Introduction

The Bushveld Complex in South Africa is the largest known layered igneous complex and contains two-thirds of the world’s PGM reserves (Jacobs, 2006). Platinum-group metals (PGMs) are concentrated in three narrow layers in the Bushveld Complex, namely the Merensky Reef, the Platreef, and the UG2 chromitite layer (Jones, 2005). PGMs occur together with base metal sulphides in the Merensky and Platreef, while the UG2 layer has a high chromite content and low concentrations of base metal sulphides. UG2 ores contain approximately 30% Cr₂O₃ compared with 0.1% Cr₂O₃ in the Merensky deposit (Jones, 2005). Mines are increasingly exploiting the UG2 as the Merensky Reef becomes depleted.

The chromite content of the UG2 ore presents a major challenge for the PGM smelting process as high levels of chromium increase the slag liquidus temperature, which necessitates higher operating temperatures. If, under non-reducing conditions, the Cr₂O₃ content of the concentrate exceeds approximately 1.8%, the chromite spinels do not dissolve in the slag at conventional slag temperatures (1500–1550°C), but build up in the furnace hearth and form a 'mushy' three-phase layer at the slag-matte interface (Eksteen 2011; Hundermark, 2011). This leads to inefficient matte segregation and difficulties in matte tapping. To achieve adequate suspension of the spinels, the furnace temperature is increased by increasing the electrode immersion depth and power density (Eksteen, 2011). Chromium control is therefore an important factor when considering furnace operating temperature. This is done by effectively controlling the concentrate blend that is fed into the furnace and adjusting the operating power accordingly (Jacobs, 2006).

FactSAGE® calculations performed by Eksteen (2011) predicted that at temperatures above 1500°C the matte will react chemically with the refractory lining. In this process chromium will be picked up in the matte and wear of magnesia-chrome refractory bricks as a function of matte temperature

by M. Lange*, A.M. Garbers-Craig*, and R. Cromarty*

Paper written on project work carried out in partial fulfilment of B. Eng. (Metallurgy)

Synopsis

The postulation that primary platinum group metal (PGM) matte will chemically react with magnesia-chrome bricks when temperatures exceed 1500°C was tested. Magnesia-chrome brick samples were heated in contact with matte at 1300°C to 1750°C for 30 minutes, after which the refractory samples were analysed using reflected light microscopy and scanning electron microscopy. The samples were all completely penetrated by matte. As the temperature increased the matte also penetrated the fused aggregate grains and disintegrated them. The chromium concentration of the matte inside the refractory samples was found to be slightly higher than that of the bulk matte. At temperatures of 1500°C and higher, MgO, FeO, and magnesium-rich silicate crystals could be identified in the matte directly adjacent to the refractory-matte interface. Phase relations clearly indicated that chemical reactions take place between primary PGM matte and the magnesia-chrome refractory material at temperatures above 1500°C, but that these reactions are more complex than expected from FactSAGE® calculations.

Keywords

refractory, magnesia-chrome bricks, penetration, fused grains.

* Centre for Pyrometallurgy, Department of Materials Science and Metallurgical Engineering, University of Pretoria, Pretoria, South Africa.

Wear of magnesia-chrome refractory bricks as a function of matte temperature

Oxygen will be transferred from the refractory to the matte according to reactions [1] and [2]:

\[
\begin{align*}
(FeCr_2O_4)_{\text{refractory}} + 2[S]_{\text{matte}} + 3[Fe]_{\text{matte}} &= \text{[1]} \\
2[CrS]_{\text{matte}} + 4[FeO]_{\text{matte}} &= \text{[2]}
\end{align*}
\]

With \(\Delta G^o = -8.478 \text{ kJ/mol at } T=1500^\circ\text{C} (\Delta G^o < 0, \text{ when } T > 1450^\circ\text{C})\)

\[
\begin{align*}
(MgCr_2O_4)_{\text{refractory}} + 2[S]_{\text{matte}} + 3[Fe]_{\text{matte}} &= \text{[2]} \\
2[CrS]_{\text{matte}} + 3[FeO]_{\text{matte}} + (MgO)_{\text{refractory}}
\end{align*}
\]

With \(\Delta G^o = +11.03 \text{ kJ/mol at } T=1500^\circ\text{C} (\Delta G^o < 0, \text{ when } T > 1650^\circ\text{C})\)

Eksteen (2011) concluded that the combination of high temperatures and sulphidation reactions would cause disintegration of the brick due to the destruction of its spinel bonding phase.

This project subsequently investigated whether chemical interaction between magnesia-chrome bricks and primary PGM matte takes place at temperatures above 1500°C, as predicted by Eksteen (2011).

### Materials

Vereeniging Refractories supplied samples of reconstituted fused-grain magnesia-chrome refractory bricks, while furnace matte and slag samples were obtained from the Anglo Platinum Waterval Smelter. According to the supplier’s specifications, the brick had a chemical composition of 57.4% MgO, 21.3% Cr₂O₃, 11.2% Fe₂O₃, 7.8% Al₂O₃, 1.5% SiO₂, and 0.8% CaO, and an apparent porosity of 16%. The matte was analysed using powder X-ray diffraction (XRD), scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDS), inductively coupled plasma optical emission spectrometry (ICP-OES), and sulphur analysis (Leco-S). The matte sample consisted mainly of nickel, copper, and iron sulphides, and contained 39% Fe, 15% Ni, 11% Cu, 34%S, 0.61% Cr, and 1% SiO₂.

### Experimental

Laboratory-scale experiments were performed in an induction furnace consisting of a graphite susceptor in an insulated, gas-tight, chamber. The furnace was purged with argon to prevent oxidation of the graphite susceptor. Power was supplied by an Ambrell Ekoheat 15/100 radio frequency power supply. Temperature was controlled by a Eurotherm 2416 temperature controller with a Type B thermocouple.

Two sample types were used to study matte–refractory interactions:

- **Design 1 – magnesia-chrome crucible containing matte and slag**
  - Design 1 (magnesia-chrome crucible, filled with matte and slag) was used for tests at 1300°C and 1500°C. This design, however, resulted in the refractory soaking up all the matte, leaving no matte in the crucible for analysis. The microstructure of the magnesia-chrome brick with soaked-up matte is shown in Figures 3 and 4.

### Results and discussion

#### Microstructure of unreacted magnesia-chrome refractory brick

The as-supplied magnesia-chrome brick consisted of large magnesia grains (dark grey phase), which contained small amounts of iron and chrome in solid solution (Figure 2). Finely exsolved spinel crystals (light grey phase) were observed in the magnesia grains. The spinels on the grain boundaries had roughly the same composition as the spinels within the magnesia grains.

#### Design 1 – magnesia-chrome crucible containing matte and slag

Design 1 (magnesia-chrome crucible, filled with matte and slag) was used for tests at 1300°C and 1500°C. This design, however, resulted in the refractory soaking up all the matte, leaving no matte in the crucible for analysis. The microstructure of the magnesia-chrome brick with soaked-up matte is shown in Figures 3 and 4.
The white phase is a penetrated Fe-rich sulphide phase, while the very light grey phase represents a Cu-Fe-Ni-based sulphide (Figure 4). The light grey phase in Figure 4 is the typical chromite spinel that is found in the refractory, with the dark grey phase surrounding it consisting of mainly magnesium oxide. The penetration that took place was minimal but uniform throughout the refractory. This experimental set-up presented numerous difficulties as there was no matte left for chemical analysis due to the complete penetration. This design also allowed the refractory to be in direct contact with the graphite suscepter of the induction furnace, thereby exposing it to a very reducing atmosphere. These reducing conditions resulted in the formation of an iron-nickel alloy within the refractory closest to the graphite suscepter.

It was subsequently decided to change the design to a set-up in which a small piece of refractory, surrounded with a large amount of matte, was placed in a large alumina crucible (Design 2). The crucible was closed with an alumina lid to limit the sulphur losses from the matte. No slag was used in this design as the slag tended to react with the alumina crucible. Alloy formation in the matte was not observed when Design 2 was used.

**Design 2 – alumina crucible containing matte and refractory sample**

Observed matte-refractory interaction is discussed in terms of matte penetration into the open porosity, matte penetration into the fused aggregate grains, and matte-refractory interaction at the interface.

**Matte penetration into open porosity**

All the examined refractory samples from Design 2 were completely penetrated by matte, similar to samples from Design 1. A penetration profile could not be distinguished as the refractory samples had a 'wicking' effect on the surrounding matte. All the samples had roughly the same outward appearance (Figure 5).

The extent of penetration as a function of temperature can be seen in Figure 6. The porosity of the unreacted brick (A) became completely filled with matte as the refractory piece came in contact with the matte at the different temperatures. The large fused grains began disintegrating as the temperature was raised and finally the matte even penetrated into the fused grains themselves.

**Matte penetration into the fused aggregate grains**

Examination of the aggregate grains at higher magnifications gave important insight into the reactions taking place at
Wear of magnesia-chrome refractory bricks as a function of matte temperature

Increasing temperatures. Except for penetration, the tests at 1300°C and 1400°C showed no clear signs of chemical interaction. It was only at temperatures of 1500°C and higher that signs of interaction were noticed. This agrees with FactSAGE® predictions.

At 1500°C and higher, spinels migrated out of the magnesia grains and collected on the grain boundaries. This left large areas of the magnesia grains exposed as they became depleted in spinels. Furthermore, matte started to penetrate into the fused grains and disintegrated them (Figure 7). EDS analysis of this penetrating matte indicated that it locally contained up to 0.7% Cr, compared to 0.3% Cr in the bulk matte.

Disintegration of the fused grains was more pronounced in the refractory samples that were reacted at 1600°C and 1700°C (Figures 8 and 9). The spinel crystals migrated out of the magnesia grains, while the matte completely disintegrated the large fused grains. At 1600°C the penetrating matte had a Cr content of 0.5% compared to 0.3% in the bulk matte, which is not a significant increase.

At 1750°C (Figure 10) the penetrating matte contained 0.8% Cr compared with a bulk matte concentration of 0.3%. A sudden increase in porosity was also observed (Figure 10), together with a large amount of sulphur gas evolution during the experiment.

As the experimental temperature increased the spinel crystals increasingly migrated out of the magnesia grains and grouped together as the magnesia grains disintegrated. This destruction of the fused grains would make the bricks more vulnerable to the effects of thermal shock, as without the finely dispersed spinel crystals the bricks would be more susceptible to crack propagation.

Matte-refractory interaction at the refractory-matte interface

It was important to carry out a detailed analysis of the interface between the refractory and the surrounding matte, as this would indicate how the actual furnace lining would react when brought in contact with the superheated matte. Tests at 1350°C and 1400°C again resulted in matte penetration only.

![Figure 6—Reflected light micrographs of matte penetration into the magnesia-chrome refractory as a function of temperature. A: Unreacted brick, B: 1300°C, C: 1400°C, D: 1500°C, E: 1600°C, F: 1700°C](image)

![Figure 7—Backscattered electron image of the microstructure of the magnesia-chrome brick reacted at 1500°C](image)

![Figure 8—Backscattered electron image of the microstructure of the magnesia-chrome brick reacted at 1600°C](image)

![Figure 9—Backscattered electron image of the microstructure of the magnesia-chrome brick reacted at 1700°C](image)
At temperatures of 1500°C and higher a magnesium-rich silicate phase could be observed to form a boundary layer at the refractory-matte interface (Figures 11 to 13). This boundary phase could have been established through the predicted formation of MgO that reacted with the silica in either the matte or refractory, as both contained small amounts of silica. On either side of the boundary, FeO crystals started to form, together with spinel crystals. The stoichiometry of these crystals started to change from $Mg_3O_4$ to $MO$. Some large spinel crystals could also be observed at the refractory-matte interface, as well as magnesia grains with finely dispersed exsolved spinel crystals.

At temperatures of 1700°C and 1750°C more FeO crystals started to form at the interface, and the stoichiometry of the magnesium-rich silicate phase was calculated to be $\text{(Mg,Fe)}_2\text{SiO}_4$ (Figures 13 and 14). The extent of spinel segregation out of the magnesia grains close to the interface was also higher at these temperatures. At 1750°C the spinels were completely removed from the fused magnesia grains close to the refractory-matte interface (Figure 14).

Conclusions
The observed amount of matte penetration into the magnesia-chrome brick samples was substantial. All the refractory samples were completely penetrated by matte. As the temperature increased the matte also started to penetrate the fused aggregate grains, and disintegrated them.

CrS was not observed as a separate phase. It was noticed, however, that the chromium content of the matte inside the refractory sample was slightly higher than that of the bulk.
Wear of magnesia-chrome refractory bricks as a function of matte temperature

matte. At temperatures of 1500˚C and higher, definite signs of MgO and FeO formation were found, as well as the gradual disintegration of the grains inside the refractory at the refractory-matte interface.

The formation of a magnesium-rich silicate boundary phase at the matte-refractory interface at temperatures above 1500ºC was unexpected and needs further investigation. Results obtained in this study clearly indicate that the reactions that took place between primary PGM matte and the magnesia-chrome refractory material are more complex than those predicted through FactSAGE® modelling.

Acknowledgements

Technical and financial support from Anglo American Platinum is gratefully acknowledged. This work is based on research supported in part by the National Research Foundation of South Africa (Grant number TP1208219517).

References


The SAIMM Library

The library has been indexed and sorted. Although it is not as big as we would like it to be, we have a fair number of reference books and a certain amount of resource material.

Access to the library and the control of the borrowing process is in the hands of Kea Shumba.

The titles are available on the website at the following link:
http://www.saimm.co.za/saimm-library?task=showCategory&catid=32

Sam Moolla, Manager: SAIMM Secretariat