



Melting of platinum group metal concentrates in South Africa

by J. Nell*

Synopsis

An overview is given of the matte melting process used for the beneficiation of South African platinum group metal (PGM) ores. Most producers use six-electrode furnaces to melt the concentrate and Pierce Smith converters to oxidize excess iron sulphide from the furnace matte. Concentrates from two reef types (the so-called Merensky and UG-2 reefs) dominate the feedstock supply. Concentrate from the Merensky Reef is low in chromium and does not pose significant melting problems. Concentrates from the UG-2 reef contain much higher levels of chromium, which results in the formation of chromium-rich spinels during melting. This is attributed to the low solubility of chromium in furnace slag under typical operating conditions (an oxygen partial pressure of 10^{-8} – 10^{-9} bar at temperatures of 1550°C to 1600°C).

During the converting process, care is needed to avoid excessively oxidizing conditions, which result in cobalt, nickel and copper losses to the slag. High nickel losses result in the formation of Fe_2NiO_4 (trevorite), which often forms solid solutions with FeCr_2O_4 and Fe_3O_4 .

In future, the main challenge in the processing of South African PGM ores will be to cope with ever-increasing levels of chromium in the concentrate. A short-term solution to the problem would be to melt the concentrate under slightly reducing conditions to promote the formation of CrO , which is more soluble in the slag than Cr_2O_3 . A longer-term solution to the problem would be to abandon the current matte-smelting process in favour of an alloy-based process, which would offer total flexibility with respect to the amount of chromium that can be tolerated in the feed.

Keywords: Merensky, UG-2, furnace, slag, matte, converting, spinel, chromium

Introduction

South Africa hosts more than 80 per cent of the world's reserves of platinum group metals (PGM). Recent reviews of the South African PGM industry focused on smelting¹, general extractive metallurgy² and the role of applied mineralogy in mineral beneficiation³. To date, little has been published on slag chemistry, the optimization of which is critical for the successful extraction of the PGMs from their ores. Here I attempt to partly fill that gap by providing a general overview of the role that slag chemistry plays during melting and converting.

History

Melting of platinum group metal (PGM) concentrates in South Africa dates back to the 1930s when blast furnaces were installed in Rustenburg to melt concentrate obtained from the Merensky Reef, one of the two main PGM-bearing reefs in the Bushveld Complex. (A third reef type, the Platreef, is mined in smaller quantities. Concentrates from the Platreef are chemically and mineralogically similar to those from the Merensky Reef and are treated in the same manner.) The concentrate had to be pelletized before melting and inadequate pellet strength and the relatively high liquidus temperature of the slag compromised the performance of the blast furnaces.

Furthermore, PGM concentrates derived from the Merensky Reef have high concentrations of base metals and sulphur and, more than anything else, it was the high sulphur emissions from the blast furnaces that led to their replacement by rectangular, six-electrode submerged arc furnaces in the 1960s. At the same time, the early Great-Falls-type converters, used for the removal of iron and sulphur from the matte produced by the melting furnaces, were replaced by more efficient Pierce-Smith units.

Currently, the amount of Merensky Reef concentrate being treated is decreasing in favour of concentrate derived from the UG-2 Reef, the second of the main PGM-bearing reefs in the Bushveld Complex. UG-2 concentrate is characterized by high concentrations of Cr_2O_3 and is much more refractory than Merensky concentrate. Six-in-line furnaces are still used for the melting of concentrates with ever increasing amounts of UG-2 ore, but they typically have much higher power densities than the earlier units. In response to the more demanding melting

* Mintek, South Africa.

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conditions, one of the three main PGM producers has opted for a circular, three-electrode furnace that has the capacity to operate with a maximum power density of 250 kW/m². In another recent development, another of the main producers is phasing out Pierce-Smith converters in favour of a continuous flash converting process². It is expected that high PGM prices will stimulate further developments in processing technology and in future an alloy collection process may well replace the current matte-based process⁴.

Process description

Dried concentrate is pneumatically transferred to the submerged arc furnaces where it is melted to produce an iron-nickel-copper-cobalt matte that acts as PGM collector. Depending on the ore type and the configuration of the concentrator plant, the concentrate is very fine (top size below 75 micron) and contains about 300 ppm PGM+Au. In the arc furnace the concentrate is melted, sometimes with the addition of lime or limestone as flux. Slag from the arc furnace typically contains less than 5 ppm PGM + Au and is usually discarded. Furnace matte is transferred to the converter where FeS is oxidized to FeO and SO₂. The FeO is fluxed with silica to form a fayalitic slag and the SO₂ is usually converted to sulphuric acid. Because of the turbulent nature of the converter operation, converter slag usually contains more than 10 ppm PGM + Au and cannot be discarded. Historically, the converter slag has been recycled to the arc furnace but, because of ever increasing chromium levels in the furnace feed, this practice has been all but discontinued. Instead, converter slag is milled and floated or it is treated in a separate slag-cleaning furnace. The latter, of course, must be able to melt the highly (electrically) conductive slag and, depending on the matte content of the converter slag, it might also be necessary to add a sulphide concentrate to improve matte collection.

Concentrate melting

Slag chemistry

As is the case with most metallurgical operations, the success of the melting process lies in the ability to form a 'good' slag. For the melting of PGM concentrates the slag should, ideally, have the following characteristics:

- ▶ A low viscosity to allow clean slag-matte separation
- ▶ A low liquidus temperature to avoid excessive superheating of the matte
- ▶ The ability to dissolve all the chromium present in the concentrate to avoid the formation of refractory chromium-bearing spinel and to avoid the transfer of chromium to the matte
- ▶ A limited solubility of nickel, copper and cobalt as oxides
- ▶ Chemical compatibility with the refractory lining in the furnace (in modern, water-cooled furnaces this consideration is less important than in the past).

Unfortunately, in the confines of the matte-melting environment, the slag composition is largely determined by the composition of the concentrate charged to the furnace and there is very little freedom to manipulate the slag composition (the only fluxing agent that is used in different

amounts by the various PGM producers is lime). The concentrate composition, in turn, depends on the relative amounts of the different ore types that are being processed. Typical compositions of Merensky concentrate and a blend of UG-2 concentrates for the Lonmin operations are given in Table I. From the data it is seen that as the ratio of UG-2-to-Merensky concentrate increases:

- ▶ The silica content increases (from 41 to 47 per cent SiO₂)
- ▶ The MgO-to-Fe ratio increases (from approximately 1 to 1.4)
- ▶ The Al₂O₃ content doubles
- ▶ The Cr₂O₃ content increases almost 7-fold
- ▶ The concentrations of the Cu, Ni and S decrease.

Slag compositions from the so-called 'Merensky' and 'UG-2' furnaces at Lonmin (Table II)¹ clearly reflect the compositional differences between Merensky concentrate and a blend of UG-2 concentrates.

The higher concentrations of MgO and Cr₂O₃ associated with increasing amounts of UG-2 concentrate in the furnace feed increases the liquidus temperature of the slag (the slag temperature in a Merensky furnaces is typically about 1350°C while in a UG-2 furnace it can exceed 1600°C). At the same time, the higher silica content leads to an increase in the slag viscosity. One therefore tends to find that matte entrainment and PGM losses to the slag increase with the UG-2 content of the furnace feed (PGM losses are exacerbated by the higher PGM grade of matte derived from UG-2 concentrates). In practice, a matte-fall of at least 15 per cent is needed to assure good collection and a high recovery of PGMs (Figure 1).

The main problem during melting is the presence of chromium in the furnace feed. Under typical operating conditions in a UG-2 furnace (slag temperature of about 1600°C and an oxygen partial pressure slightly more oxidizing than the Fe-FeO redox buffer) the solubility of chromium in furnace slag is low—typically below 2 per cent Cr₂O₃. Depending on the chromium content of the feed and the detailed operating conditions of the furnace, it frequently happens that the slag becomes saturated with a chromium-rich spinel phase. The consequences of spinel formation in the furnace are severalfold:

Table I

Typical Merensky and UG-2 concentrate analyses for the Lonmin operations¹

	Al ₂ O ₃	CaO	Cr ₂ O ₃	Cu+Ni	Fe	MgO	S	SiO ₂	PGM
Merensky	1.8	2.8	0.4	5	18	18	9	41	130
UG-2 blend	3.6	2.7	2.8	3.3	15	21	4.1	47	340

Table II

Composition of slag from the Merensky and UG-2 furnaces at Lonmin¹

	Al ₂ O ₃	CaO	Cr ₂ O ₃	Cu+Ni	Fe	MgO	S	SiO ₂
Merensky	2.0	10	1.2	0.24	28	19	0.5	44
UG-2 blend	3.9	13	2.4	0.24	9	22	0.3	47

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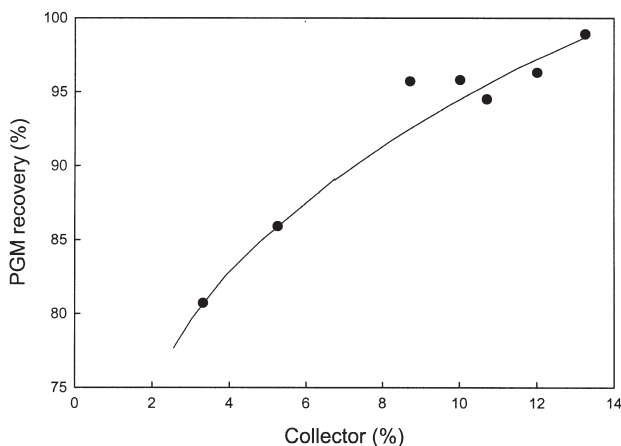


Figure 1—Relationship between PGM recovery and the amount of collector phase formed during melting. The solid line is a visual guide

- The spinel tends to accumulate at the slag-matte interface, preventing clean separation of slag and matte
- It increases the effective slag viscosity and causes emulsification of slag and matte
- Spinel freezes onto the sidewalls of the furnace and, if matte is tapped to a level where the slag-matte interface layer is brought into contact with the hearth, it also freezes onto the hearth, thereby decreasing the available furnace volume and changing the profile of the hearth
- It contaminates the matte with chromium (as FeCr_2O_4). Spinel in furnace matte causes problems with slag-matte separation during converting and increases the chromium content of converter slag. High levels of chromium in converter slag render it unsuitable for recycling to the furnace and, to recover PGMs from chromium-rich converter slag, it must either be melted in a slag-cleaning furnace or treated in a minerals processing plant.

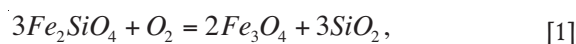
Furthermore, high levels of chromium increase the liquidus temperature of the slag, resulting in excessive superheating of the matte and severe refractory corrosion in furnaces that are not water cooled.

Factors that affect the solubility of chromium in the furnace slag

Under equilibrium conditions, the solubility of chromium in slag is controlled by temperature, oxygen potential and slag composition. These variables are briefly discussed in turn.

Temperature

Under oxygen partial pressure conditions controlled by the reaction:



(this reaction is commonly known as the QFM redox buffer, for which $\mu_{\text{O}_2} = -587474 + 1584.4T - 203.32\ln T + 0.0927T^2$ in units of joule per mole with T in kelvin)⁵ there is an almost threefold increase in the solubility of Cr_2O_3 in

silicate liquid with compositions similar to that of furnace slag as temperature increases from 1300°C to 1500°C (Figure 2)⁶. However, even at 1500°C the solubility is still only about 0.6 per cent Cr_2O_3 and from the slope of the curve it is evident that under these relatively oxidizing conditions it would not be possible to attain significant levels of chromium solubility in the slag by increasing furnace temperature only.

Oxygen potential

In the case of base metals with multiple valence states, it is generally true that the lower valence states are more soluble in silicate liquid than the higher valence states. Chromium is no exception to this general rule and it is seen that the oxygen partial pressure has a powerful effect on chromium solubility in typical furnace slag (Figure 3). Assuming that the partitioning of trace elements between slag and matte will be largely governed by the stabilities of the elements relative

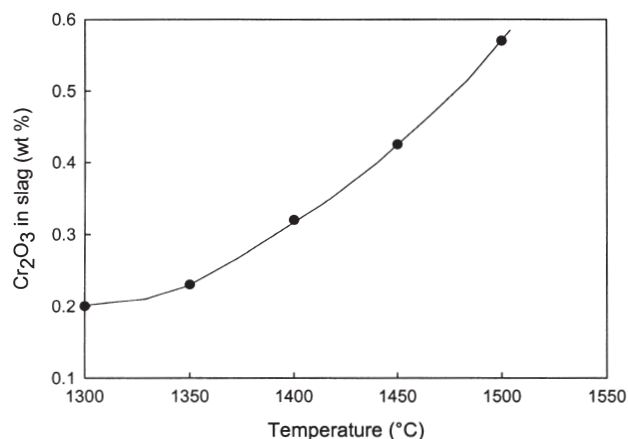


Figure 2—Chromium solubility in a komatiite liquid (45.1 per cent SiO_2 , 6.4 per cent Al_2O_3 , 10.4 per cent FeO , 30.8 per cent MgO , 5.9 per cent CaO) as a function of temperature under quartz (SiO_2)-fayalite (Fe_2SiO_4)-magnetite (Fe_3O_4) buffer conditions⁶. The solid line is a visual guide

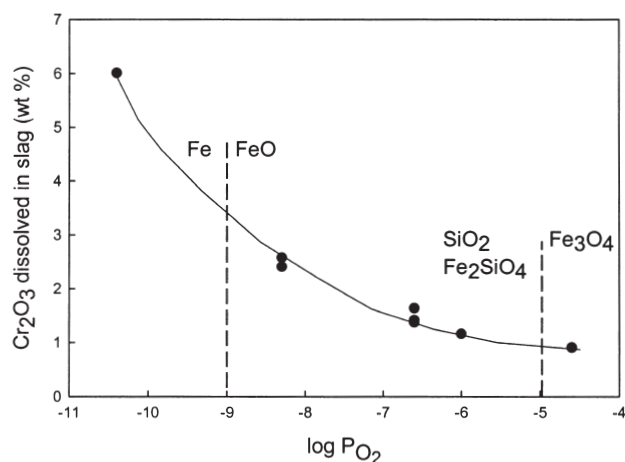


Figure 3—Chromium solubility (total dissolved chromium expressed as Cr_2O_3) in synthetic furnace slag as a function of oxygen partial pressure ($\log_{10} P_{\text{O}_2}$) at 1550°C³. The oxygen partial pressures of the iron (Fe)-iron oxide (FeO), and quartz (SiO_2)-fayalite (Fe_2SiO_4)-magnetite (Fe_3O_4) redox buffers are indicated for reference purposes. The solid line is a visual guide

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to their oxides, one can use trace element partition coefficients to bracket the oxygen partial pressure during melting (and converting). Unpublished Mintek data showed that in a typical UG-2 melting furnace running at about 1600°C, gallium partitions to the slag (as Ga₂O₃), while tin partitions to the matte (as Sn⁰). Based on the positions of the Ga₂O₃-Ga and SnO-Sn redox buffers⁷ this observation puts the oxygen partial pressure in the region of 10⁻⁸ to 10⁻⁹ bar. From Figure 3 it is evident that at an oxygen partial pressure of 10⁻⁹ bar at 1550°C it would be possible to dissolve between 2 per cent and 3 per cent chromium oxide in the furnace slag. What is more, by lowering the oxygen partial pressure further to about 10⁻¹⁰ bar it should be possible to increase chromium solubility to 6 per cent Cr₂O₃.

Under more oxidizing conditions, however, the chromium solubility rapidly decreases, and under QFM buffer conditions it is less than 1 per cent. It will be shown below that the QFM buffer sets the oxygen partial pressure in converter slag. Because of the oxidized nature of converter slag, it is not desirable to recycle it to the arc furnace since it will lower the solubility of chromium in furnace slag during melting.

The increase in chromium solubility with decreasing oxygen partial pressure is attributed to a shift in the dominant valence state from trivalent to divalent. The difference in the solubility of chromium in the divalent and

trivalent oxidation states is illustrated by binary phase diagrams for the system CrO_x-SiO₂ under oxidizing and reducing conditions, respectively (Figure 4)⁸. In the trivalent oxidation state, a liquid immiscibility gap spans across virtually the entire system and at 2100°C the solubility of Cr₂O₃ in the liquid phase does not exceed 0.1 wt per cent. Under reducing conditions, the immiscibility gap contracts and the solubility of chromium increases significantly.

To attain high solubility levels under reducing conditions, other metal oxides are also reduced. The reduction of other metal oxides could be advantageous (as for the reduction of NiO, CoO and CuO) or undesirable, as for the reduction of FeO. Excessive reduction of FeO could lead to the formation of a separate alloy phase that would unmix from the matte during smelting. Such an alloy phase would scavenge PGMs from the matte and, because of its density, settle to the furnace hearth where it is likely to freeze because of its high liquidus temperature. It is clear, therefore, that by adjusting the oxygen potential it would be possible to significantly increase chromium solubility, but this would have to be done with utmost care and under conditions of tight control over furnace chemistry to avoid over-reduction of iron oxide from the slag.

A further consequence of operating the furnace at reduced oxygen potential is an increase in the department of chromium to the matte. Under slightly 'reducing' conditions, the high solubility of chromium in the slag is a result of the reduction of Cr³⁺ to Cr²⁺. Cr²⁺ is soluble in the slag as 'CrO' but also in the matte as 'CrS'. High levels of chromium sulphide in the matte might result in the formation of large amounts of chromium spinel during converting, which, in turn, might cause operational problems.

Slag composition

The effect of slag composition on chromium solubility is less certain. Experimental work under reducing conditions shows a strong dependence on melt basicity (Figure 5)⁹. However, it is also clear that the solubility relationship depends on the redox conditions and that it is less pronounced under more

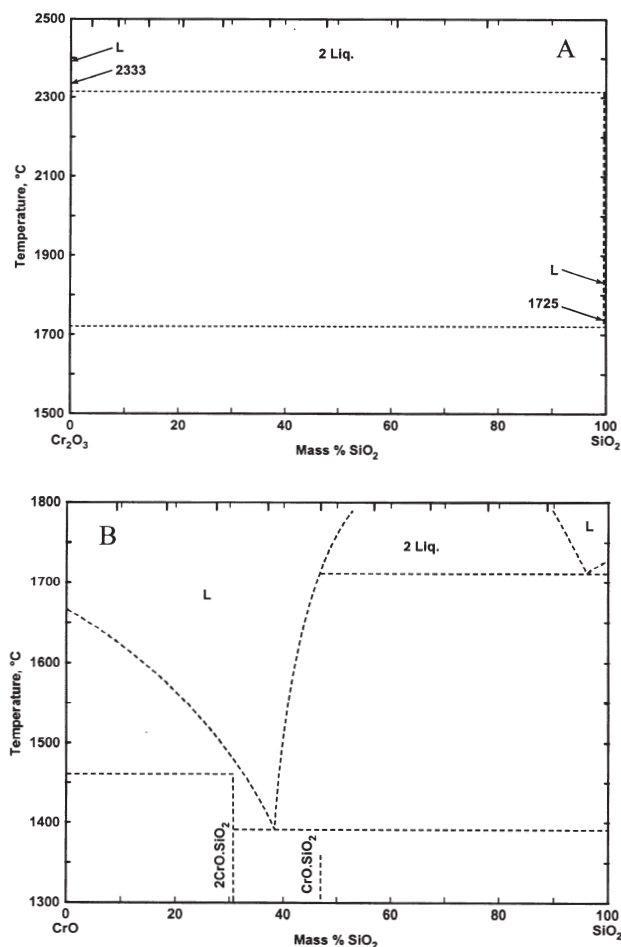


Figure 4—Phase diagrams for the system CrO_x-SiO₂ under oxidizing (A) and reducing (B) conditions, respectively⁸

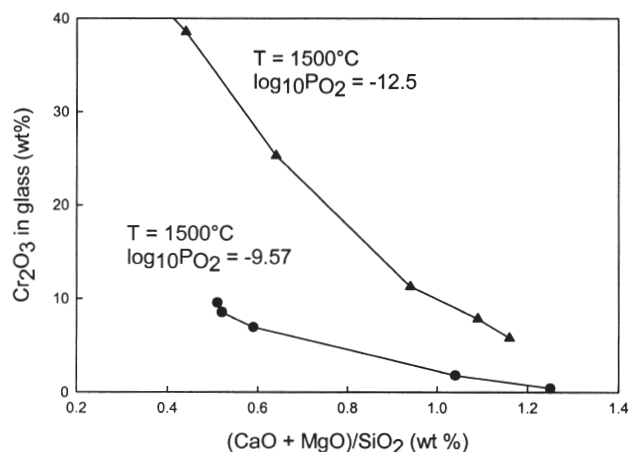


Figure 5—Chromium solubility (at spinel saturation) in the system CaO-MgO-SiO₂-CrO_x as a function of melt basicity⁹. Solid lines are visual guides

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oxidizing conditions. From these trends it is to be expected that in air chromium solubility would be less dependent on melt basicity than at an oxygen partial pressure of $10^{-9.75}$ bar (at 1500°C).

The effect of slag composition on chromium solubility in a multi-component slag system is, largely, undocumented. Plant observations (Mintek unpublished data) indicate that the solubility of chromium might depend on the concentrations of both silica and lime, but more data are needed to verify the initial observations.

From the foregoing, it is evident that the easiest way to counter the formation of chromium-bearing spinel in the slag is to lower the oxygen potential in the furnace (through the addition of reductants).

Crystallization behaviour

The liquidus temperature of chromium-bearing furnace slag is determined by the crystallization of chromium spinel (Figure 6). The temperature at which the spinel crystallizes is determined by the oxygen partial pressure and the chromium content of the slag. For slag running at 2.5 per cent Cr_2O_3 the liquidus temperature is approximately 1600°C at an oxygen partial pressure of 10^{-8} bar (Figure 6). Fortunately, the amount of spinel that forms is small (less than 3 per cent of the mass of the slag). The composition of the spinel is significantly different from that of the chromite in the feed. The latter contains about 15 per cent Al_2O_3 , 45 per cent Cr_2O_3 and 26 per cent FeO (total iron expressed as FeO). Spinel that crystallizes in the furnace contains about 5 per cent alumina and, depending on the temperature of formation, up to 65 per cent Cr_2O_3 . In general, it is found that the iron content of the spinel increases with decreasing temperature of crystallization and increasing oxygen partial pressure^{6,10}.

The first silicate phase that crystallizes from the slag at approximately 1500°C is either olivine $(\text{Mg, Fe})_2\text{SiO}_4$ or pyroxene $(\text{Mg, Fe, Ca, Al})\text{SiO}_3$. Free energy minimization shows that the activities of olivine and pyroxene are very similar at temperatures between 1400°C and 1500°C , and

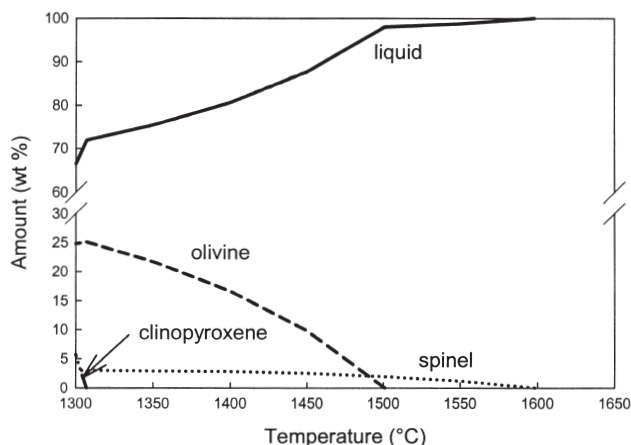


Figure 6—Crystallization behaviour of furnace slag (48.3 per cent SiO_2 , 4 per cent Al_2O_3 , 9.2 per cent FeO, 22.6 per cent MgO, 13.4 per cent CaO, 2.5 per cent Cr_2O_3) at a constant oxygen partial pressure of 10^{-8} bar modelled with the FactSage software package

subtle differences in slag composition determine the order of crystallization of the silicate phases.

Electrical conductivity

A recent study provides detailed information on the effect of slag composition and oxygen partial pressure on the electrical conductivity of furnace type slag at 1450°C ¹¹. It was found that:

- The electrical conductivity increases with basicity and iron oxide content (increasing iron oxide serves to depolymerize the slag and creates sites for electronic conduction)
- Ionic and electronic conduction mechanisms operate in slags with a high iron oxide content (above 20 per cent FeO).
- Electronic conduction depends on the oxidation state of the slag. Depending on the basicity, the conductivity reaches a maximum when the oxygen partial pressure is in the range of 10^{-4} bar (low basicity) to 10^{-7} bar (high basicity). Under these conditions the number of electronic conduction sites (which depends on both the Fe^{3+} -to- Fe^{2+} ratio and the coordination number of the Fe^{3+} ions) is at a maximum.
- For the same oxidation state, more basic slags contain a larger proportion of Fe^{3+} ions, explaining why the maximum in conductivity occurs at lower oxygen partial pressures for higher basicity slags.

Converting of furnace matte

Matte from the melting furnaces is oxidized to lower the concentrations of iron and sulphur, while at the same time increasing the PGM grade. Pierce-Smith converters are widely used to oxidize the matte but because these units operate in batch mode and because of inefficient SO_2 capturing and widely fluctuating concentrations of SO_2 in the off-gas (which is usually treated in sulphuric acid plants), Anglo Platinum has adopted flash furnace technology for the converting of their furnace matte.

Iron oxide derived from the oxidation of the matte is fluxed with silica to form a fayalitic slag. The oxygen partial pressure in converter slag is close to that of the quartz-fayalite-magnetite (QFM) redox buffer (Reaction 1), which defines an oxygen partial pressure of $10^{-8.4}$ bar at 1200°C . That this is the case is demonstrated by the fact that both NiFe_2O_4 (trevorite) and Fe-bearing Ni monoxide (containing less than 15 per cent FeO) are frequently found in converter slag. At 1200°C , NiFe_2O_4 coexists with a nickel-rich monoxide phase at oxygen partial pressures that are more oxidizing than $10^{-10.5}$ bar (Figure 7)¹². The oxidizing nature of these conditions means that high losses of cobalt, nickel and copper (as oxides) might be encountered unless blowing conditions are carefully controlled and monitored. (Incidentally, using Figure 7, the iron content of the nickel monoxide phase formed during converting can be used to estimate the oxygen partial pressure in converter slag at 1200°C .)

Under the relatively oxidizing conditions in the converter, all the chromium in the matte is oxidized to Cr_2O_3 and,

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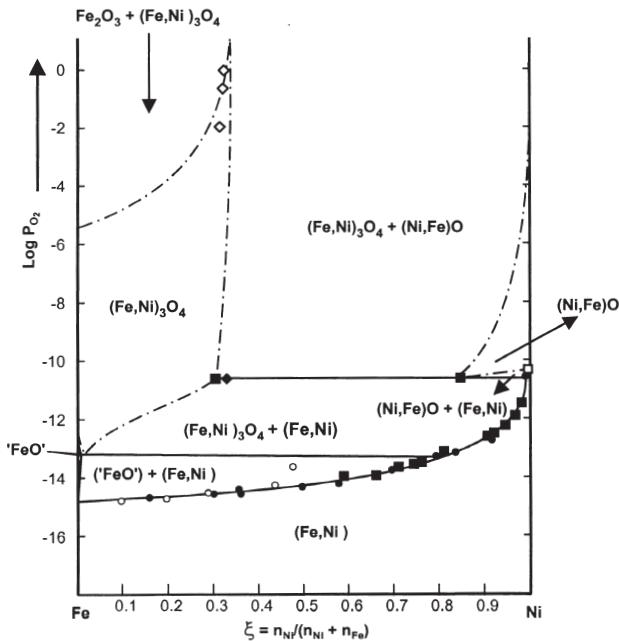


Figure 7—Phase diagram for the system Fe-Ni as a function of oxygen partial pressure at 1200°C¹²

unless care is taken to assure that the final iron content of the converter matte does not decrease below about 3 per cent, significant cobalt (and potentially also nickel) losses to the slag are experienced.

While cobalt and nickel are readily soluble in fayalitic slag, chromium is not (the solubility is less than 1 per cent Cr₂O₃ at 1250°C, which is a typical temperature for converter operations). In general, the low solubility of chromium is attributed to the low slag temperature and the oxidizing conditions in the converter. Unlike the furnace, where it is possible to operate under more reducing conditions and to increase the slag temperature, these options are not available in the converter. Chromium management in the converter, therefore, requires a different approach.

Chromium oxide in the converter crystallizes as FeCr₂O₄-Fe₃O₄-NiFe₂O₄ (spinel) solid solutions. Chromium- and nickel-bearing spinels that remain trapped in the converter matte are inert to acid attack and their presence cause considerable operational problems in the base metals refinery (BMR). As in the melting furnace, spinels in converter slag result in poor slag-matte separation and excessive PGM losses to the slag.

Discussion

From the foregoing it is evident that the main challenge in the melting of PGM concentrates from the Bushveld Complex is the ever-increasing chromium content, which is a consequence of increasing amounts of UG-2 ore being mined. Over the last few years much progress has been made in

managing the 'chromium problem'. Steps that have been taken include:

- ▶ The exclusion of converter slag from the electric arc furnaces
- ▶ Regular monitoring of arc furnace performance
- ▶ Optimization of slag basicity, coupled with an increase in operating temperature necessitated by the higher liquidus temperature of chromium-enriched concentrates
- ▶ The use of furnaces with a higher power density.

While these steps have permitted partial relaxation of chromium constraints imposed on ore processing plants, future operations might use small amounts of reductant to further increase chromium solubility in the slag. Depending on the availability of low-chromium, sulphur-rich ore concentrates (such as those obtained from the Platreef) the matte-melting process might eventually even be abandoned in favour of an alloy smelting process³, which would, in principle, allow complete flexibility with respect to the chromium content of the ore that is treated.

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