

## PHYSICO-CHEMICAL PROPERTIES OF TITANIFEROUS SLAGS

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### SYNOPSIS

The phase equilibria, viscosities and sulphur capacities of titaniferous slags were determined in the composition range of CaO = 30 to 0 per cent, MgO = 0 to 30 per cent, SiO<sub>2</sub> = 19.69 per cent, Al<sub>2</sub>O<sub>3</sub> = 13.12 per cent and TiO<sub>2</sub> = 37.19 per cent. The phase equilibria were determined by high temperature microscopy, the viscosities were measured using a rotating outer cylinder viscometer and the sulphur capacities were evaluated from the results obtained by equilibrating the slag in a gas stream of CO, CO<sub>2</sub> and SO<sub>2</sub>. The behaviour of these titaniferous slags under reducing conditions was examined. Possible use of the slags for aggregate, or slag-cement, and the possibility of extracting the TiO<sub>2</sub> are discussed.

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### INTRODUCTION

The latest phase in the exploitation of the mineral wealth of the Bushveld Igneous Complex is the erection of a plant by the Highveld Steel and Vanadium Corporation Limited near Witbank to produce steel and vanadium-rich slag from the titaniferous magnetites occurring in this rock formation. These titaniferous magnetites occur as segregations in the gabbro body and the TiO<sub>2</sub> is mainly present within the structure of other constituent minerals but also occurs in smaller amounts as ilmenite and ulvospinel. The vanadium is thought to be present in the iron oxide phase due to isomorphous replacement of the iron.

Until very recently, it was feared that the high titania content of these titaniferous magnetites would militate against their value as useful iron ores. However, the design of an integrated plant to produce both steel and vanadium-rich slag, and in which the iron-making process is conducted in submerged arc furnaces instead of in

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conventional blast furnaces, considerably alleviates the problems associated with these ores. The process, as finally developed, is as follows: The ore, together with coal and flux consisting of limestone dolomite and silica is passed through a rotary kiln at a temperature of 900°C-950°C so effecting about a 55 per cent reduction of the iron oxide content of the ore and also preheating the charge. This partially reduced charge is then fed to submerged arc furnaces. The products from the smelting operation are pig iron containing the vanadium and a titaniferous slag containing the gangue from the ore. The vanadium-bearing pig iron is then partially blown with oxygen in a shaking ladle and a vanadium-rich slag is formed. The slag may be treated for the production of vanadium pentoxide and the pig iron is converted into steel.

Assessed primarily on the basis of preliminary pilot plant tests and also on the experience of attempts to treat somewhat similar ores in other countries, it was found that additions of limestone, dolomite and silica were required to produce slags of the required characteristics during the iron-making step. However, very little information existed regarding the liquidus temperatures, phase equilibria, viscosities, sulphur capacities and other related properties of such titaniferous slags. Also, the question arose as to what the effects would be when the limestone/dolomite mixture in the original flux was replaced by dolomite alone, dolomite being less expensive than limestone under local conditions. For these reasons, an extensive research project was sponsored by the board of Highveld Steel and Vanadium Corporation Limited to determine the physico-chemical properties of the titaniferous slags in the composition range anticipated in plant operation.

#### PHASE EQUILIBRIA

The phase equilibria of the titaniferous slags were determined for slags in the following composition range: CaO = 30.0 per cent, MgO = 0.30 per cent, SiO<sub>2</sub> = 19.69 per cent, Al<sub>2</sub>O<sub>3</sub> = 13.12 per cent and TiO<sub>2</sub> = 37.19 per cent. All the phase equilibria determinations were conducted under atmospheric conditions.

For these phase studies a high temperature microscope<sup>1</sup> and a micro differential thermal analyser<sup>2, 3</sup> based on the same principle, were constructed, the micro differential thermal analyser being shown in Fig. 1. In this apparatus a 5 per cent Rh-Pt/20 per cent Rh-Pt thermocouple has a triple function, i.e., the thermocouple serves as temperature measuring device, heating element and sample holder, the unit being heated during the positive half-cycles obtained by rectifying alternating current by means of diodes. The thermo-electromotive force is isolated by means of a synchronous converter and is measured during the negative half-cycles when no power is supplied to the thermocouple. This thermocouple, with the slag sample at the thermojunction, is housed in a cell attached to a stereoscopic microscope.

The slag samples were prepared by weighing and mixing the high purity oxide components. These mixtures were placed in platinum foil containers and fused, quenched and then ground to obtain homogeneous samples.

The determination of the liquidus temperature consists of lowering and then raising the temperature of the sample on the thermocouple after melting until, near the thermojunction, a very small crystal remains in the melt without showing signs of growth or decay. These determinations were carried out in quadruplicate—a new sample being used for each determination and only two determinations being carried out on the same thermocouple. In this manner it is possible to determine the liquidus temperature of a slag with an accuracy and precision of  $\pm 5^\circ\text{C}$  in relation to a set of standard slags.

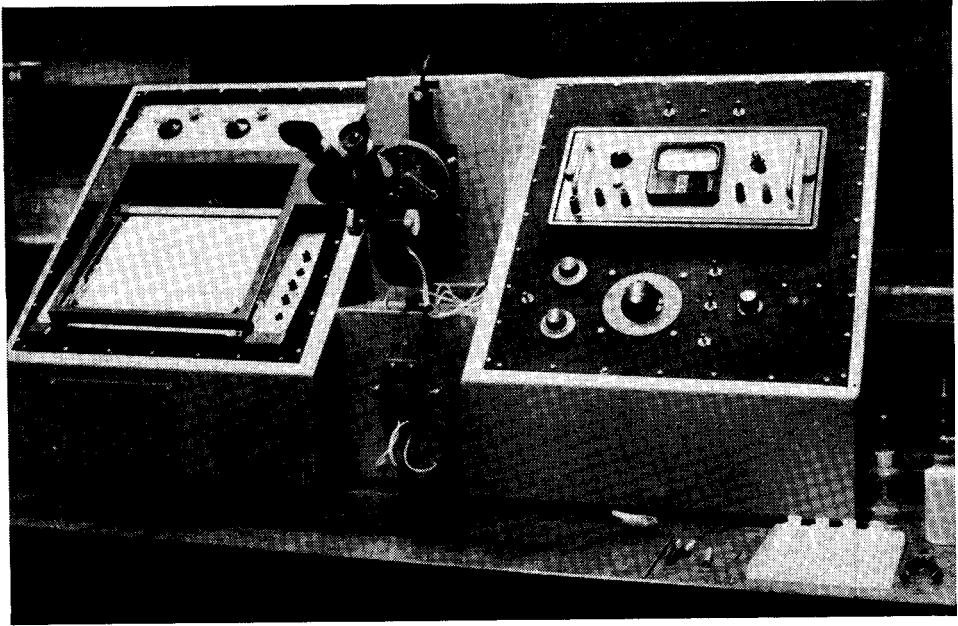


Fig. 1—View of the micro differential thermal analyzer

The method of determining the phase equilibria is described in detail in a previous publication<sup>4</sup>. In brief outline the procedure is as follows: The slag specimen on the thermocouple is cooled at a rate of 10°C per minute from 50°C above the liquidus temperature to a predetermined temperature and allowed to equilibrate at this temperature for 60 minutes. It is then either air- or water-quenched to prevent further transformation occurring. This slag specimen, of known thermal history, is then separated from the thermojunction and, after grinding, subjected to X-ray diffraction in a Debye-Scherrer camera. This method of plotting the phase equilibria was assisted by visual observation of the progress of crystallization through the microscope. When the amount of crystalline material already present was still sufficiently small to permit accurate observation of the precipitation of subsequent phases, the temperature of this subsequent appearance, determined in this manner, was correlated with that determined by the X-ray method. It is estimated that the temperature of appearance of a subsequent phase is, on an average, correct to within  $\pm 12\frac{1}{2}$ °C. This technique was repeated until the transverse section of the phase equilibria was established as shown in Fig. 2. It was decided to standardize on a 60 minute equilibrating soaking period for the slags after they had been cooled at a rate of 10°C per minute. While it is believed that this is sufficient to establish equilibrium conditions in the very small quantities of slag involved it is always possible that complete equilibrium conditions were not attained in all cases.

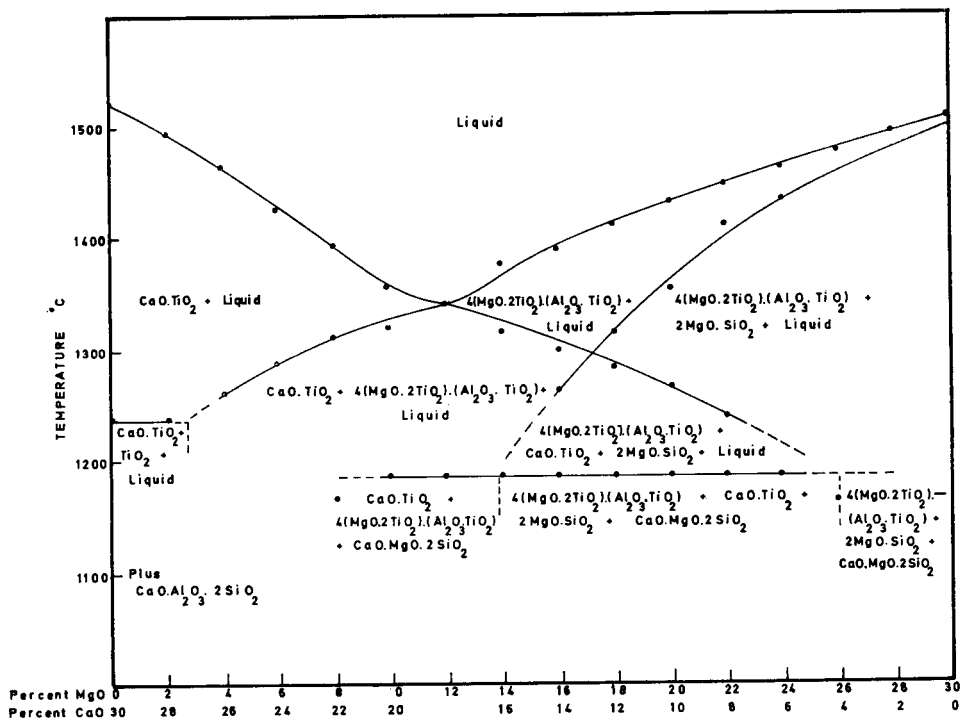


Fig. 2—Phase equilibria in the slag system: CaO = 30.0 per cent, MgO = 0.30 per cent, SiO<sub>2</sub> = 19.69 per cent, Al<sub>2</sub>O<sub>3</sub> = 13.12 per cent and TiO<sub>2</sub> = 37.19 per cent

Interest was also attached to knowledge of the behaviour of the liquidus temperatures of slags where the total (CaO + MgO) contents are 25 and 35 per cent respectively. The liquidus temperatures and primary phases for these compositions were determined in the manner as described above. The results are presented graphically in Fig. 3.

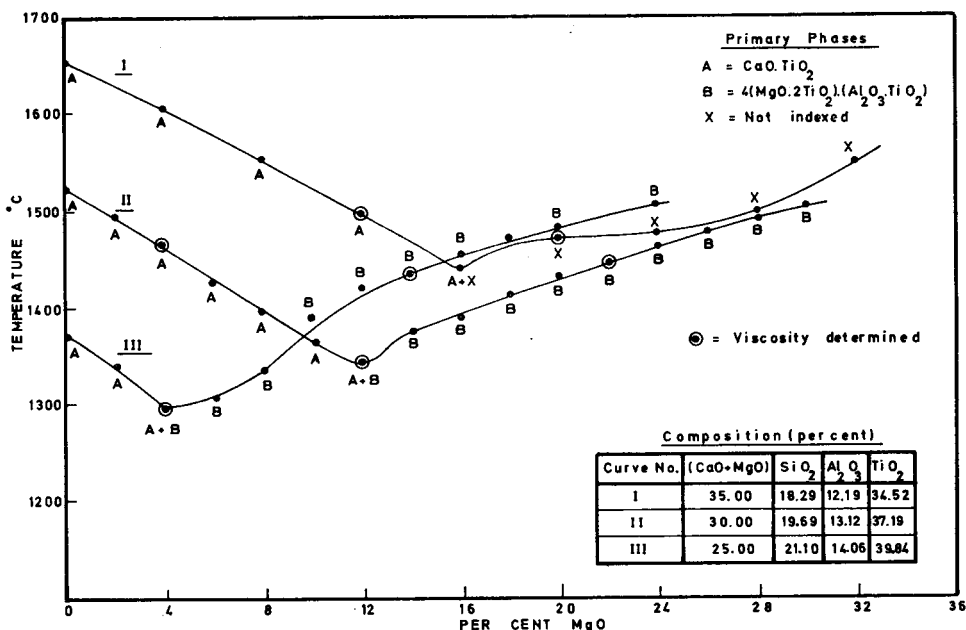


Fig. 3—Liquidus curves and primary phases for slags with (CaO + MgO) contents of 25 per cent, 30 per cent and 35 per cent respectively

VISCOSITIES

After careful consideration and several trial attempts to use a commercially available viscometer, based on the rotating inner cylinder principle, a rotating outer cylinder viscometer was constructed as shown in Fig. 4. This type of viscometer was considered to be the most suitable for these particular slags as the viscosities had been found to be low (about 1 poise) in the pilot determinations and furthermore, changes in viscosity between different slag compositions were not expected to be large.

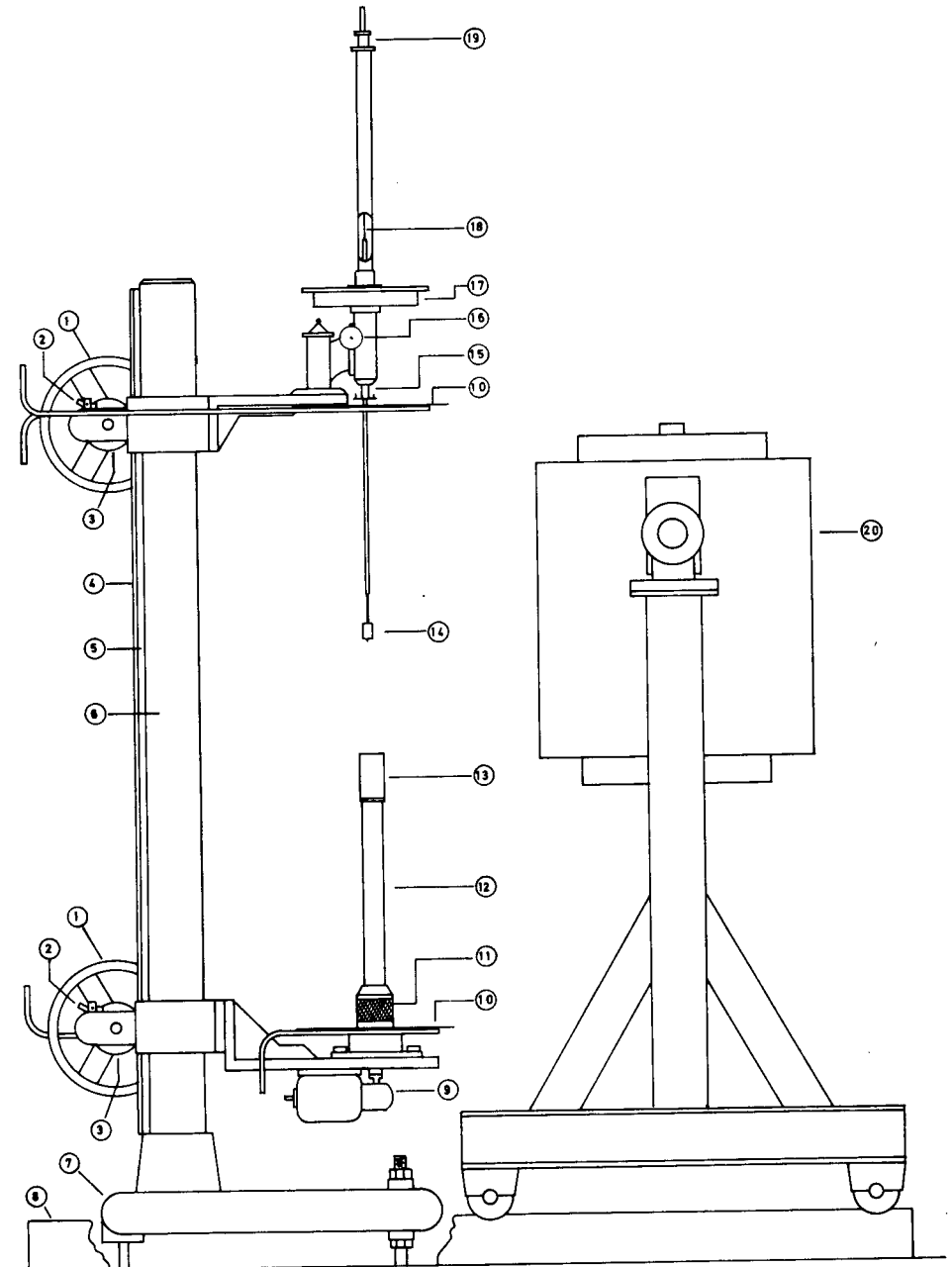


Fig. 4—Detailed drawing of the rotating outer cylinder viscometer

## Key to Fig. 4

1. Handwheel for adjustment.
2. Pawl for locking sprocket.
3. Sprocket engaging in chain rack.
4. Chain rack.
5. Tongue to prevent lateral movement of upper and lower stages.
6. Column.
7. Base.
8. Rails to permit movement of furnace.
9. Variable speed motor to rotate outer cylinder.
10. Water-cooled heat shield.
11. Collet chuck.
12. Mullite tube.
13. Outer cylinder.
14. Inner cylinder.
15. Collet with pins on insulated disc for thermocouple lead attachment.
16. Fine adjustment finger wheel.
17. Circular box fitted with glass window containing circular scale.
18. Torsion wire suspended inside brass tube.
19. Zero adjustment for torsion wire.
20. Tube furnace and frame.

In this apparatus an inner platinum cylinder, 1.58 cm in diameter and 2.53 cm long, is suspended in a rotating platinum outer cylinder of 3.81 cm diameter which contains the molten slag. These components of the viscometer are held within a vertical tube furnace. A thermocouple, threaded through the shaft supporting the inner cylinder, makes contact with the inside wall of the inner cylinder. The temperature of the slag is therefore measured as close as possible to the surface at which shear is taking place.

When a viscosity measurement is made, the temperature of the slag is noted and the thermocouple leads at the top of the inner cylinder shaft are disconnected. The angular velocity of the outer cylinder is determined. The viscous drag on the inner cylinder, caused by the rotation of the slag in the outer cylinder, is determined by the steady deflection of the copper-beryllium torsion wire from which the inner cylinder is suspended.

The viscometer was calibrated using oils; the viscosity of these oils having been determined by application of Stokes' Law. The method of determining the viscosity of the calibrating oils was checked against standard oils obtained from the United States Bureau of Commerce.

To make the calibration valid at elevated temperatures, a special inner and outer cylinder were fabricated from brass having the same dimensions as the platinum cylinders would attain at 1,400°C. Exhaustive testing of the viscometer with respect to misalignment of the cylinders, variation in slag level, etc. proved that the viscometer is capable of precision of better than  $\pm 5$  per cent.

The slags were prepared by weighing and mixing the chemically pure components (180 gm) and these were then melted in the rotating outer cylinder used in the viscometer. The inner cylinder was introduced into the molten slag and accurately positioned both with respect to depth and concentricity. The temperature of the slag was raised to some preselected temperature above the liquidus temperature and the viscosity was determined. The temperature was then decreased and the viscosity measured again until the data were obtained for a graph of viscosity versus temperature. This procedure was repeated at least once on a fresh sample of slag of the same composition.

The viscosities of the slag composition marked with a circle in Fig. 3 were determined in this manner. The results are depicted in Fig. 5.

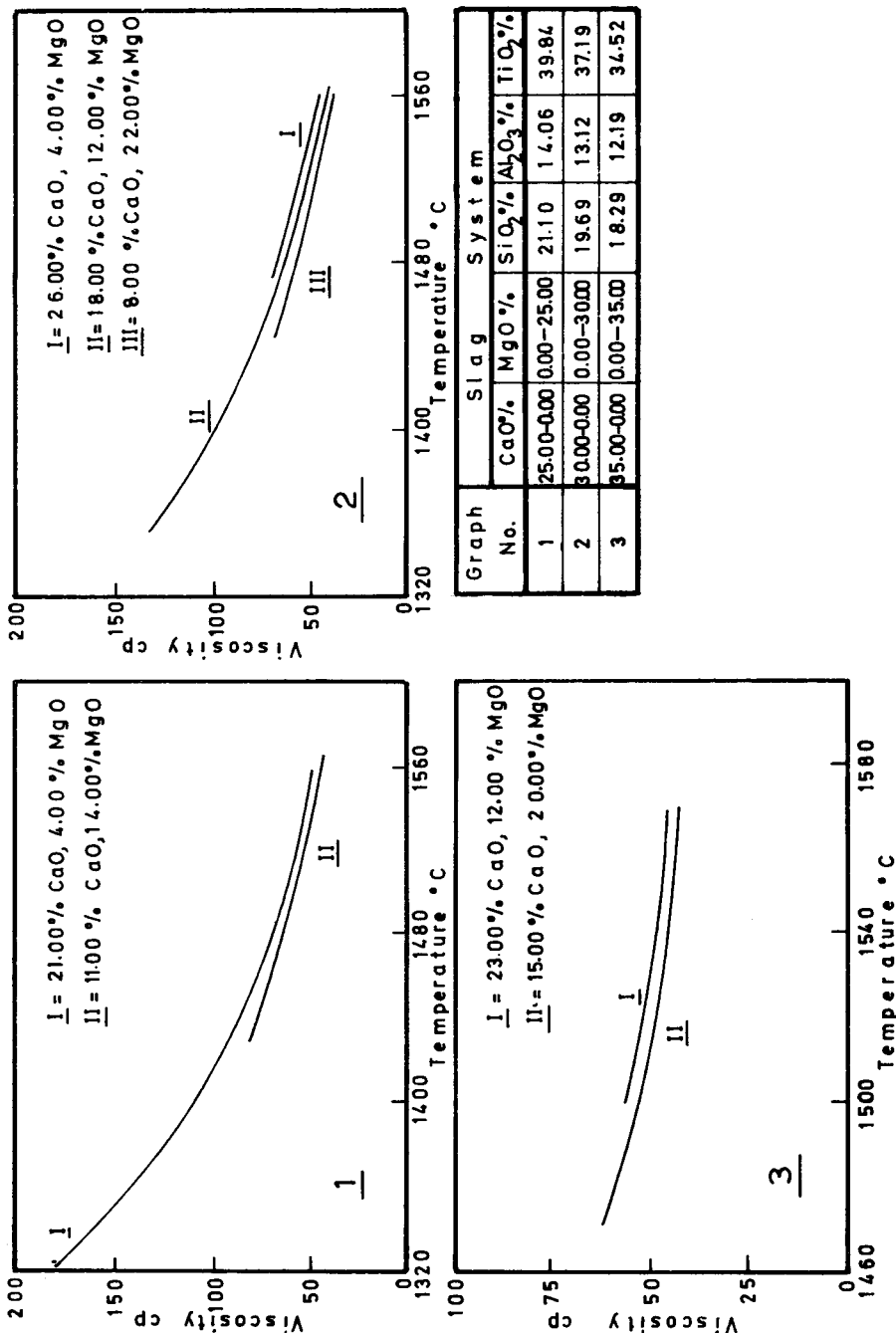


Fig. 5—Viscosities of the titaniferous slags



## DISCUSSION OF THE PHASE EQUILIBRIA AND THE VISCOSITY VALUES

The liquidus temperature of the slag is important in the operation of a submerged arc furnace since all the charge is not completely melted at any one time and it is, therefore, impossible to increase the temperature of the metal by increasing its retention time in the furnace. This is due to the fact that once the charge has reached the melting zone and has fused, it will drop away from the arc area. Consequently, the metal can only be superheated to the required degree (to permit teeming and subsequent handling in the molten state, etc.) by using a slag which has a liquidus temperature considerably higher than that of the metal. Hence it would appear that for the production of pig iron with a carbon content of 4.0-4.5 per cent, a slag with a liquidus temperature of about 1,350°-1,400°C is required.

The requirement that the liquidus temperature of the slag should be about 1,350-1,400°C implies, as is evident from Fig. 2, that the slag must contain both CaO and MgO. If the basic oxide components of the flux are changed from a limestone/dolomite mixture (CaO = 22 per cent, MgO = 8 per cent in the slag) to dolomite only (as was hoped would prove feasible) (CaO = 16 per cent, MgO = 14 per cent in the slag). Fig. 2 shows that the liquidus temperature changes from 1,395°C to 1,375°C which still meets the basic requirement. Further, the phase equilibria of the slags will change. In the slag as used on the pilot plant, the primary phase to crystallize is perovskite (CaO . TiO<sub>2</sub>) followed by 4(MgO . 2TiO<sub>2</sub>) . (Al<sub>2</sub>O<sub>3</sub> . TiO<sub>2</sub>) while in the slag produced by the employment of a dolomite flux, this order of crystallization is reversed. In addition, forsterite (2MgO . SiO<sub>2</sub>) crystallizes as the tertiary phase. The crystallization of diopside (CaO . MgO . 2SiO<sub>2</sub>) occurs at the solidus temperature and it appears that this temperature is constant over this range of slag compositions.

From Fig. 3 it can be seen that the titaniferous slags with different (CaO + MgO) contents exhibit large changes in liquidus temperatures with comparatively minor changes in basicity. Those changes, however, become much less marked as the ratio of MgO/CaO is increased until with about 16 per cent MgO the gap in liquidus temperature is reduced to about 50°C.

Each of the three graphs of liquidus temperatures shown in Fig. 3 passes through a decided minimum as the ratio of MgO/CaO is increased, the minima being 1,295°C, 1,340°C and 1,440°C respectively for the slags containing 25, 30 and 35 per cent of (CaO + MgO). These minima in liquidus temperatures occur at 4 per cent MgO for the slag containing 25 per cent (CaO + MgO), at 12 per cent MgO for 30 per cent (CaO + MgO) and at 16 per cent MgO for 35 per cent (CaO + MgO). This trough in the liquidus temperature graph is associated with a change in primary phase in each case. As the ratio of MgO/CaO is increased beyond the values corresponding with the minimum liquidus temperatures the differences in liquidus temperatures between the three curves decrease until at a content of 24 per cent MgO, for example, the liquidus temperatures are 1,505°C, 1,460°C and 1,475°C respectively.

The viscosity of the slag will affect the electric arc furnace smelting process in a number of ways. From a chemical viewpoint the most important effect is that, although the distribution of solutes in the system is governed by Nernst's Law, the kinetics of the overall reaction are governed by the rate of volume diffusion, which, in turn, may be related to fluidity. Therefore, a low viscosity enables the diffusion process in the slag to take place at a rate sufficiently high for a rapid approach to equilibrium of the slag/metal reactions and hence affects the kinetics of the process favourably.

Due to turbulence in the furnace and on tapping, small droplets of metal will occur in the slag. The rate of separation of these metal droplets from the slag is a

function of the viscosity of the slag. Also, an excessively viscous slag will give rise to operational difficulties. Firstly, the slag will tend to 'hang' in the furnace in the area adjacent to the arcs and, secondly, difficulties may be experienced in tapping the slag.

From the graphs presented in Fig. 5, it may be seen that the viscosities of the titaniferous slags are low and that the viscosity at constant temperature decreases slightly with increase in the MgO/CaO ratio in slags with constant (CaO + MgO) values. This may be attributed to the fact that  $Mg^{2+}$  has a cation field strength considerably greater than that of  $Ca^{2+}$  and hence has a greater tendency to co-ordinate itself with oxygen. This results in a relative weakening of any network structure with a corresponding reduction in the viscosity of the melt. Also, at constant temperature, the viscosity decreases with increasing basicity of the slag. This is explained by the fact that the proportion of network former, i.e., silica, is being replaced by network modifiers, i.e., CaO and MgO with an accompanying decrease in viscosity. It can also be deduced that, at a constant temperature above the liquidus temperature, the viscosities are higher for the slags which have lower liquidus temperatures. These slags also show a higher rate of reduction in viscosity with increase in temperature.

#### EFFECT OF REDUCING CONDITIONS

It is known that, under reducing conditions, the  $TiO_2$  in titaniferous slags may be reduced to lower oxides of Ti and/or to the carbide, nitride or carbo-nitride. There is considerable controversy as to the effects of this reduction but it is generally accepted that if the formation of titanium carbides and/or nitrides occurs these will separate out from the melt due to their insolubility and high melting point temperatures, causing an increase in viscosity because the slag system becomes heterogeneous. Frijdenzon *et al*<sup>5</sup> have shown that if a blast furnace slag, containing 15.0 per cent  $TiO_2$  is held under reducing conditions, the viscosity is considerably increased.

To ensure that the titaniferous slags were maintained under reducing conditions, the viscometer was modified so that the slag could be held in a rotating outer cylinder fabricated from graphite, the bottom of the furnace being closed off with a sand seal. However, during attempts to measure the viscosity of the slag as in previous tests, it was found that the liquidus temperature of the slag increased considerably although the few viscosity values which could be obtained were similar to those obtained under atmospheric conditions.

Following several unsuccessful attempts, a technique, using the basic components of the viscometer, was devised whereby the liquidus temperature could be measured at intervals while the slag was being maintained under reducing conditions. The slag was contained in a rotating graphite crucible and the inner cylinder of the viscometer was replaced by a 6 mm diameter thermocouple insulator fitted with a platinum sheath over one end. This platinum sheath was immersed in the slag and a thermocouple was threaded through the insulator and welded to this platinum sheath. The temperature of the slag was raised to above the liquidus temperature, as measured under atmospheric conditions, and after holding at this temperature the temperature was slowly decreased until a sudden deflection of the torsion wire indicated that crystals had started to precipitate on the platinum sheath. It is generally accepted that the inner cylinder in this type of apparatus is the coolest part of the system and hence initial crystallization will preferentially take place upon it. The temperature of the slag was raised again and the process repeated. In this manner it was possible to establish Fig. 6. It had previously been shown that this technique gave liquidus temperatures 10 to 15°C lower as compared with those obtained by the high temperature microscope using a standard slag.

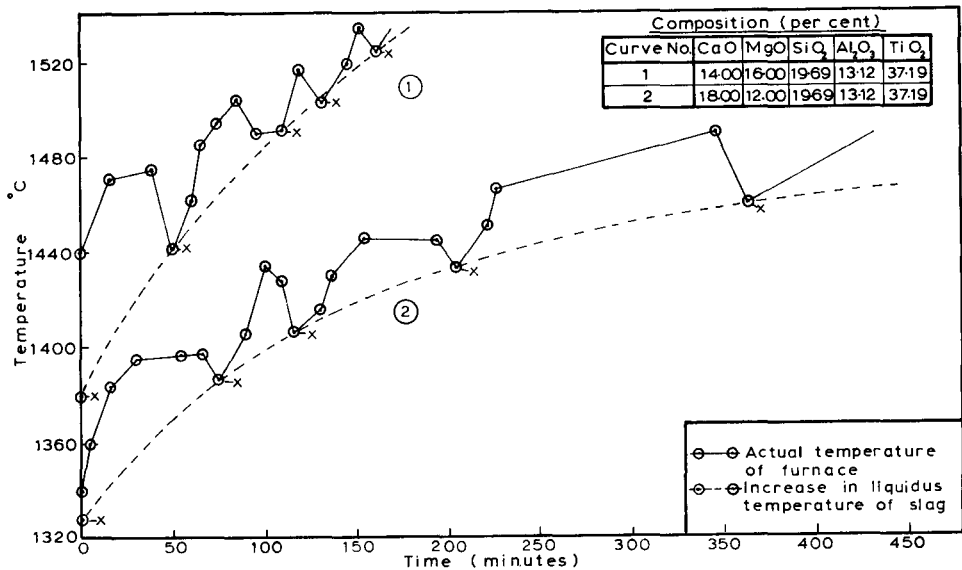


Fig. 6—Increase in liquidus temperatures of titaniferous slags with time held under reducing conditions

From Fig. 6 it is apparent that the liquidus temperature of the titaniferous slag under reducing conditions increases continuously with holding time and, after a period of four hours, the liquidus temperature has been raised by over 100°C. X-ray diffraction and thin-section microscopy revealed that these titaniferous slags (37 per cent TiO<sub>2</sub>) do not contain carbides and/or nitrides as was the case in the slags reported by Frijdenzon (15 per cent TiO<sub>2</sub>) when treated in the same apparatus. After maintaining the reducing atmosphere, the slags with the high-titania content showed no change in X-ray diffraction spectra but microscopic examination indicated that those crystalline phases which contain TiO<sub>2</sub>, viz. 4(MgO · 2TiO<sub>2</sub>) · (Al<sub>2</sub>O<sub>3</sub> · TiO<sub>2</sub>) and CaO · TiO<sub>2</sub> had become darkened. It is known that loss of oxygen and accompanying darkening in colour on heating TiO<sub>2</sub> in a reducing atmosphere can occur without the separation of a lower oxide phase, i.e., the titania can exist as a non-stoichiometric phase with an O : Ti ratio of less than 2:1.

#### SULPHUR CAPACITY

A fundamental study of the distribution of sulphur between metal and slag presents the almost insuperable problem of obtaining a crucible in which both molten metal and molten slag may be held for prolonged periods at elevated temperatures without attack on the crucible. For this reason it was decided to adopt the more common procedure of determining the sulphur capacity of slags by studying the gas/slag equilibria relationships using a mixture of CO, CO<sub>2</sub> and SO<sub>2</sub> gases. This technique has been extensively employed for the study of slags used in iron and steel making<sup>6, 7, 8</sup>.

However, in the previous section it was shown that the liquidus temperatures of the titaniferous slags were raised rapidly when maintained at a constant temperature under reducing conditions. Therefore, when equilibrating these slags under an atmosphere of CO, CO<sub>2</sub> and SO<sub>2</sub>, the liquidus temperatures can be expected to rise. If this rise in liquidus temperature is sufficiently high it is possible that at some stage during the experiment the temperature at which the slag is being equilibrated with the gas phase is actually below the liquidus temperature. This would cause crystallization to occur with inherent changes in composition of the remaining liquid which could affect the sulphur capacity of the slag.

The apparatus assembled for the sulphur capacity measurements is shown diagrammatically in Fig. 7. The slag samples were prepared by weighing and mixing the high purity oxide components. Two 1 gm samples were placed in two platinum crucibles positioned in recesses in an alundum holder which was supported by the sheath containing the thermocouple. The crucibles containing the slag were introduced into the vertical tube furnace which was then purged with nitrogen. During this time the flow of CO, CO<sub>2</sub> and SO<sub>2</sub> was started and, when the flow rates had become constant at the required rates, the gas mixture was introduced into the furnace so as to impinge on the surface of the slag samples which were held at a pre-selected temperature. The gas flow through the reaction tube was continued for 3 to 4 hours as it had been shown previously that the sulphur content in the slag attained its equilibrium value within 2 hours. The gas stream was analyzed for CO, CO<sub>2</sub> and SO<sub>2</sub>. A 150 cc sample of the incoming gas stream was analyzed periodically during each experiment to ensure that the ratio of the gases in the gas stream was as constant as possible. At the completion of an experiment the slag samples were removed from the furnace, quenched and analyzed for sulphur.

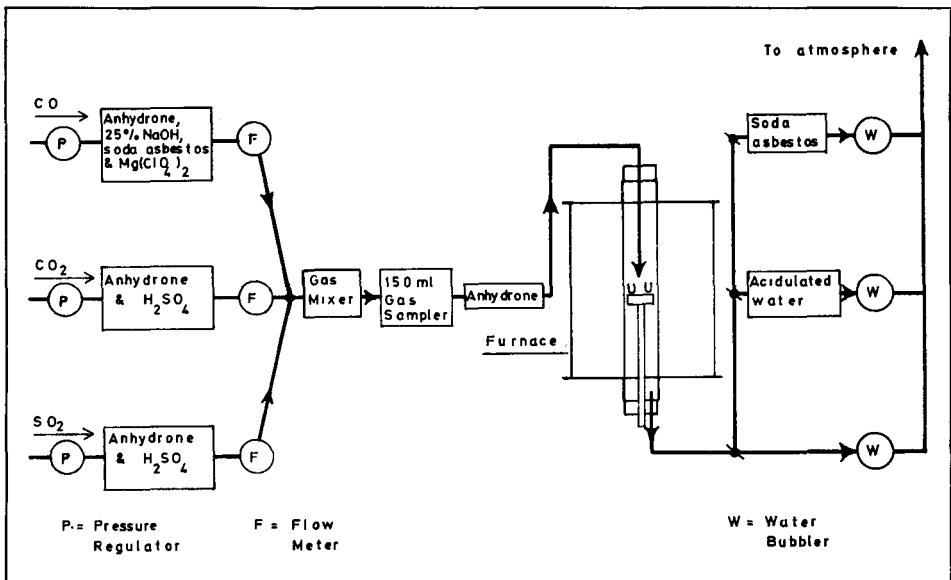


Fig. 7—Diagrammatic details of apparatus for determining sulphur capacities

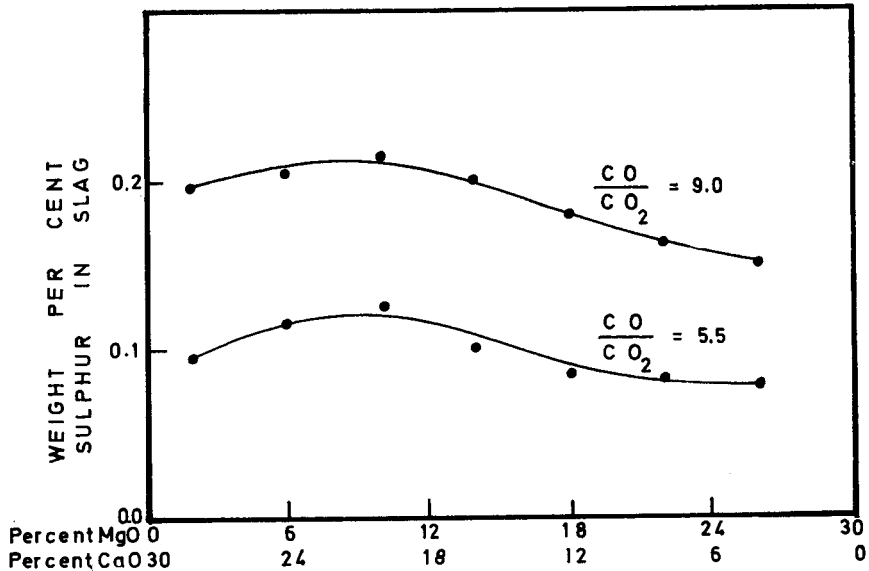
The sulphur capacity of the slags are presented in Fig. 8. In Fig. 8a the experiments were conducted at temperatures of 50°C above the liquidus temperatures of the slags as measured under atmospheric conditions. In these, as in all other sulphur capacity tests, the slags exhibited the characteristic dark blue to black colour associated with titaniferous slags when subjected to reducing conditions. Another series of experiments was conducted at a constant temperature of 1,550°C and the results are presented in Fig. 8b. The results obtained relating the effect of temperature on the sulphur capacity are presented in Fig. 9.

#### DISCUSSION OF THE SULPHUR CAPACITY VALUES

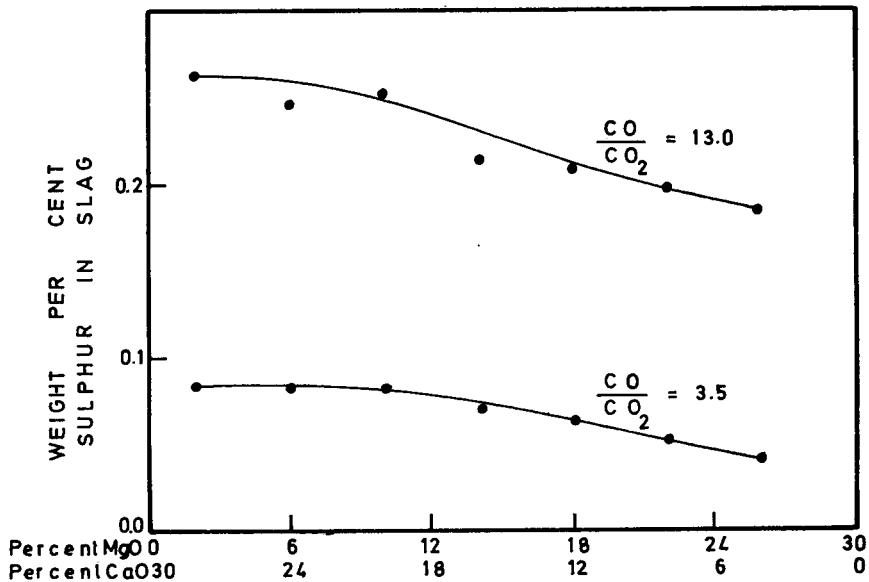
From the graphs in Fig. 8a and Fig. 8b which are for different CO/CO<sub>2</sub> ratios by volume in the gas stream, it is evident that the sulphur capacities of the titaniferous slags are low and that the sulphur capacity decreases with the progressive replacement of CaO by MgO although in Fig. 8a the sulphur capacity initially rises slightly. Since the Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> contents are maintained constant, the basicity ratios of the slags are the same and, therefore, it can be concluded that MgO confers a smaller sulphur capacity on the slag than does CaO<sup>8, 9</sup>. Experiments were actually conducted to determine the effect of the TiO<sub>2</sub>. In one series of tests the ratios of SiO<sub>2</sub>/TiO<sub>2</sub> were varied while maintaining the CaO, MgO and Al<sub>2</sub>O<sub>3</sub> contents constant and in the second series of tests the TiO<sub>2</sub> content was varied while maintaining the (CaO + MgO)/SiO<sub>2</sub> ratio constant. From these results it was evident that the TiO<sub>2</sub> cannot be regarded as a basic component of the slag but that its effect is not as detrimental to the sulphur capacity of the slags as is the presence of SiO<sub>2</sub>.

Also, from these data, it is evident that the variable that has the most pronounced effect on the sulphur capacity of these slags is the reducing power of the gas phase, viz., the CO/CO<sub>2</sub> ratio. As the CO/CO<sub>2</sub> ratio is increased the sulphur capacity is raised considerably. However, it was not possible practically in the experimental work to have the same SO<sub>2</sub> content in two gas atmospheres with differing CO/CO<sub>2</sub> ratios, i.e., it was necessary to have a considerably higher SO<sub>2</sub> content in the gas stream having the lower CO/CO<sub>2</sub> ratio. As there is published evidence that the sulphur content of a slag is related to the SO<sub>2</sub> concentration in the gas phase it can be deduced that the effect of the two different CO/CO<sub>2</sub> ratios would have been even more pronounced if the gases of differing CO/CO<sub>2</sub> ratios had the same SO<sub>2</sub> contents.

With reference to the rise in liquidus temperatures of these titaniferous slags when held under reducing conditions, it has been stated earlier that the possibility exists that the equilibrating temperature, at which a sulphur capacity was determined, may in fact have been below the liquidus temperature at the completion of a test. When crystallization occurs the composition of the liquid alters. If the primary phase contains proportionately more CaO than the remaining liquid, then the formation of primary crystals will result in a more acidic liquid having a decreased power to retain sulphur since the crystals separating out contain little, if any, sulphur<sup>10</sup>. Hence the desulphurizing efficiency of the slag decreases. As shown in Fig. 2 on the CaO-rich side of the phase diagram, the primary phase is CaO . TiO<sub>2</sub> and hence if the liquidus temperature should rise above the experimental temperature then the precipitation of this phase will cause a decreased sulphur capacity of the slag due to the fact that the remaining liquid is impoverished in CaO. On the MgO-rich side, the primary phase is 4(MgO . 2TiO<sub>2</sub>) . (Al<sub>2</sub>O<sub>3</sub> . TiO<sub>2</sub>) and hence the effect of crystallization of this phase would have less effect on the sulphur capacity as the liquid is not depleted of CaO but only of MgO which has a lesser sulphur capacity than CaO. Therefore, the decrease in sulphur capacity caused by the replacement of CaO by MgO may be more rapid than indicated by the graphs in Fig. 8.



(a) Test temperature 50°C above liquids



(b) Test temperature 1550°C

Fig. 8—Effect of the progressive replacement of CaO by MgO on the sulphur capacities of titaniferous slags

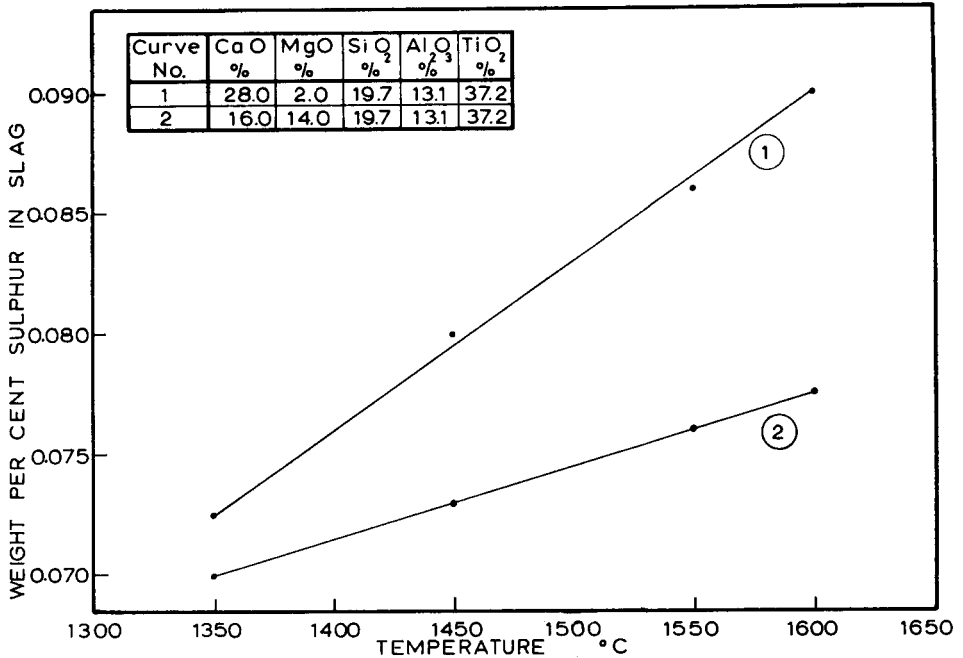


Fig. 9—Effect of increase in temperature on the sulphur capacities of titaniferous slags

#### POSSIBLE USES

When an industry develops around a newly exploited ore body and large tonnages of slags are produced then automatically the question arises as to whether there are any products which could be derived or made from the slags. The spatial demands of such a large volume of slag can be embarrassing and recently, because of demands for maximum exploitation of natural resources, every product should at least be investigated for its market potential. An especial problem in this connection is raised due to the high TiO<sub>2</sub> content of these slags and the question naturally arises as to the possibility of extracting this TiO<sub>2</sub>.

One of the most common processes for the gainful use of iron-making slags is the use of air-cooled aggregate for concrete and road making. Depending on the chemical composition, the crystalline aggregate either has a mechanical strength comparable with that of rocks normally used for aggregate, or it may disintegrate into a powder. This disintegration of air-cooled slag is mainly caused by lime unsoundness (dicalcium silicate) and magnesia unsoundness (periclase) with a relatively minor part played by sulphur unsoundness. Since, as can be seen from Fig. 2, neither of these phases crystallize it should be possible, at least from these considerations, to use the slags as aggregate. However, aggregate is a low-priced material and apparently can only be profitably marketed if it is used in road construction near the plant.

When iron-making slags are to be used for slag-cement manufacture (which, as opposed to aggregate, is a comparatively profitable by-product) they are treated on

a granulation plant where the molten slag stream is subjected to the action of high pressure water jets which split the slag into small granules which are cooled extremely rapidly. This is done to achieve as high a glass content as possible (in excess of 80 per cent), experience having shown that by this procedure the best cement quality is obtained from a given slag. The various hydraulicity indices which are often expressed in mathematical form are in effect various expressions indicating the basicity of the slag. Due to the high  $\text{TiO}_2$  content, these titaniferous slags are expected to display poor hydraulic properties. However, even more important is the fact that because of the low viscosities of these slags as shown in Fig. 5, it can be assumed that their crystallization potentials will be high since the rate of crystal growth varies as the inverse of the square of viscosity. When these slags were subjected to cooling rates of  $50^\circ\text{C}$  per second on the micro differential thermal analyzer, to simulate the quenching conditions obtaining on a granulation plant<sup>11</sup> the amount of crystalline material formed was far in excess of the maximum permissible for slag-cement manufacture.

From Fig. 2 it is clear that the  $\text{TiO}_2$  crystallizes either as perovskite ( $\text{CaO} \cdot \text{TiO}_2$ ) or as a solid solution  $4(\text{MgO} \cdot 2\text{TiO}_2) \cdot (\text{Al}_2\text{O}_3 \cdot \text{TiO}_2)$  depending on the lime and magnesia contents of the liquid. Only at very high CaO contents does  $\text{TiO}_2$  crystallize as a separate phase and then only as a comparatively small amount of secondary phase. The ions  $\text{Si}^{4+}$  and  $\text{Ti}^{4+}$  have very high cation field strengths and hence there will be a strong tendency for both  $\text{Si}^{4+}$  and  $\text{Ti}^{4+}$  to co-ordinate themselves completely with oxygen. This is shown in the  $\text{TiO}_2$ - $\text{SiO}_2$  system which exhibits complete immiscibility in the solid state and even very extensive immiscibility in the liquid state. Hence, by increasing the  $\text{SiO}_2$  content of these slags it may be possible to cause considerable changes in the phase relationships with the possibility that the  $\text{TiO}_2$  may crystallize in a more readily extractable form.

A slag of the following composition: CaO = 18.00 per cent, MgO = 12.00 per cent,  $\text{SiO}_2$  = 19.69 per cent,  $\text{Al}_2\text{O}_3$  = 13.12 per cent and  $\text{TiO}_2$  = 37.19 per cent (i.e., intermediate between that derived from the limestone/dolomite and solely dolomite flux) was studied to determine the phase changes which occur when the  $\text{SiO}_2$  content is increased. The method employed was the same as described previously and the results are depicted in Fig. 10.

As expected, increased contents of  $\text{SiO}_2$  increase the viscosity of the slag and this is marked by the appearance of glass, probably an alumina-silicate containing CaO and/or MgO. With  $\text{SiO}_2$  contents between 30.76 per cent and 34.70 per cent the primary phase is still  $4(\text{MgO} \cdot 2\text{TiO}_2) \cdot (\text{Al}_2\text{O}_3 \cdot \text{TiO}_2)$  but the secondary phase is now the most stable polymorphous structure of  $\text{TiO}_2$ , namely, rutile.  $\text{SiO}_2$  contents in excess of 34.70 per cent lead to the formation of  $\text{TiO}_2$  as primary phase with  $4(\text{MgO} \cdot 2\text{TiO}_2) \cdot (\text{Al}_2\text{O}_3 \cdot \text{TiO}_2)$  as secondary phase and at  $\text{SiO}_2$  additions between 42.64 per cent and 48.18 per cent, rutile is the primary phase over a long temperature interval followed by the crystallization of diopside. This latter range of compositions can be cooled at rates required to produce suitable crystallization of the  $\text{TiO}_2$  and, provided the cooling rate is in excess of  $10^\circ\text{C}$  per minute below temperatures of about  $1,200^\circ\text{C}$  down to say  $500^\circ\text{C}$ , then the product will consist of crystals of rutile in a glassy matrix since the diopside will not crystallize at these cooling rates.  $\text{TiO}_2$  may therefore be made to crystallize in a form more readily extractable by mineral-processing techniques. The expense associated with this complete operation is no doubt excessive but it should be borne in mind that the product after extraction of most of the  $\text{TiO}_2$  has been found to be suitable for the production of  $\text{TiO}_2$ -nucleated slag-ceramics.



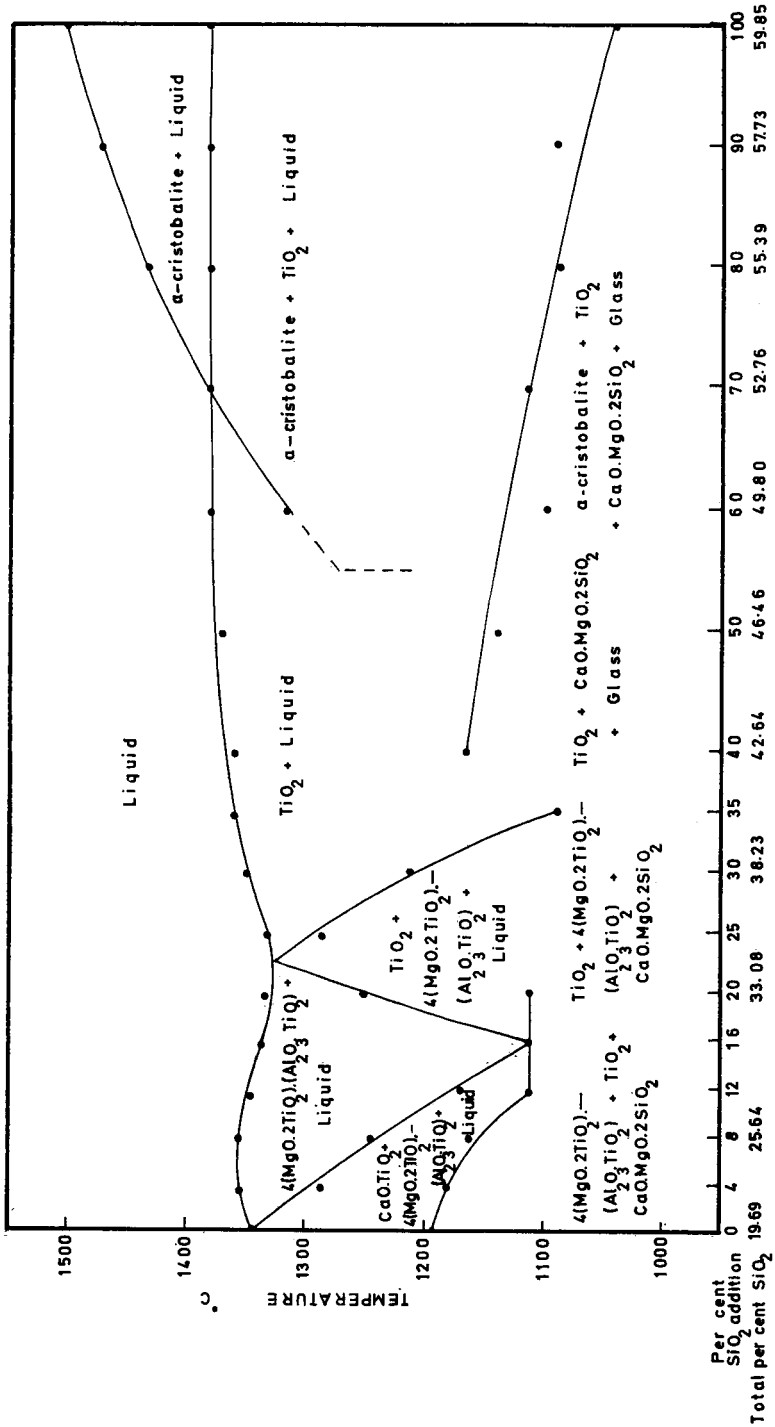


Fig. 10.—Phase equilibria of a titaniferous slag with increasing additions of SiO<sub>2</sub>.

## CONCLUSIONS

It has been shown that both CaO and MgO are necessary to obtain the required liquidus temperatures. The (CaO + MgO) content is of prime importance and should not deviate significantly from a total of 30 per cent. Furthermore, if the (CaO + MgO) content of 30 per cent is used, it is possible to vary the CaO/MgO ratio within quite wide limits and yet obtain a slag with the required liquidus temperature, hence indicating that complete replacement of limestone by dolomite in the limestone/dolomite flux is possible—at least from these considerations.

A blast furnace slag is considered to be fluid if it has a viscosity of 150 centipoise. Therefore, the titaniferous slags are all of low viscosity as their average viscosities are less than 100 centipoise and changes in composition within the limits investigated would have little effect on the furnace operation from a consideration of viscosities.

From the tests conducted under reducing conditions, it becomes obvious that a much more important property of these slags than phase constitution or viscosity under atmospheric conditions is the reduction of the TiO<sub>2</sub> in the slags. This is associated with a marked rise in liquidus temperature but with apparently little change in viscosity above liquidus temperature.

The sulphur capacities of these slags are comparatively low due to the low basicity. By the replacement of CaO by MgO the sulphur capacities are still further reduced.

It would appear that although the slag cannot be used for the production of slag-cement, it should be capable of use as aggregate. Also, although it is possible to make the TiO<sub>2</sub> in the slag more amenable to extraction by the addition of SiO<sub>2</sub> to the slag in a separate slag-treatment plant and to use the glassy product, still containing some TiO<sub>2</sub>, for production of slag-ceramic this, most probably, would not be economically feasible.

## ACKNOWLEDGEMENTS

This paper is a correlation of three post-graduate research projects conducted in the Department of Metallurgy, University of the Witwatersrand. These projects were sponsored by the Highveld Steel and Vanadium Corporation Limited, to whom the authors are greatly indebted.

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