frac{1}{2}O_2(g) = [O]_{1\%(\text{Mn})} \quad \Delta G_{(19)}^{\circ} = -302\,265 + 57.78T, \text{ J/mole [14].} \quad (19)$$

The temperature dependence of the Gibbs energy of reaction (18) can be described by equation

$$\Delta G_{(18)}^{\circ} = -270\,656 + 154.42T, \text{ J/mole.}$$

The calculated Gibbs energies and equilibrium constants of reaction (18) for the temperatures characteristic to the refining processes of ferromanganese alloys are given below.

|                                           |         |         |         |
|-------------------------------------------|---------|---------|---------|
| $T, K$                                    | 1873    | 1973    | 2073    |
| $\Delta G_{(18)}^{\circ}, \text{ J/mole}$ | 18 573  | 34 015  | 49 457  |
| $\lg K_{(18)}$                            | –0.5178 | –0.9030 | –1.2458 |

In the course of interaction of oxygen and carbon in the melt, along with the formation of carbon monoxide, carbon dioxide can be formed [30] according to reaction

$$[C]_{\text{Mn}} + 2[O]_{\text{Mn}} = CO_2(g) \quad K_{(20)} = \frac{p_{CO_2}}{([ \%C ] f_C)([ \%O ] f_O)^2}, \quad (20)$$

which can be represented as a sum of reaction (16) and reactions

$$O_2(g) = 2[O]_{1\%(\text{Mn})} \quad \Delta G_{(21)}^{\circ} = -604\,574 + 115.56T, \text{ J/mole [14];} \quad (21)$$

$$C + O_2(g) = CO_2(g) \quad \Delta G_{(22)}^{\circ} = -396\,720 + 0.08T, \text{ J/mole [14].} \quad (22)$$

The temperature dependence of the Gibbs energy of reaction (20) can be described by the equation

$$\Delta G_{(20)}^{\circ} = 290\,838 - 126T, \text{ J/mole},$$

It follows that reaction (20) can proceed ( $\Delta G_{(20)}^{\circ} < 0$ ) only at temperatures of above 2308 K. This must be taken into account when calculating oxygen concentrations in manganese melts in equilibrium with carbon.

For reaction (18), the concentration of oxygen in equilibrium with a given carbon content can be calculated according to the equation

$$\lg[\%O]_{\text{Mn}} = \lg K_{(18)} + \lg p_{\text{CO}} - \lg[\%C]_{\text{Mn}} - \left[ e_{\text{C}(\text{Mn})}^{\text{C}} + e_{\text{O}(\text{Mn})}^{\text{C}} \right] [\%C] - \left[ e_{\text{O}(\text{Mn})}^{\text{O}} + e_{\text{C}(\text{Mn})}^{\text{O}} \right] [\%O]_{\text{Mn}}. \quad (23)$$

The  $[\%O]$  value in the right-side term of Eq. (23) can be expressed using the ratio  $(K_{(18)} p_{\text{CO}} / [\%C]_{\text{Mn}} f_{\text{C}} f_{\text{O}})$ . Because of the small oxygen solubility one can assume  $(K_{(18)} p_{\text{CO}} / [\%C]_{\text{Mn}} f_{\text{C}} f_{\text{O}}) \approx (K_{(18)} p_{\text{CO}} / [\%C]_{\text{Mn}})$  [14]. This substitution gives no appreciable error in the calculations. Then

$$\lg[\%O]_{\text{Mn}} = \lg K_{(18)} + \lg p_{\text{CO}} - \lg[\%C]_{\text{Mn}} - \left[ e_{\text{C}(\text{Mn})}^{\text{C}} + e_{\text{O}(\text{Mn})}^{\text{C}} \right] [\%C]_{\text{Mn}} - \left[ e_{\text{O}(\text{Mn})}^{\text{O}} + e_{\text{C}(\text{Mn})}^{\text{O}} \right] (K_{(18)} p_{\text{CO}} / [\%C]_{\text{Mn}}). \quad (23a)$$

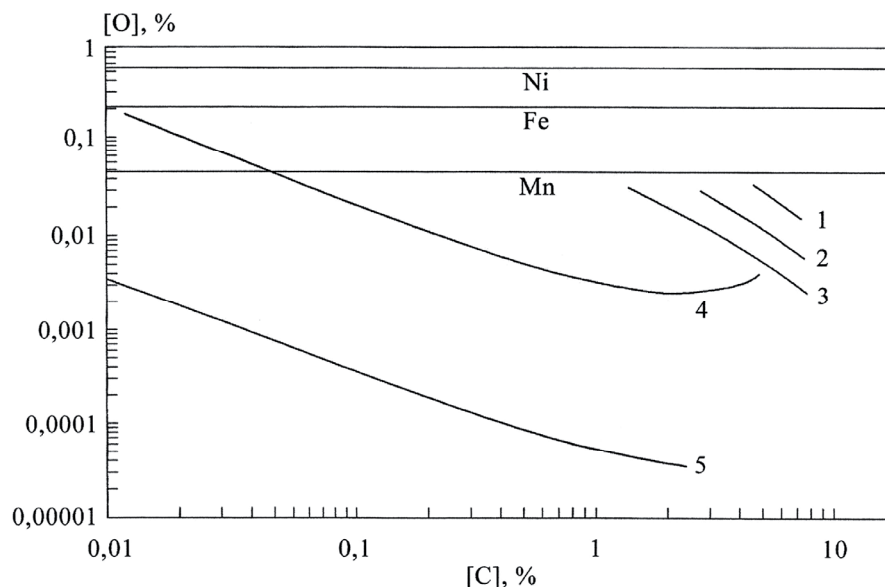
At  $p_{\text{CO}} = 1$  atm (0.1MPa) and the interaction parameters  $e_{\text{C}(\text{Mn})}^{\text{C}} = 0.149$  [26];  $e_{\text{O}(\text{Mn})}^{\text{O}} = -0.207$  (see above);  $e_{\text{O}(\text{Mn})}^{\text{C}} = -0.0979$  [25];  $e_{\text{C}(\text{Mn})}^{\text{O}} = -0.0724$  [27], Eq. (23a) becomes

$$\lg[\%O]_{\text{Mn}} = \lg K_{(18)} - \lg[\%C]_{\text{Mn}} - 0.0511[\%C]_{\text{Mn}} + 0.2794(K_{(18)} / [\%C]_{\text{Mn}}). \quad (24)$$

The equilibrium concentrations of oxygen in manganese-based melts at 1873–2073 K as a function of carbon concentration calculated from Eq. (24) are shown in Table 3 and Fig. 3, and compared to those of iron- and nickel-based melts [31]. Since there are no published parameters at other temperatures and taking into account the fact that the interaction parameter depends weakly on temperature, the above values of these parameters were used in calculations at all temperatures, supposing this assumption to give no appreciable error.

**Table 3:** Oxygen concentration of liquid manganese depending on the carbon content

| [C], % | [O], %  | [C], % | [O], %  |
|--------|---------|--------|---------|
| 1873 K |         | 8.20   | 0.00587 |
| 5.0    | 0.03505 | 2073 K |         |
| 7.0    | 0.01957 | 1.5    | 0.03252 |
| 7.96   | 0.01532 | 2.0    | 0.02285 |
| 1973 K |         | 3.0    | 0.01346 |
| 3.0    | 0.03008 | 5.0    | 0.00635 |
| 5.0    | 0.01411 | 7.0    | 0.00358 |
| 7.0    | 0.00793 | 8.43   | 0.00251 |



**Figure 3:** Oxygen concentration of manganese (1–3), iron (4) [31], and nickel (5) melts depending on the carbon content [31] (1, 4, 5 – 1873 K; 2 – 1973 K; 3 – 2073 K)

As is seen in Fig. 3, the deoxidation ability of carbon in manganese melt is considerably lower in comparison with iron and nickel melts, since manganese has a higher affinity to oxygen than the those metals (at 1873 K,  $\gamma_{C(Mn)}^\circ = 0.414$  [8];  $\gamma_{C(Fe)}^\circ = 0.538$  [4];  $\gamma_{C(Ni)}^\circ = 0.82$  [14];  $\gamma_{O(Mn)}^\circ = 1.131 \cdot 10^{-4}$  (see above);  $\gamma_{O(Fe)}^\circ = 1.05 \cdot 10^{-2}$  [4];  $\gamma_{O(Ni)}^\circ = 0.357$  [22]). With an increase in the temperature, the deoxidation ability of manganese increases since the bond strengths of base with the dissolved elements become weaker; however, in all cases, this process occurs at sufficiently high carbon contents. The results obtained are in good agreement with the above conclusion that the refining of high-carbon manganese with carbon requires high temperatures of 1973–2073 K.

The horizontal lines in Fig. 3 demonstrate the saturated concentrations of oxygen in manganese, iron, and nickel at 1873 K ( $[O]_{Mn}^{sat} = 0.0472\%$  (see above);  $[O]_{Fe}^{sat} = 0.235\%$  [33];  $[O]_{Ni}^{sat} = 0.60\%$  [32]). The maximum carbon concentration in the curves corresponds to its saturation concentration in these molten metals at the given temperature ( $[C]_{Mn(1873\ K)}^{sat} = 7.96\%$ ,  $[C]_{Mn(1973\ K)}^{sat} = 8.20\%$ ,  $[C]_{Mn(2073\ K)}^{sat} = 8.43\%$  [33];  $[C]_{Fe(1873\ K)}^{sat} = 5.30\%$  [34];  $[C]_{Ni(1873\ K)}^{sat} = 2.59\%$  [33]).

## 6 CONCLUSIONS

1. Composition of the oxide phase in equilibrium with the oxygen-containing Mn-Fe melts was determined in the whole range of alloy compositions. The oxide phase contains mainly MnO. This is connected with the fact that manganese has considerably higher affinity to oxygen than iron.
2. The equilibrium oxygen concentrations in the Mn-Fe melts were calculated in a wide range of alloy compositions. Addition of manganese into iron causes a considerable decrease in the oxygen solubility. At a manganese content of 19.32%, a minimum is observed in the oxygen solubility curve, which corresponds to an oxygen content of  $5.136 \cdot 10^{-3}\%$ .
3. The saturated oxygen concentration in liquid manganese at 1873 K is 0.0472%. The interaction parameter  $e_{O(Mn)}^O = -0.207$  and activity coefficient  $\gamma_{O(Mn)}^\circ = 1.131 \cdot 10^{-4}$  were calculated.
4. Interaction of carbon with oxygen dissolved in liquid manganese oxide can develop appreciably at temperatures of 1973–2073 K depending on the carbon concentration. The deoxidation ability of

carbon in the manganese-based melts is considerably lower in comparison with the iron- and nickel-based melts because of the higher affinity of manganese to both oxygen and carbon. With increasing temperature, the deoxidation ability of carbon in the manganese melts increases. However, in all cases, this process develops appreciably at sufficiently high carbon contents.

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