POST MORTEM ANALYSIS OF A TAPPING CHANNEL FROM A PLATINUM SMELTER

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ABSTRACT
In a platinum smelter Platinum group metal (PGM) matte is tapped through an alumina-chrome brick lined tapping channel. Penetration of PGM matte into these tap-hole bricks leads to detrimental refractory wear which can cause furnace breakouts. The extent to which matte penetration and chemical interaction takes place was investigated through a post mortem study of a tapping channel removed from the Anglo American Platinum Mortimer smelter in South Africa. Matte penetration in regions surrounding the hole in the refractory tapping module was the main focus. The investigation also included determining whether residual tap-hole clay is present in the tapping channel and how oxygen lancing impacts on refractory wear. SEM-EDS and XRD analyses were done on samples taken from the position of the new tapping module condition as well as the worn hole, both on the tap hole side of the brick (the hot face) and at the edge of the brick (the cold face). It was found that upon solidification, the penetrated matte crystallised to form sulphides with different concentrations of iron, copper and nickel, or combinations of these elements. Chalcopyrite ($CuFeS_2$), pentlandite ($(Fe, Ni)_9S_8$) and pyrrhotite ($Fe_{1-x}S$) were the dominant phases. Oxidation of both iron and copper was observed. This resulted in the formation of a $CuFe_2O_4$ – Fe_3O_4 solid solution spinel phase in the areas surrounding the worn hole, and a more complex Cu-Fe-Al-Cr-based spinel phase in the position of the original hole. Residual tap-hole clay could not be identified. SiO_2 observed in the bricks is associated with CaO, MgO and iron oxide which indicates that slag also came in contact with the matte tap-hole bricks.

INTRODUCTION

PGM processing is complex. In South Africa PGM-containing ore is mined from the Merensky, UG2 and Platreef reefs of the Bushveld Complex. Ore from the Merensky and Platreef reefs are similar, where PGMs occur together with base metal sulphides, while ore from the UG2 reef has a high concentration of chromite with low concentrations of base metal sulphides. The base-metal sulphide minerals in these ores are mainly pyrrhotite ($Fe_{1-x}S$), pentlandite ($(Fe, Ni)_9S_8$), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). The UG2 ore undergoes comminution and gravity concentration followed by a flotation step to concentrate the sulphides. The sulphide rich flotation concentrate forms the feed to the smelter. Matte from the smelter, which is Fe-Ni-Cu – based, is fed to the converter to produce a PGM-containing nickel-copper matte. Finally hydrometallurgical processes are used to separate the base metals from the precious metals, and recover the PGMs individually [1].

PGM producers in South Africa feed a blend of Merensky, UG2 and Platreef concentrate to the smelter. With decreasing supplies of Merensky concentrate, increasing amounts of UG2 concentrate are used. The high chromium content of the UG2 concentrate increases the slag liquidus temperature. Smelters are forced to operate above the slag liquidus temperature to avoid the refractory chromite building up in the furnace hearth as chromium spinel [2]. The slag operating temperatures can therefore range from 1460-1650°C depending on the feed composition. The high slag operating temperatures result in matte superheats of 300-650°C, which implies the matte is extremely fluid, can easily penetrate the refractory bricks and thereby increase refractory wear. The increased temperature also places greater demands on the refractories in the tapping channel.

Anglo American Platinum use six-in-line electric arc furnaces in their smelting processes. Upon melting two distinct liquid phases form. The slag, which contains silica (52%), magnesia (23%) and iron oxides (11%) with some alumina (5%), CaO (5%) and Cr_2O_3 (2%) [3], separates from the denser matte, which mainly contains iron, nickel and copper [4]. During tapping, molten matte moves through the tapping channel into ladles, from where it is further processed. As molten matte moves through the tapping channel it causes considerable damage to the refractory materials. Wear of the refractories occurs through a three step process [5]: Wear is initiated when the molten matte penetrates into the refractory bricks. Once penetration has occurred, parts of the brick can corrode. Erosion occurs as pieces of the brick are removed along with the molten matte during consequent taps. Wear of tapping channels leads to a decrease in the control possible during tapping. It also leads to greater safety risks as the possibility of a burn-through and a reopening of the tap-hole become a larger possibility [5].

The matte tap-hole is opened through drilling and oxygen lancing. At the end of a tap, the tapping channel is closed through plugging with tap-hole clay using a mud gun [5]. The tap-hole clay hardens and strengthens during the curing process to become sufficiently hard and strong to ensure that reopening of the tap-hole does not occur. Oxygen lancing can damage the tap-hole refractories significantly due to thermal spikes as well as unwanted oxidation, which can cause the tap-hole to shift from the centre position. This can lead to premature refractory failure, or in extreme cases water explosions if the lancing becomes so skew that accidental lancing into the water-cooled tap-hole assembly occurs [6].

A better understanding of the interaction between the matte and the refractory materials and the wear mechanisms in the tapping channel can lead to the use of better suited materials or better operating conditions and procedures to ensure that the lifetime of the refractories are maximised. This paper reports on how matte penetration and oxygen lancing impacts on wear of matte tap-hole bricks from a PGM smelter. If the tap-hole clay can form a layer on the refractory bricks, it can provide protection against matte penetration during tapping [4]. The post mortem analysis therefore also established whether any residual tap-hole clay was present in the tapping channel after use.

MATERIALS AND METHOD

Materials before Use

Phosphate bonded alumina-chrome tap-hole bricks were used. Quantitative XRD analysis indicated that it contained 43% alumina (Al_2O_3) and 54% of an alumina-chrome solid solution phase ($(Al,Cr)_2O_3$.

The tap-hole clay that is used is resin bonded and contains, according to the data sheet, alumina (71%), SiO_2 (13%), Fe_2O_3 (1.5%), TiO_2 (2.5%) and SiC+C (11.5%).

Sample Preparation and Analysis

The tap block consisted of seven bricks. Brick 7 (Figure 1), bordered the matte in the furnace, where higher temperatures were experienced, while brick 1 (Figure 1) was closest to the outside of the furnace, where temperatures were lower.

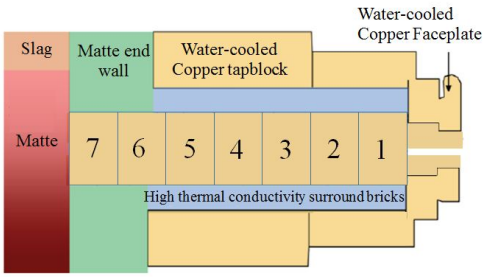

Fig. 1: Schematic of the tapping channel [3]

The bricks retrieved from the tapping channel had to be reconstructed, as they fell apart on removal. Different parts of the reconstructed brick were then selected for phase chemical analysis.

Sections from the hot face of the tap-hole towards the cold face were removed and analysed to establish compositional changes with changing position relative to the tap-hole. Regions to the bottom of the tap-hole (**Fig. 2**, region C) and the side of the tap-hole (**Fig. 2**, region B) were considered, as well as the regions around the original position of the tap-hole (**Fig. 2**, region A) before drilling and oxygen lancing caused the tap-hole to move from its original position. Polished sections were prepared for SEM-EDS analysis along paths A, B and C (in one centimetre increments) as shown by the arrows (**Fig. 2**). XRD analyses were also performed on samples from the hot face (**Fig. 2**, A1, B1, C1), samples from the cold face (**Fig. 2**, A3, B2, C2) and a sample in the middle of the original tap-hole (**Fig. 2**, A2).

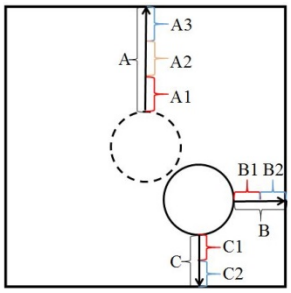

Fig. 2: Schematic diagram that shows where samples were taken from the post mortem bricks

The focus of the analyses was threefold. Firstly the extent of matte penetration and the interaction between the matte and the brick was investigated. Secondly the effect of oxygen lancing on a chemical level was investigated. Since the conditions during processing are reducing (partial pressures of 10^{-8}-10^{-9} bar [7]), any oxidation of phases in the tapping channel was accepted to be due to oxygen lancing. Finally there was also a focus on whether any residual tap-hole clay could be detected in the used brick. This would indicate that under operating conditions, the tap-hole clay could provide the brick with protection against matte penetration.

RESULTS AND DISCUSSION

Matte – brick interaction

Distinct changes in the compositions of the bricks were observed, with definite matte penetration and chemical interaction having occurred. The backscattered electron images (BEI) of typical microstructures observed in brick 7 and brick 1 are shown in Figures 3 - 8 and Figures 9 – 13 respectively.

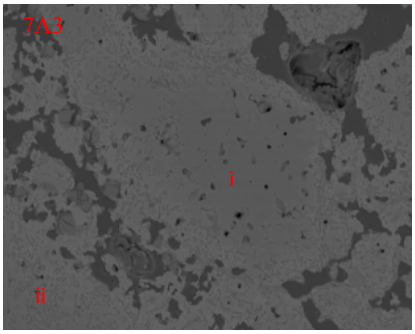

Figure 3: BEI of brick 7, position A3 (1cm = 53μm). (i = Al_2O_3; ii = $(Al,Cr)_2O_3$)

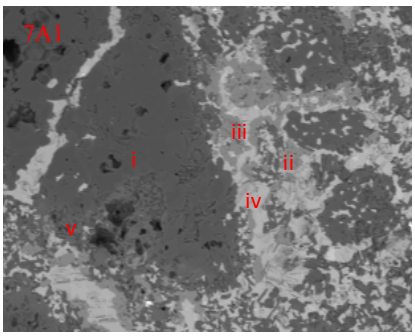

Figure 4: BEI of brick 7, position A1 (1cm = 48μm). (i = Al_2O_3; ii = $(Fe,Ni)_9S_8$; iii = $(Cu,Fe,Al,Cr)_3O_4$ spinel; iv = $Fe_{1-x}S$; v = $(Al,Cr)_2O_3$)

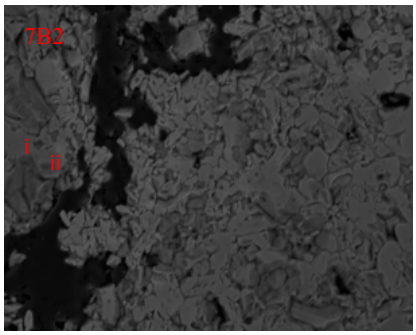

Figure 5: BEI of brick 7, position B2 (1cm = 22μm). (i = $(Al,Cr)_2O_3$; ii = Al_2O_3)

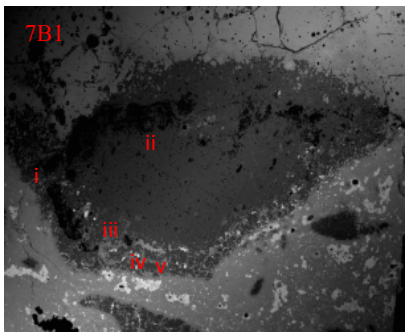

Figure 6: BEI of brick 7, position B1 (1cm = 445μm). (i = Fe_3O_4 (magnetite); ii = Al_2O_3; iii = Fe_2SiO_4 (fayalite); iv = $CuFeS_2$; v = $(Fe,Ni)_9S_8$)

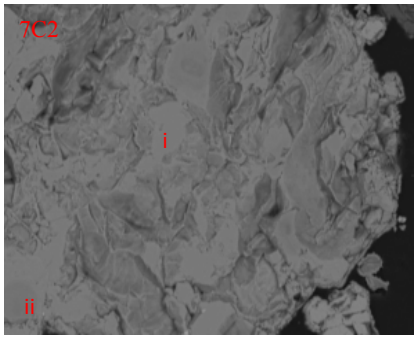

Figure 7: BEI of brick 7, position C2 (1cm = 25µm). (i = $CuFeS_2$; ii = $(Fe,Ni)_9S_8$)

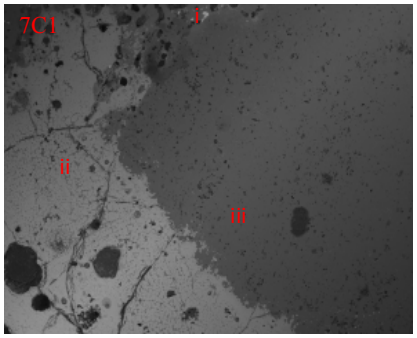

Figure 8: BEI of brick 7, position C1 (1cm = 315µm). (i = $(Fe,Ni)_9S_8$; ii = $(Cu,Fe,Al,Cr)_3O_4$ spinel; iii = Al_2O_3)

The cold face of the analysed sections (brick 7: A3, B2 and brick 1: A3, B2, C2) proved to be largely unaffected by the matte, with the phases present being alumina and an alumina chrome solid solution. An exception to this is brick 7C2 (Figure 7) which contained chalcopyrite and pentlandite. The XRD analysis of 7C2 confirmed that the extent of matte penetration towards the bottom of the tap-hole seems to be more significant than towards the side of the tap-hole (7B2), and even more significant than the penetration to the cold side of the original tap-hole (7A3).

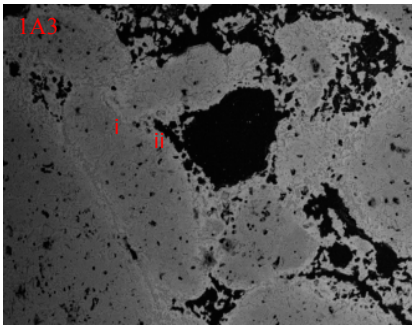

Figure 9: BEI of brick 1, position A3 (1cm = 122µm). (i = Al_2O_3 (Alumina); ii = $(Al,Cr)_2O_3$)

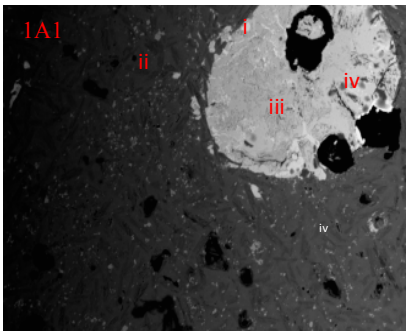

Figure 10: BSE image of brick 1, position A1 (1cm = 118µm). (i = Fe_3O_4; ii = $Ca(Mg,Fe)Si_2O_6$ (diopside); iii = $Fe_{1-x}S$; iv = $(Fe,Ni)_9S_8$)

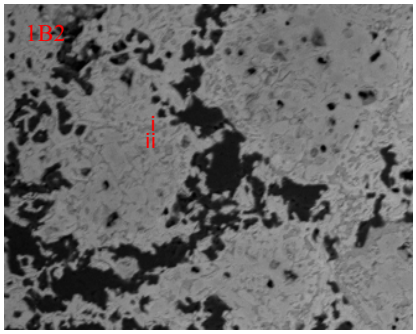

Figure 11: BEI brick 1, position B2 (1cm = 52µm). (i = $(Al,Cr)_2O_3$; ii = Al_2O_3)

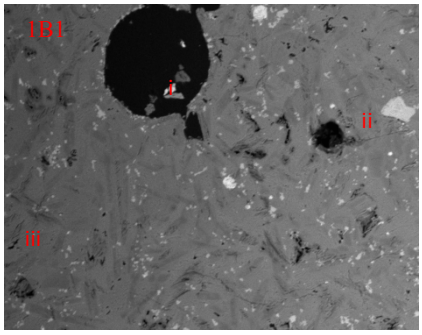

Figure 12: BEI of brick 1, position B1 (1cm = 77µm). (i = $CuFeS_2$; ii = $Ca(Mg,Fe)Si_2O_6$; iii = $Fe^{2+}(Fe^{3+},Cr)_2O_4$ spinel)

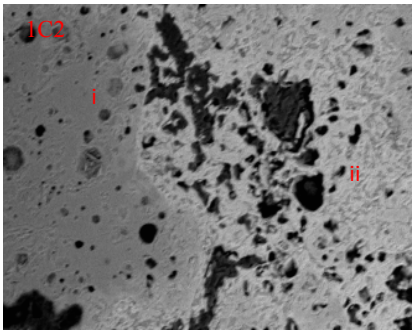

Figure 13: BEI of brick 1, position C2 (1cm = 56µm). (i = Al_2O_3; ii = $(Al,Cr)_2O_3$)

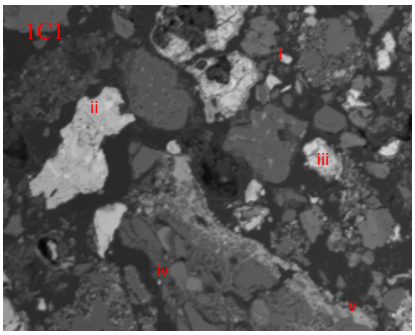

Figure 14: BEI of brick 1, position C2 (1cm = 49µm). (i = $Fe_{1-x}S$; ii = $(Fe,Ni)_9S_8$; iii = $CuFeS_2$; iv = Fe_3O_4; v = $Fe^{2+}(Fe^{3+},Cr)_2O_4$ spinel)

In the regions surrounding the tap-hole (brick 7: A1, B1, C1 and brick 1: A1, B1, C1) the penetrated matte crystallised on cooling to form sulphides with different concentrations of iron, copper and nickel, or combinations of these elements. The main phases identified were chalcopyrite ($CuFeS_2$), pentlandite ($(Fe, Ni)_9S_8$) and pyrrhotite ($Fe_{1-x}S$). Quantitative XRD indicated that matte penetration into brick 7 was significantly more than into brick 1. Matte penetration was observed in all the samples taken from brick 7 (i.e. samples A1, A2, A3, B1, B2, C1 and C2), while matte was only observed in the areas

adjacent to the original and shifted tap hole in brick 1 (i.e. samples A1, B1 and C1).

Effects of Oxygen Lancing

Oxygen lancing subjects the refractory materials to extreme temperatures and oxidising conditions. In this study it is clear that drilling and lancing led to an increase in the size of the tap-hole and a loss of its circular shape. The bricks before use had a 40 mm diameter hole, while after use the hole shifted and became elongated, with a length of 50 mm in the horizontal direction and 60 mm in the vertical direction. The off-centre position of the tap-hole in the refractory brick is indicative of both skew drilling and lancing.

The oxidation effects of lancing were evident from the SEM-EDS analyses. Oxidation of both iron and copper from the matte were observed, resulting in the formation of a $CuFe_2O_4$ – Fe_3O_4 solid solution spinel phase (Figure 15). A more complex $(Cu,Fe,Al,Cr)_3O_4$ - based spinel phase surrounding the original tap-hole, could also be distinguished (Figures 4, 8 and 15). This complex $(Cu, Fe,Al,Cr)_3O_4$ - based spinel presumably formed through interaction between the alumina-chrome brick and the $CuFe_2O_4$ – Fe_3O_4 solid solution spinel phase.

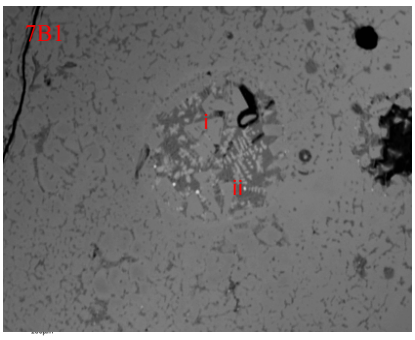

Figure 15: BEI of brick 7, position B1 (1cm = 94μm). (i = $(Cu,Fe,Al,Cr)_3O_4$ spinel, ii = $CuFe_2O_4$ – Fe_3O_4 solid solution spinel)

Residual Tap-hole Clay

Based on the chemical composition of the tap-hole clay, the alumina from the tap-hole clay would be indistinguishable from the alumina from the brick. The distinguishing factor by which the clay can be identified is the presence of SiO_2, since the clay originally contained 13% SiO_2 and 11.5% SiC.

It was found that whenever SiO_2 was present in a brick sample, FeO, MgO and CaO were also present (as diopside, $Ca(Mg,Fe)Si_2O_6$). This implies that slag is a more likely source of SiO_2 than the tap-hole clay. Although slag is not tapped through the matte tap-hole as part of the standard operating practice, matte levels may be reduced down to the matte tap-hole elevation in preparation for deep tap-hole repairs. In such case slag may be tapped through the matte tapping channel. Significant reaction between the furnace slag and alumina – chrome bricks was however not observed.

CONCLUSIONS

Wear of matte tap-hole bricks in a PGM smelter proceeds mainly through matte penetration. Oxygen lancing and penetration by furnace slag also contribute to wear.

Oxygen lancing oxidises iron and copper in the matte to form a $CuFe_2O_4$ – Fe_3O_4 solid solution spinel phase. These solid solution spinel phases then react with the alumina-chrome brick to form a $(Cu,Fe,Al,Cr)_3O_4$ - based spinel phase.

Residual tap-hole clay could not be found in the tapping channel. No evidence therefore exists that the tap-hole clay provides the refractory bricks with any level of protection against matte penetration during tapping.

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