

Viscosities, electrical resistivities, and liquidus temperatures of slags in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ under reducing conditions

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SYNOPSIS

Selected members of the slag system were reduced in graphite crucibles in an argon atmosphere, and the physico-chemical properties of the reduced derivatives of the slags were determined in inert crucibles.

It was found that slags having magnesium aluminium titanate as the primary phase before reduction underwent an increase in liquidus temperature, accompanied by a change in the primary phase. No analogous behaviour could be detected for the slags having perovskite as the initial primary crystallization product. In most instances, the viscosity of the melt passed through an initial minimum, followed by an increase as the reduction time was extended. Increased MgO/CaO ratio, basicity, titania content, and reduction temperature all served to accelerate thickening. During reduction, the electrical conductivity of the slags tended to rise relative to the value for the unreduced melt.

SAMEVATTING

Geselekteerde slaksamestellings is met koolstof gereduseer in 'n argon atmosfeer. Die fisiko-chemiese eienskappe van die gereduseerde slakke is daarna bepaal in onaktiewe kroesies.

Dit is vasgestel dat slakke wat magnesium aluminium titanaat voor reduksie as primêre fase gehad het, gedurende reduksie 'n smeltpuntverhoging ondergaan wat teweeggebring word deur 'n verandering van die primêre fase. Slakke wat aanvanklik perovskiet as primêre fase het, ondergaan nie sodanige verandering nie. In die meeste gevalle gaan die viskositeit van die slak aanvanklik deur 'n minimum, maar by verdere reduksie verdik dit. Verdikking word verhaas deur 'n verhoogde MgO/CaO verhouding, basisiteit, titaanhoud en reduksietemperatuur. Die elektriese geleidingsvermoë van die slakke was geneig om te vermeerder gedurende reduksie.

Introduction

In an earlier paper¹ it was shown that the slags in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ are very fluid under neutral conditions. However, because practical difficulties are experienced during the smelting of titaniferous burdens, it was necessary to determine the physico-chemical properties of these slags under the reducing conditions existing in a furnace.

The effect of reducing conditions on the viscosity of titaniferous slags has been the subject of many investigations²⁻¹⁰. While it is generally agreed that the reduction of titanium oxide is at the root of the problems, which are variously described as high viscosity, accretion formation, and difficult tapping, some controversy remains over the mechanism affecting furnace operation.

It is possible that oxygen loss from a slag to a degree corresponding to the existence of lower oxides of titanium can influence the viscosity. More recent investigations have proved that such conditions can increase the liquidus temperatures of slags⁸⁻¹⁰, which partly explains thickening under reducing conditions at a constant temperature as reported earlier^{2, 3}. Handfield *et al.*¹⁰ made additions of titanium oxides to a $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ slag, and found that TiO and Ti_2O_3 increased the liquidus temperature substantially after a slight decrease at low concentrations of the oxides. On the basis of the activation energy for viscous flow, they

found Ti_2O_3 to be a better network modifier than either TiO or TiO_2 . Gruzdev *et al.*⁹ actually linked the changes in liquidus temperature with accompanying changes in primary phase, but their results appear to prove the opposite of those of Handfield *et al.*¹⁰ with respect to the relative effects of TiO_2 and Ti_2O_3 upon viscosity.

Ohno and Ross⁵ measured the viscosity of slags in the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ continuously and isothermally while the slags were contained in graphite crucibles in an argon atmosphere. The technique would considerably mask the appearance of a new more-refractory phase, but the authors did mention the possibility to explain the very rapid increase in the viscosity of a 50 per cent TiO_2 slag at temperatures up to 1550°C, as compared with the more gradual thickening of the same slag at 1600°C. It was also shown that increased temperature, a higher alumina content, and replacement of the argon with nitrogen in the furnace atmosphere all increased the thickening rate, and that carbon as the reductant was a prerequisite for thickening. The viscosity did not increase when CO was the reducing agent.

An alternative thickening mechanism could be that causing the appearance of finely dispersed reaction products consisting of titanium carbide, nitride, or a solid solution of these. Ohno and Ross⁵ discarded the suggestion since these solid phases could be expected to form surface layers. Semik³, working on blast-furnace type slags, found that sufficient carbide was formed after prolonged reduction in graphite crucibles to cause marked thickening. Freidenzon⁶ attributed the change in viscosity occurring in members of the system $\text{CaO-SiO}_2\text{-}$

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$\text{Al}_2\text{O}_3\text{-TiO}_2$ to heterogeneity in the slag due to the presence of TiC and TiN in finely dispersed form. Using the Einstein equation

$$\eta = \eta_0(1 + 2,5\phi),$$

where ϕ is the degree of heterogeneity of the system as derived from the analyses of the slag and metal fractions of the 'buckshot slag' recovered from a blast furnace, he calculated an approximate viscosity value of 2,8 Ns/m² for the slag. Gruzdev *et al.*⁹ measured the increase in viscosity brought about by the addition of TiC in finely dispersed form.

Apart from their effect on the viscosity of a slag, these very high melting compounds may separate from the melt and grow outward and upward in the hearth into the slag layer in the blast furnace. The constriction resulting from this would give rise to a higher than normal slag level, leading to the normal symptoms of trouble. Eventually the accretion could interfere with the flow of materials above the tuyère line. Such a mechanism was proposed by Delve *et al.*⁴.

In the research work described here, it was assumed that the formation of solid reduction products would have a deleterious effect on furnace operation. The work was therefore confined to slags that had been reduced by carbon but that contained no TiC. As smelting in an electric-arc furnace was the operation that prompted the research, reduction was carried out in an argon atmosphere in the absence of nitrogen. The most important reaction was consequently the reduction of TiO_2 to lower oxides.

Selection and Preparation of Slag Samples

The entire range of slag compositions and the reasons for their selection have already been stated¹. The twenty mixtures were all tested during the present investigation as well, but in this paper only the measurements conducted on seven slags are reported (Table I). This selection is based on the composition of B14, which was of immediate interest to a South African plant.

Table I includes three series of slag compositions:

- A5-B14-C23, in which the basicity and the CaO/MgO ratio were constant, the variable being the concentration of $(\text{TiO}_2 + \text{Al}_2\text{O}_3)$ in mass per cent;
- B13-B14-B15, in which the $(\text{TiO}_2 + \text{Al}_2\text{O}_3)$ and $(\text{CaO} + \text{MgO})/\text{SiO}_2$ were constant and the CaO/MgO ratio varied;
- B11-B14-B17, in which the $(\text{TiO}_2 + \text{Al}_2\text{O}_3)$ and CaO/MgO were constant, while the basicity ratio varied from 1,7 to 0,8.

The slags, which had been premelted in an argon

atmosphere, were reduced in graphite crucibles for selected time intervals in preparation for the measurements of viscosity and electrical resistance. Full experimental details are given elsewhere¹¹.

The reduction times chosen had to meet the following requirements:

- (1) the resulting degree of reduction with respect to titanium had to be realistic in terms of plant practice;
- (2) the absence of titanium carbide was essential;
- (3) the overall slag composition was not to be altered materially during reduction.

A reduction time of 45 to 60 minutes at 1550°C proved to be realistic. The removal of silicon from the slag was significant only for the most acidic slag (B17), in which the SiO_2 content was reduced from 31,10 to 27,02 per cent after reduction for 2 hours at 1550°C. The average carbon content of the reduced slags was 0,06 per cent, and more detailed investigations¹¹ revealed that no TiC (or SiC) was present in the reduced samples.

It is concluded that any change in the properties of the slags during reduction must be due only to the reduction of TiO_2 to lower oxides, except in the case of very acidic slags, where the reduction of SiO_2 to SiO is significant.

Experimental Method

The reduced samples were removed from the graphite crucibles and transferred to molybdenum crucibles for the measurement of viscosity and electrical resistance, which also provided approximate values of the liquidus temperature. All the measurements were made in an argon atmosphere as described in detail elsewhere¹¹.

Results and Discussion

Liquidus Temperature and Primary Phase

The results are given in Table II and for some slags also in Figs. 1 to 5. The approximate liquidus temperatures are those obtained from viscosity measurements except for slag B14, where the values derived from the measurements of electrical resistance were also available. The two sets of values agree surprisingly well. X-ray-diffraction camera samples of B14 that had been reduced for 90 minutes at 1550°C were prepared in the cell of the high-temperature microscope in argon by quenching down from temperatures ranging from 1390 to 1460°C. The liquidus temperature was shown to lie between 1440 and 1460°C, which is in good agreement with the values obtained from indirect methods.

There is an obvious relationship between the behaviour

TABLE I

INITIAL COMPOSITIONS OF THE SYNTHETIC SLAGS INVESTIGATED

| Slag group | Slag no. | $(\text{TiO}_2 + \text{Al}_2\text{O}_3)$ % | CaO+MgO | | TiO_2 % | Al_2O_3 % | SiO_2 % | CaO % | MgO % |
|------------|----------|--|---------|----------------|------------------|---------------------------|------------------|--------|--------|
| | | | | SiO_2 | | | | | |
| A | 5 | 36,000 | 1,401 | 1,000 | 24,800 | 11,200 | 26,650 | 18,675 | 18,675 |
| B | 11 | 44,000 | 1,699 | 1,000 | 30,200 | 13,800 | 20,750 | 17,625 | 17,625 |
| B | 13 | 44,000 | 1,400 | 2,000 | 30,200 | 13,800 | 23,330 | 21,780 | 10,890 |
| B | 14 | 44,000 | 1,400 | 1,000 | 30,200 | 13,800 | 23,330 | 16,335 | 16,335 |
| B | 15 | 44,000 | 1,400 | 0,500 | 30,200 | 13,800 | 23,330 | 10,890 | 21,780 |
| B | 17 | 44,000 | 0,801 | 1,000 | 30,200 | 13,800 | 31,100 | 12,450 | 12,450 |
| C | 23 | 54,000 | 1,397 | 1,000 | 37,180 | 16,820 | 19,190 | 13,405 | 13,405 |

of the melting temperature during reduction and the primary phase of the unreduced slag. If the primary crystallization product is magnesium aluminium titanate (M), the melting temperature tends to increase during reduction. Examples of this are slags B14 (see also Fig. 3), B15 and B17 (see also Fig. 4), and C23. However, when the original slag had perovskite (P) as the primary phase, the change in liquidus temperature was insignificant, e.g. slags A5 (see also Fig. 1), B11 (see Fig. 2), and B13.

To investigate the possibility that slags with M as primary phase undergo a change of primary phase, further investigations were undertaken using B14 and B11 as examples of the two types of slag.

(a) *Slags with M as Primary Phase (Example B14)*

Highly refractory reaction products could be expected to be concentrated at the slag-graphite and slag-gas interfaces. Powdered specimens were therefore removed from the surfaces of the sample of B14 that had been reduced at 1550°C for 90 minutes. On the surfaces that had been in contact with graphite, M and P, which were known to be

the primary and secondary phases of unreduced B14, were readily identified. The remaining lines were best interpreted as belonging to a mixture of lower titanium oxides (higher than $TiO_{1.5}$) with Ti_3O_5 (anosovite) predominating. On the surface that had been in contact with the gas, the slag was in the glassy state. A hole was drilled along the axis of the cylindrical slag sample, and the resulting powder was melted and quenched from 1440°C. (The approximate liquidus temperature from the viscosity measurement was 1456°). The simple set of lines obtained by X-ray-diffraction analysis of the quenched specimen clearly belonged to $MgO \cdot Al_2O_3$. By a classical quench technique, the bulk samples of the reduced slag were shown to have a primary phase consisting of a mixture of M and S (spinel, $MgO \cdot Al_2O_3$). The same mixture was also confirmed in other reduced derivatives of B14, as shown in Table II.

(b) *Slags with P as the Primary Phase (Example B11)*

The slag sample that had been reduced for 90 minutes at 1550° was treated in essentially the same

TABLE II
LIQUIDUS TEMPERATURES, PRIMARY PHASES, VISCOSITIES, AND ELECTRICAL RESISTIVITIES OF REDUCED AND UNREDUCED SLAGS AT SELECTED TEMPERATURES

| Slag no. | Reduction temp. °C | Reduction time min | Approx. liq. temp. °C | Primary phase* | Viscosity (Ns/m ² × 10 ³) and resistivity† (Ωm × 10 ³) at °C: | | | | | | | | | | | | | | | | |
|----------|--------------------|--------------------|-----------------------|----------------|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|------|------|------|------|-----|--|
| | | | | | 1360 | 1380 | 1400 | 1420 | 1440 | 1460 | 1480 | 1500 | 1520 | 1540 | 1560 | 1580 | 1600 | 1620 | 1640 | | |
| A5 | — | — | 1361 | P | | 156 | 142 | 129 | 118 | 108 | 99 | 91 | | | | | | | | | |
| | 1550 | 15 | 1361 | | | 150 | 132 | 117 | 105 | 94 | 83 | 73 | 65 | | | | | | | | |
| | 1550 | 30 | 1358 | | | 130 | 111 | 96 | 84 | 75 | 66 | 58 | | | | | | | | | |
| | 1550 | 60 | 1374 | P | | 178 | 128 | 109 | 95 | 85 | 78 | 73 | 70 | | | | | | | | |
| B11 | — | — | 1455 | P | | | | | | 94 | 87 | 80 | 74 | 68 | 63 | | | | | | |
| | 1550 | 15 | 1466 | | | | | | | | 87 | 64 | 59 | 56 | 54 | 53 | 52 | 51 | | | |
| | 1550 | 30 | 1472 | | | | | | | | 63 | 55 | 50 | 47 | 45 | 43 | 43 | 41 | | | |
| | 1550 | 45 | 1475 | P | | | | | | | 154 | 124 | 106 | 95 | 87 | 80 | 75 | | | | |
| | 1550 | 90 | 1483 | | | | | | | | | 283 | 238 | 208 | 185 | 167 | 148 | 132 | | | |
| | 1600 | 30 | 1473 | | | | | | | | | 144 | 124 | 107 | 94 | 83 | 75 | 67 | 60 | 55 | |
| | 1600 | 60 | 1490 | | | | | | | | 154 | 130 | 112 | 98 | 86 | 76 | 67 | 67 | 59 | | |
| B13 | — | — | 1337 | P | 166 | 144 | 126 | 110 | 96 | 85 | 75 | 66 | 59 | 52 | | | | | | | |
| | 1550 | 15 | 1340 | | 126 | 101 | 83 | 71 | 61 | 54 | 47 | 42 | 37 | | | | | | | | |
| | 1550 | 30 | 1337 | | 114 | 98 | 86 | 76 | 68 | 61 | 54 | 49 | 44 | | | | | | | | |
| | 1550 | 45 | 1350 | | 118 | 103 | 97 | 90 | 84 | 79 | 75 | 72 | 68 | | | | | | | | |
| | 1550 | 60 | 1350 | | 197 | 165 | 142 | 127 | 114 | 103 | 92 | 85 | 75 | | | | | | | | |
| B14 | — | — | 1335 | M | 139 | 126 | 114 | 103 | 94 | 86 | 78 | 72 | 66 | 61 | | | | | | | |
| | 1500 | 30 | 1365 | | (1,03) | (0,96) | (0,89) | (0,83) | (0,77) | (0,72) | (0,68) | (0,63) | | | | | | | | | |
| | 1500 | 60 | 1413 | | | 83 | 71 | 64 | 59 | 55 | 52 | 51 | 50 | 48 | | | | | | | |
| | 1500 | 90 | 1430 | M+S | 106 | 84 | 72 | 63 | 56 | 52 | 48 | 45 | 42 | 42 | 74 | 65 | | | | | |
| | 1550 | 15 | 1347 | | | | | | | | | | | | | | | | | | |
| | 1550 | 30 | 1383 | | | 130 | (0,80) | (0,73) | (0,68) | (0,64) | (0,60) | (0,56) | (0,52) | (0,47) | (0,43) | | | | | | |
| | 1550 | 45 | 1438 | M+S | | | | | | | | | | | | | | | | | |
| | 1550 | 60 | 1463 | | | | | | | | | | | | | | | | | | |
| | 1550 | 90 | 1456 | M+S | | | | | | | | | | | | | | | | | |
| | 1550 | 120 | 1463 | | | | | | | | | | | | | | | | | | |
| | 1550 | 180 | 1481 | M+S | | | | | | | | | | | | | | | | | |
| | 1600 | 20 | 1420 | | | | | 129 | 108 | 97 | 90 | | | | | | | | | | |
| | 1600 | 30 | 1491 | | | | | | | | | | | | | | | | | | |
| 1600 | 45 | 1527 | | | | | | | | | | | | | | | | | | | |
| 1600 | 90 | 1530 | | | | | | | | | | | | | | | | | | | |
| 1600 | 120 | 1528 | | | | | | | | | | | | | | | | | | | |
| B15 | — | — | 1492 | M | | | | | | | | 132 | 113 | 97 | 84 | | | | | | |
| | 1550 | 15 | 1492 | | | | | | | | | | 101 | 85 | 76 | 72 | | | | | |
| | 1550 | 30 | 1504 | | | | | | | | | | 151 | 126 | 116 | 111 | | | | | |
| | 1550 | 45 | 1524 | | | | | | | | | | | 202 | 170 | 156 | 148 | | | | |
| B17 | — | — | 1420 | M | | | | 330 | 281 | 240 | 206 | 177 | 154 | 133 | 116 | | | | | | |
| | 1550 | 15 | 1461 | | | | | | | | | | | | | | | | | | |
| | 1550 | 30 | 1481 | | | | | | | | 259 | 224 | 201 | 183 | 165 | 152 | 140 | 130 | 126 | | |
| | 1550 | 45 | 1489 | | | | | | | | | 187 | 160 | 146 | 139 | 134 | 130 | 128 | 125 | | |
| | 1550 | 90 | 1523 | | | | | | | | | | 147 | 139 | 134 | 131 | 128 | 125 | | | |
| | 1600 | 10 | 1463 | | | | | | | | | | | 126 | 112 | 102 | 95 | 88 | | | |
| | 1600 | 20 | 1524 | | | | | | | | 292 | 255 | 230 | 211 | 193 | 177 | 163 | 151 | | | |
| | 1600 | 40 | 1547 | | | | | | | | | | | 190 | 168 | 155 | 145 | 137 | 131 | 126 | |
| 1600 | 60 | 1547 | | | | | | | | | | | | 141 | 128 | 118 | 109 | 102 | | | |
| C23 | — | — | 1447 | M | | | | | | 108 | 95 | 83 | 74 | 65 | 58 | | | | | | |
| | 1550 | 60 | 1516 | | | | | | | | | | 154 | 126 | 112 | 103 | 97 | | | | |

*P = perovskite, M = magnesium aluminium titanate, S = spinel

†Resistivity values are given in brackets. The italic figure values are for approximately (liquidus temp. + 50°C).

way as the corresponding sample of B14. The surface powders again contained, in addition to P, what appeared to be a mixture of lower titanium oxides. The core powder, quenched from 1430°, showed only the pattern of P. The primary and secondary crystallization products of the bulk reduced slag were shown to be P and M respectively.

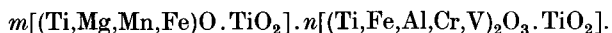
In the system MgO-Al₂O₃, phase 4(MgO.2TiO₂).Al₂O₃.TiO₂ (M) lies on the join MgO.2TiO₂-Al₂O₃.TiO₂. These two end members are both isomorphous with pseudo-brookite, Fe₂O₃.TiO₂. The phase relationships along the join have been studied by Boden and Glasser¹². Above 1262° the sub-solidus phase distribution shows complete solid solubility between the two end members. The X-ray *d*-spacings measured by these authors increase linearly with the concentration in mole per cent of MgO.2TiO₂. Above 1375° the two spinels 2MgO.TiO₂ (inverse) and MgO.Al₂O₃ (normal) are also completely miscible, and the X-ray *d*-spacings are linear functions of composition, increasing as the Mg₂TiO₄ content increases.

It is also significant that the homogeneous ternary spinel field is in the shape of a wedge with its base on the MgO.Al₂O₃ join, the wedge terminating on the composition Mg₂TiO₄. The *d*-spacings of the ternary spinel solid solutions go through the wedge almost parallel with the iso-magnesia contours. According to Boden and Glasser, these lines show that a spinel containing 32 per cent MgO, 44 per cent Al₂O₃, and 19 per cent TiO₂ by mass has the same unit cell size as stoichiometric MgO.Al₂O₃.

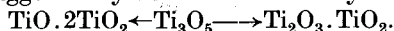
The proposed melting temperatures of the most important end members in the system are as follows^{13, 14}:

| | |
|--|--------|
| 2MgO.TiO ₂ | 1732°C |
| MgO.TiO ₂ | 1630°C |
| MgO.2TiO ₂ | 1652°C |
| MgO.Al ₂ O ₃ | 2135°C |
| Al ₂ O ₃ .TiO ₂ | 1860°C |

According to Reznichenko¹⁵, the most important mineral group occurring in industrial high-titania slags (of approximately Sorel type) is the anosovite group, which consists of solid solutions based on the Ti₃O₅ structure (orthorhombic). The proposed general formula is



The possibility of complete mutual dissolution is strongly suggested by the variable valency of Ti in Ti₃O₅:



The ionic radii of the mutually substituting divalent cations mentioned above for the anosovite group are sufficiently similar to make substitution feasible¹¹. The same applies to the trivalent cations.

On the other hand, CaO.TiO₂ is known to be a very stable phase. It has a melting temperature of approximately 2000°C compared with, for example, FeO.TiO₂(1470°C), MgO.TiO₂(1630°C), and MgO.Al₂O₃(2100°C).

There are clear indications (to be discussed later) that, as the reduction time is extended, the oxygen content of the reduced slags tends to a level corresponding to the stoichiometry of Ti₃O₅. It has also been indicated, although not proved conclusively, that the reduction product at the slag-graphite interface appears to contain

a high concentration of the same compound. In the light of the above discussion, the disproportionation of Ti₃O₅ in a system reduced to a level at which the oxygen content is suitable appears to be feasible. The disproportionation products are isomorphous with the end members MgO.2TiO₂ and Al₂O₃.TiO₂ in the MgO-TiO₂-Al₂O₃ system, so that Ti²⁺ can replace Mg²⁺, and Ti³⁺ can replace Al³⁺, in the compound 4(MgO.2TiO₂).Al₂O₃.TiO₂. In the limiting case, replacement under severely non-equilibrium conditions as exist at the phase boundary must lead to the separation of a lower titanium oxide. It has been shown that, even in the oxidized state, the spinel phase MgO.Al₂O₃ accompanies M when the latter is the primary crystallization product¹⁶. Replacement of Mg²⁺ with Ti²⁺ and of Al³⁺ with Ti³⁺ must lead to at least a change favouring the spinel phase in the bulk of the slag. The spinel in its pure form is a stable high-temperature phase. Lower titanium oxides at the molar O/Ti ratio in which they are present in this system (down to 1.67) are probably not congruently melting, but the general temperature where a true liquid is expected to exist is above 1800°C.

This mechanism appears to be in accord with the observations made in the present study when the slag with M as the original primary phase was investigated in the as-reduced condition. The phase S, reported as present in the core powders of such reduced slags, is not expected to conform stoichiometrically with pure spinel, but rather to be a member of the solid-solution series containing MgO, Al₂O₃, and TiO₂. The results of Boden and Glasser¹² appear to confirm such a possibility.

However, the increased melting temperatures reported here are those of homogenized melts in which lower oxides of titanium were not identified. The primary phase was a mixture of M and S. It is suggested that the lower oxides of titanium containing Ti²⁺ and Ti³⁺ were redistributed, a pseudo-brookite solid solution phase of composition similar to the one suggested by Reznichenko¹⁵ was reconstructed, and, because of mutual substitution, the spinel phase persisted. The appearance of the refractory spinel can be expected to raise the liquidus temperature of the slag.

Viscosity

The results are summarized in Table II, and the behaviour of selected slags is also shown in Figs. 1 to 4. These diagrams show the following:

- neither the viscosity nor liquidus temperature of slag A5 was greatly affected (Fig. 1);
- the liquidus temperature of slag B11 was virtually constant but the viscosity rose (Fig. 2) — slag B13 is similar;
- both the liquidus temperature and viscosity of slag B14 increased (Fig. 3) — slags B15 and C23 are similar;
- the liquidus temperature of slag B17 rose and the viscosity decreased (Fig. 4).

Effect of a Change in Basicity

The different behaviour of the three slags B11, B14, and B17 (decreasing basicity index) under reducing conditions at 1550°C is apparent from Figs. 2 to 4. For all the slags, there is an initial period during which there

is no thickening. For the more acidic slags, the liquids actually become more fluid during this interval, and in the case of B17 (the most acidic member of the series), the 'thinning' persists for reduction times of up to 90 minutes. The other two slags thicken considerably after passing through a viscosity minimum.

The possible relationship between the degree of reduction of titanium oxide and the viscosity of a particular slag will be discussed elsewhere. Merely on the basis of the results presented here, certain suggestions can be made. During the reduction sequence $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti^{2+}$, there is a marked decrease in the cationic field strength, I , also due to the increase in the cationic radius (0,68 Å through 0,76 Å to 0,94 Å). If a high field strength is associated with a low co-ordination number and a pronounced network-forming tendency, progressive removal of oxygen from these titaniferous melts must give rise to improved fluidity.

In the more detailed work¹¹, an explanation was offered for the high fluidity of the slags under oxidizing conditions. In the behaviour pattern of reduced slags, the viscosity minimum is thought to be associated with (a) small losses of silicon as SiO from the system, and (b) the disappearance of any tetrahedrally co-ordinated titanium.

The viscosity-lowering effect of (b) is not great (the trough is a shallow one) because of the mixed and predominantly higher co-ordination existing in the first instance, and because of the comparatively mild change brought about by a change in the co-ordination number of titanium.

The overridingly important thickening effect is due to the loss of oxygen from the melt. Not only does this lead to more extensive sharing of oxygen between silicate tetrahedra, but also possibly to a change in the role of alumina. The lowered field strength of titanium ions in

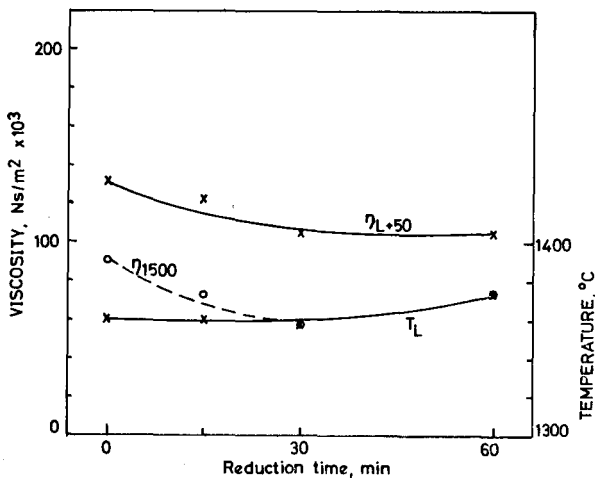


Fig. 1—Viscosity and liquidus temperature of slag A5, reduced at 1550°C

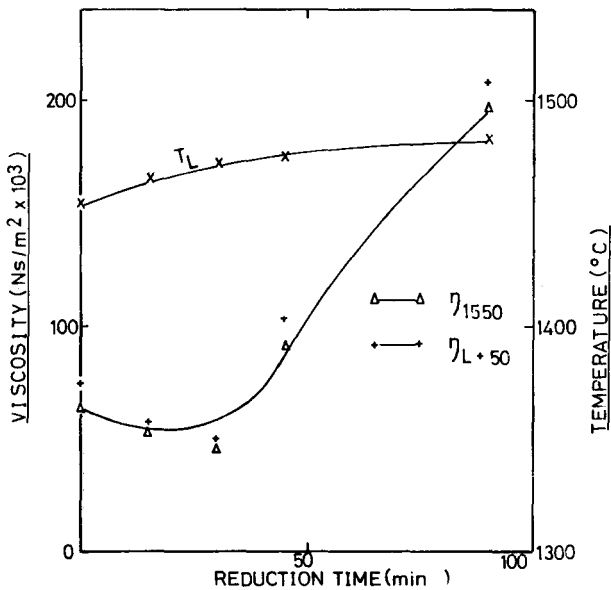


Fig. 2—Viscosity of slag B11, reduced at 1550°C

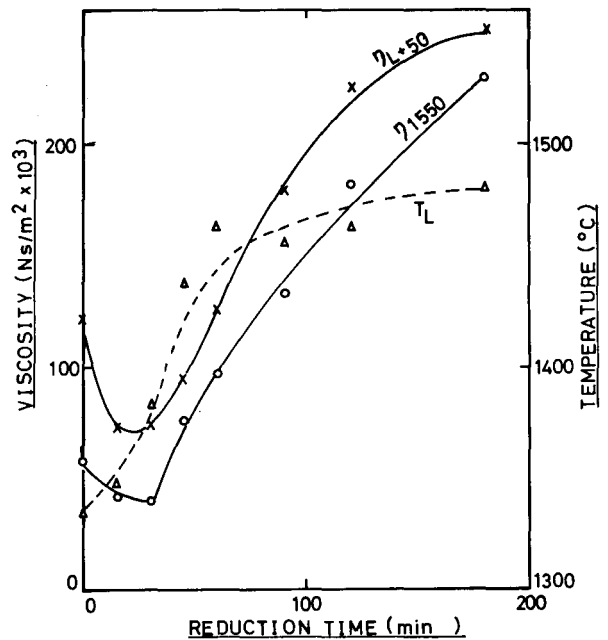


Fig. 3—Properties of slag B14, reduced by carbon at 1550°C

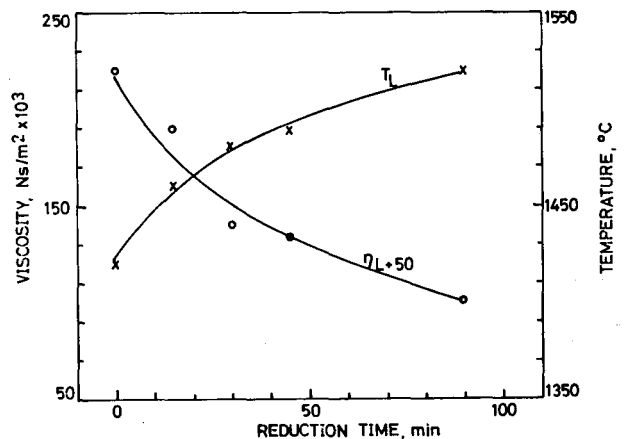


Fig. 4—Viscosity and liquidus temperature of slag B17, reduced at 1550°C

the melt is almost entirely cancelled by these effects. The role of Ti^{2+} , which must eventually be formed in considerable concentration, should then be seen as one of network distortion with pronounced bridging.

The effect of a high initial silica concentration is to retard the rate of reduction of TiO_2 and to cause a decrease in viscosity during reduction owing to the removal of SiO. The overall effect is to delay the start of the thickening process.

Effect of CaO/MgO ratio

The effect of the CaO/MgO ratio is shown for slags B13, B14, and B15 in Tables II and III, the latter being a summary of the relevant data in Table II.

The overall behaviour pattern, which involves an initial drop in the viscosity at 50°C above liquidus temperature (η_{L+50}) followed by an increase, is recognizable for all three slags. However, the slag with the high MgO content (B15) starts thickening relatively early. These comments are based on metal oxide concentrations expressed as mass per cent. In an earlier paper¹ on the properties of unreduced slags, it was pointed out that a decrease in the mass ratio CaO/MgO means an increase in the molar basicity index $(CaO+MgO)/SiO_2$. This may explain the fact that the high MgO slag thickened more quickly. Moreover, Mg^{2+} has a greater field strength than Ca^{2+} . In the reduced slag, Mg^{2+} may therefore be expected to have a greater 'bridging' effect and to aid the thickening process in the system, which is deficient in oxygen.

Effect of $(TiO_2+Al_2O_3)$ Content

For slags A5, B14, and C23, the effect of the $(TiO_2+Al_2O_3)$ content is shown in Tables II and IV and in Figs. 1 and 3.

If it is assumed that the 'viscosity minimum' is common to all the slags, A5 may have passed the minimum, but it is still more fluid than the original slag. Fig. 3 shows that the viscosity of B14 is increasing (at 60 minutes), although the difference in the table is insignificant. C23 has apparently passed its minimum, and the thickening appears to be particularly marked. This may be due to two factors.

(a) The increased concentration of TiO_2 from 30,2 to

37,2 per cent (B14 to C23) must have a pronounced effect on oxygen activity and therefore on the rate of reduction of TiO_2 .

(b) The increase in the titania concentration is accompanied by an increase in the alumina content from 13,8 to 16,8 per cent. In an oxygen-deficient liquid, Al^{3+} may be forced to enter into fourfold co-ordination to a greater extent as the concentration of Al_2O_3 is raised.

Effect of Changes in the Reduction Temperature (see Table II)

The choice of slag compositions to illustrate this effect was based on basicity only (B11, B14, and B17), while comprehensive testing at three different temperatures was carried out only on slag B14.

For slag B11 there was a viscosity minimum when the reduction was performed at 1550°C. At 1600°C the minimum was either absent altogether or occurred very soon after reduction commenced. It appears as though the rate of thickening at 1600°C was not much faster than at 1550°C for reduction times longer than 30 minutes. This may be due to the fact that the initially very fluid basic slag has a high initial reduction rate, reaching the point where a high viscosity starts to inhibit the reaction sooner as the reduction temperature is raised.

For slag B14 at the 30-minute level, η_{L+50} for samples reduced at all three temperatures was below that of the original slag. The value for a reduction temperature of 1600° was only slightly below, showing that in this case the viscosity minimum had been passed. At 90 minutes, only the slag reduced at 1500° had a viscosity approximating that of the unreduced slag. At higher temperatures the corresponding melts were relatively much more viscous.

In the case of B17 with $(CaO+MgO)/SiO_2$ equal to 0,8, η_{L+50} was lowered more or less continuously when the reduction was carried out at 1550°C. At 1600° this measure of viscosity was beginning to increase after reduction for 90 minutes.

Electrical Resistivity

Fig. 5 is a summary of the experimental data available for the reduced derivatives of B14. (These are also given

TABLE III
THE EFFECT OF THE CaO/MgO RATIO ON VARIATION IN VISCOSITY DURING REDUCTION

| Slag no. | CaO/MgO | η_{L+50} ($Ns/m^2 \times 10^3$) for reduction times of: | |
|----------|---------|---|--------|
| | | 0 min | 45 min |
| B13 | 2 | 134 | 97 |
| B14 | 1 | 123 | 95 |
| B15 | 0,5 | 91 | 150 |

TABLE IV
EFFECT OF $(TiO_2+Al_2O_3)$ CONCENTRATION ON VARIATION IN VISCOSITY DURING REDUCTION

| Slag no. | $(TiO_2+Al_2O_3)$ mass % | η_{L+50} ($Ns/m^2 \times 10^3$) for reduction times of: | |
|----------|-----------------------------|---|--------|
| | | 0 min | 60 min |
| A5 | 36 | 135 | 106 |
| B14 | 44 | 123 | 126 |
| C23 | 54 | 85 | 109 |

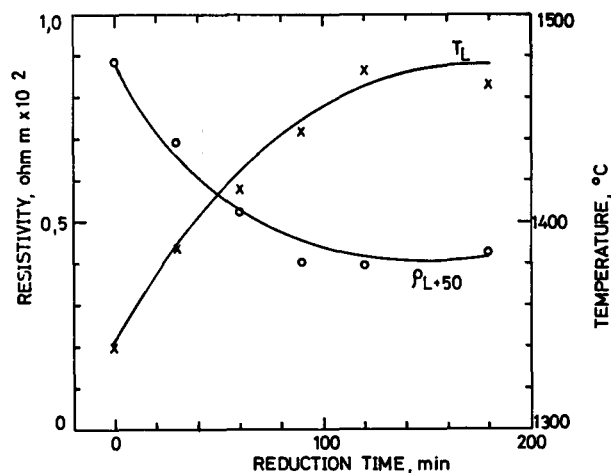


Fig. 5—Resistivity and liquidus temperature of slag B14, reduced at 1550°C

in Table II.) Reduction by carbon caused a marked decrease in the electrical resistivity of the slag at least over the first 90 minutes. Only thereafter did there appear to be a slight increase in the resistance of the melt. This is in sharp contrast to the viscosity data shown in Fig. 3.

This system in which the electrical properties are influenced by the valency of a transition metal ion is not unique. As might be expected from the mechanism of semi-conduction, Fe^{2+} and Fe^{3+} represent limiting conditions in slags that contain iron oxide. At either $x=0$ or $x=1$, where $x=Fe^{3+}/Fe$, ionic conduction is the only mode of charge transfer. The value $x=0.5$ frequently corresponds to a conductivity maximum associated with electronic conduction. As emphasized before, electronic conduction is thought to be significant even in unreduced titaniferous slags. While studies of the degree of reduction cannot be discussed here, it must be concluded for the time being that prolonged reduction increases the contribution of electronic conduction to such an extent that the indirect effect of anionic size is cancelled out to a considerable degree.

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Ion exchange and solvent extraction

During the past ten years, there has been an upsurge of interest in hydrometallurgical techniques for the extraction of metals and for the purification of the solutions produced during mineral processing. The need to treat low-grade and complex ores, the unavoidable air pollution caused by many pyrometallurgical operations, and the successful industrial application of selective reagents and resins for solvent extraction and ion exchange are but three of the many reasons for the current ascendancy of hydrometallurgy.

In 1976, the fundamental aspects of ion exchange and solvent extraction were presented in considerable detail at an SAIMM Vacation School entitled 'Hydrometallurgy: Theory and Practice'. The time is now right for industrial processes and equipment to be discussed,

and these will be the subjects of a symposium that will be held early in 1980. Contributions from leading international authorities in the fields of ion exchange and solvent extraction will ensure the value and success of the symposium.

The symposium is being organized jointly by the National Institute for Metallurgy, the South African Institution of Chemical Engineers, and the South African Institute of Mining and Metallurgy, and it will be held in NIM's Auditorium at Randburg.

Authors wishing to read papers at the symposium should send titles and abstracts to The Head: Liaison and Information Division, National Institute for Metallurgy, Private Bag X3015, 2125 Randburg. Tel. (011) 793-3511.

Hydrometallurgy

The Society of Chemical Industry is proposing to hold, as part of its Centenary Celebrations in June 1981, a 3 or 4-day conference on hydrometallurgy at U.M.I.S.T., Manchester.

Conference dates are June 30 to July 3, 1981.

Sessions will be devoted to unit operations in hydrometallurgy including

- leaching
- solid-liquid separation
- solvent extraction
- ion exchange
- membrane processes

precipitation methods
electrowinning.

The programme will include both invited and contributed papers, and the proceedings will be published.

Further information is obtainable from Conference Secretariat, Society of Chemical Industry, 14 Belgrave Square, London SW1X 8PS, England, or from Dr M. Cox, Secretary Solvent Extraction and Ion Exchange Group, School of Natural Science, The Hatfield Polytechnic, P.O. Box 109, Hatfield, Hertfordshire, AL10 9AB, England, or by telephone from Dr A. K. Haines at Johannesburg 836-1121.