A study of the liquidus temperatures of titano-magnetite smelting type slags

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ABSTRACT

This study is limited to the compositions of slags normally encountered in the current electric smelting operation at BHP New Zealand Steel and can be described by the five-component system TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO and the six-component TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO - FeO and TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO - MnO systems.

A melting - holding - quenching technique was employed in the determination of the liquidus temperatures of these slags. It revealed that the state of reduction of the slag had a very strong influence on the liquidus point. Reduction of all the Ti in the employed slag from (4+) to (3+) oxidation state increased the liquidus temperature by 140 °C. The liquidus temperature was not affected up to 4.5 wt.% FeO and 5.3 wt.% MnO in the slag within the range of experimental error (+20°C).

The primary crystallisation phase was a spinel (magnesium meta-aluminate $MgAl_2O_4$) or a solid solution spinel of magnesium meta-aluminate and magnesium meta-titanate $MgTi_2O_4$. The state of reduction of the slag affects the content of Ti in the primary spinel phase. Reduction of Ti from Ti^{4+} to Ti^{3+} increases the Ti_2O_3 content of the spinel phase from 0 to 14.1 wt.%.

1. INTRODUCTION

BHP Steel operates in New Zealand a process in which titaniferous sands are pre-reduced in rotary kilns and smelted in submerged arc electric melters. The properties of the slag, generated in the melter, are the subject of the present investigation.

The number of studies on the liquidus temperatures of titaniferrous slags of the complexity of the BHP New Zealand Steel melter type one is limited. Additionally, the reported values from different investigators are not in good agreement. The difference in the reported liquidus temperatures goes up to 300 °C. It should be noted, however, that small variations in the composition of such slags result in substantial changes in the liquidus temperature. For this reason it is quite difficult to extrapolate from the available information to areas which have not been measured.

One of the most comprehensive studies on the liquidus temperatures of the five-component TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO and the six-component TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO - FeO systems is that of Holmes et al.[1] They used both the melting-holding-quenching method and the hot stage microscope method to study a wide range of compositions. The established liquidus temperatures in the five-component system varied between 1217 °C and 1667 °C, while in the six-component system they were between 1241 °C and 1900 °C. Some of the compositions studied fall close enough to the composition of NZS melter slags to allow for some qualitative trends to be drawn. Figures 1, 2 and 3 show some trends derived from their study in the composition range of NZS melter type slags. Generally, when the TiO_2 content of the slag was 35 or 36 wt.%, Al_2O_3 was between 15 and 24 wt.% and MgO was between 5 and 15 wt.%, the liquidus temperature went through a minimum with increase in the CaO/SiO_2 ratio. The observed minima were at ratios of 0.8 to 1.0. When the MgO and Al_2O_3 content increased by 5 and 10 wt.% respectively, the liquidus temperatures increased by 50 to 150 °C at CaO/ SiO_2 ratios between 0.6 and 2.0. In this work the state of reduction of the slag was not reported and the measurements were carried out under nitrogen.

Dongsheng Xie et al.[2] studied the viscosity and liquidus temperatures of the five-component TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO system at TiO_2 contents up to 33 wt.%. The liquidus temperatures were estimated from the breaks in the viscosity polytherms. They found that reduction of TiO_2 by carbon caused rapid increase in the viscosity of the slag, but did not seem to influence the liquidus temperature.

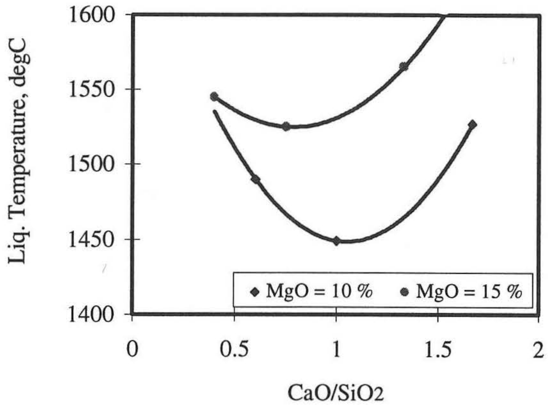

Fig. 1. Variation of the liquidus temperature with the CaO/SiO_2 ratio and MgO content. (TiO_2 = 35 wt.%, Al_2O_3 = 15 wt.%)

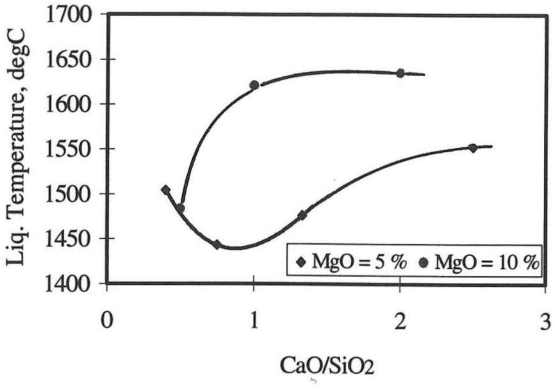

Fig. 2. Variation of the liquidus temperature with the CaO/SiO_2 ratio and MgO content of the slag. (TiO_2 = 36 wt.%, Al_2O_3 = 24 wt.%)

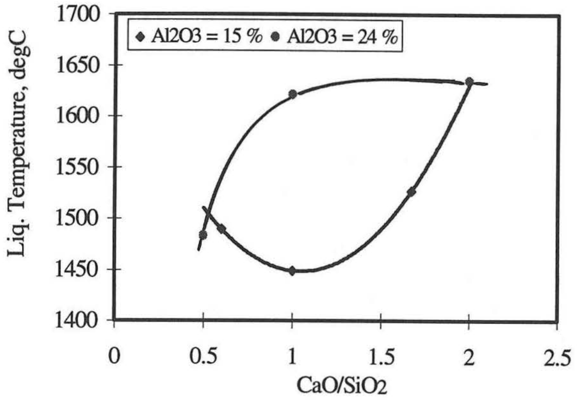

Fig. 3. Variation of the liquidus temperature with the CaO/SiO_2 ratio and Al_2O_3 content of the slag. (TiO_2 = 36 wt.%, MgO= 24 wt.%)

Furthermore, the increase in viscosity could not be attributed to the formation of TiC, because TiC was not always present in slags of high viscosity. The increase in viscosity, however, was always accompanied by reduction of TiO_2 to oxides of lower oxidation state of Ti. The authors of the paper concluded that a possible change in the structure of the slags during reduction resulted in the increase in viscosity. This implies that either polymerisation or clustering is taking place during reduction, which is contrary to what would be expected from theoretical considerations. One would expect that the lower oxides would exhibit less tendency towards polymerisation[8] and would have a lower degree of coordination. In light of the findings in the present work and those of Holmes et al.[1] there are some doubts as to whether the reported values by Dongsheng Xie et al.[2] are not the solidus rather than liquidus temperatures.

Jochens et al.[3] studied the phase equilibria in a slag system containing 19.69 wt.% SiO_2 , 13.12 wt.% Al_2O_3, 37.19 wt.% TiO_2 and 30 wt.% (CaO+MgO) with various ratios of CaO/MgO. The technique employed was high temperature microscopy. They found that comparatively small variations in the basicity ((CaO+MgO)/ SiO_2) of the slag result in considerable variations in the liquidus temperatures. The substitution of CaO by MgO initially lowered the liquidus temperature of the slag and after that tended to raise it, the minima being at 4, 12 and 16 wt.% MgO in slags having 25, 30 and 35 wt.% (CaO+MgO) respectively. The influence of MgO and the absolute values of the estimated liquidus temperatures are in disagreement with those of Holmes et al.[1]

Jun et al.[4] studied the influence of MnO on the viscosity and melting points of the six component system TiO_2 - Al_2O_3 - SiO_2 - CaO - MgO - MnO. They found that addition of 1.5 wt.% MnO decreased the melting temperature of slags containing between 20 and 30 wt.% TiO_2 by up to 80 °C. In their measurements the slags were held in graphite containers under an Ar atmosphere for 2 hours prior to the measurement and thus titanium was extensively reduced to the Ti^{3+} and Ti^{2+} states. The final analysis of the reduced forms of Ti in the slags are reported in the paper, but the total composition including the MnO content is not. It is not clear whether the observed effect was due to retarded TiO_2 reduction in the presence of MnO, nor whether the composition of the slags was constant during viscosity measurements at different temperatures.

Nityanand et al.[5] measured the liquidus temperatures of the ternary CaO - Al_2O_3 - TiO_2 system at different oxygen potentials. They found that the liquidus temperature of a slag is higher at oxygen partial pressure of 10^{-16} atm than at 0.21 atm. Although the slags could not be analysed chemically because of the small amounts involved in the measurements, they attributed the observed effect to the reduction of Ti^{4+} to Ti^{2+} and emphasised the importance of the state of reduction of Ti on the liquidus temperature [6].

Tricklebank and Kelly[7] measured the influence of FeO on the viscosity of NZS Melter type slags and from the discontinuity in the viscosity versus temperature plots were able to determine the liquidus temperatures. The CaO content in their slag was 10 wt.% and the SiO_2 was 19.6 wt.%. The liquidus temperatures measured in Mo lined graphite crucibles were found to decrease from 1510°C to 1442 °C when 8 wt.% FeO was added to the slag. When TiB_2 crucibles were used, the measured liquidus temperatures were approximately 30°C higher. The difference was attributed to failure of the Mo lining which separated the graphite container from the slag.

The intent of the present investigation was to establish the liquidus temperatures of NZS Melter type slags at different degrees of reduction as well as the influence of CaO/ SiO_2 ratio and small additions of MnO and FeO. The idea to re-examine the liquidus points came from a study on the electrical conductivities of commercial and synthetic NZS Melter type slags. Breaks in the electrical conductivity polytherms were observed at temperatures in excess of 1550 °C, which were substantially higher than the perceived melting points of these slags. The experimental apparatus used in that study, however, did not allow determination with the required degree of precision.

2. EXPERIMENTAL TECHNIQUE

The method employed in the present study was the so called melting-holding-quenching technique. Slags of predetermined composition were prepared from reagent grade TiO_2 , Al_2O_3 , SiO_2 , CaO, MgO, MnO and Fe_2O_3 chemicals. Some of the slags were premelted in Pt crucibles in air so that Ti was completely oxidised to Ti^{4+}. In order to generate certain amounts of Ti^{3+} some slags were premelted in graphite crucibles under an Ar atmosphere. The premelted slags were introduced in Mo crucibles and heated under purified Ar to the desired temperatures and held until they reached thermal equilibrium, which was about one hour. Slags were quenched on a massive Mo rod and Mo strip immersed into the slag.

Each slag was analysed after premelting, prior and after quenching. The content of the major slag components including the Ti^{3+} content did not show any significant change during the experiments.

Polished sections were prepared from the quenched samples. As these slags show a tendency towards very high crystallisation rates, it is important to be able to discriminate between crystals formed during quenching and the ones present in the melt. The criteria chosen in this work was the presence of crystals larger than 100 μm within 500 μm of the Mo rod/strip - slag interface. The crystals in samples quenched from temperatures higher than the liquidus were smaller than 10 μm. The large crystals observed in samples quenched from temperatures below the liquidus were usually larger than 100 μm. An example of the interface area in samples with and without primary phase precipitation is shown in Figure 4. The temperature was varied in 15 or 20 degrees increments, which largely determined the precision of the measurement. Apart from the chemical analysis, SEM and EPMA analysis were performed on the polished sections, which allowed the composition of the phases, precipitated at different temperatures, to be established.

3. RESULTS AND DISCUSSION

The compositions of the investigated slags are represented in Table I.

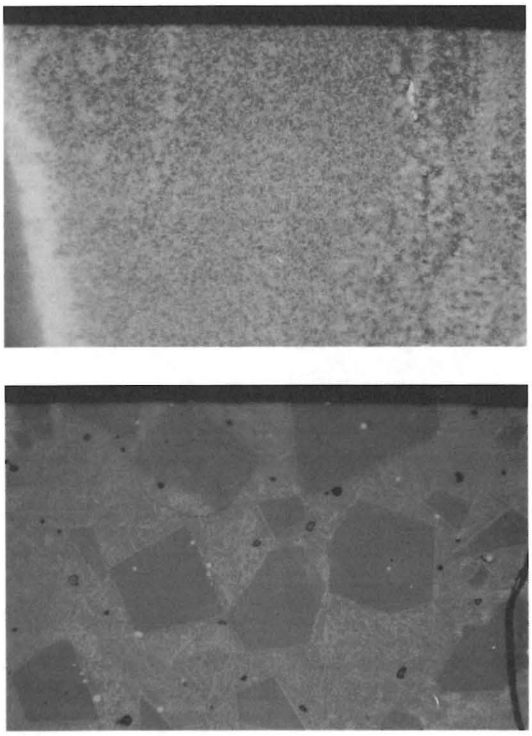

Fig. 4. Quenched samples without (above) and with (below) primary phase precipitation.

Table I Composition of the slags used in the investigation

Exp. No.	TiO_2 wt.%	Al_2O_3 wt.%	CaO wt.%	SiO_2 wt.%	MgO wt.%	FeO wt.%	MnO wt.%	Ti^{3+} wt.%
1	37.2	18.8	14.7	14.9	14.5	0	0	4.55
2	36.7	19.5	14.8	14.3	14.8	0	0	6.29
3	36.2	19.0	15.4	14.8	15.7	0	0	20.0
4	35.9	19.5	14.3	14.2	14.7	0	0	1.76
5	35.2	19.0	13.5	13.8	14.3	0	3.8	1.38
6	32.1	20.6	12.3	13.6	14.1	0	5.3	1.66
7	35.9	18.9	13.7	14.2	14.5	0	1.0	2.18
8	35.4	18.5	13.7	13.8	14.3	2.3	0	1.68
9	34.5	18.7	13.2	13.1	13.9	4.5	0	2.01
10	36.0	19.5	12.3	17.6	14.5	0	0	1.96

It was found that below a certain temperature, large cubic crystals precipitated from the liquid. The analyses of these crystals showed that they were a spinel phase of the type $MgAl_2O_4$ containing Ti. The amount of Ti increased from 1.4 to 9.4 wt.%, when the Ti^{3+} increased from 8.1 to 92.7 wt.% of the total Ti in slag, the remainder being Ti^{4+}.

Figure 5 shows an EPMA image of a slag quenched from 1500 °C. Apart from the primary spinel phase which precipitates at temperatures higher than 1600°C, a secondary phase is present in the form of needle-like crystals. The secondary crystalline phase was rich in TiO_2. The TiO_2 content in this phase varied between 68.6 and 75.7 wt.% when the Ti^{3+} content was low and dropped to 43.9 wt.% when all Ti^{4+} was reduced to Ti^{3+}.

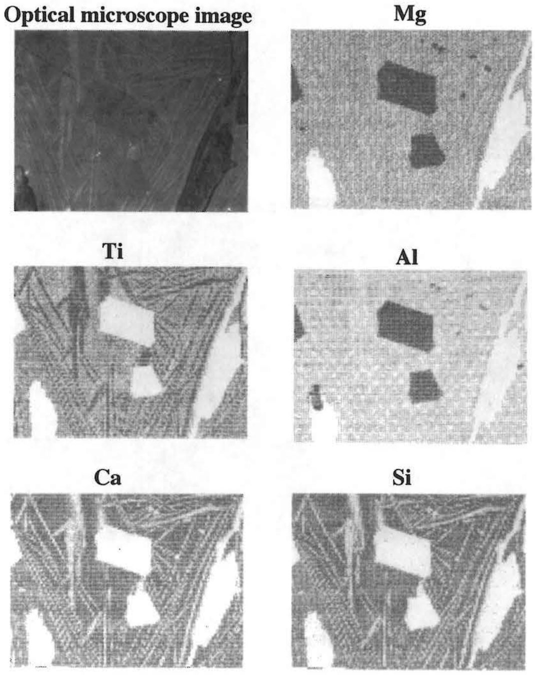

Fig. 5. Distribution of the major elements within the crystal structure of a sample quenched from a temperature below the liquidus one.

The other major constituents of this phase were Al_2O_3 and MgO but their relative amount decreased at higher degrees of reduction, while the content of SiO_2 and CaO increased from 7.5 to 47.2 total wt.%. Whether this phase is armalcolite as suggested by Crawford et al.[9] is not clear, but it is obvious that the degree of reduction of the slag influences the composition of the Ti rich phase which may be the target of beneficiation.

Figure 6 shows the variation of the composition of the primary spinel phase. It is obvious that Al_2O_3 is substituted by Ti oxide and it appears that, on a molar base 1 mole of Al_2O_3 is substituted by 1 mole of Ti oxide. This allows to speculate, on the basis of electrical neutrality, that the form of spinel formed is magnesium meta-titanate, $MgTi_2O_4$, rather than magnesium ortho-titanate, Mg_2TiO_4, which would require substitution of two moles of Al by one mole of Mg and one mole of Ti ions ($Mg^{2+} + Ti^{4+} = 2Al^{3+}$).

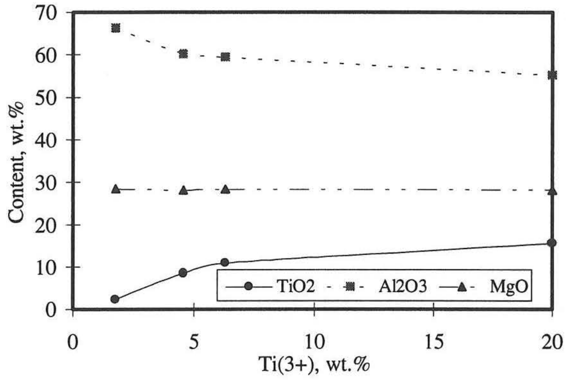

Fig. 6. Variation of the composition of the large crystals with the Ti(3+) content of the slag.

The influence of the amount of Ti^{3+} on the composition of the Ti-rich needle like crystals is represented in Figure 7. The amount of Ti is lower at higher degrees of reduction, being substituted by CaO and SiO_2. As these crystals form at temperatures below 1500°C, which is well below the liquidus temperature, detailed study of them is considered beyond the scope of the present work.

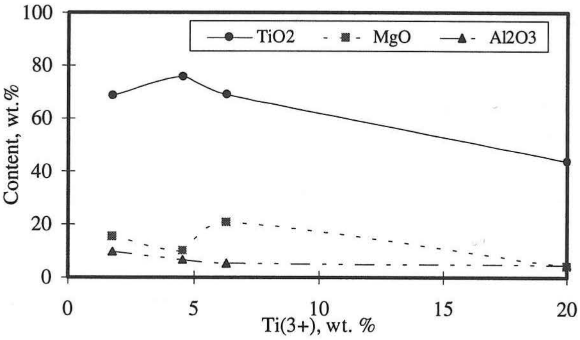

Fig. 7. Variation of the composition of the needle-like crystals with the Ti(3+) content of the slag.

Figure 8 shows the variation of the measured liquidus temperatures with the Ti^{3+} content of the slag. The effect of the state of reduction of Ti in the slag seems to be quite remarkable as complete reduction of Ti^{4+} to Ti^{3+} increases the liquidus temperatures by about 150 °C at a fixed ratio of the main slag components.

It should be remembered that the total Ti content of the slag was 21.6 wt.% and in the present study Ti was not reduced beyond Ti^{3+}. Although it is of substantial theoretical interest to study the influence of Ti^{2+} , there is

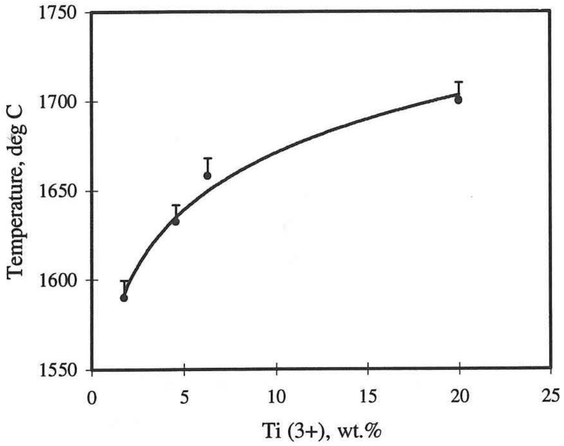

Fig. 8. Variation of the liquidus temperature of a synthetic slag, containing 21.6 wt.% Ti, with the degree of reduction.

no immediate practical incentive since during the melter operation Ti is hardly reduced to that extent. Chemical analysis of melter slags show that less than 50 % of the total titanium is reduced to Ti^{3+} the balance being Ti^{4+}. The detected TiC in some slag samples suggests that Ti^{2+} may be present in small amounts, but is probably limited to the char-slag interface.

Figure 9 shows the influence of MnO on the liquidus temperatures of the slag. In disagreement with the literature results[4], MnO did not show any significant influence on the melting point of the slag. In the present investigation the effect does not exceed 20 °C, since this is the error level. This is a great deal less than the value of 80°C, reported by Jun et al.[4], and is in agreement with the influence of MnO on the melting point of blast furnace slags.

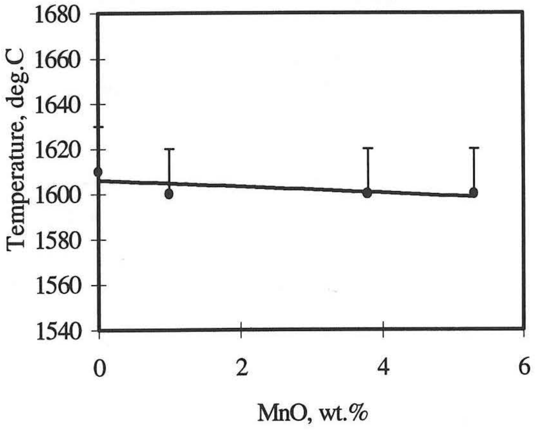

Fig. 9. Variation of the liquidus temperature of a synthetic slag, containing 21.6 wt.% Ti, with the MnO content.

The influence of small additions of FeO is represented in Figure 10. Within the range of experimental error, the liquidus temperature was not affected up to 4.5 wt.% FeO in the slag. This means that the difference in temperature is below 20°C.

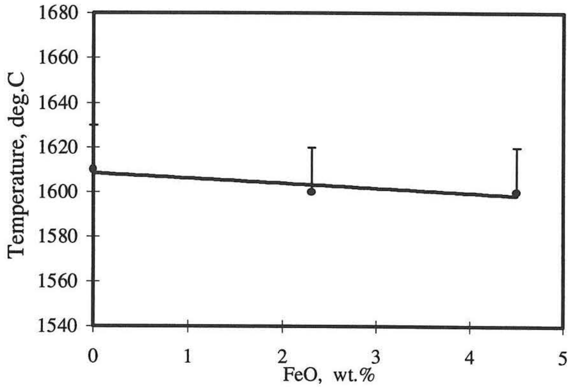

Fig.10. Variation of the liquidus temperature of a synthetic slag, containing 21.6 wt.% Ti, with the FeO content.

Figure 11 shows the influence of CaO/SiO_2 ratio on the liquidus temperature. At the slag composition employed in this study, decreasing the ratio of CaO/SiO_2 from 1 to 0.7 sharply decreased the liquidus temperature of the slag. The results are in fair agreement with Holmes et al.[1], but more experiments are required in order to establish precisely this influence, especially at higher degrees of reduction.

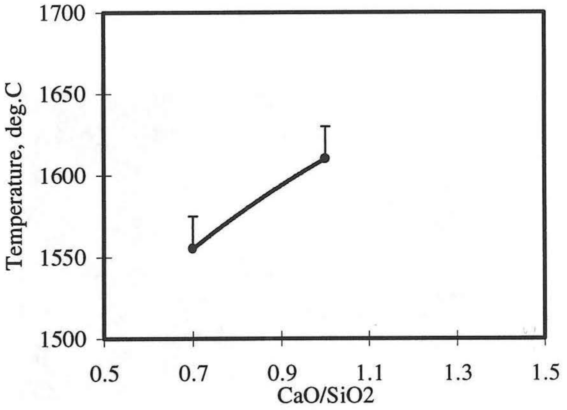

Fig.11. Variation of the liquidus temperature of a synthetic slag, containing 21.6 wt.% Ti, with the CaO/SiO_2 ratio.

During the course of the study it was noticed that the XRF analysis of the content of the major constituents of the slags, quenched from different temperatures, showed a systematic deviation below the established liquidus temperatures. This was an independent and unexpected validation of the observed transformation points. An example of this phenomenon is represented in Figure 12.
Below the detected liquidus temperature, the levels of Al_2O_3 and MgO was progressively decreasing while those of SiO_2, TiO_2 and CaO were increasing. XRF was used for

analysis of the total slag composition which should have been constant during the whole measurement. Phase transformation within the slag could influence the analysis only if it led to segregation and thereby ultimately affect the sampling or sample preparation practice. A study of the phase segregation of the slag in the Mo container revealed that the spinel crystals tend to segregate to the bottom of the crucible.

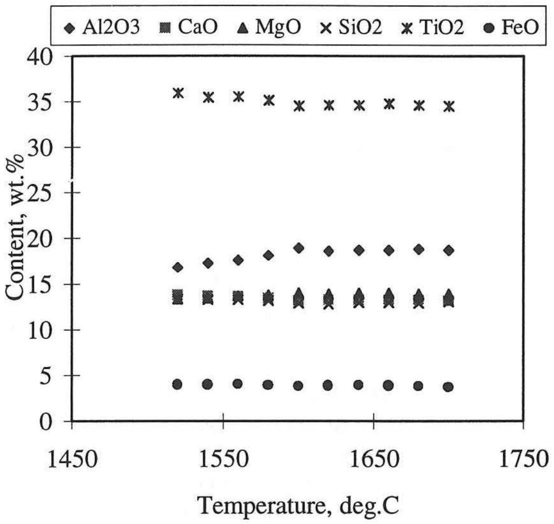

Fig. 12. XRF analysis of samples, quenched from different temperatures during the Experiment No. 9 (See Table I).

Fig. 13 Segregation of spinel crystals within the Mo container.

Figure 13 shows an optical microscopic image of the border between the areas occupied by and free of spinel crystals.

Horizontally sliced sections of the solidified slag samples from both the top and bottom of the sample were analysed. The analysis showed severe segregation in the vertical direction. Figure 14 shows the segregation of Ti expressed as TiO_2 in a few experiments in which this phenomenon was studied. The difference in the TiO_2 content was up to 9.2 wt.%. This was largely a result of the temperature from which the slag was cooled, the thickness of the analysed layers and the conditions of cooling.

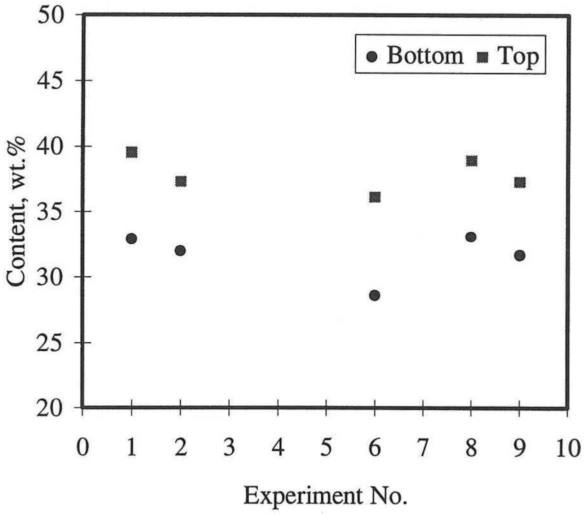

Fig. 14 Segregation of TiO_2 within the slag.

Figures 15 and 16 show the segregation of Al_2O_3 and CaO. The Al_2O_3 level was high in the bottom part of the crucible, the difference going up to 13 wt.%. Conversely, CaO concentration was high in the top part of the slag. SiO_2 behaved in a manner similar to CaO, while MgO followed the behaviour of Al_2O_3 .

The observed segregation may have a serious impact on the performance of the Melter in which the slag exists in a relatively quiescent bath.

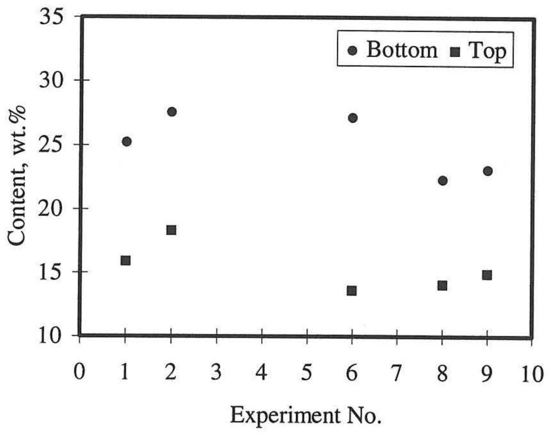

Fig. 15 Segregation of Al_2O_3 within the slag.

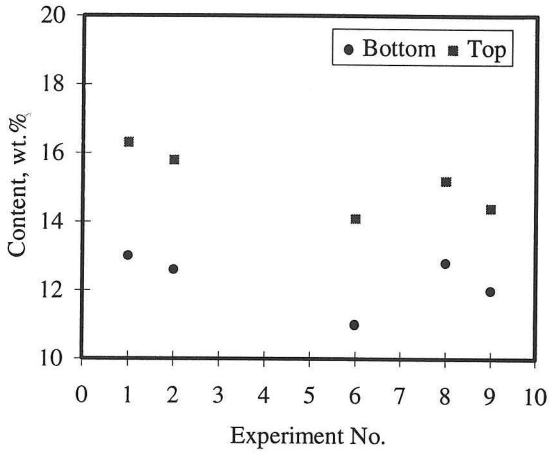

Fig. 16 Segregation of CaO within the slag.

The presence of a solid phase will affect the flow characteristics of the slag and may create problems during tapping. The amount of the spinel phase will vary with the slag composition, temperature and degree of oxidation of Ti. It is premature to attempt to prescribe operational conditions which will eliminate this problem of non-homogeneity and is altogether beyond the purpose of the present study, but a few qualitative trends deserve mention. Increasing the temperature in itself is not a solution, since the presence of carbon would bring about faster reduction of the slag. Employing higher temperatures of the slag (generally in excess of 1550 °C), is beneficial but should be considered in combination with the state of reduction of the bath. The latter relates to the amount of FeO in the slag and is controlled by addition of ore.

At the levels of TiO_2, Al_2O_3 and MgO used in this study, decreasing the CaO/SiO_2 ratio from 1.0 to 0.7 decreases the liquidus temperature by 50°C. It is desirable to reduce the Al_2O_3 and MgO content, but as they come from the gangue of the ore, there is little that can be done in this respect. Varying the CaO/SiO_2 ratio is operationally feasible by fluxing, but it affects a number of operational parameters like energy consumption, refining capabilities and productivity. Considering a possible decrease of the melting point of the slag via fluxing requires careful examination of the implications on the overall performance of the Melter.

4. CONCLUSIONS

1. A melting - holding - quenching technique employed in the determination of the liquidus temperatures of NZS Melter type slags revealed that the state of reduction of the slag has a very strong influence on the liquidus.

2. Reduction of all Ti in a slag, containing 21.6 wt.% Ti, from (4+) to (3+) oxidation state increases the liquidus temperature by 140 °C.

3. Within the range of experimental error (+20°C), the liquidus temperature was not affected up to 4.5 wt.% FeO and 5.3 wt.% MnO in the slag.

4. The primary crystallisation phase is a spinel (magnesium meta-aluminate $MgAl_2O_4$) or a solid solution spinel of magnesium meta-aluminate and magnesium meta-titanate $MgTi_2O_4$.

5. The state of reduction of the slag affects the content of Ti in the primary spinel phase. Reduction of Ti from Ti^{4+} to Ti^{3+} increases the Ti_2O_3 content of the spinel phase from 0 to 14.1 wt.%.

6. Below the liquidus temperature the precipitated spinel crystals segregate to the bottom of the container. Due to a wide temperature difference between the solidus and liquidus, at temperatures substantially lower than the liquidus, the composition of the liquid fraction of the slag is substantially different from that determined by bulk analysis.

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