

**CORROSION OF TAPHOLE CARBON REFRACTORY
BY CaO-MnO-SiO₂-Al₂O₃-MgO SLAG FROM A SiMn PRODUCTION FURNACE**

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ABSTRACT

The taphole is one of the high wear areas in any furnace. In SAFs producing SiMn, carbon blocks are typically installed as taphole refractory material and cold ramming paste utilised for taphole rebuild. In this study, mechanisms responsible for wear of taphole refractory are investigated using the stationary crucible test method. Crucibles made of micropore carbon block or prebaked cold ramming paste were filled with industrial SiMn slag and heated for 4 hours in an argon atmosphere at 1400°C, 1500°C or 1600°C using an induction furnace. Analysis indicates that the mechanisms responsible for wear of the refractory materials include densification and potentially corrosion.

KEYWORDS: Corrosion, tap hole, micropore carbon refractory, cold ramming paste, SiMn.

1. INTRODUCTION

For the production of standard SiMn, typically containing 68% Mn, 20% Si, 2% C and 10% Fe by mass, the process temperatures range between 1600°C and 1650°C [1]. The tapped slag typically consists of 9% MnO, 45% SiO₂, 16% Al₂O₃, 21% CaO and 9% MgO by mass, and tap temperature is 1600°C. Metal, slag and carbon are said to approach equilibrium [1].

In many furnaces, the taphole area is the main wear area adversely influencing furnace reliability. Furnace tapping schedules expose the taphole to fairly large temperature cycles at regular intervals. A CFD model under transient conditions predicts temperature cycles of 568°C at the taphole refractory cold face and 130°C at the hot face for SiMn production, where the average tap temperature is 1600°C [2].

For industrial SiMn production, two main refractory design philosophies are applied: insulating [3] and conductive [4]. In insulating linings, carbon blocks, silicon carbide (SiC) or magnesia (MgO) refractory materials are utilised and in conductive linings carbon blocks and graphite sleeves. During tapping, slag or metal is in contact with carbon block in insulating linings, and in conductive linings with graphite sleeves [3, 4]. For taphole rebuild purposes carbon-based cold ramming paste is utilised [3, 5].

Carbon bricks or blocks are produced from electrically or gas calcined anthracite, calcined coal, petroleum coke, carbon black, artificial graphite or combinations thereof as aggregate, with petroleum pitch or coal tar as binder. For carbon blocks, the raw materials are mixed, shaped and baked at 800-1400°C to carbonise the binder. To produce graphite blocks, an additional graphitising step at 3000°C is required [4, 6, 7]. To reduce the porosity of carbon bricks or blocks, the fired material is impregnated with binder material and re-fired [7]. To strengthen the bond matrix, generate micro-porosity or improve wear resistance properties, metallic Si, SiC, Al₂O₃, Ti or TiO₂ is added [6, 7]. Cold ramming paste typically consists of electrically calcined anthracite as aggregate and coal tar pitch as binder [8].

Refractory wear mechanisms reported for SAFs producing manganese ferroalloys are corrosion, densification, spalling and erosion. *Corrosion* is caused by slag or metal components dissolving refractory components it is not saturated with or chemical reactions between refractory and slag, metal or gas consuming the refractory materials [9]. Examples are alkali attack of carbon tamping paste [3], slag attack of carbon paste and tar dolomite brick [3], oxidation by water leakages [6] and metal attack of carbon refractory [6]. *Densification* is caused by slag/metal penetrating pores and/or reacting with refractory [9]. Examples are alkali attack of alumina brick with subsequent volume increase [3] and metal penetrating open pores [6]. *Spalling* is caused by thermal stress across a single refractory body [9], for example when hot face refractory material fractures and breaks away due to densification and/or thermal stress [10]. *Erosion* is caused by slag, metal and solid material abrading refractory [9]. Of these mechanisms, corrosion, erosion and spalling are all potentially applicable to the taphole area.

Laboratory experiments are conducted to simulate furnace conditions and study refractory wear mechanisms under these conditions. Static wear tests simulate conditions for corrosion, while dynamic wear tests incorporate the effect of erosion. The crucible (or cup, brick or cavity) test is a type of static wear test in which the corrosive medium is melted in a crucible made of the refractory material under investigation. Wear resistance is evaluated based on the depth of densification (permeation via open porosity without chemical reaction), and chemical wear (penetration, involving chemical reaction, of the corrosive liquid into the refractory or the loss in thickness from the original surface of the refractory) [11].

Mølnås [5] applied the crucible test method to study the interaction between five different types of refractory material, including carbon block and cold ramming paste, and two types of industrial slag from a SiMn furnace. Cups of refractory material were filled with finely ground slag and heated in a vertical resistance furnace at 1367°C, 1467°C and 1600°C for ramming paste and 1467°C for carbon block, for 4 hours in an argon atmosphere. For ramming paste, he observed no wear at 1367°C, some corrosion and densification at 1467°C and some corrosion and significant densification at 1600°C. For the carbon block he observed some corrosion only. As corrosion product he observed the formation of SiC at or near the slag/refractory interface. The aim of the present study was to further investigate the refractory wear mechanisms observed by Mølnås and to determine the effect of temperature on these wear mechanisms when exposing carbon block or cold ramming paste refractory materials to industrial CaO-MnO-SiO₂-Al₂O₃-MgO slag.

2. EXPERIMENTAL METHOD

As-received industrial SiMn slag was crushed, milled and sieved to < 425 µm. The bulk chemical composition of three representative samples was determined by wet chemistry methods. Phase composition was determined by SEM (scanning electron microscopy) and FEGSEM (field emission gun scanning electron microscopy) with EDS (energy dispersive spectroscopy) at 15 kV as area analysis. Elemental maps were obtained with EDS at 20 kV.

Samples of as-received carbon block and ramming paste were analysed using proximate analysis techniques to determine the inherent moisture, ash and volatile matter contents. Inherent moisture is the percentage loss in weight of 1 gram of air-dried sample after drying to a constant weight at 105°C (typically for 90 minutes). Volatile matter is determined by the percentage loss in weight of 1 gram of sample heated for 7 minutes at 900°C in the absence of air, less the percentage inherent moisture. Ash is determined by the percentage weight remaining of 1 gram of slowly heated coal after complete combustion in a ventilated muffle furnace at 815°C. The heating schedule is from room temperature to 500°C in 60 min, held at 500°C for 30 min, then raised to 815°C over a period of 30 min and held there for 60 min. The carbon content was calculated by difference.

The mineral composition of the ash from the proximate analysis was determined by XRD (X-ray diffraction). The relative phase amounts (weight %) was estimated using the Rietveld method. As-received materials were also submitted for XRD. Phase composition was studied with LOM (light optical microscopy), SEM, FEGSEM and EDS.

The carbon block was machined into crucibles with OD (outer diameter) 65 mm, ID (inner diameter) 25 mm, EH (external height) 70 mm and IH (internal height) 45 mm. Cold ramming paste crucibles required an outer shell machined from graphite with OD 65 mm, ID 55 mm, EH 70 mm and IH 60 mm. Ramming paste was rammed by hand around a spacer creating a cavity with ID 25 mm and IH 45 mm. Rammed crucibles were placed in steel cans with a layer of carbon powder, covered with refractory paper and carbon powder, heated in a muffle furnace to 950°C at a rate of 40°C per hour and baked for 30 minutes. The furnace was switched off and cooled to room temperature. The ID of each crucible was measured using callipers.

A crucible filled with slag was placed in a high-frequency induction furnace, to 1400°C, 1500°C or 1600°C in 1 hour, held at temperature for 4 hours and cooled in the furnace to room temperature. The experiments were conducted in argon passed through a column containing zirconium turnings at 300°C. Once the furnace was sealed, the chamber was flushed with argon at a flow rate of 1.8 l/min for 40 minutes. Once the temperature ramp-up started the argon flow rate was reduced to 0.7 l/min. The chamber volume was 0.074 m³. The experimental apparatus is shown in figure 1.

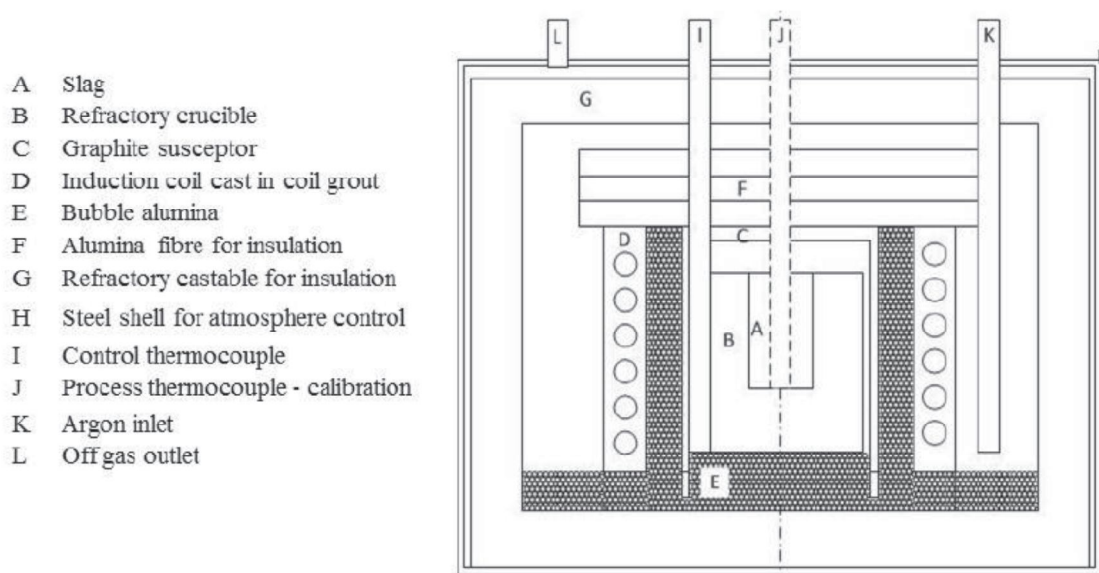


Figure 1: Experimental apparatus utilised in crucible tests

Cooled samples were removed from the furnace and filled with resin to keep the process material in position. Once the resin cured the samples were sliced in half. One half was used for sampling and preparation of polished sections and the other for wear profile measurements. Polished sections were studied by LOM, SEM, FEGSEM and EDS.

3. RESULTS AND DISCUSSION

The normalised, average bulk chemical analysis of the as-received slag – 8 % MnO, 45 % SiO₂, 23 % CaO, 7% MgO and 17% Al₂O₃ by mass – was similar to published compositions of industrial SiMn slag. The as-received slag did not consist of an amorphous oxide phase only but also included a phase rich in silicon and two metal phases as indicated in figure 2. The silicon rich

phase was silicon carbide. Two distinctly different types of metal were identified: MnS and a metal phase rich in Mn (79%) and Si (18%) which also contained Fe (2%) by mass and C. The average chemical composition of the amorphous slag phase was 4% MnO, 47% SiO₂, 23% CaO, 7% MgO and 19% Al₂O₃. The MnO content of the bulk chemical analysis was twice that of the amorphous phase due to the inclusion of the Mn-rich metal phases. The analyses for the other components were fairly similar and the SiO₂ content of the bulk slag was not significantly influenced by Si-rich metal and silicon carbide phases.

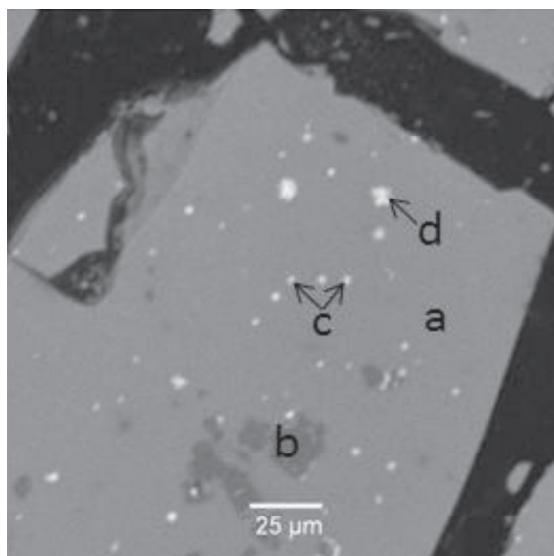


Figure 2: SEM backscattered electron image of typical slag particle in the as-received industrial SiMn slag with (a) amorphous slag phase, (b) silicon carbide, (c) metal phase rich in Mn and Si and (d) MnS

The proximate analysis of the as-received carbon block indicated that the ash content (22.8%) is similar to that of micropore brick (20%) and significantly higher than that of other carbon bricks ($\leq 2\%$) [12]. The ash content of the ramming paste (7.5%) is typical of carbon refractories [12]. As the ramming paste was in the unfired state, it had a higher volatile matter content (6.1% vs 0.8%) than the carbon block. The calculated fixed carbon content (86.4%) of the ramming paste was higher than that of the carbon block (76.4%) due to the significantly lower ash content in the ramming paste. All results were reported on a dry basis. The moisture content, on an air dried basis, of the ramming paste was 2.5% and of the carbon block 0.2%.

The ash from the proximate analysis of the as-received carbon block was analysed using XRD (table 1).

As metallic Si, SiC and Al₂O₃ are typically added to micropore brick [7], the presence of corundum and moissanite was expected. XRD analysis of the as-received carbon block (table 1) showed no metallic silicon was detected, but moissanite and corundum were present. Traces of hematite, cristobalite and quartz were detected but could not be quantified. SiO₂-bearing minerals in the ash from the proximate analysis formed during the (oxidising) ash preparation process rather than being added intentionally to the refractory material during manufacturing. Elemental maps indicate that the moissanite was finely dispersed throughout the matrix of the refractory while the corundum particles were present as larger, discrete particles. The carbon block contained amorphous carbon – not quantified – as well as graphite explaining the high ash content reported in the XRD results compared to the proximate analysis.

Table 1: XRD analysis of ash samples prepared from ramming paste and carbon block and as-received carbon block and ramming paste, weight %

Mineral	Ideal formula	Carbon block ash	Carbon block as received	Ramming paste ash	Ramming paste as received
Anhydrite	CaSO ₄	-	-	13	-
Corundum	Al ₂ O ₃	33	18	11	-
Hematite	Fe ₂ O ₃	3	-	15	-
Mullite	Al ₆ Si ₂ O ₁₃	7	-	14	-
Quartz	SiO ₂	10	-	21	-
Cristobalite	SiO ₂	39	-	-	-
Moissanite	SiC	8	12	27	2
Graphite	C	-	70	-	98

The ash from the proximate analysis of the ramming paste was analysed using XRD (table 1). All of the minerals except for corundum and moissanite were typical for coal ash [13] and probably originated from the ash in the electrically calcined anthracite. As was the case for the micropore carbon block, corundum and moissanite could have been added intentionally by the manufacturer, and to confirm their presence the as-received ramming paste was analysed using XRD (table 1). No corundum was detected, but moissanite was. Elemental maps for the as-received ramming paste indicated that the Si and Fe were finely dispersed throughout the matrix of the refractory, while Al and Ca were both finely dispersed and present as larger, discrete particles. The finely dispersed components would be typical of coal ash or moissanite. The ramming paste contained amorphous carbon – not quantified – as well as graphite. Yet the ash content reported in the XRD results is lower than reported in the proximate analysis. The lower ash content and absence of Al and Fe in the XRD results are attributed to the detection limit of XRD being between 1% and 2%.

After testing in contact with slag (crucible tests), no significant change in the diameter of any of the samples could be determined by visual inspection and measurement. LOM of the post-mortem samples indicated that in both refractory materials densification occurred where the slag penetrated the pores of the material. The depth of penetration in each refractory material as a function of temperature was determined from stitched LOM images prepared for each sample and is reported in table 2. The depth of penetration was not uniform over the whole slag-crucible contact region and the results in table 2 were for the maximum depth observed in the samples analysed. The extent of penetration for the two materials was fairly similar, while the depth of penetration decreased with decrease in temperature.

Table 2: Depth of penetration (mm) of slag into refractory as measured on the LOM images

Temperature	Carbon block	Ramming paste
1600°C	3.9 - 4.1	2.1 - 3.8
1500°C	0.5	0.8
1400°C	-	-

SEM backscattered electron images of the as-received carbon block and the post-mortem sample of the carbon block exposed to the slag at 1600°C are presented in figure 3. The phases identified in the as-received sample were carbon aggregate, carbon matrix, moissanite and corundum. The phases identified in the post-mortem sample were slag, SiC, metal, carbon aggregate and carbon matrix material, with no discrete Al-bearing phases other than slag present.

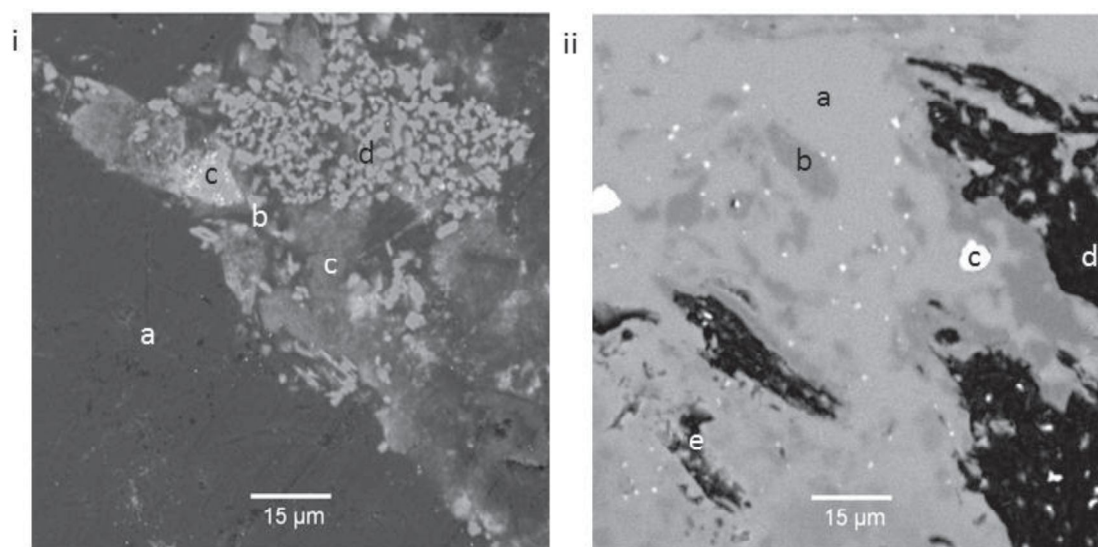


Figure 3: SEM backscattered electron image of (i) as-received carbon block with (a) carbon aggregate, (b) carbon matrix, (c) moissanite and (d) corundum and (ii) slag-refractory interface for carbon block exposed to industrial slag at 1600°C for 4 hours in a crucible test with (a) slag, (b) SiC, (c) metal, (d) carbon aggregate and (e) remnant of carbon matrix

In the elemental maps of the post-mortem sample of the carbon block exposed to the slag at 1600°C, three zones were identified: the bulk slag zone, the reaction zone (where slag penetrated the refractory) and the refractory zone not penetrated by slag. The maps indicate that the Si, and to some extent Ca, were finely dispersed throughout the matrix of the refractory but more concentrated in approximately the first 1.6 mm from the slag/refractory interface. This is the reaction zone, confirmed by the presence of discrete metal particles indicated by high concentrations of Mn and Fe. The metal in the refractory had a lower Mn:Fe ratio than the as-received slag (8 vs 15 by mass) probably a reaction product involving the reduction of iron oxide present in the refractory. The Si concentration was higher in the reaction zone than in the bulk slag or the refractory, with distinctly different areas of high and lower concentration in the reaction zone. The areas of high concentration were SiC and those of lower concentration, amorphous slag. The SiC originated from the as-received slag and carbon refractory. The Al concentration was higher in the refractory than in the reaction zone or bulk slag. In the refractory, discrete areas of high concentration Al were present, but not in the reaction zone and bulk slag. The Al_2O_3 particles added to the matrix to improve the properties of the refractory dissolved in the slag and caused a localised change in the composition of the slag.

SEM backscattered electron images for the as-received ramming paste and the post-mortem sample, of the ramming paste exposed to the slag at 1600°C are presented in figure 4. The phases identified in the as-received sample were carbon aggregate and carbon matrix. Phases rich in Ca, Fe, Mg and Si were also observed. The phases identified in the post-mortem sample were slag, SiC, metal, carbon aggregate and carbon matrix. In the elemental maps for the post-mortem sample, three zones were identified: the bulk slag zone, the reaction zone, and the refractory zone not penetrated by slag. The Si was present in distinctly different areas of high and lower concentration in the bulk slag and in the reaction zone. The areas of high concentration were SiC and those of lower concentration, amorphous slag. The SiC originated from the as-received slag, and potentially through the reaction of SiO_2 in the slag with carbon in the refractory. The metal in the refractory had a lower Mn:Fe ratio than the as-received slag (5 vs 15 by mass) probably a reaction product

involving the reduction of iron oxide present in the refractory.

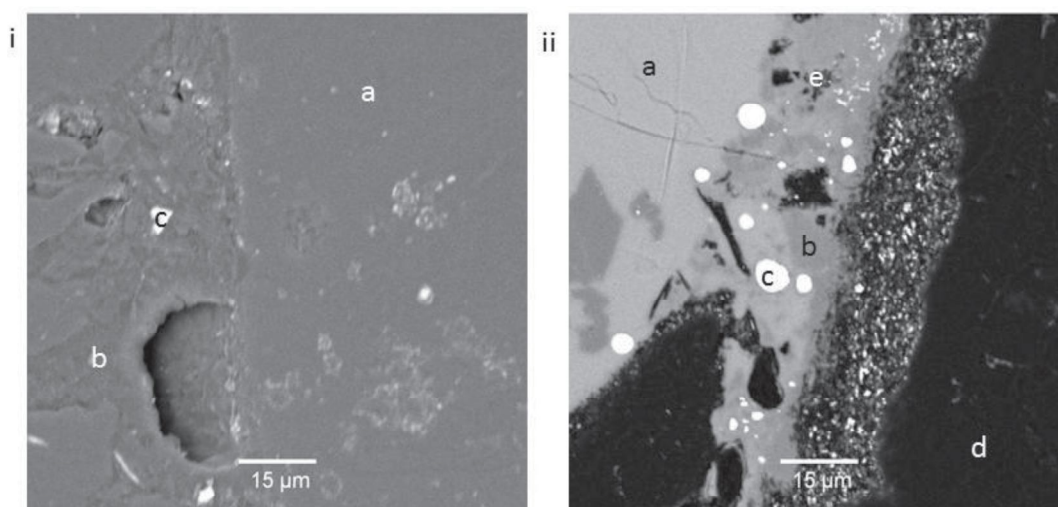


Figure 4: SEM Backscattered electron image of (i) as-received ramming paste with (a) carbon aggregate, (b) carbon matrix and (c) Si-rich particle and (ii) slag-refractory interface for ramming paste exposed to industrial slag at 1600°C for 4 hours in a crucible test with (a) slag, (b) SiC, (c) metal, (d) carbon aggregate and (e) carbon matrix

4. CONCLUSIONS

In a stationary crucible tests, carbon block or cold ramming paste were exposed to industrial SiMn slag at 1400°C, 1500°C and 1600°C for four hours in an argon atmosphere. The wear mechanisms observed were densification and corrosion. Densification occurred in both the carbon refractory and ramming paste as the slag penetrated the pores. Temperature had a significant influence on the depth of penetration. At 1600°C penetration was between 2 mm and 4 mm, at 1500°C less than 1 mm and at 1400°C zero. The extent of penetration was fairly similar for the two materials. First indications are that corrosion occurred in the ramming paste where the SiO_2 in the slag reacted with carbon in the refractory to form SiC. Thermodynamic calculations indicate that this reaction is likely to occur.

5. RECOMMENDATIONS

On a practical level, based on the observations made in the investigation reported here, SiC could be considered as a choice in tap hole refractory material. As part of the on-going study to obtain a better understanding of the wear mechanisms involved when using carbon-based material, next steps include testing the following hypothesis: *the main mechanism responsible for the wear of the carbon refractories under investigation in the $\text{CaO-MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag system is corrosion caused by the interaction of carbon with slag to form SiC. This mechanism can be counteracted by the presence of SiC, to locally saturate the system in SiC.*

4. ACKNOWLEDGEMENTS

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5. REFERENCES

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