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Partial pressure of oxygen and activity of manganese monooxide in the molten system Fe-Mn-Si-O (1)/CaO-MgO-MnO-FeO-Al₂O₃-SiO₂ (1) at the temperature of 1600 °C was investigated using electrochemical methods. The dependence of the activity of MnO on its content in the mixture and on the optical basicity of the melt was determined. Dependence of the distribution coefficient of manganese on the partial pressure of oxygen and the optical basicity of the ionic melt was obtained.

Reactions in the molten system Fe-Mn-Si-O (1)/ CaO-MgO-MnO-FeO-Al₂O₃-SiO₂ (1) are of interest from the point of view of metallurgy (to the content of 2 mass % of MnO) [1] and of electrical arc welding under the layer of flux (content of MnO ca. 20 mass %). The most important for welding are the heterogeneous reactions which determine the distribution of oxygen, silicon, and manganese between the slag and the metal. These reactions are usually treated separately even if they should be considered as a set of simultaneous reactions. What makes the theoretical treatment of this process difficult is that the exact temperature of welding is not known (it is in the range of 1870-2300 K) and that the system is not in an equilibrium [2]. Nevertheless, it is generally accepted that the resulting composition of welding metal is determined by the heterogeneous reaction between the molten metal and the ionic melt. Thus knowledge of the thermodynamic data for this system is important for predicting of the direction and the extension of the reactions taking place at welding. Thermodynamic data on multicomponent ionic systems containing MnO are rather scarce. Therefore the properties of the flux and their influence on the content of manganese in the weld are often estimated using empirical rules [2, 3].

The aim of this work is to investigate the distribution of manganese between the molten metal and ionic melt on the basis of direct electrochemical measurement of the partial pressure of oxygen in both heterogeneous phases and to determine the activity of MnO. Moreover, the influence of basicity of the ionic melt on the activity of MnO and the distribution coefficient of manganese in the system was determined.

EXPERIMENTAL

Investigation of the distribution of manganese between slag and molten metal was done both in a model multicomponent system and in the sample taken from the flux used for welding in industrial conditions. In the former case the samples of the system CaO-MgO-Al₂O₃-SiO₂ were premelted in a platinum crucible at 1600 °C and after cooling crushed and ground. The used chemicals were of anal. grade purity. Manganese monooxide was added to this mixture. Metal phase was prepared from iron of the purity 99.5 % containing 0.0025 mass % of oxygen. For laboratory measurement iron was deoxidized by aluminium to the content of 0.001 % of oxygen. The amount of oxygen was determined by the apparatus LECO TC 436.

The apparatus used for measurements was described in detail in paper [4]. Heating graphite tube was insulated inside by a sintered alumina tube. Sintered alumina crucible contained *ca.* 50 g of molten metal and 25 g of slag. The temperature was measured by Pt30Rh-Pt6Rh thermocouple which was immersed in the melt. The measurement was carried out in argon atmosphere. For faster reaching of equilibrium the melt was mixed by bubbling of argon (flow rate 2×10^{-3} dm³ s⁻¹) for 600 s. After this time EMF of galvanic cell (I)

was measured. The reference oxygen electrode was formed by the solid electrolyte $ZrO_2(Y_2O_3)$. It was shaped as semi-closed tube filled with Cr— Cr_2O_3 as reference mixture in which a molybdenum wire was immersed. The measurement of EMF in the ionic

Sample	×/%						w/%		a(O in Fe)
	MnO	FeO	CaO	MgO	Al ₂ O ₃	SiO ₂	Mn	Si	×10 ³
1	4.5	1.2	44.9	0	47.5	1.9	0.87	0.02	4.1
2	6.0	0.9	43.4	0	47.8	1.9	0.87	0.02	4.3
3	3.1	0.5	45.0	14.6	35.8	0.8	0.87	0.02	2.9
4	4.3	0.5	40.3	17.9	36.1	0.8	0.93	0.01	4.0
5	6.3	0.6	38.4	20.1	33.3	1.0	0.90	0.01	6.0
6	0.5	0.4	48.0	17.0	31.3	0.8	0.57	0.01	1.2
7	3.5	0.6	39.5	19.0	34.3	3.0	0.79	0.03	7.0
8	4.9	2.4	42.0	16.9	33.4	0.3	0.77	0.03	4.2
9	1.2	0.5	51.1	0	39.0	8.3	0.27	0.02	2.8
10	2.4	0.6	46.4	0	42.4	8.3	0.30	0.02	4.5
11	7.5	0.9	41.7	0	38.4	11.4	0.51	0.01	8.3
12	0.7	0.1	51.4	0	39.4	8.4	0.49	0.06	0.7
13	1.7	0.5	48.4	0	41.1	8.4	0.61	0.01	1.9
14	3.8	0.4	44.7	0	43.3	7.8	0.62	0.01	3.3
15	0.9	0.3	49.2	0	29.1	21.0	0.47	0.06	2.1
16	2.6	0.5	44.4	0	32.9	19.6	0.63	0.03	3.6
17	5.1	0.8	39.7	0	38.4	16.0	0.65	0.02	3.4
18	7.1	0.7	40.1	0	36.5	15.4	0.58	0.03	6.0
19	0.7	0.3	46.4	0	35.1	17.5	0.27	0.15	1.3
20	2.9	0.4	43.0	0	36.9	16.7	0.70	0.05	1.7
21	4.3	0.5	43.0	0	36.6	15.6	0.54	0.03	4.4
22	0.9	0.4	43.8	18.6	35.9	0.3	0.56	0.02	0.9
23	5.5	1.4	35.8	0	36.8	20.4	0.37	0.03	6.6
24	14.5	1.6	10.8	17.4	15.1	36.7	0.61	0.13	7.8
25	17.2	1.5	9.6	18.4	15.0	35.6	0.66	0.07	8.0
26	20.4	1.8	9.2	20.6	13.8	30.5	0.68	0.14	12.0
27	20.7	2.3	8.3	21.1	12.6	32.2	0.67	0.05	13.0
28	21.7	2.2	8.5	21.5	10.4	32.7	0.65	0.04	15.0
29	22.9	3.0	8.9	19.6	11.6	31.7	0.60	0.05	18.0

Table 1. Composition of the Ionic Melt and the Content of Manganese and Silicon in the Metal after EMF Measurement, Calculated Activity of Oxygen in Fe

and metallic melts has been discussed in paper [4]. Reproducibility of the measurement was \pm 15 mV, temperature of the melt was (1600 \pm 10) °C. After EMF measurement, the metal and the slag were sampled by evacuated silica tube and quenched in water. It was found that because of dissolution of alumina crucible and silica tube during sampling the content of alumina in the melt increased by 10 mass % and the content of silica by 1 mass %, respectively. Chemical analysis was done by AAS method. Fe(II) was determined by the bichromatometric method. The content of Fe(III) was very low (0–0.2 %).

RESULTS AND DISCUSSION

Composition of the oxide and metal phases and equilibrium activity of oxygen are summarized in Table 1. The content of oxygen in the metal is not included in this table because the electrochemical determination of $p(O_2)$ in situ gives more reliable results for thermodynamic calculations than the analysis of oxygen content in quenched sample. The samples 1-24 correspond to the model system and 24-29 to the flux used in industry.

The following reactions take place in the investigated heterogeneous system:

Fe (1) + 1/2 O_2 (g) \implies FeO (in the slag) (A)

Mn (in Fe) + $1/2 O_2(g) \implies$ MnO (in the slag) (B)

1/2 Si (in Fe) + 1/2 O₂ (g)
$$\leq$$
 1/2 SiO₂
(in the slag) (C)

Partial pressure of oxygen was measured using the galvanic cell (I). The EMF of the cell is given by eqn (1) which holds for low pressure of oxygen

$$E = \frac{RT}{F} \ln \frac{{}^{r} p_{\Theta}^{1/4} + {}^{r} \rho(O_{2})_{ref}^{1/4}}{{}^{r} p_{\Theta}^{1/4} + {}^{r} \rho(O_{2})^{1/4}}$$
(1)

R is the gas constant (J K⁻¹ mol⁻¹), *T* is the thermodynamic temperature (K), and *F* is the Faraday constant (C mol⁻¹), ${}^{r}p_{\Theta}$ is the partial pressure of oxygen corresponding to the case when the electron conductivity equals to the ionic conductivity and ${}^{r}p(O_2)_{ref}$ is the partial pressure of oxygen in the reference mixture Cr—Cr₂O₃. Index r denotes that all pressures are related to the standard state of 101325 Pa. For the calculation of ${}^{r}p_{\Theta}$ the following equation was used [5]



Fig. 1. Dependence of EMF on the composition of the system at 1600 °C ($y = x(MnO)x(FeO)[x(SiO_2)/w(Si)]^{1/2}/w(Mn))$.

$$\log p_{\Theta} = -58974 / T + 15.49$$
 (2)

 $p(O_2)_{ref}$ was calculated according to [6]

$$RT \ln p(O_2)_{ref} = -755200 + 171.2 T$$
 (3)

The relationship between the partial pressure of oxygen and its activity is given by the equilibrium of the reaction [7] with the corresponding Gibbs energy

$$1/2 O_2(g) \leq O(in Fe)$$
 (D)

$$\Delta G_D^{\circ} / (J \text{ mol}^{-1}) = -117152 - 2.887 T \quad (4)$$

Relationships between the activities of specific oxides, partial pressure of oxygen, composition of the melt and EMF have been discussed in paper [1]. For EMF of cell (I) of the system which does not contain MgO and which has a low content of MnO the following relationship was derived

$$E = E' - \frac{RT}{6F} \ln \left[\frac{x(\text{FeO})x(\text{MnO})}{w(\text{Mn})} \left(\frac{x(\text{SiO}_2)}{w(\text{Si})} \right)^{1/2} \right]^{1/2}$$
(5)

E' includes the sum of standard potentials of reactions (*A*—*C*), the activity coefficients of oxides and $p(O_2)_{ref}$, *x* is the mole fraction and *w* is the mass fraction in percent. For w(Mn) < 1% and w(Si) < 1%the Henry activity coefficients equal to one. The expression $x(MnO)x(FeO)[x(SiO_2)/w(Si)]^{1/2}/w(Mn)$ will be denoted as *y*. For the dependence of $p(O_2)$ on the content of MnO, FeO, and Mn in the system CaO—Al₂O₃—SiO₂—FeO—MnO and temperature 1600 °C the following empirical equation has been derived [1]

$$\log {}^{r}\rho(O_{2}) = -8.664 + 0.904 \log \frac{x(FeO)x(MnO)}{w(Mn)}$$
(6)



Fig. 2. Comparison of the experimental and calculated (eqn (6)) partial pressure of oxygen in the melt.

Correlation coefficient of eqn (6) has been found to be 0.93 [1].

In this work, the composition range of the investigated systems was extended up to 23 mass % MnO and of the addition of another component, viz. MgO. The dependence of EMF vs. parameter y is shown in Fig. 1. Slope of this plot was obtained by the treatment of the data by the least-squares method and equals to RT/nF. It follows that the charge number n = 5.76. This is in good agreement with the theoretical value of 6. This also proves that SiO does not take part in the reactions (A-C). Correlation coefficient of this dependence was found to be 0.92. The values of ${}^{r}p(O_{2})_{theor}$ were calculated according to eqn (6) and compared with the experimental data (Fig. 2). From a good agreement it can be concluded that also in the systems having high content of MgO, MnO, and SiO₂ the oxidation potential is determined by the activities of FeO and MnO. Observed linear dependence of EMF vs. y can be explained by the assumption that the abovementioned components influence the activity coefficients of FeO, MnO, and SiO₂ in such a way that their influence compensates and thus the value of E' in the relationship (5) remains constant. The obtained results also suggest that for the prediction of the content of Mn in metal it is not sufficient to consider only the parameter which determines the acid-base properties of the flux. It is necessary to take into account also the contribution of the given component to the oxidation potential of the system.

The activity of oxygen in Fe was calculated according to eqn (*D*) from the electrochemical measurements of $p(O_2)$. On the basis of a(O in Fe) and of composition of the metal the activity of MnO was determined according to eqn (*E*). The equilibrium constant is given by eqn (7) [8]. Standard state of MnO is the pure liquid of this substance.

Mn (in Fe) + O (in Fe) = MnO (in the slag) (E)
log
$$K = (12\ 760/T) - 5.68$$
 (7)

Experimentally determined values of activity of MnO are presented in Table 2. The Raoult activity coefficient γ (MnO) changes from the value of 0.38 for the most acid mixture to 2 for highly basic slag.

In the next we will show how the value of a(MnO) can be calculated on the basis of composition of the melt and the concept of basicity. The basicity of the melt used in this work is defined as the optical basicity Λ described in paper [9]. It can be calculated according to the equation

$$\Lambda = \sum_{i}^{n} \Lambda_{i} r_{i} \tag{8}$$

where Λ_i is the optical basicity of the oxide and r_i is the ionic fraction of the oxide Me_uO_v which can be calculated according to the relationship

$$r_i = v_i x_i / \sum_{i}^{n} v_i x_i$$
(9)

The definition and calculation of ionic fractions and the values of Λ_i are presented in paper [10]. The values of optical basicity of samples *1*—29 are presented in Table 2.

Dependence of the activity of MnO on the mole fraction x(MnO) and parameter Λ as it was derived on the basis of our experimental data, is described by eqn (10). Correlation coefficient equals 0.91.

$$a(MnO)_{calc} = -0.28 + 0.53 x(MnO) + 0.41 \Lambda$$
 (10)

Dependence of the distribution coefficient of manganese on $p(O_2)$ and basicity of the melt was investigated as well. The thermodynamic distribution coefficient L(Mn) equals the ratio of the Raoult activity of MnO in the slag and of the Henry activity of Mn in the metal. The manganese distribution for practical use can be also defined as L'(Mn) = x(MnO)/w(Mn).

Experimentally determined values of L'(Mn) in this work and in paper [1] were fitted into a linear equation with two independent variables, *viz*. log $p(O_2)$ and Λ by the least-squares method

$$\log L'(Mn)_{calc} = 7.25 + 0.56 \log p(O_2) - 2.78 \Lambda (11)$$

It follows that the distribution coefficient of manganese remarkably decreases with increasing basicity and it rises with increasing partial pressure of oxygen in the melt. The correlation coefficient of eqn (11) is 0.9.

Table 2. Optical Basicity of the Ionic Melt and Experimentally Determined Activities of Manganese Monooxide at the Temperature of 1600 °C

Sample	Λ	a(MnO)	Sample	Λ	a(MnO)
1	0.713	0.049	16	0.686	0.031
2	0.714	0.052	17	0.686	0.030
3	0.737	0.035	18	0.696	0.048
4	0.733	0.051	19	0.685	0.004
5	0.743	0.071	20	0.685	0.016
6	0.745	0.009	21	0.692	0.032
7	0.728	0.070	22	0.731	0.007
8	0.749	0.044	23	0.648	0.032
9	0.710	0.010	24	0.635	0.064
10	0.701	0.019	25	0.641	0.065
11	0.707	0.057	26	0.663	0.116
12	0.708	0.005	27	0.689	0.108
13	0.704	0.016	28	0.663	0.119
14	0.702	0.029	29	0.668	0.138
15	0.690	0.012			

CONCLUSION

The experimental results show that even for high contents of MnO (up to 23 mass %) and 14–22 mass % MgO in the slag the partial pressure of oxygen of the system ionic melt—molten metal can be described as a function of the content of FeO and MnO in the slag and of Mn in the metal. It was shown that the optical basicity is a suitable parameter for characterizing the acid-base properties of the melt. This parameter and $p(O_2)$ determine the distribution of manganese between the metal and the ionic phase and the activity of manganese monooxide.

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