ELECTRICAL CONDUCTIVITY OF MELTS IN THE SYSTEM Fe₂O₃-FeO-CaO

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ABSTRACT

The paper discusses the mechanism of the electrical conductivity of the slags consisting of Fe₂O₃, FeO and CaO. From the experimental results the contributions of individual ionic species and of electrons to the overall transfer of charge were determined. The ionic component of the conductivity has been considered and discussed in terms of the assumed structure of the melt. The discussion of the electronic conductivity is carried out from the point of view of the mechanism of exchange of electrons between Fe²⁺ and Fe³⁺ cations.

INTRODUCTION

As a result of an increasing interest in the possibility of the application of the calcium-ferrite slags in pyrometallurgical extraction processes it has become necessary to know their physical properties and to better understand the structure of this unconventional type of slag. The electrical conductivity of the conventional electrolytic melts is very sensitive to their structure. The conductivity depends on the amount of the charge carriers present in the melt and on their mobilities. It is well known that in the melts of oxides the transfer of charge is carried out exclusively by simple cations (e.g. Na⁺, K⁺, Ca²⁺ etc.) Other cations (e.g. Si⁴⁺, P⁵⁺, B³⁺) create long structural units that have extremely low mobility. Oxides of amphoteric metals (e.g. Al³⁺, Fe³⁺) may behave either as network formers or as network modifiers. Their participation in the transfer of charge in the melt depends on the type of their behaviour. Slag systems containing polyvalent metals in two different valency states (e.g. Fe²⁺ and Fe³⁺ or Bi⁺ and Bi³⁺) exhibit also an electronic conductance. This is the reason why it is virtually impossible to arrive at any definite conclusion concerning their structure in
the molten state simply on the basic of experimentally de-
termined electrical conductivities.

In an attempt to describe the mechanism of the electronic conductivity two different approaches have been used. The first is based on the band theory of electronic structure. Due to the disturbances in the stoichiometry of a chemical compound free electrons appear in a conductive band or va-
cancies are being created in a valency band. In the case
of the slag system investigated in this work this theory has only limited validity as it can describe the behaviour of the slag at the extremely high or extremely low oxygen potentials. Moreover, the band theory is based on the per-
riodicity of a lattice potential which implies the existen-
ce of a longe-range order in a solid. When the solid melts, band boundaries become distorted and broadened and new energy levels may appear in the so far forbidden zones which is why it is virtually impossible to find an analy-
tical expression for the description of the electrical conductivity (1).

The melts investigated in this paper behave in accordance with the polaron theory according to which electrons and electron holes are localized on the ions. Electronic con-
ductivity of the melts is direct consequence of the jump of an electron from a cation in its lower valency state to the one in the higher one. The exchange of electrons may occur between cations with different valencies and the electrons can be exchanged at appreciably high frequencies even in the case that the distance between the pair of ions between which the electron is being exchanged is several times longer than the atomic radius, particularly when the bridging groups are present in the melt (2).

The objective of this investigation was to assess the con-
tribution of individual ions and electrons to the transfer of charge in the melt, to find a correlation between the structure of the melt and its ionic conductivity and, last but not least, to verify the applicability of the jumping electron model of the electronic conductivity to the melts of the Fe2O3-FeO-CaO system.

**EXPERIMENTAL**

As the calcium ferritic slags are highly corrosive with respect to the refractory oxides and alloys of the metals of platinum group and also because the composition of the melt was strongly dependent on temperature and oxygen po-
tential, the electric conductivity measurements were rat-
er elaborate. The final version of the experimental as-
sembly and the range of temperatures that have been finally adopted should therefore be considered as a compromise between what was available in terms of equipment and what was necessary from the point of view of what we intended to achieve.

A bridge circuit method was used for measurements. The simplified schematic diagram of the circuit is depicted in Fig 1. The most important unit of the circuit was the RCL radio-frequency Wayne-Kerr bridge. Two platinum electrodes 2 mm in diameter situated 12 mm apart were used. The melt was held in platinum or magnesia under purified nitrogen at temperatures between 1550-1600 K. The composition of the furnace gas was monitored by using gas chromatography. Samples of melts were quenched and chemically analysed for Fe$^{2+}$ and Fe$^{3+}$ contents, other constituents of the slag were analysed by Atomic absorption spectrometer.

RESULTS

The chemical composition of the melts and the corresponding results of their electrical conductivities are summarized in Tab.1.

Table 1: Chemical analysis and specific conductivity in the Fe$_2$O$_3$-FeO-CaO system at 1573 K

| Chemical analysis (mol.%) | specific conductivity (S.m$^{-1}$) |
|---------------------------|----------------------------------|
| FeO | Fe$_2$O$_3$ | CaO | total | reg | tun |
| 52.12 | 18.43 | 27.8 | 2440 | 2250 | 1927 |
| 54.47 | 21.52 | 22.21 | 2505 | 2326 | 2689 |
| 26.31 | 22.96 | 50.71 | 1591 | 1436 | 1475 |
| 25.02 | 20.04 | 46.12 | 1651 | 1512 | 1267 |
| 20.36 | 29.39 | 50.24 | 1479 | 1347 | 834 |
| 18.72 | 33.81 | 47.46 | 1442 | 1324 | 659 |
| 11.92 | 40.30 | 47.77 | 1022 | 923 | 330 |
| 49.01 | 16.19 | 33.63 | 2194 | 1997 | 2068 |
| 49.88 | 15.82 | 33.15 | 2252 | 2053 | 1972 |
| 52.21 | 15.07 | 31.42 | 2425 | 2221 | 1889 |
| 6.85 | 43.72 | 45.3 | 686 | 602 | 143 |
| 6.74 | 49.33 | 43.91 | 680 | 604 | 145 |
| 56.45 | 19.08 | 24.45 | 2537 | 2346 | 2482 |
| 23.35 | 33.89 | 42.75 | 1727 | 1606 | 972 |
| 7.96 | 45.09 | 46.93 | 812 | 726 | 183 |
| 30.74 | 24.78 | 44.46 | 1777 | 1625 | 1724 |
| 26.11 | 29.83 | 44.04 | 1648 | 1515 | 1404 |

205
The variation of the conductivity of the melt with the composition can be fitted to the following equation:

\[ \mathcal{K} = \sum_{i=1}^{n} z_i \cdot F \cdot u_i \cdot c_i \]  

(1)

where \( c_i \) is the concentration of the conductive particles having the charge \( z_i \), \( u_i \) is the mobility and \( F \) Faraday's constant.

Concentrations of individual ionic species were determined from the results of the density measurements and calculated as the ratio of molar fraction and molar volume. The number of electrons that participated in the transfer of charge in the melt was estimated on the basis of assumption that an electron may jump from \( \text{Fe}^{2+} \) ion as long as the \( \text{Fe}^{3+} \) ion is present (3). The concentration of cations in the melt can be calculated from the relation:

\[ C(e^-) = 2 \cdot X_{\text{Fe}_2\text{O}_3} \cdot X_{\text{FeO}} / V_m \]  

(2)

We used multiple regression method for the determination of the coefficients of the following equation:

\[ \mathcal{K} = - A + B_1 \cdot C \text{ (Ca}^{2+}) + B_2 \cdot C \text{ (Fe}^{2+}) + B_3 \cdot C \text{ (Fe}^{3+}) + B_4 \cdot C \text{ (O}^2-) + B_5 \cdot C \text{ (e}^-) \]  

(3)

Best correlations were obtained on the assumption that \( \text{Ca}^{2+} \), \( \text{Fe}^{2+} \) and \( e^- \) were the only species that participated in the transfer of charge. The mobilities of the charge transferring species were calculated from the coefficients \( B_i (u = B_i / z_i F) \) and the diffusion coefficients calculated from the Nernst/Einstein's equation. The results are summarized in Tab.2.

Table 2: Regression coefficients, mobilities and diffusion coefficients of the particles \( \text{Ca}^{2+}, \text{Fe}^{2+} \) and \( e^- \) in the \( \text{Fe}_2\text{O}_3-\text{FeO}-\text{CaO} \) system at 1573 K

| Parameter | \( \text{Ca}^{2+} \) | \( \text{Fe}^{2+} \) | \( e^- \) |
|-----------|------------------|------------------|-------|
| \( B \) S.m\(^2\).mol\(^{-1}\) | 3.6369.10\(^{-3}\) | 5.8252.10\(^{-3}\) | 0.2739 |
| \( u.10^8 \) m\(^2\).s\(^{-1}\).V\(^{-1}\) | 1,88 | 3,02 | 283.9 |
| \( D.10^9 \) m\(^2\).s\(^{-1}\) | 1,3 | 2,1 | 384,8 |

206
DISCUSSION

The magnitudes of the calculated coefficients of the equation (3) allow us to assume that Ca2+, Fe2+ ions and electrons have the highest contributions to the transfer of charge. The size of O2- ion is relatively large hence it exhibits low mobility. Statistical insignificance of the coefficients B2 of equation (3) stems from tendency of Fe2+ cation to create larger structural units which can be represented by the general formula FeXOYz-. This property depends on the magnitude of the ratio Fe3+/O2-. Any increase in the concentration of O2- anion in the melt brings about a gradual change in the coordination number of the Fe2+ ion which can be represented in a following manner:

\[ \text{Fe}^{3+} \rightarrow \text{FeO}^+ \rightarrow \text{FeO}^-_2 \rightarrow \text{Fe}_2\text{O}_3^- \rightarrow \text{Fe}_2\text{O}_4^- \]

This assumption has been indirectly confirmed at our laboratory by the result obtained from the density viscosity and surface tension measurements. Mobilities of large ferrite anions are small and the contribution of Fe3+ ion to the overall conductivity is insignificant. Mobilities of Ca2+ and Fe2+ cations are very similar and their diffusion coefficients are higher than in the silicate melts. These conclusions are in a good agreement with low viscosities that were measured in calcium ferrite slags. To our surprise, both the mobility and the diffusion coefficient of Fe2+ cation exceed those of Ca2+ cation.

The mobility of electrons is by two orders of magnitudes higher than the mobility of any other charge transferring specie. For this reason the electronic conductivity may greatly exceed the contribution of ions to the overall conductivity. The magnitude of the electronic component of conductivity depends however on the concentration of Fe2+, Fe3+ ion in the melt. According to the electron jumping model (1), the frequency of an electron jump may be expressed in the following manner:

\[ \nu_r = \frac{ue \cdot 6 \cdot kT}{(e \cdot r^2)} \]

where \( e \) is the charge of an electron, \( u_e \) the mobility of electron, \( r \) the distance between Fe2+ and Fe3+ cations, \( k \) the Boltzmann constant, \( T \) temperature.

The applicability of this model has been tested by calculating the frequency of electron jump from the experimentally determined conductivities and by comparison with the results calculated from the theory. The frequencies determined from the experiments were expressed as the ratio \( \kappa \cdot F \cdot C(e^-) \) whe-
re as the electronic conductivities were determined after subtracting ionic portion of conductivity from the overall conductivity and applying the regression coefficients from equation (3).

The fact that the plot \( \log \gamma \) vs \( r \) is linear (Fig. 2) is in accord with the electron jump model. The slope of the line corresponds to the effective potential energy barrier of the exchange of one electron between the ions. If \( \mathcal{L} = 0.25 \times 10^{-10} \) m\(^{-1}\) is substituted to the equation (7) which assumes the transfer of an electron by its tunneling through the effective energy barrier

\[
\mathcal{L} = \left( \frac{2 m_e}{H} \right)^{1/2}
\]

where \( m_e \) is the mass of an electron, \( H \) is the height of the energy barrier, \( \hbar = h/2\pi \) and \( h \) is the Planck’s constant.

The calculated value of \( H \) is equal to 0.3 eV and its magnitude is similar to 0.375 eV found in wustite on the basis of quantum theory approach (4).

Mott (3) expressed the electronic conductivity in the melts that consisted of transition metals in the following manner:

\[
\kappa = \frac{\nu X(1-x) \cdot f^2/(R \cdot T \cdot N \cdot r) \cdot \exp(-2 \cdot r) \cdot \exp(-W/RT)}{\exp(-W/RT)}
\]

where \( \nu \) is the phonon frequency, \( X, (1-X) \) are the mole fractions of the two valency states of a metal and \( W \) is the activation energy. The electronic conductivities calculated from the Mott’s model were then compared with the electronic conductivities calculated as a product:

\[
\kappa = B_5 \cdot c (e^-)
\]

Satisfactory agreement has been found between the results calculated by two methods. The existing discrepancies may have been caused by the fact that the term \( \exp(-W/RT) \) in equation (8) was approximate. Nevertheless one can assume that the activation energy of the electronic conductivity is small in system rich in Fe\(_2\)O\(_3\) (Fig. 3).

CONCLUSION

In oxidic melts comprising Fe\(_2\)O\(_3\), FeO and CaO, Fe\(^{2+}\), Ca\(^{2+}\) and free electrons have been found to be the main carriers of the charge. Fe\(^{3+}\) cations may create the ferrite anions that do not participate in the transfer of charge. Mobilities of electrons are by two orders of magnitudes higher than those of cations. Electronic conductivity occurs through the exchange of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) ions. According to quantum theory tunneling phenomenon, the
height of an effective potential energy barrier is lower than 0.5 eV. We have found satisfactory agreement between the electronic conductivity calculated on the basis of the electron jump model and the one determined from the regression analysis.

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Figure 1. Schematic diagram of the measuring circuit
1- RCL bridge 2- oscilloscope 3- high-frequency generator 4- electrode 5- electrical furnace

Figure 2. Log calculated jump frequency vs average exchange pair separation

Figure 3. Electronic conductivity calculated according to Mott's model and regression analysis