

Původní práce

ELECTROCHEMICAL MEASUREMENT OF FERROUS OXIDE
ACTIVITY IN $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x \text{FeO}$ MELTS

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On the basis of measuring the electrochemical voltage of the cell $\text{Fe(s)} | \text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x \text{FeO(l)} | \text{ZrO}_2 (\text{CaO}) | \text{Ni, NiO(s)} | \text{Mo(s)}$ the activity of ferrous oxide was determined for $x(\text{FeO}) = 0.005-0.06$ at $1300-1400^\circ\text{C}$. At temperatures of $1300-1350^\circ\text{C}$, the FeO activity exhibits a negative deviation from Raoult's law and at 1400°C approaches the ideal behaviour.

A linear relationship between EMF and $\log x(\text{FeO})$ was found, the values of standard electromotive force E° and the number of exchanged electrons n were determined; the values are in agreement with theoretical assumptions. The results indicate that it is in principle possible to measure $a(\text{FeO})$ in commercial glass melts by means of the given arrangement.

INTRODUCTION

Knowledge of the thermodynamic activities of components in oxidic melts (glass, slag) would allow the state of the system to be assessed and the course of homogeneous and heterogeneous reactions in the melt to be controlled. By means of solid electrolytes showing ionic conductivity (O^{2-} , Na^+) it is possible to arrange galvanic cells for direct activity measurement in these melts at high temperatures. The activity of the MeO component can be measured with a chemical cell using a common electrolyte (1),



where the symbol (MeO) represents the oxide dissolved in the melt.

The chemical cell (1) consists of a metallic and an oxygen electrode and its voltage is determined by a change in Gibbs's energy of the cell reaction. The metallic electrode must not reduce any of the melt components, should produce a Nernstian response to the Me^{n+} ions, and formation of a mixed potential has to be ruled out. The problem has not so far been quite satisfactorily resolved for high-temperature electrochemical measurements. In the use of Pt— O_2 electrode as an oxygen one, the gas may come into contact with the metallic electrode and bring about its increased dissolution [1]. It is therefore necessary to design suitable oxygen electrodes using solid electrolytes with ionic conductivity for measurement in oxidic melts.

The present study had the aim to measure ferrous oxide activity in the $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2$ melt by means of a chemical cell. The activity of FeO in the $\text{Na}_2\text{O}-\text{SiO}_2$ system was already measured [2, 3], but only up to 1300°C and at lower SiO_2 contents.

From the practical point of view, the composition of the system is identical with that of binary technical glass. The system may serve as a model for studying the problem of colouring container glasses with iron oxides. It is also significant in the development of new steelmaking processes [4] where the system $\text{Na}_2\text{O}-\text{FeO}-\text{SiO}_2$ arises in the refining of pig iron by means of Na_2CO_3 at temperatures up to 1400°C . In this case, the activity of FeO influences the distribution of components between the metallic and the ionic melt.

EXPERIMENTAL

The initial substances for sample preparation were Fe_2O_3 , Na_2CO_3 and SiO_2 of A.R. purity. The binary system $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ was prepared in advance by standard melting in a platinum crucible at 1300°C for 3 hours in the SF 2 muffle furnace. The mixture of Fe_2O_3 and $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ in the given stoichiometric ratio was placed in an iron crucible in Tamman's furnace provided with an inner protective tube of Al_2O_3 in argon atmosphere. The partial pressure of oxygen, $p\text{O}_2$, in the furnace atmosphere was determined by the Gapolyt instrument and amounted to 10^{-9} Pa.

The experimental arrangement is shown in Fig. 1. The EMF measuring procedure was as follows: Following the melting, a PtRh 6—PtRh 30 thermocouple in a protective tube of Al_2O_3 was placed in the sample. The sample was kept for 1 hour at 1300°C to establish an equilibrium between the solid iron and liquid oxides. A measuring electrode of pure iron was immersed in the melt

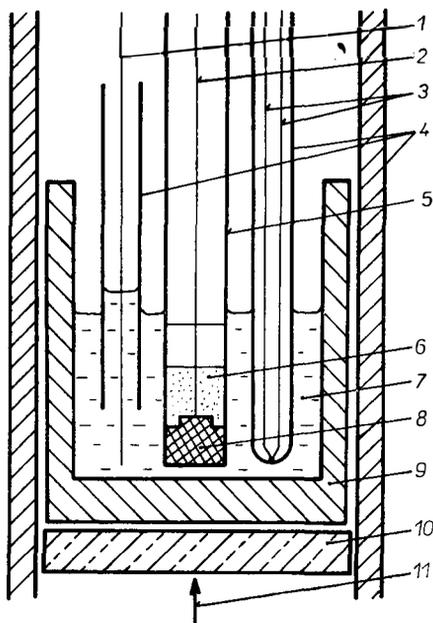


Fig. 1. Measuring apparatus; 1 — iron electrode, 2 — molybdenum wire, 3 — thermocouple, 4 — protective tube of Al_2O_3 , 5 — silica glass tube, 6 — reference mixture, 7 — melt, 8 — solid electrolyte, 9 — iron crucible, 10 — stand of Al_2O_3 , 11 — argon supply.

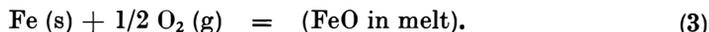
and kept there throughout the experiment. The oxygen electrode was immersed in the liquid just for a certain period of time. The electrode consisted of a solid disk-shaped ZrO_2 (CaO) electrolyte fused in a silica glass tube. The reference medium of a given pO_2 was an Ni—NiO mixture with a molybdenum lead. The immersion of the oxygen electrode resulted in cooling of the melt, so that re-equalization of temperature took about 30 seconds. The equilibrium values of electromotive force were established within 60—240 seconds according to the FeO content. Simultaneous analog recording of EMF and temperature was provided by the Goerz SE 461 recorder having a large input resistance. The reversibility of the electrode reaction was checked by shorting the electrodes, after which the original EMF value was regained within several seconds. The reproducibility of the EMF values in several serial measurements at constant temperature and composition amounted to ± 8 mV. Following concluded measurements, the sample was cooled in argon atmosphere and analyzed bichromatometrically for the content of bivalent and trivalent iron.

RESULTS AND DISCUSSION

The EMF of cell (2) was measured in the system $Na_2O \cdot 3 SiO_2 - x FeO$ 1300, 1350 and 1400 °C respectively.



The FeO content varied from 0.5 to 6 mole %. Reaction (3) proceeded in the cell:



The EMF is given by equation (4)

$$E = E^0 - \frac{RT}{nF} \ln \frac{a(FeO)}{a(Fe) (p(O_2)_{ref}/p^0)^{1/2}}, \quad (4)$$

where E^0 is the standard electromotive force (V), R is the universal gas constant ($J \text{ mole}^{-1} K^{-1}$), T is absolute temperature (K), n is the charge number, F is Faraday's charge (C), $a(FeO)$ is the activity of ferrous oxide (1), $a(Fe)$ is the activity of the metallic electrode (1), $p(O_2)_{ref}$ is the partial pressure on the oxygen electrode (Pa), p^0 is the standard pressure (101,325 Pa).

The activity of FeO was determined from equation (4). The E^0 value was calculated from equation (5) given in the literature [5].

$$E^0 = \frac{1}{2F} (259,408 - 62.50T). \quad (5)$$

The number of electrons exchanged was assumed to be $n = 2$ and the activity of iron metal was considered to be unity.

The partial pressure of oxygen, $p(O_2)_{ref}$ in the reference electrode was determined according to [6] with the use of equation (6)

$$RT \ln \frac{p(O_2)_{ref}}{p^0} = -468,316 + 169.78T. \quad (6)$$

The values of a_{FeO} obtained by measurement are plotted in Fig. 2. At 1300 and 1350 °C, a negative deviation from Raoult's law was found up to $x(\text{FeO}) = 0.06$, and at 1400 °C the system behaved ideally up to $x(\text{FeO}) = 0.04$. These results cannot be compared with data from the literature, because no

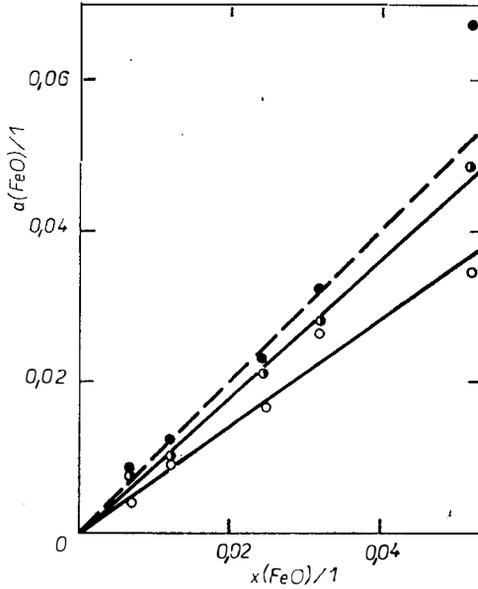


Fig. 2. Activity of FeO vs. molar fraction in the system $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$. The points (○) 1300 °C, (◐) 1350 °C, (●) 1400 °C, — — — ideal solution.

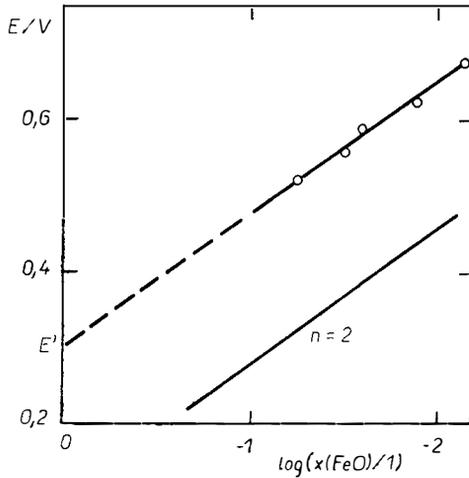


Fig. 3. Electromotive force of the chemical cell vs. the molar fraction of FeO in the system $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$ at 1300 °C.

measurements in this system have so far been published. However, a negative deviation was also found in the system $\text{Na}_2\text{O}-2\text{SiO}_2-x\text{FeO}$ at temperatures up to 1300°C [2, 3].

To assess the correctness of the FeO activity calculation, the assumptions on the cell reaction and the electrode function of the iron electrode, the following analysis of results was carried out. Figs. 3 and 4 show the dependence of EMF on the molar fraction of ferrous oxide at 1300 and 1400°C respectively. The linear course of this relationship allows equation (4) to be used in the form (7) in the determination of n and E^0 on the assumption that the activity coefficient $\gamma(\text{FeO})$ is constant.

$$E = E^0 - 2.303 \frac{RT}{nF} \log \frac{\gamma(\text{FeO})}{(p(\text{O}_2)_{\text{ref}}/p^0)^{1/2}} - 2.303 \frac{RT}{nF} \log x(\text{FeO}). \quad (7)$$

The values obtained were processed by the least squares method to determine the parameters n and E' , where E' are the first two terms on the right-hand side of equation (7). These were used to compute the standard electromotive force E^0 . The results for the temperatures of $1300-1400^\circ\text{C}$ are listed in Table

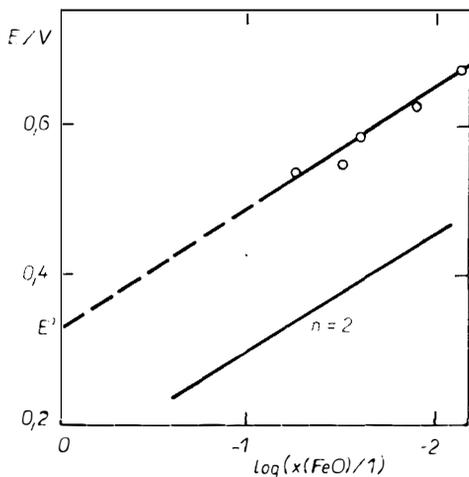


Fig. 4. Electromotive force of the chemical cell vs. molar fraction of FeO in the system $\text{Na}_2\text{O} . 3 \text{SiO}_2 - x\text{FeO}$ at 1400°C .

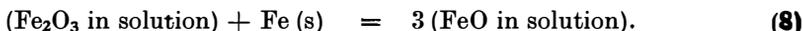
Table I

The values of standard electromotive force and the number of electrons exchanged

Temperature $^\circ\text{C}$	$\frac{E'}{V}$	$\frac{E^0_{\text{exp}}}{V}$	$\frac{n_{\text{exp}}}{1}$	$\frac{E^0_{\text{theor}}}{V}$
1300	0.334	0.832	1.96	0.835
1350	0.337	0.831	2.09	0.819
1400	0.308	0.792	1.91	0.802

I and show a satisfactory agreement of the E^0 values calculated according to equation (5) and the experimental ones. The number of electrons exchanged likewise agrees with the cell reaction assumed.

The reaction between $x(\text{Fe}_2\text{O}_3)$ and $x(\text{FeO})$ in the system measured is given by equation (8):



The equilibrium constant of this reaction is of the order of 10^3 for 1400 °C. It might therefore be assumed that the melt contains solely iron in the second oxidation degree. In our instance, however, the ratio $x(\text{Fe}_2\text{O}_3) / (x(\text{Fe}_2\text{O}_3) + x(\text{FeO}))$, established by chemical analysis of solidified samples, amounts to 0.2. The higher contents of Fe_2O_3 compared to the assumed ones, are obviously due to the small values of $\gamma(\text{Fe}_2\text{O}_3)$ in the melt measured. Insofar as the cooling of the sample would involve distinct changes in the ratio $\text{Fe (III)} / \text{Fe (II)}$, it would not be possible to obtain an agreement of the theoretical and experimental values of E^0 and n .

The results obtained indicate that with the given experimental arrangement, it was explicitly the EMF of the chemical cell that was measured, that the iron electrode was reversible with respect to Fe^{2+} ions and that no mixed potential was created. The experimental arrangement is analogous with the design of the TSO probe for measuring oxygen activity in melted metals. It only differs in the reference mixture employed. The TSO probe can therefore be used in measurements in melted glasses containing FeO .

With respect to practical application, it is possible to consider e.g. measurement in glass melts for the manufacture of container glasses containing iron oxides.

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ELEKTROCHEMICKÉ MĚŘENÍ AKTIVITY OXIDU ŽELEZNATÉHO V TAVENINÁCH $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$

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Práce se zabývá použitím chemických galvanických článků pro měření aktivity složek v oxidových taveninách pomocí experimentálního uspořádání uvedeného na obr. 1.

Byla určena aktivita FeO v tavenině $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$ při teplotách 1300–1400 °C na základě měření EMN článku (2) pomocí vztahu (4). Hodnoty E^0 a $p(\text{O}_2)$ byly určovány ze vztahů (5, 6).

Hodnoty $a(\text{FeO})$ vykazují při teplotách 1300 a 1350 °C negativní odchylku od Raoultova zákona. Při teplotě 1400 °C se systém do $x(\text{FeO}) \cong 0,04$ chová ideálně (obr. 2).

Lineární průběh závislosti EMN na $\log x(\text{FeO})$ umožnil stanovit hodnoty E^0 a n v článkové reakci (3) podle vztahu (7), které jsou v dobré shodě s teoretickými předpoklady. Dosažené výsledky ukázaly, že při těchto měřeních nevzniká smíšený potenciál železné elektrody.

Experimentální uspořádání bylo shodné s konstrukcí sondy TSO používané k měření aktivity kyslíku v roztavených kovech. Existuje zde principiální možnost použití sondy TSO k měření v roztavených sklovinách obsahujících oxidy železa za předpokladu, že výsledky budou interpretovány ve smyslu chemických galvanických článků.

- Obr. 1. Měřicí aparatura — 1 — železná elektroda, 2 — molybdonový drát, 3 — termočlánek, 4 — ochranná trubice z Al_2O_3 , 5 — trubice z křemenného skla, 6 — referenční směs, 7 — tavenina, 8 — tuhý elektrolyt, 9 — železný kelímek, 10 — podstavec z Al_2O_3 , 11 — přívod argonu.
- Obr. 2. Závislost aktivity FeO na molárním zlomku v systému $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$. Body (○) 1 300 °C, (◐) 1 350 °C, (●) 1 400 °C, — — — — ideální roztok.
- Obr. 3. Závislost elektromotorického napětí chemického článku na molárním zlomku FeO v systému $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$ při teplotě 1 300 °C.
- Obr. 4. Závislost elektromotorického napětí chemického článku na molárním zlomku FeO v systému $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$ při teplotě 1 400 °C.

ЭЛЕКТРОХИМИЧЕСКОЕ ИЗМЕРЕНИЕ АКТИВНОСТИ ОКСИДА ДВУХВАЛЕНТНОГО ЖЕЛЕЗА В РАСПЛАВАХ $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x \text{FeO}$

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Предлагаемая работа занимается использованием химических гальванических элементов для измерения активности компонентов в расплавах оксидов с помощью экспериментального упорядочения, приводимого на рис. 1.

Определили активность FeO в расплаве $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x\text{FeO}$ при температурах 1 300—1 400 °C на основании измерения EMN элемента (2) с помощью отношения (4). Величины E^0 и $p(\text{O}_2)$ выводили из отношений (5, 6).

Величины a (FeO) при температурах 1 300 и 1 350 °C имеют отрицательное отклонение от закона Рауля. При температуре 1 400 °C система до $x(\text{FeO}) = 0,04$ ведет себя идеально (рис. 2).

Линейный ход зависимости EMN от $\log x(\text{FeO})$ предоставляет возможность определить величины E^0 и n в реакции элемента (3) согласно отношению (7), находящиеся в хорошем согласии с теоретическими предположениями. Полученные результаты показали, что при данных измерениях не возникает смешанный потенциал железного электрода. Экспериментальное упорядочение совпадало с конструкцией зонда TSO, применяемого для измерения активности кислорода в расплавленных металлах. Предоставляется принципиальная возможность использования зонда TSO для измерений, проводимых в расплавленных стекломассах, содержащих оксиды железа при предположении, что результаты будут объясняться в смысле химических гальванических элементов.

Рис. 1. Измерительная аппаратура; 1 — железный электрод, 2 — молибденовая проволока, 3 — термоэлемент, 4 — защитная трубка из Al_2O_3 , 5 — трубка из кварцевого стекла, 6 — референцирующая смесь, 7 — расплав, 8 — твердый электролит, 9 — железный тигель, 10 — подставка из Al_2O_3 , 11 — подача аргона.

Рис. 2. Зависимость активности FeO от молярной доли в системе $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x \text{FeO}$: ○ — 1 300 °C, ◐ — 1 350 °C, ● — 1 400 °C, — — — — идеальный раствор.

Рис. 3. Зависимость электродвижущего напряжения химического элемента от молярной доли FeO в системе $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x \text{FeO}$ при температуре 1 300 °C.

Рис. 4. Зависимость электродвижущего напряжения химического элемента от молярной доли FeO в системе $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2 - x \text{FeO}$ при температуре 1 400 °C.