

The effects of Chromium oxide, Iron oxide and Calcium oxide on the liquidus temperatures, viscosities and electrical conductivities of slags in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ †

M. S. Rennie* B.Sc. Hons. (Natal), M.Sc. (Eng.) Rand (Visitor)

D. D. Howat** B.Sc. (Glas.), Ph.D. F.I.M. (Fellow)

P. R. Jochens* Pr. Eng. M.Sc. (Eng.) Rand., Ph.D., A.I.M. (Member)

SYNOPSIS

The slags arising from ferrochromium plants were simulated by additions of CaO and Fe_2O_3 (6 per cent each), Cr_2O_3 (7 and 12 per cent), and Fe_2O_3 and Cr_2O_3 together (6 and 12 per cent respectively) to slags in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. These additions were made to slags having an SiO_2 content of 45 per cent and an MgO -to- Al_2O_3 ratio of 4 to 3 or 3 to 4. The effect of these oxide additions on the liquidus temperatures, electrical conductivities, and viscosities was determined.

The additions of CaO and Fe_2O_3 , although having little effect on liquidus temperatures, decreased viscosity and increased electrical conductivity. The addition of Cr_2O_3 raised the liquidus temperatures considerably, and tended to decrease viscosity in the temperature range 1 700 to 1 800°C and to increase electrical conductivity.

SINOPSISIS

Die slakke afkomstig van ferrochroom aanlegte is gesimuleer met byvoegings van CaO en Fe_2O_3 (6 persent elk), Cr_2O_3 (7 en 12 persent) en Fe_2O_3 en Cr_2O_3 gesamentlik (6 en 12 persent respektiewelik) tot slakke van die $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ stelsel. Hierdie byvoegings is gemaak tot slakke met 'n silika inhoud van 45 persent en 'n MgO tot Al_2O_3 verhouding van 4 tot 3 of 3 tot 4. Die invloed van hierdie oksiet byvoegings op smeltpunt, elektriese geleidingsvermoë en viskositeit is bepaal.

Alhoewel die toevoegings van CaO en Fe_2O_3 min invloed uitoefen op smeltpunt, verminder dit die viskositeit en vermeerder die elektriese geleidingsvermoë. Die teenwoordigheid van Cr_2O_3 verhoog die smeltpunt aansienlik en vir temperature van 1 700 tot 1 800°C, is dit geneig om die viskositeit te verlaag en die elektriese geleidingsvermoë te verhoog.

INTRODUCTION

In the smelting operations used in the production of high-carbon ferrochromium and ferrochromium silicide by the slag process, the major slag constituents are magnesia, alumina, and silica. All the major constituents of the slags generally used in smelting processes in South Africa are included in the ternary region of the oxide system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ shown in Fig. 1, i.e. the region bounded by an SiO_2 content of 25 to 45 per cent and an MgO -to- Al_2O_3 ratio of 0,5 to 2,0. Also present in ferrochromium slags are considerable quantities of iron oxide and chromium oxide. The normal maximum concentrations of chromium (reported as Cr_2O_3), iron (reported as FeO), and CaO in these slags are 14, 6, and 6 per cent respectively. In this investigation, additions of these oxides were made both singly and in combination to selected slags in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, so that these synthetic slags would be representative of the slags encountered in smelting plants. Preliminary investigation had shown that the liquidus temperatures of slags of low silica content were in the region of 1 800°C, and these slags were excluded from the investigation because of the experimental difficulties that would arise with the existing apparatus. The following two compositions were chosen as the basic

slags to which various additions would be made: a silica content of 45 per cent, and an MgO -to- Al_2O_3 ratio of 4 to 3 or 3 to 4. These compositions are represented by points A and B in Fig. 1.

Because of the high temperatures involved in the study of this slag system, comparatively little experimental work has been done on the physicochemical

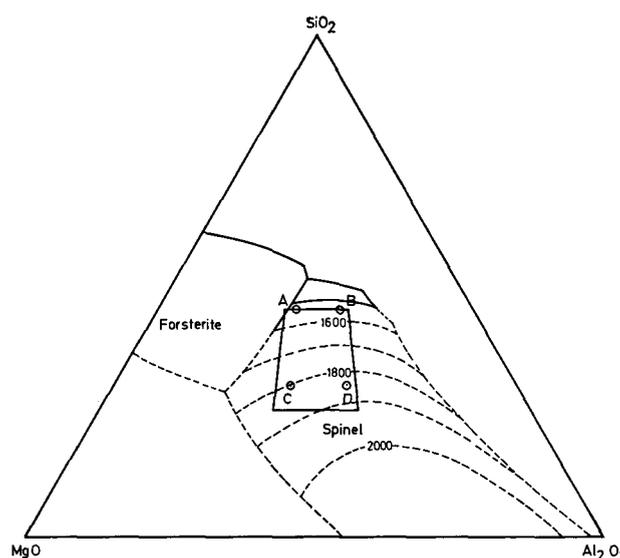


Fig. 1—The system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ indicating the region of slag compositions used in the production of ferrochromium

* Pyrometallurgical Research Group, National Institute of Metallurgy

** Professor and Head, Department of Metallurgy, University of the Witwatersrand

† This paper is based on a thesis submitted to the University of the Witwatersrand.

properties of these slags. Bobkova¹, Zhilo^{2,3}, and Liutikov and Tsylev^{4,5} have investigated the viscosity of the slag system MgO-Al₂O₃-SiO₂ for slag compositions similar to those used in the production of high-carbon ferrochromium and ferrochromium silicide. However, only Liutikov and Tsylev have undertaken a systematic study of the effects of chromium oxide on the physicochemical properties of the system.

LIQUIDUS TEMPERATURE

The liquidus temperature of a slag is important. The charge reacts and is heated as it descends towards the hot zone of the furnace, and it is not practically possible for the temperature of the alloy to be raised by an increase in its retention time in the furnace because, once the charge has reached the smelting zone and has fused, it will drop away from the area of intense heat surrounding the arcs and will settle to the bottom of the furnace. Consequently, for the alloy to be superheated to the required degree, the liquidus temperature of the slag must be sufficiently high to ensure that the slag is only sufficiently fluid for the products of smelting to drain away from the arc zone once the alloy has been heated to above its liquidus temperature.

Experimental technique

The liquidus temperatures of the slags investigated were determined by high-temperature microscopy, which involves the simultaneous heating of a thermocouple and the measurement of its temperature, with the thermocouple acting as the heater element and

sample-holder. The apparatus used was developed by Sommer and Jochens⁶, based on the work of Welch⁷. When Pt-5% Rh/Pt-20% Rh thermocouples are used, the precision is about $\pm 5^\circ\text{C}$ at 1700°C, and, although the accuracy of the thermocouple is only $\pm 5^\circ\text{C}$ at 1700°C, agreement with standards was generally as good as $\pm 5^\circ\text{C}$. Crystal phases were identified from crystals grown on the hot-stage microscope, the remaining melt being quenched to a glass and the finely ground sample analysed in a Phillips Debye-Sherrer X-ray-diffraction camera.

Experimental results

Initially, 1 g samples of the required compositions were made up and the liquidus temperatures of these homogeneous premelts were determined. The liquidus temperatures of the slags containing chromium oxide could not be measured by the technique of high-temperature microscopy because of thermocouple contamination. After electrical conductivity and viscosity measurements had been completed, samples of the slags were taken and analysed (Table I). The liquidus temperatures of all the slags not containing chromium oxide were redetermined, and these results were found to be in good agreement with those obtained initially. The liquidus temperatures and primary phases are given in Table II. It may be noted that spinel (MgO·Al₂O₃) was the primary phase in all cases.

Samples of the A and B slags containing 7 and 12 per cent chromium oxide, when quenched from 1680°C in air, revealed the presence of small rose-coloured crystals in a glassy matrix, i.e., even at this temperature,

TABLE I

COMPOSITION OF SLAGS USED IN THE INVESTIGATIONS OF ELECTRICAL CONDUCTIVITY AND VISCOSITY

From platinum crucibles							
Slag as analysed	MgO	Al ₂ O ₃	SiO ₂	CaO	Cr ₂ O ₃	FeO	Fe ₂ O ₃
A	31,03	24,01	43,17	0,57		0,62	
A+6%CaO	28,99	22,33	41,40	6,03		0,69	
A+6%Fe ₂ O ₃	29,85	23,14	40,97	0,63		2,34	3,02
B	23,04	32,5	43,84				
B+6%CaO	22,04	31,29	41,36	5,63			
B+6%Fe ₂ O ₃	22,48	31,36	41,03			2,86	2,27
From molybdenum crucibles							MoO ₃
A+7%Cr ₂ O ₃	29,51	21,78	41,33	1,40	6,52	0,28	
A+12%Cr ₂ O ₃	27,62	19,38	40,20	0,69	10,26	0,49	0,57
A+6%Fe ₂ O ₃							
+12%Cr ₂ O ₃	25,70	20,78	35,35	0,59	10,85	3,43	0,98
B+7%Cr ₂ O ₃	21,75	27,45	39,73	0,38	6,59	0,28	1,75
B+12%Cr ₂ O ₃	18,69	28,62	36,04	0,43	9,07	0,95	2,73

TABLE II

LIQUIDUS TEMPERATURES AND PRIMARY PHASES OF THE SLAGS INVESTIGATED

Slag	A	A + 6%CaO	A + 6%Fe ₂ O ₃	B	B + 6%CaO	B + 6%Fe ₂ O ₃
Liquidus temperature	1 519°C	1 529°C	1 524°C	1 554°C	1 554°C	1 542°C
Primary phase	Spinel	Spinel	Spinel	Spinel	Spinel	Spinel

the slag was below its liquidus temperature. X-ray-diffraction analysis showed the existence of a spinel structure corresponding closely to the composition $MgO \cdot Al_2O_3$, and electron-microprobe analysis for the chromium ion showed that almost all the chromium was contained within the spinel structure, only a small amount remaining in the glassy phase. The liquidus temperatures could be estimated from the viscosity measurements: as soon as crystal growth occurred on the spindle, indicating that the temperature of the slag was below liquidus, the rotary movement became erratic. It was estimated that the liquidus temperatures of the A series of slags with Cr_2O_3 additions were between 1 700 and 1 800 °C, and those of the B series were above 1 800 °C.

Discussion

The liquidus temperatures of slags A and B are in general agreement with the phase diagram compiled by Osborn and Muan⁸. CaO and Fe_2O_3 have little influence on the liquidus temperature, CaO raises the temperature, as found by Osborn et al.⁹ in their work on the liquidus temperatures of blast-furnace slags. In their study of the phase assemblages of the system $MgO - Al_2O_3 - SiO_2$ with Cr_2O_3 additions, Liutikov and Rudneva¹⁰ found that rose-coloured crystals of spinel were always observed in samples of slags containing 35 to 40 per cent SiO_2 and more than 6 to 9 per cent chromium oxide when these were quenched from 1 800 °C. A considerable increase in the liquidus temperatures of slags on the addition of Cr_2O_3 was also found by Keith¹¹ and Kats et al.¹²

ELECTRICAL CONDUCTIVITY

The relative importance of the electrical conductivity of the slag is still under debate. Heating in the electric-arc furnace during the smelting of ferro-alloys of chromium can occur to a considerable degree by resistance heating, the resistance being supplied by the furnace contents at the electrode tips. The contents of the furnace in this area consist of chromite ore in various stages of reduction, flux additions that have undergone incipient fusion, the reducing agent, and the products of the smelting operation, namely, alloy and slag.

Although, as in most smelting processes in the submerged-arc furnace, the carbon reducing agent is expected to supply the major proportion of the current paths available, the slag may contribute considerably to the overall resistivity at the electrode-tip area because of the high slag-to-metal ratio in this process. It is therefore logical that the conductivity of the final slag should be examined, especially as the composition can be varied in practice. However, it must be pointed out that it is not known to what degree the slag contributes to the electrical resistance of the furnace, which is normally between 0,8 and $1,2 \times 10^{-3}$ ohm, or how this final slag is related to the 'primary' slag formed higher up in the furnace.

Experimental technique

Conductivity was determined at high temperatures by measurement of the resistance of the slag with a suitable electrode system and conversion of the results according

to a resistance—conductivity calibration curve obtained from appropriate liquids of accurately determined conductivity. Two parallel metal electrodes held in position by an alumina rod dipped into the slag to form one arm of an impedance bridge, which incorporated provision for variation in supply frequency and separate measurement of the resistance and capacitance of the slag. The design was based on the experimental work of Riebling and Logel¹³. At temperatures of up to 1 650 °C, a molybdenum resistance furnace was used with platinum electrodes and crucibles in an air atmosphere. For higher temperatures, an Intertherm 500 kHz induction furnace was used with molybdenum electrodes and crucibles in an argon atmosphere.

The resistance of a slag is inversely proportional to its conductivity, and thus

$$RK = G,$$

where R is the resistance of the slag in the cell,

K is the conductivity of the slag, and

G is the cell constant.

G depends on the geometry of the cell and should remain constant with changes in resistance and conductivity or with changes in the applied frequency. Preliminary investigation revealed that the resistance of the slag was independent of frequency down to about 2 000 Hz, and the precision was greatest at 10 kHz.

For the derivation of a calibration curve based on standard solutions, the above equation was used in the form

$$\log R + \log K = \log G.$$

Thus a plot of $\log_{10} R$ versus $\log_{10} K$ should be a straight line with a gradient of -1 . However, when an attempt was made to calibrate the electrical conductivity cell at 10 kHz with aqueous sodium chloride and potassium chloride solutions, it was found that there was considerable deviation from linearity, especially for more concentrated solutions. Also, it was noted that there was a change in capacitance from 0,0024 to 0,54 μF from the least concentrated to the most concentrated solutions. This change was attributed to polarization of the electrodes by means of the ions in solution. So that reactance-free impedances would be obtained, it was decided to consider resistance as that value which would be measured at infinite frequency. This was accomplished by extrapolation to infinite frequency of the resistance values on a curve of resistance versus the reciprocal of frequency. Riebling and Logel¹³ and Tickle¹⁴ also used reactance-free calibration curves.

The best straight line was obtained by a least-squares fit. The line was given as

$$\log_{10} R = 0,9942 \log_{10} K - 0,1514.$$

The standard deviation was 0,01, and the correlation coefficient was $-0,9999$.

Experimental results

Electrical-conductivity measurements were made in platinum crucibles in air in the temperature range 1 500 to 1 640 °C for the A and B series with CaO and Fe_2O_3 additions. Although it was realized that the slags would be below their liquidus temperatures, further measurements were made on composition A with chromium oxide additions, so that correlation could be

obtained with later high-temperature work carried out in the induction furnace. It was not possible to do the same with the B composition or with the combined chromium and iron oxide additions because this resulted in attack on the crucible and in a slag of uneven and moving surface due to oxygen evolution in this temperature range. These results are shown in Fig. 2. In molybdenum crucibles and under an argon atmosphere, a check run was performed on slag A+6 per cent CaO.

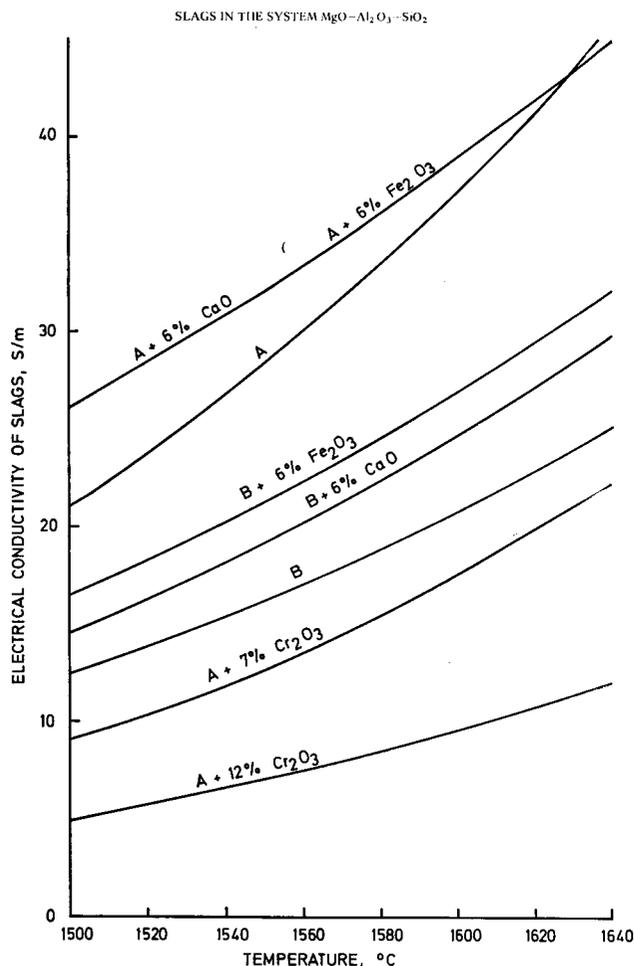


Fig. 2—Change in the electrical conductivity of slags after additions of CaO, Fe₂O₃, and Cr₂O₃.

The precision of the measurement was found to be good, and the results were in good agreement with those obtained previously with the platinum crucibles. For the slags containing chromium oxide, it was possible to obtain resistance readings only for slag A+7 per cent Cr₂O₃ and slag A+6 per cent Fe₂O₃+12 per cent Cr₂O₃ at high temperatures, and the accuracy and precision was poor because of the low resistances measured and interference from the furnace. For the B series of slags with chromium oxide additions, no readings were obtained to which significance could be attached, because the slags had not settled even after several hours at 1 800 °C. Table III gives the equation of slag conductivity or the slags investigated, together with activation energy (E_K), standard deviation (σ), and correlation coefficient (r). These results were obtained from the

calibration equation, and the best straight line was obtained from a least-squares fit.

Discussion

The results of the present investigation were interpreted according to the ionic nature of silicate slags as given by Bockris et al.¹⁵ and according to the interpretation of the effects of cations on the electrical conductivity of molten silicates¹⁶ in terms of their oxygen-ion attraction I (after the work of Dietzel¹⁷). Slag A has a greater conductivity than slag B because of its higher MgO-to-Al₂O₃ ratio. Additions of CaO and Fe₂O₃ increase the conductivity of both A and B, and, for slag B, Fe₂O₃ increases the conductivity more than CaO. CaO has a lower I value than either FeO or Fe₂O₃ and would thus be expected to increase the conductivity more than either of these two. The increase in conductivity as a result of the Fe₂O₃ addition may be explained by the high oxygen-ion attraction of the Fe³⁺ ion, which would distort the silicate structure, having a similar effect to that of a breakdown of the structure. Conduction would be due to the Fe²⁺ ion, which has a high mobility because of its small radius. The high mobility of the Fe²⁺ ion was confirmed by subsequent work. Although the presence of CaO and Fe₂O₃ considerably decreased the activation energy for slag A, the CaO addition slightly increased the activation energy for slag B. As CaO has a low I value, it would be expected that the activation energy would decrease, as was found by Bockris et al.¹⁵. However, the conductivity increases because of the magnitude of the frequency factor (A_K).

The effects of Cr₂O₃ may be divided into two classes: those revealed by measurements below the liquidus temperature in platinum crucibles in air, and those by measurements above the liquidus in molybdenum crucibles in an argon atmosphere. The measurement in platinum crucibles shows that Cr₂O₃ decreases the conductivity considerably. This finding is in accordance with the fact that the melt was considerably below its liquidus temperature and, as the primary phase is MgO.(Al,Cr)₂O₃, the number of cations available for conduction is reduced. The high-temperature results obtained in molybdenum crucibles in an argon atmosphere give a different picture. The conductivity increases with additions of Cr₂O₃ and is highest for the melt with 6 per cent Fe₂O₃ and 12 per cent Cr₂O₃. As can be seen in Table III, the activation energy for slag A+7 per cent Cr₂O₃ is considerably different for measurements above and below the liquidus temperature. The differences may be explained by the fact that an inert atmosphere will favour the conversion of the Cr³⁺ ion to Cr²⁺, the equilibrium ratio depending on the oxygen partial pressure. In addition, as the liquidus temperature is approached, more cations are released from the primary phase. It is believed that the I value of CrO is similar to that of MgO, but no precise confirmation of this could be found in the literature. The presence of molybdenum oxide in the melt, as shown by the analyses (Table I), may be another factor affecting conductivity. The oxide results from the evolution of oxygen in the conversion of Cr₂O₃ to CrO at high temperatures. This oxygen attacks the molybdenum crucible,

TABLE III

EQUATION OF SLAG CONDUCTIVITY, SHOWING ACTIVATION ENERGY, STANDARD DEVIATION, AND CORRELATION COEFFICIENT

(a) In the molybdenum resistance furnace:

Slag	Equation	E_K kJ/mol	σ	r
A	$\ln K = -185,4 \times 10^2 \times \frac{1}{T} + 8,918$	154,1	0,3090	-0,975
A + 6%CaO	$\ln K = -129,9 \times 10^2 \times \frac{1}{T} + 5,993$	108,1	0,0177	-0,981
A + 6%Fe ₂ O ₃	$\ln K = -131,4 \times 10^2 \times \frac{1}{T} + 6,067$	109,2	0,0144	-0,981
A + 7%Cr ₂ O ₃	$\ln K = -214,3 \times 10^2 \times \frac{1}{T} + 9,702$	178,2	0,0262	-0,979
A + 12%Cr ₂ O ₃	$\ln K = -202,2 \times 10^2 \times \frac{1}{T} + 8,470$	168,2	0,0281	-0,978
B	$\ln K = -168,0 \times 10^2 \times \frac{1}{T} + 7,401$	139,7	0,0259	-0,987
B + 6%CaO	$\ln K = -172,2 \times 10^2 \times \frac{1}{T} + 7,794$	143,2	0,0214	-0,988
B + 6%Fe ₂ O ₃	$\ln K = -160,6 \times 10^2 \times \frac{1}{T} + 7,262$	133,6	0,0253	-0,986

(b) In the induction furnace:

A + 6%CaO	$\ln K = -116,7 \times 10^2 \times \frac{1}{T} + 5,276$	97,0	0,0099	-0,995
A + 7%Cr ₂ O ₃	$\ln K = -154,0 \times 10^2 \times \frac{1}{T} + 7,454$	128,0	0,0188	-0,974
A + 6%Fe ₂ O ₃ + 12%Cr ₂ O ₃	$\ln K = -122,8 \times 10^2 \times \frac{1}{T} + 6,088$	102,1	0,0096	-0,997

and molybdenum oxide goes into solution. The attack is greater as the percentage of chromium oxide in the slag increases, and is very much greater for the B slags, for which the oxide melts were made up in molybdenum crucibles (for the A slags, the melts had already been made up in platinum crucibles). By analogy with most metal oxides, molybdenum oxide should increase the conductivity, but no work on the effect of molybdenum oxide in any slag system seems to have been reported.

THE EFFECTS OF CHANGES IN FREQUENCY AND CURRENT ON THE MEASURED RESISTANCE OF THE CELL

Electric reduction furnaces are run at a frequency of 50 Hz and at very high current densities. So that a greater understanding of the conduction and electrode processes could be obtained, an attempt was made to determine the effects of variation in frequency and current on the resistance of the slags.

Preliminary investigations

So that polarization at low frequencies would be

limited, a single platinum rod of 4.7 mm diameter was constructed to act as the central electrode and the crucible was used as the other electrode. Heavier connections were used to permit a greater current to be carried. For an electrode power density similar to Kelly's¹⁸ value for high-carbon ferrochromium, it was calculated that the electrode current should be about 20 A.

The bridge employed in the conductivity measurements was used in the determination of the variation of resistance with frequency. Higher capacitances were encountered, and these had to be balanced out. Because the slag was heated locally by the passage of current in the vicinity of the electrode, a Pt-6 per cent Rh/Pt-30 per cent Rh thermocouple was positioned in the slag next to the electrode. Because of possible contamination, new thermocouple ends were used for each slag.

It was found that dissolution of the electrode began with a current of 10 A, which appreciably heated the slag as it passed through. For the clearer interpretation of current effects, the slag resistance was measured at different current levels but at a constant temperature.

This was accomplished by a lowering of the furnace temperature by the required amount. It was found that, when the current was increased by more than 1 A, all the slags showed the same trend, viz, an increase in resistance for an increase in current, the rate of increase depending on the resistance of the slag. As will be explained, this trend was to be expected, and currents greater than 2 A were generally not passed through the slag.

Results and discussion

The effects on the cell resistances of a change of current and frequency for the slags investigated are shown in Figs. 3 to 7. For purposes of comparison, the two graphs for each slag are shown in the same figure. The temperature range of the investigation, 1 540 to 1 620°C, was above the liquidus temperatures of all the slags, except those containing chromium oxide. Because the greatest variation occurs over a comparatively small range of low frequencies the logarithm of the frequency values was taken. As can be seen from the graphs at the limit of low current and low frequency, the resistance values are in fair agreement, except in Fig. 7. The resistance measured by the current and voltage ratio was generally less than the bridge-circuit measurement for low current values. The agreement in the region of 0,5 A was found to be good.

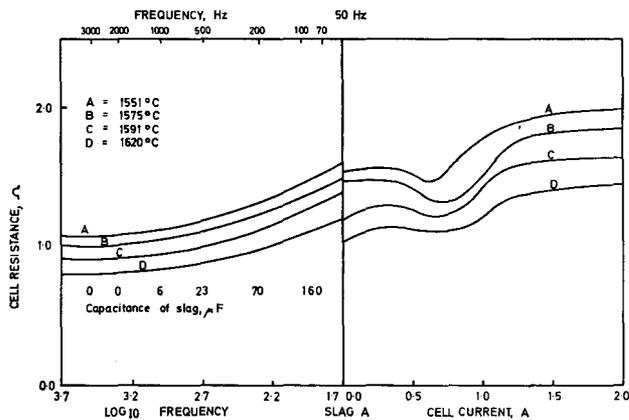


Fig. 3—Variation in cell resistance with changes of frequency and current for slag A

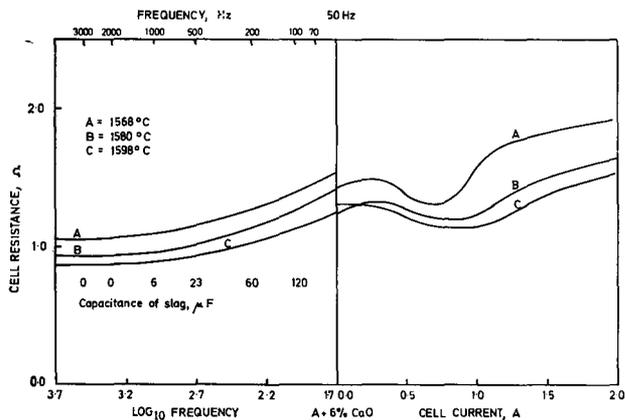


Fig. 4—Variation in cell resistance with changes of frequency and current for slag A + 6% CaO

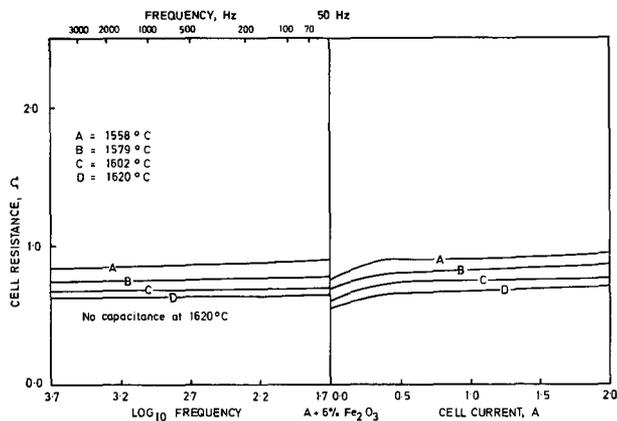


Fig. 5—Variation in cell resistance with changes of frequency and current for slag A + 6% Fe₂O₃

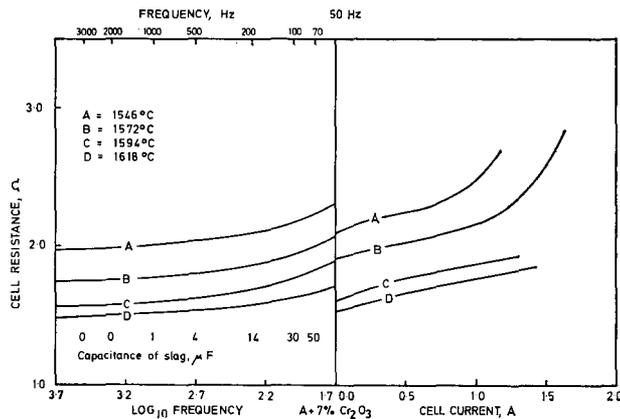


Fig. 6—Variation in cell resistance with changes of frequency and current for slag A + 7% Cr₂O₃

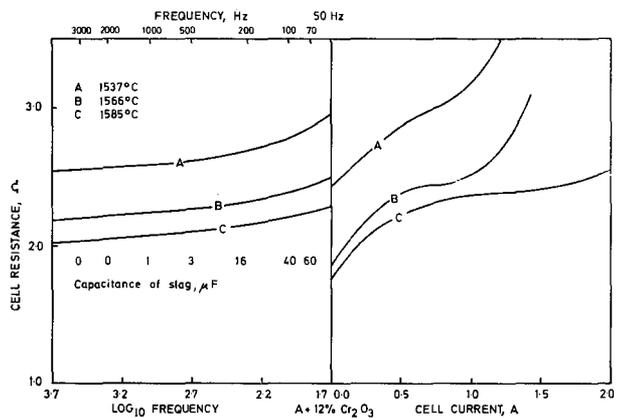


Fig. 7—Variation in cell resistance with changes of frequency and current for slag A + 12% Cr₂O₃

TABLE IV
CHANGE IN MEASURED RESISTANCE OF THE SLAGS WITH CHANGE IN FREQUENCY FOR ALL TEMPERATURES IN THE RANGE 1 520 TO 1 620°C

Slag	Increase in resistance from 3 000 to 50 Hz %
A	22
A + 6% CaO	22
A + 6% Fe ₂ O ₃	2
A + 7% Cr ₂ O ₃	13
A + 12% Cr ₂ O ₃	11

The percentage change in the measured resistance of the slags over the frequency range 3 000 to 50 Hz is given in Table IV. Fig. 3 shows that, for slag A, the resistance increases fairly considerably from 3 000 to 50 Hz. At the same time the capacitance increases very rapidly. It can be deduced that electron transfer at the electrode—slag interface decreased and diffusion was being hindered by the build-up of ions, increasing both resistance and capacitance. The addition of CaO has little effect on the characteristics of slag A (Fig. 4), whereas the addition of Fe_2O_3 to slag A causes only a very small change in resistance with change in frequency (Fig. 5). This small change in resistance is probably due to distortion of the melt structure by the Fe^{3+} ion, which because of its high I value, permits greater mobility of the Fe^{2+} ion, which has a lower I value. The fact that CaO has a lower I value than FeO and yet has little effect on the electrical characteristics of the slag shows that the Fe^{3+} ion must be important in these processes. The percentage change in resistance with frequency for slag A with additions of 7 and 12 per cent Cr_2O_3 is 13 and 11 per cent, compared with 22 per cent for slag A alone. Thus the presence of Cr_2O_3 in the slag resulted in a smaller variation of resistance with frequency. The lower capacitance of the slags with additions of Cr_2O_3 (only about half that of slag A) can be explained by the presence of a relatively mobile cation, which would probably be Cr^{2+} . The higher resistance of slag A with additions of Cr_2O_3 is assumed to be due to the fact that the Cr^{3+} ion has caused the formation of high-temperature spinel crystals — $\text{MgO}(\text{Al},\text{Cr})_2\text{O}_3$ — because of the higher melting points, thus removing a large proportion of the conducting cations from the melt. This interpretation is in accordance with the findings from high-temperature measurements performed in the induction furnace. As can be seen in Figs. 3 to 7, the slags with higher capacitances exhibit some form of electrode effect at cell currents between 0 and 1 A. The slag containing Fe_2O_3 , which has a lower capacitance, follows the trend that would be expected — a slight increase in resistance as the current is increased over this same range. The other slags follow this trend at cell currents greater than 1 A, except that the increase in resistance is larger because of the higher resistivity of these slags. The increase in resistance occurs because the furnace temperature was being lowered so that a constant temperature would be maintained in the slag as the slag temperature was being increased by resistance heating. However, only the slag in the immediate vicinity of the electrode, where the temperature is being measured, is being heated. The bulk of the slag is close to furnace temperature. The slags with Cr_2O_3 exhibit a more pronounced temperature increase because the higher resistance of these slags results in greater resistance heating ($I^2 R$). (Compare Figs. 6 and 7 with Figs. 3 to 5).

The capacitance of the slags at higher current values was determined with a phase meter. There was no detectable change in ϕ , although the test for capacitance was positive. The absence of capacitance was confirmed by the calculation

$$\cos \phi = (w^2 c^2 R^2 + 1)^{-\frac{1}{2}},$$

where $R = 1 \Omega$,
 $c = 150 \mu\text{F}$, and
 $w = 2\pi \times 50 \text{ rads}^{-1}$

Thus

$$\cos \phi = (10^4 \times 9,873 \times 225 \times 10^2 \times 10^{-12} + 1)^{-\frac{1}{2}} = 0,999 -$$

a reading that cannot be differentiated from unity on the instrument.

VISCOSITY

Viscosity must be low if the diffusion processes in the slag are to occur quickly enough for the reactions between slag and alloy to approach equilibrium rapidly and so affect the kinetics of the process favourably. Because of turbulence both in the furnace and when the furnace is tapped, small droplets of metal will occur in the slag, and the rate at which these metal droplets are separated from the slag phase is a function of the viscosity of the slag. In addition, an excessively viscous slag will give rise to operational difficulties during tapping.

Technique of measurement

A Brookfield Syncro-Lectric Viscometer was used for viscosity measurements. The instrument is quick and simple to operate and of high precision, having springs of different torsion constants available and a wide range of motor speeds. The inner cylinder is driven through a copper-beryllium helical spring by a variable-speed synchronous motor, and the spring is attached to a pointer that moves over a scale. When the torque on the inner cylinder equals the restoring torque of the spring, the position of the pointer is a measure of the viscosity.

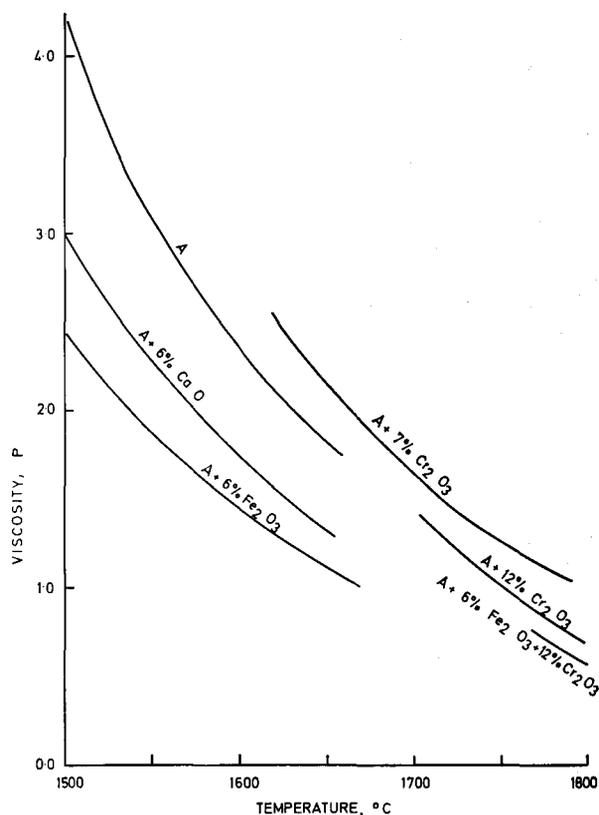


Fig. 8—Change in viscosity of slags after additions of CaO, Fe_2O_3 , and Cr_2O_3

TABLE V
EQUATIONS OF SLAG VISCOSITY SHOWING ACTIVATION ENERGY, STANDARD DEVIATION, AND CORRELATION COEFFICIENT

Slag	Equation	E_{η} kJ/mol	σ	r
A	$\ln \eta = 191,0 \times 10^3 \times \frac{1}{T} - 9,392$	159,0	0,0158	0,998
A + 6%CaO	$\ln \eta = 184,5 \times 10^3 \times \frac{1}{T} - 9,341$	153,5	0,0147	0,998
A + 6%Fe ₂ O ₃	$\ln \eta = 180,6 \times 10^3 \times \frac{1}{T} - 9,297$	150,2	0,0237	0,996
A + 7%Cr ₂ O ₃	$\ln \eta = 214,9 \times 10^3 \times \frac{1}{T} - 10,43$	173,9	0,0384	0,988
A + 12%Cr ₂ O ₃	$\ln \eta = 321,5 \times 10^3 \times \frac{1}{T} - 15,90$	267,4	0,0260	0,978
A + 6%Fe ₂ O ₃ + 12%Cr ₂ O ₃	$\ln \eta = 414,5 \times 10^3 \times \frac{1}{T} - 20,57$	344,7	0,0305	0,948

The viscometer was calibrated with calibrating oils obtained from the United States Bureau of Standards, and was adapted for high-temperature work by means of a specially constructed molybdenum spindle.

Experimental results

The induction furnace was used, viscosity measurements being made in molybdenum crucibles in an argon atmosphere. For the slags of higher chromium oxide content, comparatively few readings could be taken below 1 800°C because the growth of crystals around the spindle shaft impeded the rotary movement of the spindle. Except for the presence of these crystals, the chromium oxide slags were found to be very fluid. The viscosity of slag A with additions of calcium oxide, ferric oxide, and chromium oxide is shown in Fig. 8. All the readings were combined to give the best straight-line equation for the variation of log viscosity with $1/T^\circ$ K for each slag, and the activation energies were obtained from the slope of these lines. The computed results are given in Table V.

Discussion

Additions of CaO and Fe₂O₃ caused a decrease in the viscosity of slag A in a manner similar to that when the conductivity is increased as a result of a further breakup of the melt structure. The greatest effect of these additions was on the activation energy, which is influenced by the cations in the conduction process and the anions during viscous flow. Thus E_K was lowered considerably by CaO and Fe₂O₃ additions, but E_{η} was lowered only slightly by the same additions. The addition of 7 per cent Cr₂O₃ increased the viscosity, but a further increase in the Cr₂O₃ content decreased the viscosity. The high I value of the Cr³⁺ ion and its network-forming properties would explain the increase in viscosity. It is possible that the decrease with additional Cr₂O₃ may be the result of contamination by molybdenum oxide or

the lower silica content of the slag. Alternatively, most of the chromium ions might be in the divalent form at high temperatures and thus have an effect on the viscosity of the slag similar to that of MgO. The activation energies of the slags with additions of Cr₂O₃ were increased considerably. The viscosity measurement of the slag with 7 per cent Cr₂O₃ is believed to be reasonably accurate, but, as considerable difficulty was experienced in the measurement of the viscosities of the slags with the higher chromium oxide additions, these results may be less accurate.

CONCLUSION

The general trends found in the present investigation were that CaO and Fe₂O₃ additions decrease the viscosity and increase the electrical conductivity of slags in the MgO-Al₂O₃-SiO₂ system with a 45 per cent silica content. CaO and Fe₂O₃ additions have little effect on the liquidus temperatures, but Cr₂O₃ increases the liquidus temperatures considerably. Below the estimated liquidus temperatures of the slags, Cr₂O₃ additions decrease the electrical conductivity, but cause an increase above the liquidus temperatures. The viscosity increases with the addition of 7 per cent Cr₂O₃, but decreases for higher concentrations of Cr₂O₃ for temperatures above the liquidus temperature. These trends are in agreement with the work of Zhilo^{2, 3}, Bobkova¹, and Liutikov and Tsylev^{4, 5}. However, the absolute values obtained in the present investigation differ considerably from those of the above workers, who, in turn, were not in agreement with one another. The present investigation was in fair agreement with the research undertaken by other investigators of the National Institute for Metallurgy using the same experimental technique. (Ossin¹⁹ and Johnston²⁰). The results showed that the true conductivity of the slags is

independent of frequency, the observed variation in conductivity being due largely to electrode effects. This was demonstrated by the fact that, where there are no electrode-capacitance effects (as in the slag to which 6 per cent Fe_2O_3 was added), resistance is independent of frequency.

ACKNOWLEDGEMENT

This paper is published by permission of the Director, National Institute for Metallurgy, Johannesburg.

REFERENCES

1. BOBKOVA, O. C. Viscosity of slags belonging to the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. *Fiz. Khim. Proizvodsta Stalii. Aka d.Nauk. SSSR., Inst. Met. Im. A.A. Baikova Trudy 3r et Kong.* 1955. pp. 488-496.
2. ZHILO, N. L. A study of the viscosity of synthetic and natural slags of silico-chromium production. *Izv. AN. SSSR. Otd. Tekhn. Nauk. Metall. i Toplivo*, No. 3. 1961. pp. 17-24.
3. ZHILO, N. L. Viscosity of slags of ferrochromium production. *Teoriya i Praktika metallurgii. Chelyabinsk Sb.* No. 5. 1963. pp. 3-7.
4. LIUTIKOV, L. A., and TSYLEV, L. M. Viscosity and electrical conductivity of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ melts. *Izv. AN. SSSR. Otd Tekhn. Nauk. Metall. i Gorn. Delo*, No. 1. 1963. pp. 41-52.
5. LIUTIKOV, L. A., and TSYLEV, L. M. Effect of chromium oxide on the viscosity and electrical conductivity of melts of the $\text{SiO}_2-\text{MgO}-\text{Al}_2\text{O}_3$ system. *Izv. AN. SSSR. Otn. Met. i Gorn. Delo*, No. 2. 1963. pp. 59-66.
6. SOMMER, G., and JOCHENS, P. R. Techniques of micro-thermal analysis based on a thermocouple as a heating source and specimen holder. *Miner. Sci. Engng*, vol. 3, No. 1. 1971. pp. 1-16.
7. WELCH, J. H. A simple microscope attachment for observing high temperature phenomena. *J. Sci. Instrum.*, vol. 31. 1954. pp. 458-462.
8. OSBORN, E. F., and MUAN, A. System $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. PHASE DIAGRAMS FOR CERAMISTS. LEVIN, E. M., ROBBINS, C. R., and MCMURDIE, H. F. Columbus (Ohio), Amer. Ceram. Soc. Inc., 1964. p. 246.
9. OSBORN, E. F. et al. Optimum composition of blast furnace slags as deduced from liquidus data for the quaternary system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. *J. Metals, N.Y.*, vol. 33. Jan. 1954. pp. 33-45.
10. LIUTIKOV, L. M., and RUDNEVA, A. V. Mineral composition of chromium slags. *Isvest. Akad. Nauk. SSSR. Met. i Gorn. Delo*, No. 6. 1963. pp. 82-89.
11. KEITH, M. L. Phase equilibria in the system $\text{MgO}-\text{Cr}_2\text{O}_3-\text{SiO}_2$. *J. Amer. Ceram. Soc.*, vol. 37, No. 10. 1954. pp. 490-496.
12. KATS, M. S. et al. Phase compositions of slags of carbon-containing ferrochromium during operation with magnesia-containing chromium ores. *Akad. Nauk. SSSR. Izvest. Met.*, vol. 6, No. 1.
13. RIEBLING, E. F., and LOGEL, P. C. Dipping electrode electrical conductance instrument for use to 1700°C . *Rev. scient. Instrum.*, vol. 36, No. 4. Apr. 1965. pp. 425-428.
14. TICKLE, R. E. The electrical conductance of molten alkali silicates — part 1. *Soc. of Glass Tech. and Chem. of Glasses*, vol. 8. 1967. pp. 101-124.
15. BOCKRIS, J. O'M. et al. Electrical conductance in liquid silicates. *Trans. Farad. Soc.*, vol. 48. 1952. pp. 75-91.
16. BOCKRIS, J. O'M. et al. Electrical conductivity of silicate melts; systems containing calcium, magnesium and aluminium. *Disc. Farad. Soc.*, No. 4. 1948. pp. 265-281.
17. DIETZEL, A. The cationic field strengths and their relations to devitrification processes, the formation of compounds and the melting points of silicates. *Z. Electrochem.*, vol. 48, No. 1. 1942. pp. 9-23.
18. KELLY, W. M. Design and construction of the submerged arc furnace. *Carbon and Graphite News*, No. 5. 1958.
19. OSSIN, D. I. et al. Liquidus temperatures, viscosities, and electrical conductivities of lime-containing slags produced during the smelting of high-carbon ferrochromium and ferrochromium silicide alloys. Paper presented at 29th Electric Furnace Conference, Toronto, Dec. 1971. To be published in *Trans. AIME*.
20. JOHNSTON, G. H. Private communication.