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Liquidus temperature and viscosity of melter slags

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The liquidus temperature and viscosity of a range of melter slags produced in South Africa were determined. Drop-quench experiments were carried out on the supplied plant samples to determine the liquidus temperature and phase relations at sub-liquidus temperatures. The temperature measurement range covered 1300°C to 1630°C. Results from these experiments show liquidus temperatures for the melter slags to be in excess of 1500ºC with the chromium containing spinel as the primary crystalline phase. At lower temperatures, an olivine or pyroxene phase co-existed with the spinel phase.

The viscosity of the slags was determined over a temperature range of 1350 to 1550°C, under a controlled atmosphere. Results show two orders of magnitude variation in the viscosity (0.2 to 20 Pa s) with strong effects of slag chemistry and temperature. Slags with lower SiO_2 and Cr_2O_3 concentrations were more fluid. Slags with the lowest FeO_x and highest SiO_2 concentrations were the most viscous. These observations are in accord with general behaviour of silicate slags. While the presence of a spinel phase may have an effect on the viscosity of the melter slags, results obtained to date indicate a much stronger effect due to the presence of an olivine or pyroxene phase at lower temperatures.

Keywords: phase equilibria, liquidus, viscosity, slags, olivine, spinel, pyroxene

Introduction

The production of platinum group metals (PGM) in South Africa is based on the melting of a mixed low grade copper-nickel sulphide concentrate produced from the Bushveld complex in the North West Province. The PGMs follow the sulphide phases in a conventional smelting/converting process and are recovered from a high grade matte using hydrometallurgical operations. The slag produced in the initial melting stage, called melter slag, contains high levels of silica and magnesia and is fluxed with up to 10% lime. These slags are produced in large electric furnaces. Increasing levels of chrome in the concentrate, due to the co-treatment of UG2 ore is creating problems in the handling of melter furnace slag and the recovery of PGMs from the process.

The composition of the slags used in this study are presented in Table I. The major components in all the slags are SiO_2, MgO and FeO. The slags also contain minor amounts of Al_2O_3, CaO and Cr_2O_3. The phase equilibria and liquidus boundaries of the FeO-MgO-SiO_2 system was first established by Bowen and Schairer[1]. They showed the continuous solid solution of the olivine phase between the $2MgO{\cdot}SiO_2$ and $2FeO{\cdot}SiO_2$ end members, as well as the extent of the pyroxene phase field at high silica levels. The CaO-FeO-MgO-SiO_2 system was studied by Tromel, Koch and Grobkurth[2]. They showed the extent of the liquid region and phase fields at 1600°C. Hejja, Eric and Howat[3] studied the viscosity and liquidus temperature and viscosity of synthetic slags in the CaO-MgO-SiO_2-Al_2O_3-FeO system. The compositions of their synthetic slags were similar to the slags produced during the melting of concentrates produced from Merensky ore. Their measured liquidus temperature ranged from about 1300 to 1380°C as the slag basicity, (CaO+MgO)/SiO_2, was increased from 0.6 to about 1. They also found that the oxidation state of the slag (expressed as Fe^{2+}/Fe_{total}) tended to influence liquidus by about 30°C. Hejja *et al.* showed that the viscosity decreased as the silica content decreased and, at a fixed silica and FeO content, the CaO/MgO ratio had only a small effect on viscosity. The magnitude of the viscosity of the plant slag was similar to the synthetic slags (0.1 to 0.4 Pa.s) at temperatures above the 1350°C. Schwesinger and Muan[4] investigated spinel-silicate equilibria in the MgO-FeO-Fe_2O_3-Al_2O_3-Cr_2O_3-SiO_2 system at temperatures between 1309 and 1471°C.

There is a lack of phase equilibria and liquidus temperature information of slag systems relevant to the operation of South African melter furnaces. In particular there are several research questions that needed to be examined:

- The effect of chrome on the stability of oxide phases, and liquidus temperature
- The effect of chrome spinel, and other phases (olivine

Table I
Assays of supplied plant melter slag samples

Slag	Al_2O_3 (%)	CaO (%)	Cr_2O_3 (%)	Cu_2O (%)	FeO* (%)	MgO (%)	NiO (%)	SiO_2 (%)	S (%)
A	6.7	8.1	1.1	0.06	12.1	19.7	0.17	49.8	0.21
B	7.3	3.5	1.1	0.04	9.3	21.0	0.17	56.1	0.23
C	3.6	7.0	0.9	0.10	27.5	14.5	0.33	42.5	0.90
D	5.0	10.5	2.3	0.10	12.6	21.3	0.22	45.7	0.30
E	4.3	5.4	1.1	0.30	23.5	17.5	0.53	46.7	<0.2
F	5.1	4.9	3.4	0.20	12.4	24.2	0.50	49.1	<0.2

*Total iron expressed as FeO

and pyroxene) on the viscosity of slags with suspended solid phases.

The present work is part of an AMIRA International project on metallurgical processes called *Slags, Refractories and Processes,* which includes characterization of some South African melter furnace slags. This paper reports on the effects of temperature and bulk slag chemistry on the stability of oxide phases and viscosity of melter furnace slags at elevated temperatures.

Experimental

Drop quench experiments

The drop quench technique was used to measure the liquidus temperature and range of stability of high temperature phases in the supplied South African melter slags. The drop quench technique can determine:

- The liquidus temperature of the system at a known composition
- The primary (and secondary) phases of a slag of particular composition and temperature
- The composition of solid and liquid phases that are in equilibrium at a given temperature (i.e. determine tie lines) below the liquidus.

In principle the technique involves equilibrating a small amount of slag at a high temperature with a gas of particular composition. The structure of the high temperature slag is preserved by quenching in a water bath. The composition and identification of solid and liquid phases in the slag are determined using optical and electron microscopy.

In this work, small samples of slag were melted under argon gas. The aim was to replicate the conditions, particularly oxidation state of the slags in the furnace. The slag sample was contained in small envelopes made from 25 μm thick platinum foil. During the equilibration time contact between the slags and platinum capsules caused iron from the slag to dissolve into the platinum and hence result in a decrease in the iron content of the slag. To counteract this, the melter slags were doped with previously prepared wustite (FeO). Experiments were performed on as received slag as well as on slags with additions of 15 and 30 wt% FeO.

The drop quench experiments were performed in a sealed vertical tube furnace. The loaded platinum envelopes were held in place by a Pt alloy wire. The wire ran inside an alumina lance and was clamped at the top. The alumina lance was fixed to the top end cap and was used to centre the samples in the hot zone of the furnace, which was about 3 cm long. The temperature variation in the hot zone of the furnace was less than ±2°C. The slag samples were lowered into the furnace by adjusting the position of the alumina lance. The bottom furnace end cap was sealed with a film of polyethylene. This film was in contact with water, which prevented the film rupturing during the experiments. This water was also the quenching medium. Purified argon gas was introduced into the furnace tube through the bottom end cap and removed through the top end cap. A bubble seal on the exit gas ensured the furnace tube operated under a slight positive pressure. An R type thermocouple positioned near the platinum capsules measured the temperature during the experiment. A PID regulated power supply controlled the furnace temperature to within ±1°C.

The following procedure was used for each experiment:

About 300 mg of melter slag was weighed and loaded into a small platinum capsule. Up to five slag compositions were treated during each experiment. The capsules were hooked into place on the Pt-Rh wire and were suspended in the cold zone at the top of the furnace tube. The furnace tube was then flushed with dried and deoxygenated argon (Ar) gas (at 100 ml/min) for about 30 minutes. The temperature of the furnace was then increased and once the furnace reached the set temperature, the slag capsules were then lowered into the hot zone of the furnace. The flow of Ar gas through the furnace was maintained at about 100 ml/min. The slag samples were allowed either 30 or 60 minutes to reach thermal equilibrium. The slag capsules were then quenched by releasing the clamp on the Pt-Rh wire. The slag capsules were recovered from the water, dried and weighed. Some slag was removed from the capsules and mounted in resin prior to polishing and examination by SEM microprobe and EDX techniques. The remaining slag was pulverized and analysed for major elements using conventional ICP techniques.

Viscosity measurements

The experimental apparatus for measuring the viscosity of slags is shown in Figure 1 and the equipment detail has been described elsewhere[5]. In this study, Mo crucible and viscometer bob and hangers were used instead of Pt components. A Mo crucible (70 mm diameter, 100 mm high) containing about 400 g of slag was used together with a 25 mm diameter by 25 mm height bob with a 3 mm diameter shaft. An inert atmosphere in the furnace was maintained by dried and deoxygenated Ar or N_2. The gas flow-rate was controlled by calibrated mass flow controllers. Gases exiting the furnace passed through bubblers to maintain a slight positive pressure in the furnace. The oxygen and nitrogen levels in the gas were monitored by a mass spectrometer.

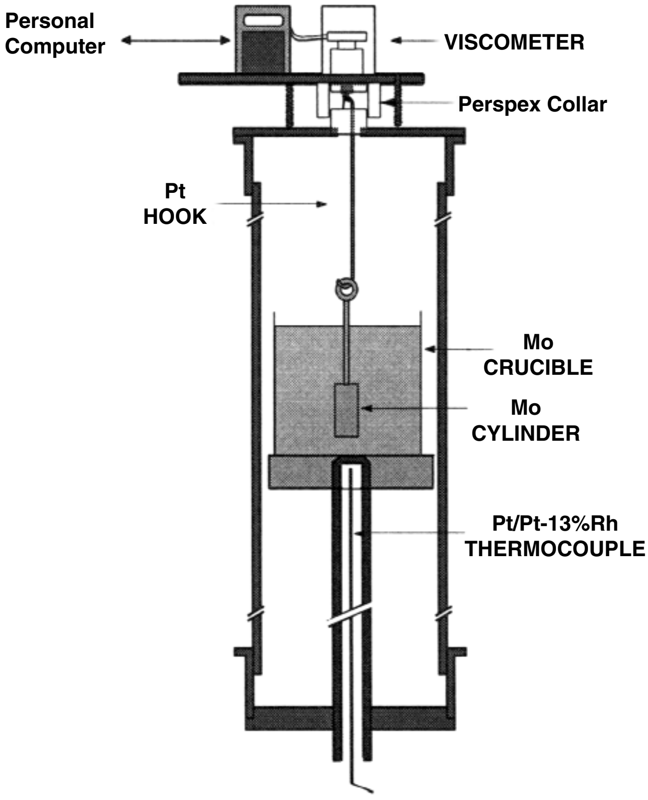

Figure 1. Schematic of furnace work tube and viscosity apparatus (not to scale)

In a typical experiment, slag was weighed into the crucible and loaded into the cold furnace. The viscometer was set in position with the bob suspended just above the slag. The furnace was then slowly heated up to temperature while a flowing Ar atmosphere was maintained in the work tube. When the slag was molten, the crucible was very slowly raised so that the bob was immersed into the melt, then the viscometer was turned on and the slag allowed to equilibrate for 20 minutes. The immersion depth in the melt was established by lowering the spindle into the melt until the top surface was just submerged. The spindle was then lowered a further 10 mm to the desired depth. The torque was then measured at several rotation speeds with either 100 or 200 readings collected at each speed over a period of 5 minutes. Twenty minutes was allowed between temperature changes for the system to regain thermal/chemical equilibrium. After measurement at the maximum temperature, the rotation of the viscometer was stopped, the crucible lowered so that the bob was out of the melt, and the furnace was programmed to slowly cool down to room temperature. Visual inspection of the bob confirmed that it did not act as a nucleation site for site crystals.

Results and discussion

Phase equilibration and liquidus temperature

Figure 2 summarizes the results in terms of the maximum temperature when spinel and olivine (pyroxene for slag B instead of olivine) phases were stable in the melter slags. The results are presented in the increasing order of Cr_2O_3 content (0.94 to 3.4 wt%) in the samples. It is shown that the maximum temperatures when spinel phase was stable, increase with increasing Cr_2O_3 level. The olivine phase was stable up to 1475°C in some melter slags. The spinel phase contained a high proportion of chrome. For two of the melter slags (D and F) spinel crystals were present above 1630°C. For the other melter slags the liquidus was mainly between 1550–1600°C.

Optical, SEM and XRD examination of the drop quenched slag samples indicated that at temperatures below 1450°C, the slags contained the solid solution phases: spinel ($(Mg,Fe)O\cdot(Al,Cr,Fe)_2O_3$) and either olivine ($[Mg,Fe,Cr]_2SiO_4$) or pyroxene ($[Fe,Mg,Cr]SiO_3$). As shown in Figure 3, at temperatures close to 1350°C, a high concentration of solid phases was present in slag F. A similar phenomenon was also observed for slags A, B and D. Analysis of the phases by SEM-EDS provided additional information on the composition of the phases. The Cr content of the spinel crystals ranged from 34 to 45 wt%, while for the olivine crystals ranged from 0.08 to 0.5 wt% and for pyroxene crystals ranged from 0.3 to 0.6 wt%. The Cr content of these phases agree well with data from Schwessinger and Muan[4] on the equilibrium between crystal phases at temperatures below 1471°C. In one case, pyroxene and spinel were the solid phases present at the temperature range studied. The olivine phase was relatively rich in MgO and low in FeO. The chromium content of the glassy phase varied between 0.3 and 1.3 wt%, depending on the temperature and slag chemistry. It is interesting to note that the liquidus temperatures of the slags studied in the present work were above 1540°C and increased with increasing chromium content. Comparison of these results with those obtained by Hejja *et al.*[3] on chromium-free slags indicates that the presence of 1 wt% Cr_2O_3 in the melter slags had increased the liquidus temperature by about 200°C, through stabilizing the spinel solid solution as the primary solid phase.

Olivine/pyroxene stability in melter slags

Olivine is an orthosilicate phase with the general chemical formula $(Mg,Fe,Cr)_2SiO_4$. The stability of the olivine phase in melter slags is primarily related to the temperature, the magnesia (MgO) and the silica (SiO_2) content of the slag. Figure 4 shows that the olivine stability in the melter slags increases with the MgO/SiO_2 ratio. The same trends were observed in the liquidus study by Hejja *et al.*[3] on 5% Al_2O_3-(14–18%) CaO-(15–25%) FeO-(14–18%)-MgO-

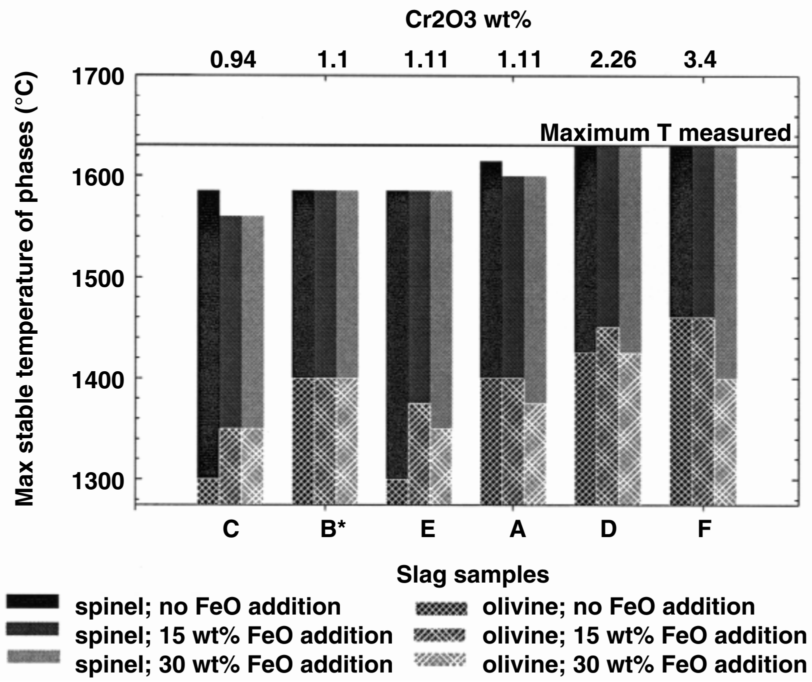

Figure 2. Measured maximum temperature when spinel and olivine (pyroxene instead of olivine) phases were stable in the melter type slags

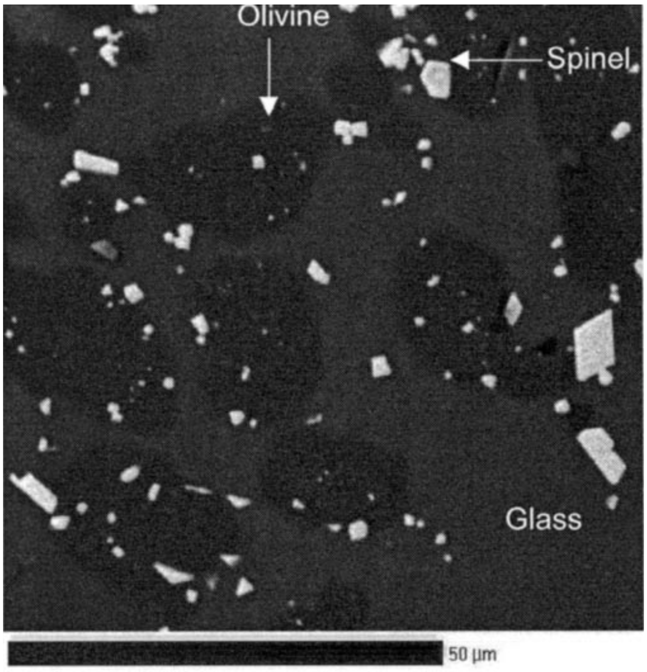

Figure 3. SEM micrograph of quenched slag F from 1350°C, with initial Cr_2O_3 and MgO content of 3.36 and 24.2wt%, respectively

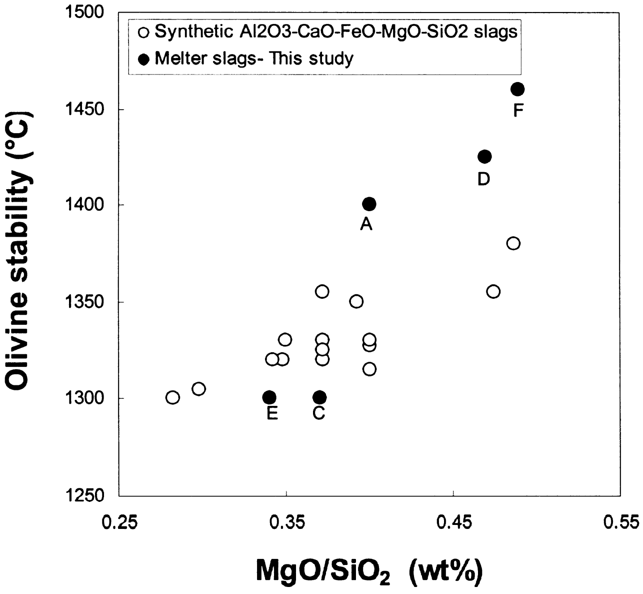

Figure 4. Comparison of the olivine stability observed for melter slags with that observed with synthetic Al_2O_3-CaO-FeO_x-MgO-SiO_2 slags[3]

(40–45%) SiO_2 slags with fixed Al_2O_3 content[3]. For slags with a constant MgO/SiO_2 ratio, the iron content of slag should have only a minor effect on the melting point temperature in the composition range of the melter slags, based on phase diagram data for the MgO-FeO-SiO_2 system[6].

The olivine stability of the as received melter slags is directly related to the MgO/SiO_2 ratio. The slags with the highest olivine stability (D and F) have the highest MgO/SiO_2 ratio. The slags with the lowest olivine stability (C and E) have the lowest MgO/SiO_2 ratio. However, the phase field can shift from olivine to pyroxene when the SiO_2 content of the slag becomes high enough to enter the pyroxene stable region. This was observed in slag B where the SiO_2 content was 56.1% and the slag contained less than 10% iron oxide.

Spinel stability in melter slags

The primary phase in all the melter slags was spinel. Table II shows the Cr and MgO content of as received melter slags as well as the range of temperature in which the liquidus temperature falls. According to Table II the two slags with the highest liquidus temperature (D and F) also had the highest chrome content, while the slags with the lowest chrome content (C) had the lowest liquidus temperature. The apparent dependence of the spinel stability on the chrome and magnesia content of slags is in accord with other published studies on stability of chromium containing slags[7–9]. It is thus reasonable to conclude that the spinel is strongly stabilized by increasing levels of chrome and magnesia in melter slags.

Viscosity of melter slags

The chemical compositions of the melter slags are as given in Table I. The final slag chemistries were determined from samples taken from the slow cooled slags at the completion of the viscosity measurements. The concentration of molybdenum in the slags was low, and unlikely to have had a significant influence on the viscosity. The composition of all the other major components, including SiO_2 and Fe^{2+} were essentially unaltered, within analytical and experimental uncertainties.

The viscosity-temperature relationship for the melter slags are summarized in Figure 5. At 1500–1550°C, the relative viscosity of the slags varies with silica content, which is also shown in Figure 6, i.e., the higher the silica content, the higher the viscosity. Figure 6 compares the viscosity of the fluid melter slags at 1400°C with viscosity measurements of synthetic Al_2O_3-CaO-FeO_x-MgO-SiO_2 slags and operating melter slags[3]. The viscosity increases as the silica content increases and the agreement between this work and the earlier study is good.

Based on results from the liquidus studies, the slags in most viscosity measurements contained some solid phases. As shown for slag D in Figure 7, at higher temperatures, Newtonian behaviour was broadly followed, in which case the torque increased linearly with rotation speed and extrapolated back to the origin. This suggests that the small fraction of solid spinel in the slag does not influence the slag's viscous characteristics. However, at lower temperatures, below 1450°C non-Newtonian (Bingham) behaviour is apparent. The transition from Newtonian to Bingham behaviour was probably due to the precipitation

Table II
Liquidus temperature and chrome and magnesia content of melter slags

Slag	Cr (wt %)	MgO (wt %)	Liquidus temp. (°C)
A	0.73	19.7	1600–1630
B	0.75	21.0	1570–1600
C	0.64	14.5	1550–1600
D	1.55	21.3	>1630
E	0.76	17.5	1570–1600
F	2.30	24.2	>1630

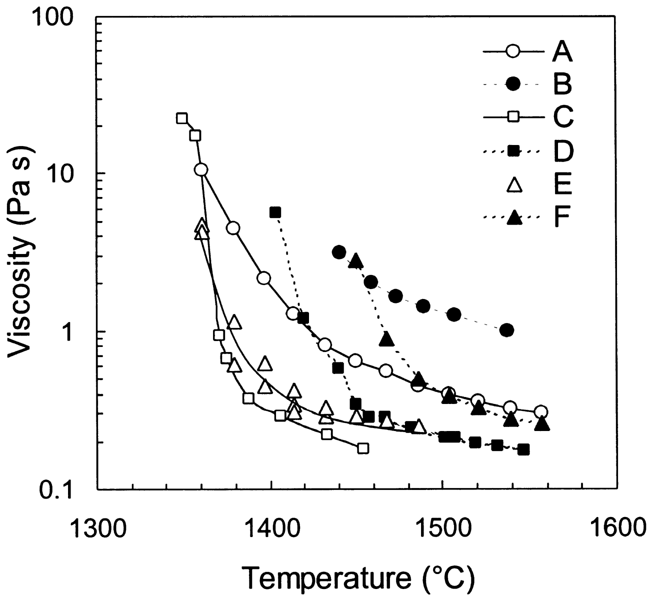

Figure 5. Temperature-viscosity relationship of the melter slags

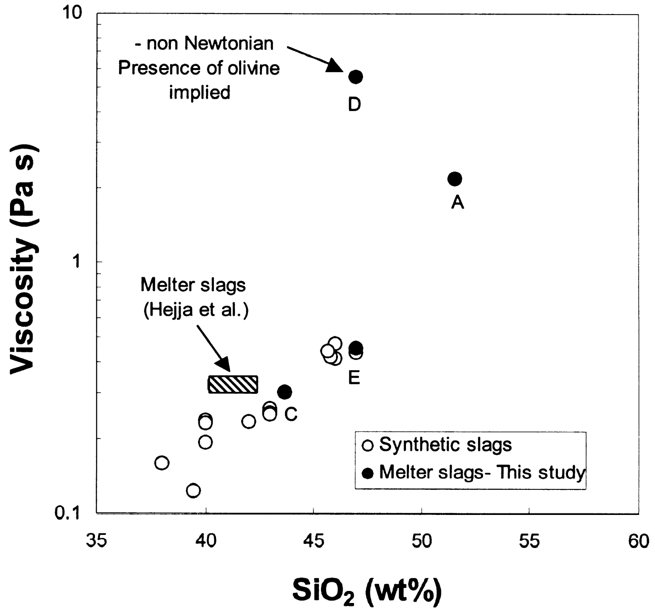

Figure 6. Comparison of the viscosity at 1400°C of the melter slags from this study with previous plant measurements and synthetic slags[3]

of the olivine phase in the slag. In Figure 8, the transition temperature from the viscosity results and the estimated stability of olivine from the drop quench experiments are compared; both are plotted against the MgO content of the slag. A broad correlation is obvious, i.e. increasing stability of olivine corresponds to higher transition temperatures. The discrepancies may be due to secondary effects of spinel contents, minor differences in slag chemistry in the drop quench, and the viscosity measurements in addition to other experimental uncertainties.

Conclusions

High temperature phase equilibria studies on a number of chromium containing melter slags produced in South Africa revealed that spinel was the primary solid phase and the

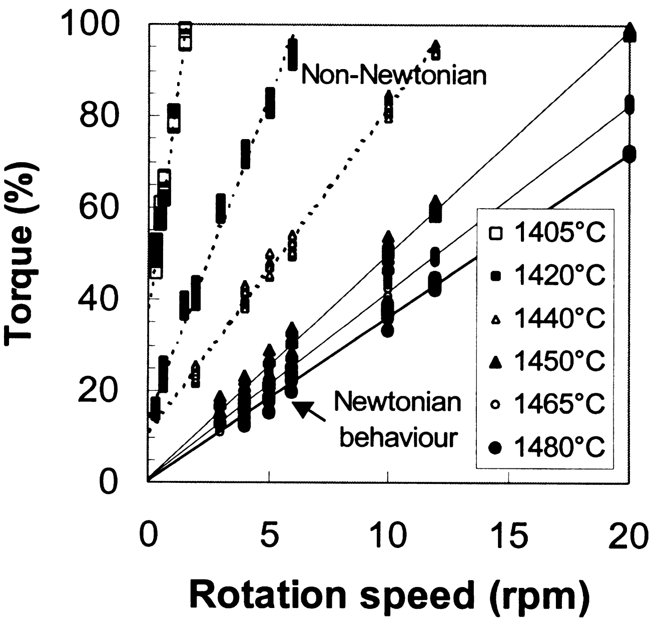

Figure 7. Measured viscometer torque as a function of the rotation speed for slag D

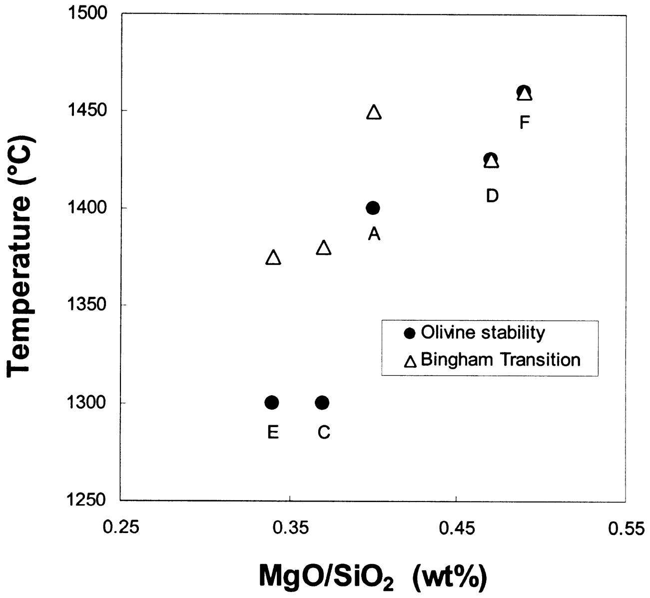

Figure 8. Observed transition temperature of Bingham to Newtonian behaviour and the highest melting temperature where olivine phase was found from the liquidus study correlated with the MgO/SiO_2 content in the slags

stability of spinel crystals was directly related to the chrome content of the slag. Olivine and pyroxene were found to be secondary solid phases in the melter slags studied. The stability of the olivine phase increased as MgO/SiO_2 ratio or MgO content of the slag increased. Formation of these secondary phases took place at temperatures well below the liquidus temperature and for slags with about 1 wt% Cr_2O_3, the temperature difference was about 200°C. The liquidus temperature for these slags increased from about 1550°C to in excess of 1630°C as the Cr_2O_3 was increased from about 0.9 to 3.4 wt%.

The viscosity of melter slags increases as their silica and/or chrome content increases. The Cr spinel crystals in these melter slags were small, well dispersed in the melt, and do not have a large impact on the liquid viscosity.

At high temperatures the slags showed Newtonian behaviour, but at lower temperatures a departure from Newtonian behaviour was observed. The transition coincided with the precipitation of the secondary olivine/pyroxene crystals in the slag.

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