The Viscosities and Electrical Conductivities of Slags Associated with the Production of High-carbon Ferromanganese Alloys

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SYNOPSIS

Viscosities and electrical conductivities of the five-component system SiO_2—Al_2O_3—CaO—MgO—MnO at 10 mole per cent Al_2O_3 were measured. The compositions (calculated on a mole per cent basis) investigated were similar to those of slags associated with the production of high-carbon ferromanganese alloys.

The SiO_2 content was found to play a major role in determining the magnitude of both properties investigated. Of the basic oxides involved, MnO has the greatest potential for decreasing the viscosity and increasing the electrical conductivity. MgO displays a somewhat variable, but less significant, influence on both these properties.

The results, presented as pseudo-ternary sections at 1500°C, permit prediction of the effect of changes in composition on the viscosities and electrical conductivities of the slags.

INTRODUCTION

This paper describes a contribution to the physicochemical data for the oxide system characteristic of slags associated with the production of high-carbon ferromanganese alloys, i.e., the system SiO_2—Al_2O_3—CaO—MgO—MnO. This type of study is consistent with a trend in technologically oriented research that is receiving increasingly widespread attention in the metallurgical industry and that shows an awareness of the need for a greater use of fundamental metallurgical and electrometallurgical data in furnace technology[1]. The particular properties studied in the work described here were viscosity and electrical conductivity.

A substantial amount of work has been published in the area of immediate interest[2-10]. However, most of these reports considered compositions low in alumina (0 to 10 per cent by mass). Some interest has been shown in slags with higher Al_2O_3 contents[10-12], for which there are considerably less data available. The system with an Al_2O_3 content of 10 mole per cent (approximately 16 per cent by mass) was therefore selected for study. The compositions chosen (Table 1) typically represented high-carbon ferromanganese discard slags produced both in the blast furnace and in the electric smelting furnace. Compositions bordering those common to enriched slags were also included in this study. Unless otherwise stated, compositions mentioned in this paper are expressed in mole per cent.

GENERAL TECHNIQUE

It is well known that manganese possesses different oxidation states. The oxide that occurs in the final slags during high-carbon ferromanganese production is stoichiometric MnO, i.e., manganese in its divalent state. The first priority in the present work was therefore to ensure that the manganese in the melt was in this divalent state during physicochemical measurements. Of the various ways that have been used to achieve this, reduction of the melt initially containing manganese in both divalent and trivalent states was chosen. The reducing atmosphere used was a mixture of about 5 per cent hydrogen with high-purity nitrogen, and the procedure adopted was as follows.

Manganese was introduced in the form of analytically pure MnO_2. The other oxides were also of analytical grade and had previously been preheated at 1000°C to remove traces of absorbed moisture and carbon dioxide. The total mass of MnO and the other oxide components in each sample was 200 grams. The sample was premelted under atmospheric conditions, during which the MnO_2 decomposed thermally, liberating much of its oxygen. (For the more viscous melts, this oxygen evolution produced uncontrollable foaming, and pure MnO was therefore used instead of MnO_2. The MnO was produced by the reduction of MnO_2 with pure hydrogen at 1000°C.) After the melt had been equilibrated at about 1500°C for one hour, the manganese was present as a mixture of Mn_3O_4 and MnO[13]. The melt was then removed from the premelt furnace and allowed to cool. The final reduction of the trivalent manganese to its divalent state was effected immediately before the measurement of the viscosities and electrical conductivities, which was done after the melt had again been equilibrated at between 1450 and 1500°C. The hydrogen—nitrogen mixture was passed over the melt for 1½ hours. Thereafter, and during the measurements, the hydrogen content of the gas atmosphere was reduced to less than 1 per cent, which was sufficient to ensure that no reoxidation of the manganese ion occurred. Attack of the platinum crucible by the melt under these conditions was not significant.

So that this reduction procedure would not have to be used twice for each sample, equipment was designed to enable measurements of viscosity and electrical conductivity to be done consecutively. The apparatus consisted of a solid, upright post on which two independent collars could move vertically. The lower collar supported the crucible support, the crucible, and the gas-seal apparatus, and the upper collar supported the turret on which the viscometer, the electrodes, and a sampling device were mounted. The turret could swing in a horizontal plane and locate in three different positions, each of which brought one of the measuring devices vertically above the crucible. The mountings of these devices allowed horizontal adjustment so that the measuring probes (viscometer spindle, electrodes, and sampling rod) could be carefully aligned with the crucible. Vertical movement of the viscometer and electrodes on the turret was effected by means of rack-and-pinion devices, and the positions were indicated on vernier scales.

A vertical, molybdenum-wound resistance furnace was mounted on rails so that it could move into and out of the working position. The temperature was measured with a

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Pt—6%Rh/Pt—30%Rh thermocouple in an impervious alumina sheath with an accuracy of ± 10°C.

With the furnace out of the working position, each measuring probe was carefully aligned with the crucible. Upper and lower collars were then moved so that the furnace could be pushed into position. The crucible was introduced into the furnace, and the reducing cycle just described was performed. After the hydrogen content of the gas atmosphere had been diminished, the electrodes were introduced into the top of the furnace, and the slag level was established by the point on the vernier scale at which the slag just bridged the electrodes and completed an electric circuit. The electrodes were then immersed 8mm in the slag, and the resistance was measured at intervals of 20 to 30°C from about 1550°C to a temperature sufficiently low to indicate liquidus (see later). Thirty to forty minutes were allowed for equilibration at each temperature, and measurements were made in both a cooling and a heating cycle.

After the electrodes had been removed from the furnace, the turret was relocated so that the viscometer was brought into position. The viscometer spindle was introduced into the furnace and immersed in the slag to a depth of 3,75cm. The viscosity was then measured at 20 to 30° intervals during both a heating and a cooling cycle for the same temperature range as that covered in the resistance measurements. As before, equilibration for 30 to 40 minutes at each temperature was allowed. After the viscosity run, a slag sample was taken with a copper chill-rod. Analysis showed that the Mn^{3+} content in all samples was negligible.*

VISCOSITY

Experimental Method

The technique of a rotating inner cylinder was used for the measurement of viscosity. The inner cylinder was a hollow platinum spindle, 2,6 cm in height and 1,6 cm in diameter, that was attached to a spindle shaft made partly of platinum and partly of Inconel tubing. The spindle shaft was 55 cm long and was suspended from the viscometer by a hook. The crucible, in which the sample produced a melt depth of about 5,7 cm, formed the stationary outer cylinder. It was made of pure platinum, and was 7,62 cm in height and 3,81 cm in diameter.

The instrument used was a Brookfield Synchroelectric viscometer[15]. The spindle, suspended from the viscometer, was driven through a copper helical spring by a variable-speed synchronous motor. The spring was attached to a pointer that moved over a scale. Viscous drag on the inner cylinder (or spindle) created a torque that produced a restoring torque in the spring. When the two opposing torques were equalized, the position of the pointer on the scale gave a measure of the viscosity.

The instrument was calibrated at normal temperatures by the use of standard oils supplied by the Cannon Instrument Company. A brass crucible and spindle were constructed according to the respective dimensions that the platinum crucible and spindle would have at 1400°C.

Table 1

Measurement of viscosity

Slag no.	Composition, mole %					Viscosity, N s/m²		Conductivity, S/m		Approx. liquidus temperature °C
	MnO	Al_2O_3	SiO_2	CaO	MgO	*A*	*B*x10^{-4}	*C*	*D*x10^{-4}	
D1	26,60	10,00	27,00	15,40	21,00	−11,24	1,59	11,12	1,16	1457
D2	24,49	10,00	32,00	14,18	19,33	−12,96	1,95	12,01	1,36	1383
D3	22,38	10,00	37,00	12,96	17,67	−13,65	2,16	10,26	1,11	1435
E1	31,03	10,00	27,00	17,97	14,00	−11,34	1,60	10,77	1,10	1458
E2	28,57	10,00	32,00	16,54	12,89	−11,37	1,66	11,75	1,29	(1330)
E3	26,11	10,00	37,00	15,11	11,78	−12,60	1,95	13,34	1,63	1291
F1	35,47	10,00	27,00	20,53	7,00	−11,72	1,66	9,64	0,88	1455
F2	32,65	10,00	32,00	18,90	6,44	−11,10	1,62	10,86	1,16	1434
F3	29,84	10,00	37,00	17,27	5,89	−13,50	2,11	12,26	1,44	1353
G1	16,33	10,00	27,00	25,67	21,00	−12,34	1,83	11,90	1,34	1446
G2	15,04	10,00	32,00	23,63	19,33	−12,67	1,94	10,86	1,20	1416
G3	13,74	10,00	37,00	21,59	17,67	−13,85	2,22	15,18	1,99	1390
H1	19,06	10,00	27,00	29,94	14,00	−11,94	1,75	10,86	1,15	1457
H2	17,54	10,00	32,00	27,57	12,89	−12,62	1,94	12,31	1,45	1448
H3	16,03	10,00	37,00	25,19	11,78	−14,54	2,33	12,98	1,62	1357
I1	21,78	10,00	27,00	34,22	7,00	−12,38	1,83	11,56	1,30	1441
I2	20,05	10,00	32,00	31,51	6,44	−11,29	1,71	11,95	1,39	1449
I3	18,32	10,00	37,00	28,79	5,89	−13,73	2,18	11,84	1,41	1384
J1	7,93	10,00	27,00	34,07	21,00	−12,07	1,80	12,01	1,38	1425
J2	7,30	10,00	32,00	31,36	19,33	−12,04	1,86	10,36	1,11	1457
J3	6,67	10,00	37,00	28,66	17,67	−14,68	2,38	14,94	1,97	(1300)
K1	9,26	10,00	27,00	39,74	14,00	−13,18	2,01	11,85	1,36	1408
K2	8,52	10,00	32,00	36,59	12,89	−13,44	2,10	11,72	1,38	1466
K3	7,79	10,00	37,00	33,44	11,78	−12,25	1,96	13,38	1,72	1397
L1	10,58	10,00	27,00	45,42	7,00	−10,94	1,60	11,68	1,34	(1450)
L2	9,74	10,00	32,00	41,82	6,44	−12,66	1,97	11,80	1,42	1480
L3	8,90	10,00	37,00	38,21	5,89	−12,81	2,05	11,78	1,44	1475

*The analytical technique used was that of Glasser[14] with a few minor modifications.

Detailed measurements were made to determine the optimum position of the inner cylinder with respect to the outer cylinder and the depth of slag. It is estimated that the viscosity values quoted are accurate to within 10 per cent.

Results and Discussions

The results are presented in Table 1 according to the Arrhenius relation

$$\ln \text{ visc (N s/m}^2) = A + B/T, \qquad (1)$$

and as contours of equal viscosity on pseudo-ternary sections at 1500°C in Figures 1 and 2. T is the absolute temperature. The values of the constants A and B were obtained by a least-squares line-fitting procedure.

Silica was found to exert the major influence on viscosity. Thus, the viscosity is increased as the SiO_2 content increases at a constant ratio of the basic oxide components MnO, MgO, and CaO. Further, at any particular CaO-to-MnO ratio, the viscosity is dependent primarily on the silica content, the proportion of MgO showing only a minor influence (Figure 1).

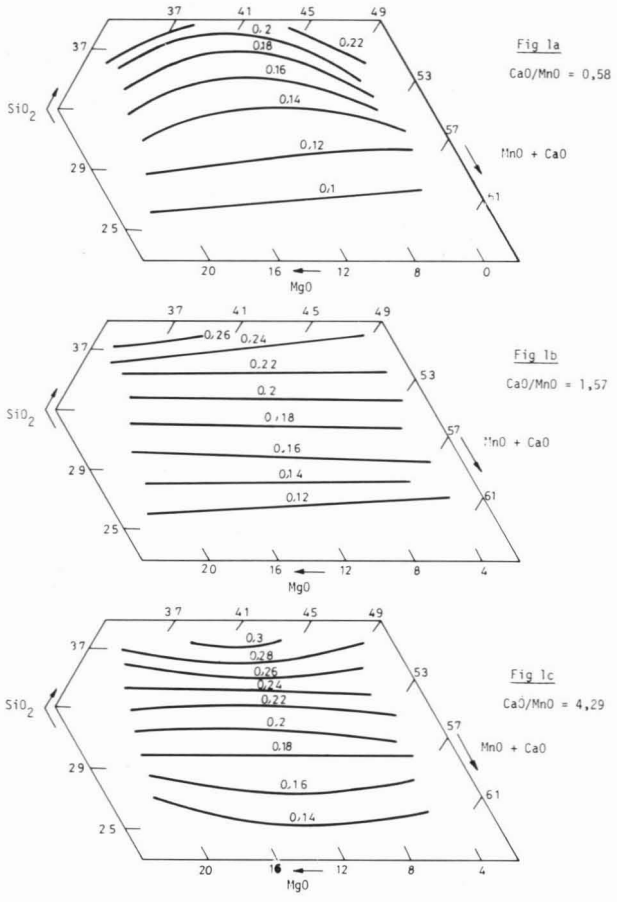

Figure 1

Viscosities (N s/m²) at 1500°C in the system SiO_2—MgO—MnO—CaO at 10 per cent Al_2O_3

A direct comparison of the viscosity-reducing effects of the three basic oxides is afforded by Figure 2, which shows pseudo-ternary sections at different SiO_2 levels. MnO is seen to display the greatest potential for reducing the viscosity of these melts. Thus, an increase in the MnO content decreases the viscosity at all the SiO_2 and MgO levels investigated.

The effect of MgO on the viscosity is variable. At 27 per cent SiO_2 an increase in the MgO content at constant ratios of CaO to MnO in most instances increases the viscosity, although the reverse is seen to occur if MgO is

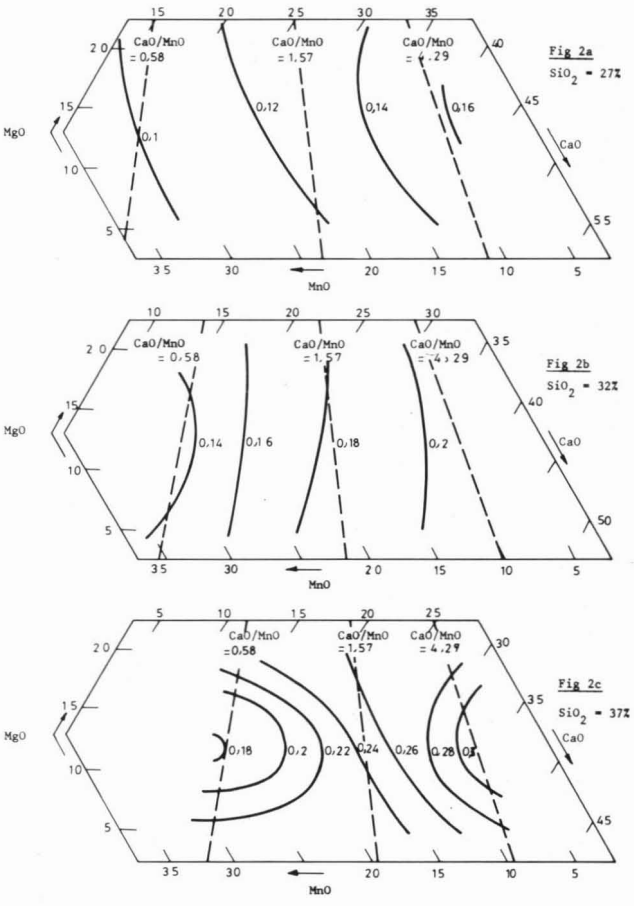

Figure 2

Viscosities (N s/m²) at 1500°C in the system SiO_2—MgO—MnO—CaO at 10 per cent Al_2O_3

substituted for CaO at constant levels of MnO. At 32 per cent SiO_2, increases in MgO content decrease the viscosity when either the MnO content or the CaO-to-MnO ratio is held constant. At 37 per cent SiO_2, the influence of MgO depends on the MnO content. At low MnO levels, an increase in the proportion of MgO increases the viscosity to a maximum and then decreases it, whereas, at high levels of MnO, the viscosity passes through a minimum as the MgO content increases. Replotting the data on a mass per cent basis clearly demonstrates that the replacement of CaO by MgO is accompanied by a more significant decrease in viscosity than is apparent on a mole per cent basis.

The results are broadly consistent with established ideas on the structure of molten silicate systems. The basic concept of these ideas is the polymerization —depolymerization reaction

$$\text{—Si—O—Si—} + O^{2-} \rightleftharpoons 2\text{—Si—O} \qquad (2)$$

The reaction shows that an increase in the concentration of O^{2-} ions (derived from the basic oxides) will lead to a breakdown of silicate structure. If this 'structure' is regarded as a system of polyanions, breakdown of the structure implies that the average size of the polyanions decreases, which would be expected to decrease the viscosity. Expression (2) suggests that the extent of the breakdown of the silicate structure would be determined primarily by the proportion of O^{2-} and silica in the melt. It is not surprising, therefore, that the silica content plays a dominant role in determining the viscosity of the melts studied. Present theory cannot successfully predict in detail, even for relatively simple systems, how the type of basic cation will affect the viscosity.

ELECTRICAL CONDUCTIVITY

Experimental Method

Parallel dipping electrodes were used in the measurement of electrical conductivity. The electrodes were made of platinum rod 2 mm in diameter, and their separation was 10 mm between centres. The electrical conductivity of a melt was established by measurement of the resistance, R, between the electrodes immersed 8 mm in the melt. The resistance is inversely proportional to the electrical conductivity, K. The constant of proportionality, G, is known as the cell constant and is characterized by the cell geometry. Thus,

$$R = G/K. \qquad (3)$$

The value of G for the cell used was established by measurement, in the cell, of the resistance of aqueous sodium and potassium chloride solutions whose electrical conductivities were known. For these calibrations, resistance was measured by use of an a.c. bridge.

Recent development work[16] at the National Institute for Metallurgy has shown that a more elegant technique than the a.c. bridge is available for the measurement of the electrical resistances of slags. In addition to providing a continuous readout of the cell impedance, it achieves high-precision measurement of low impedances. A 10 kHz oscillator impresses a steady a.c. voltage in the cell circuit by means of an input coil. The current that flows in the cell circuit is therefore dependent on the impedance of the circuit. This current is monitored through a second coil by a detector circuit that gives a continuous voltage readout. For slags containing MnO in appreciable quantities (more than 7 per cent), conduction is purely resistive. The cell impedance, therefore, was also purely resistive and was obtained by calibration of the voltage readout against a standard resistance box. The melt resistance was then calculated by subtraction, from the measured resistance, of the lead resistance, which had previously been determined as a function of furnace temperature. The values quoted are considered to be accurate to within 10 per cent.

Results and Discussion

The results are presented in Table 1 according to the Arrhenius relation

$$\ln \text{conduct (S/m)} = C - D/T, \qquad (4)$$

and as contours of equal conductivity of pseudo-ternary sections at 1500°C in Figures 3 and 4. The values of the constants C and D were obtained by the use of a least-squares line-fitting procedure. An increase in the silica content leads to a decrease in conductivity. As it is generally recognized that conduction in slags is predominantly cationic, it is not surprising to find that the type of basic cation in a melt plays a more important role in the conduction process than it did in viscous flow. Increases in MnO contents increased the conductivity in much the same way as they decreased the viscosity (i.e., almost linearly in many instances). At SiO_2 contents of 27 and 32 per cent, an increase in the MgO content increases the conductivity to a maximum and then decreases it. The reverse occurs at an SiO_2 content of 37 per cent. In addition, the influence of MgO in increasing the conductivity becomes more significant as the CaO-to-MnO ratio increases.

A more extensive examination of the conductivity of these melts is limited by the lack of data on transport numbers. This is particularly important in view of the

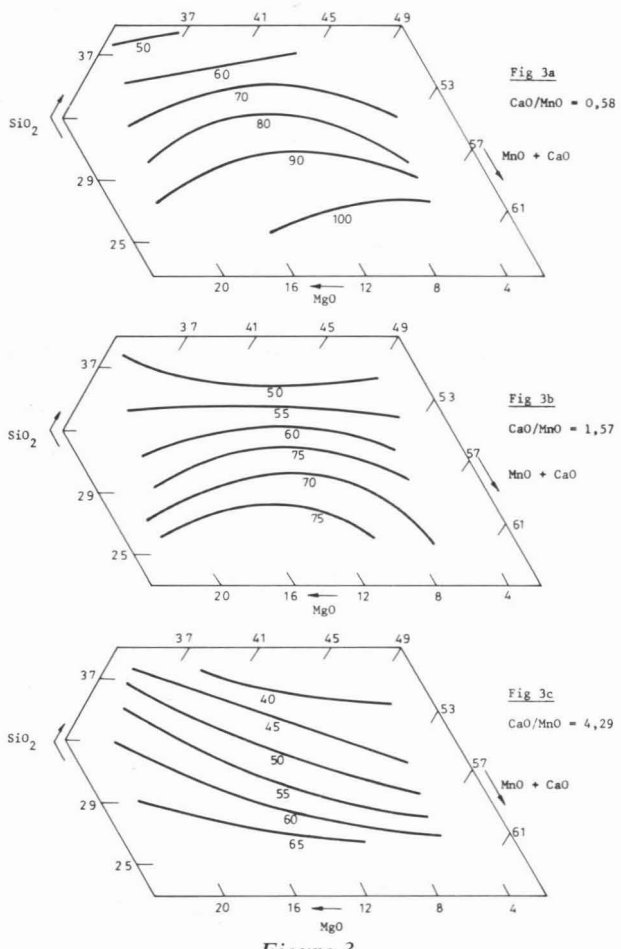

Figure 3

Electrical conductivities (S/m) at 1500°C in the system SiO_2—MgO—MnO—CaO at 10 per cent Al_2O_3

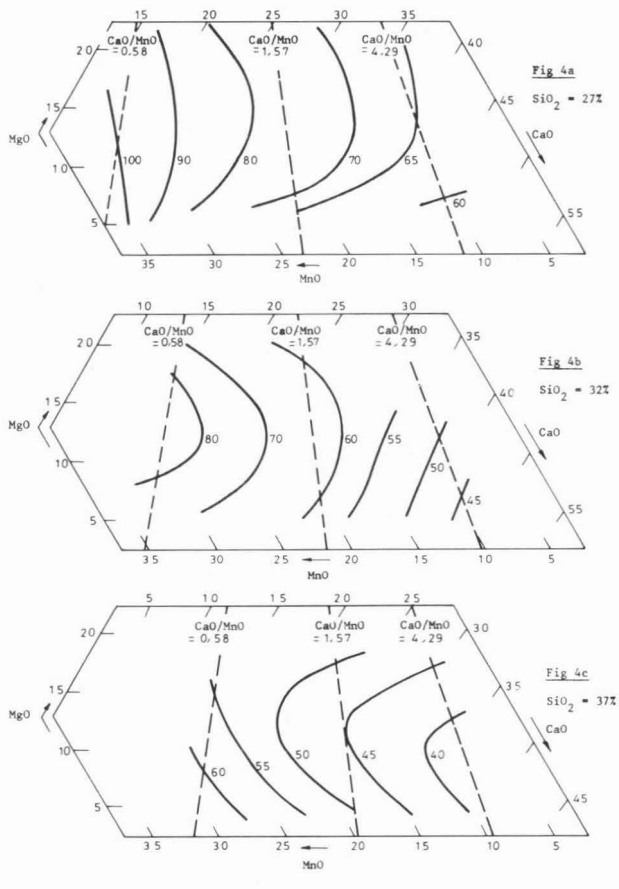

Figure 4

Electrical conductivities (S/m) at 1500°C in the system SiO_2—MgO—MnO—CaO at 10 per cent Al_2O_3

probability that conduction in these melts is partially electronic. Derge and his co-workers[17-19] have investigated this possibility in a quantitative manner and have shown that it does in fact occur in melts containing ions of the transition metals iron and manganese. Because of the greater conductivity associated with electronic conduction, the nearly linear increase in conductivity with increasing MnO content supports, to a degree, the contention that electronic conduction occurs in the melts studied. Stronger support for this view can be obtained from the observation of the purely resistive nature of the conduction process in these melts, as opposed to a reactive nature for many silicate melts that do not contain transition metal ions[1,20,21]. The reactive component of the melt impedance in the latter melts is normally explained as being capacitative and originating partly from the nature of the electrode—melt interface and partly from the dielectric nature of the bulk of the melt. In both cases the capacitance is described as being derived from the 'polar' nature of the constituents of a silicate melt and from the alignment of these constituents in an alternating field. Johnson[1] has suggested that an average separation of the cationic and large anionic species in a silicate system can be considered to function as a polar system:

$$Mn^{2+} \rightleftharpoons Mn^{3+} + e. \qquad (5)$$

If electronic motion through the agency of a reaction similar to that shown above can occur in a melt, the relaxation time for adjustment of the internal to the external electric field will be significantly shorter than in an equivalent system in which no electronic conduction can occur. This, accompanied by the faster rate of transfer of charge across the electrode—melt interface that reaction (5) would yield, would lead to a very much less significant reactive component of the melt impedance.

APPROXIMATE LIQUIDUS TEMPERATURES

The precipitation of solid matter as well as the resultant change in composition of the melt would affect the measured viscosity or electrical conductivity of that melt. The effect takes the form of a change of slope in an Arrhenius plot. The temperature at which a change of slope occurs can therefore provide an estimate of the liquidus temperature. (It should be noted that deviation from Arrhenius behaviour would also produce a change of slope.) Such estimates are approximate, and this is particularly evident when the possible effects of supercooling on this estimate are considered. The liquidus temperatures derived in this manner are presented in Table 1. Correlation of these values with those of Warren[12] and Osborne[22] indicate the following general features.

The liquidus temperature decreases with increasing silica content. At the three silica levels considered, i.e. 27, 32, and 37 per cent, there appears to be a liquidus trough at about 14 mole per cent MgO (approximately 8 per cent by mass). A high liquidus region exists at low MnO and low MgO contents but disappears gradually as the silica content increases from 27 to 37 mole per cent.

CONCLUSIONS

The composition of a slag determines its general physicochemical properties. Through the influence of these properties on furnace operation, the composition of the slag offers an important means of control of the smelting process. Although all the slags investigated had a constant Al_2O_3 content of 10 mole per cent (16 per cent by mass), the general trends of changes in the viscosities and electrical conductivities as a function of changes of the proportions of SiO_2, CaO, MgO, and MnO would be expected to apply to slags of slightly lower and higher Al_2O_3 contents. The results presented in Table 1 and Figures 1 to 4 therefore permit prediction of the effect of changes in composition on the physicochemical properties of these slags.

Slags with relatively low viscosities are required for good furnace operation. Also, low viscosities are beneficial for rapid chemical reaction because the higher rates of bulk diffusion in the slag increase the rate of reduction of MnO. Although slags having MnO contents display low viscosities, it is not desirable for MnO to be regarded as a fluxing agent that can be used to reduce viscosity. Such a role is usually delegated to CaO and, especially, to MgO. Additions of MgO, by reducing the molar proportion of silica, reduce the viscosity and increase the activity coefficient of MnO[12]. Both these factors assist in reducing the MnO content of the slag and thus improve recovery.

The results show that viscosities in the composition range examined are generally low but the electrical conductivities tend to be relatively high, especially for slags having high MnO contents. Selection of the optimum slag for a particular operation also has to take account of factors such as the activity coefficients of MnO and SiO_2, the liquidus temperatures, and the slag-to-metal ratios.

ACKNOWLEDGEMENT

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DISCUSSION

Mr D. Ossin:*

Did you find a relation between viscosity and conductivity, or, owing to the possibility of semiconduction, did you find Walden's rule to be inapplicable?

Mr Woollacott:

There is indeed a relation between viscosity and electrical conductivity, as can be noted in the diagrams in my paper. However, the relation is not such that it can be used. If we derived a parameter, for example by dividing viscosity by the conductivity, or perhaps an even more fundamental parameter, it would be found that the parameter would vary randomly with composition in the system I investigated. In a system without MnO, similar effects occur; but for a particular slag composition there is definitely a relation between viscosity and electrical conductivity.

Mr W. Gericke†:

You have gone to great trouble to ensure that the manganese oxide was in the divalent oxidation state. What effect would manganese in the trivalent state have on the viscosity and electrical conductivity of the slag system under discussion?

Mr Woollacott:

Trivalent manganese is an 'intermediate', in slag terminology. Its effect would be similar to that of silica but less marked. Thus, the viscosity would increase and the conductivity decrease. This is, of course, for the slag above the liquidus temperature.

Mr L.A. Kok:*

Will some one with experience in operating with slags of higher Al_2O_3 content than those normally occurring in South Africa please comment on this?

Mr S. Selmer-Olsen†:

I think that quite a few of us have experience in making discard slag with higher alumina content than we have here in South Africa. This applies especially when Ghana ore, with considerably higher alumina content, is used. With a higher alumina content, the furnace operation is easier because the resistance is higher and the slag can be worked out further. In enriched-slag operation, the high alumina content is not so important.

Mr N.W. Hanf‡:

Please elaborate on the method employed for determining the valence of Mn in the slag.

Mr Woollacott:

The determination of the valence of Mn in the slag is a reasonably easy and established technique, which distinguishes only between the divalent and trivalent states.

*Dr J. Taylor**:*

Dr Jochens indicated that, for highly basic slags, the attainment of a fully liquid slag necessitated high temperatures at which manganese volatilization becomes a possibility. Was this observed in your work, and were precautions taken against this possibility?

Mr Woollacott:

The problem that you refer to here is the volatilization of manganese metal. I was dealing only with slags. I found some volatilization – this could possibly have been MnO.

Mr K.J. Edwards‡‡:

Is it the intention to publish viscosity and conductivity data that can be used by furnace managers?

Mr Woollacott:

This is a very pertinent matter to raise at this stage because it can justify the position of a fundamental research worker in metallurgy. The difficulties encountered in trying to measure the viscosity of a wide range of slag compositions in more complex systems such as the one I reported (and there could be additional components), and the variation in compositions that has to be covered in order to supply the plant metallurgists with comprehensive information are very large. It is a problem I faced in motivating my project, and it led me to cut down on the alumina content. Another problem is that we are as yet unaware of the oxidation states of some of the components, such as iron oxides. The problem could be solved by doing a great deal of 'donkey work' or by carrying out fundamental research into simple slag systems. From the understanding obtained about slag structure, one could, it is hoped, predict, for example, the viscosity for more complex systems. As our knowledge of slag chemistry improves, so these predictions will be more accurate. I am quite sure that, as far as the plant metallurgist is concerned, if we could give him a figure that is accurate to within 20 per cent, it would be better than no data at all. So here we find a valid justification for research that at first glance, appears to be out of the composition range of immediate interest.

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