

Interaction of MgO-MgR₂O₄(R: Al, Cr, Fe) refractories with SO₂-containing gases

N. Z. Fotoyi and R.H. Eric *

Mintek, Randburg, South Africa

University of the Witwatersrand, Johannesburg, South Africa *

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Abstract – The reaction mechanisms occurring when MgO-MgR₂O₃ refractories are exposed to SO₂-containing gas atmospheres were examined. The study examined the characteristic structures of magnesite-chrome, chrome-magnesite and magnesite refractories exposed to SO₂-O₂ gas mixture at temperatures of 700°C to 1350°C. The phase characterization was conducted with scanning electron microscopy (SEM) and powder X-ray diffractometry (XRD). The results show that the physical characteristics of the refractory matrix along the grain boundaries are important refractory features during chemical attack from SO₂-containing gas. Upon heating in SO₂-containing gas, the changes in phase-chemical compositions and accompanying grain growth causes loosening of the structure and the pore volume promotes gas diffusion. The chemical reactions that occur form stable sulfate compounds identified as MgSO₄, CaSO₄ and CaMg₃(SO₄)₄, and lead to disintegration of various phase structures and consequently erosion of the refractory. In conclusion, the reaction mechanisms in MgO-MgR₂O₃ refractories exposed to SO₂-containing gases progress through a combination of structural disintegration and chemical attack.

INTRODUCTION

Refractories are known as primary materials capable of maintaining good chemical, thermal, and physical features at high temperatures. These physical characteristics determine the refractory life during service in campaigns. The basic refractories used for lining of the Peirce-Smith converters in non-ferrous industries are mainly chrome-magnesite and magnesia-chrome.¹ The purpose of a converting process is to remove the iron and sulfur from copper matte or white metal in blister copper by oxidation at high-temperatures between 1200°C and 1350°C. In studies carried out on Peirce-Smith converters,⁸⁻¹² the presence of sulfides (MgS) and sulfates (MgSO₄ and CaSO₄) in refractory linings has led to different suggestions about the cause of refractory failure. Various corrosive gases (SO₂, S₂, SO₃) are formed in the region of the converter above the matte; in the freeboard SO₂ has a high equilibrium pressure.¹³ During matte conversion, the MgSO₄ found in refractories is reported to be a stable for temperatures up to 850°C,¹⁴ while CaSO₄ is stable up to 1550°C.¹⁵ However, the varying partial pressures of SO₂ and O₂ increase the equilibrium temperature of MgSO₄ to ~930-1050°C.^{14, 8}

Investigations into understanding the causes of refractory failure and wear mechanisms in converters are inconclusive.⁷⁻⁹ This is because various chemical

reactions occur with different phases (slag, matte, gas and possibly metal) at different temperatures, and the changes in phase-chemical composition¹⁶⁻¹⁹ indicated cause structural erosion and refractory failure. There are no specific service conditions documented for the cause of failure. The focus has been on refractory materials that have been used in different service campaigns,^{14-15,20-23} and the change in conditions from reducing to oxidizing atmosphere promote sulfide and sulfate formation^{14,22-23}. Therefore, there is a limited understanding of the processes when refractories are exposed exclusively to SO₂-containing gases. The equilibrium decomposition temperatures of MgSO₄ and CaSO₄ range from 1000 to 1428°K.²⁴⁻²⁵

In describing the cause of refractory failure associated with sulfate formation, it is important to assess independently the processes that occur when refractories are exposed to SO₂-containing gases. This will indicate reaction mechanisms²⁶⁻²⁸ involved which can be classified into various combinations of infiltrated SO₂-containing gases, MgO and CaO reaction, oxidation of sulfide products at low temperatures, and disintegration and erosion of magnesia grains.¹⁰ The aim of the present study was to examine in detail the reaction mechanism of the unused chrome-magnesite and magnesia-chrome refractories when exposed to the SO₂-containing gases, and evaluate the refractory structure and phase-chemical composition.

EQUIPMENT AND EXPERIMENTAL PROCEDURES

In the investigations, three different types of commercially available basic refractories were used; they were magnesite (M), chrome-magnesite (CM1) and magnesite-chrome (MC1) refractories. The refractories were supplied by Vereeniging Refractories in South Africa. The physical properties provided by manufacturer and the average chemical composition determined by powder X-ray diffractometry are listed in Table I. Samples were taken from the interior of the refractories and acetone was used as a lubricant when the refractories were sectioned. The samples were dried overnight at 105°C before exposure to SO₂-containing gases. The gases used in the investigation were 99.9% SO₂ and 99.5% O₂, both supplied by Afrox.

Table I: Bulk-chemical composition, density and porosity of refractories

	Refractory		
	Magnesite-Chrome D60/100	Chrome-magnesite A	Magnesite
Al ₂ O ₃	7.64	8.65	0.14
CaO	1.19	0.94	1.88
Cr ₂ O ₃	20.3	22.5	0.31
Fe ₂ O ₃	8.97	9.49	0.21
MgO	51.9	47.3	92.1
SiO ₂	2.03	3.01	0.52
TiO ₂	0.18	0.22	<0.008
Bulk density (kg/m³)	3225	3180	2920
Apparent porosity (%)	16	17	17

The experimental apparatus used to conduct the investigation is shown in Figure 1. The experiments were conducted in a vertical-tube furnace fitted with silicon carbide heating elements. The furnace temperature was controlled by a B-type thermocouple and the gas atmosphere was controlled with mass flow controllers. A quartz tube was used as a reactor in which the three different types of refractory samples were contained when exposed to experimental conditions that ran for varying periods of time. Inside the reactor the samples were placed on a silica-wool bed used as a holder and alumina bubbles were poured in-between refractories, which separated and prevented refractories from contacting each other during experiments. A K-type thermocouple inserted from the top of the reactor was used to monitor the sample temperature for experimental conditions below 1000°C; a B-type thermocouple was used at higher temperatures. Once the experiment was completed the reactor was lowered from the furnace and the refractories were allowed to cool to room temperature.

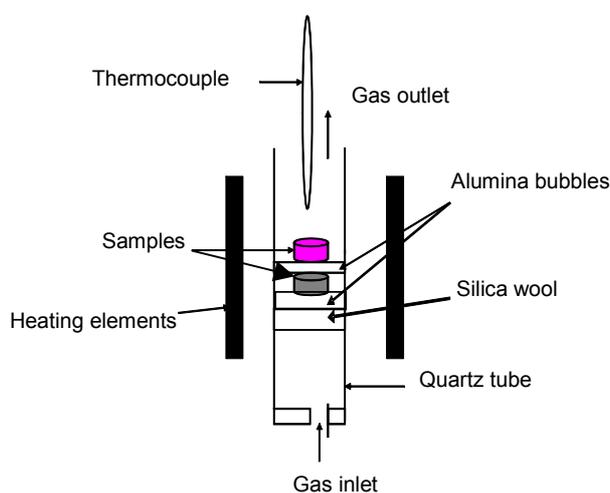


Figure 1: Schematic diagram of the apparatus

The experiments were conducted in two gas compositions, namely, one of 100% O₂ and the other of 20% SO₂-80% O₂ (by volume). For each gas composition a total flow rate of 100 ml/min was provided by mass flow controllers. In a gas composition of 20% SO₂-80% O₂ two flow controllers were used to deliver 80 ml/min O₂ and 20 ml/min SO₂. Each experimental condition comprised three samples at a time weighing between 14 and 18 g each, a gas composition, and a predetermined temperature within the range 700–1350°C.

In the first set of tests all the refractories were exposed to 100% O₂ at 1350°C for 2 weeks to examine the behaviour of the refractory structure and the phase-chemical composition in oxidizing conditions at high temperatures. In the second set of tests all the refractories were exposed to a gas composition of 80% O₂-20% SO₂ at 1350°C for 2 weeks to examine the effect of SO₂-containing gases at high temperatures. The third set of tests was conducted under similar gas compositions at 700°C; refractories were exposed for 7 days and 2 weeks. This was done to observe the extent of the SO₂-containing gas processes on the

different refractories. In the fourth set of tests, the refractories were exposed to a gas composition of 80% O₂-20% SO₂ between 700°C and 1000°C; the tests ran for varying times from 14 to 84 hours at a 21-hour increment between tests. This was done to determine the relative conversion percentages in the refractories with time. The magnesite-chrome and chrome-magnesite refractories were exposed to similar gas compositions at 1200°C; tests ran for similar varying times. This was done to confirm sulfate formation above 1000°C and observe conversion percentages.

All samples were weighed before and after testing and sectioned in half. A representative sub-sample was milled and sent for phase chemical analysis by powder X-ray diffractometry (XRD). For scanning electron microscopy (SEM) separate samples were mounted in epoxy resin and polished. The refractories tested for seven days were analysed for sulfate content (SO₄²⁻) by a chemical technique, the gravimetric analytical method. For each test the proportion of MgO converted to MgSO₄ was calculated based on the mass gain in the sample. The approach ignores the presence of CaO and the formation of CaSO₄ since the CaO content is relatively low. This approach was adopted because MgO was the dominant component in various refractories.

RESULTS

Macroscopic observations

The microstructural analyses of the refractories exposed to O₂ and SO₂-containing gases were compared with the original microstructure. Figures 2a and 2b show the original microstructure of the magnesite refractory and the microstructure exposed to the SO₂-O₂ gas mixture at 1350°C for 2 weeks, respectively. The phases identified in the as-received magnesite refractory were MgO (periclase) and Ca₃SiO₅ (tricalcium silicate). In the refractory exposed to SO₂-O₂ gas mixture the phase-chemical composition of the silicate changed and the identified phases were MgO (periclase), Mg₂SiO₄ (forsterite) and CaSO₄ (calcium sulfate). When heated at 1350°C the microstructure of the grains changed and small sub-grains grew to large magnesia grains, but the phase-chemical composition of MgO was uniform. The porosity of the refractory was affected with open pores occurring often at grain boundaries. The new CaSO₄ phase identified formed with refractory aggregates at the grain boundaries, where the Ca₃SiO₅ often occurred in the original refractory. The Mg₂SiO₄ (forsterite) identified was in association with the sulfate phase and often formed between the unreacted magnesia grains and the sulfate phase.

Figures 3a and 3b show the original microstructure of the magnesite-chrome D60/100 refractory and the microstructure exposed to O₂ at 1350°C for 2 weeks, respectively. The as-received refractory comprised MgO (periclase) and spinel phases identified as (Mg²⁺, Fe²⁺)(Fe³⁺, Cr³⁺, Al³⁺)₃O₄ (chromite spinel), and MgCr₂O₄ (magnesiochromite). The MgCr₂O₄ (magnesiochromite) is a dominant spinel and the phase-chemical composition of the secondary spinels formed with sesquioxides of Al₂O₃ (corundum), Cr₂O₃ (eskolaite) and Fe₂O₃ (hematite) within the magnesia spinels varied. The Cr₂O₃ sesquioxide occurred as

precipitated spinels that form clusters (C2) surrounded by blocky angular structures (C3) within the magnesia matrix. When heated the microstructure of the sesquioxides within the magnesia matrix changed: the crystal size and distribution of Cr₂O₃ sesquioxide grew to elongated structures (C4) that occurred at the expense of the blocky structure (C3). When exposed to SO₂-O₂ atmosphere at 1350°C no sulfates were identified.

Figures 4a and 4b presents the original chrome-magnesite A refractory and the microstructure exposed to O₂ at 1350°C for 2 weeks, respectively. The refractories comprised the same phases identified in the magnesite-chrome D60/100 refractory. However, the phase compositions of the sesquioxides within the structures were different. In the MgCr₂O₄ (magnesiochromite) grains, the Cr₂O₃ sesquioxide in the spinel clusters (C2) were less compact, while blocky angular structures (C3) and elongated structures (C4) occasionally occurred within the matrix. When exposed to O₂, complete separations of spinel phases from which the Cr₂O₃ sesquioxide migrated from the MgCr₂O₄ grain to the grain boundaries and coalesced into rounded, soft and friable remnants of primary chromite spinel, (Mg²⁺, Fe²⁺)(Fe³⁺, Cr³⁺, Al³⁺)₃O₄. This resulted in grain growth and an MgFe₂O₄ (magnesioferrite) interior having fine Fe₂O₃ sesquioxide surrounded by a rim of Cr₂O₃ sesquioxide towards the grain periphery. The grain growth caused cracks and pores to occur. At 1350°C, no sulfates were identified under all gas atmospheres.

When the refractories were exposed to SO₂-containing gases at 700°C for 7 days and two weeks, microstructural changes were observed. Figures 5a and 5b shows the microstructure of magnesite refractory exposed for 7 days and two weeks, respectively. The identified phases were MgSO₄, CaMg₃(SO₄)₄ and CaSO₄. After 7 days, the CaSO₄ formed between the sub-grains of magnesia occurred as minute particles distributed evenly within the porous material and occurred as rims (bright) around the silicate interface. The sulfates formed between the grains comprised a mix of MgSO₄ (dark), CaMg₃(SO₄)₄ (light grey) and CaSO₄ (bright) in highly porous particles. After exposure for 2 weeks, microstructural changes in the matrix showed large amounts of sulfate and elongated structures occurred within sulfates with high SO₃ contents. Within the boundaries the attack on the refractory matrix formed MgSO₄ of a collective spongy material while CaSO₄ and CaMg₃(SO₄)₄ formed as coupled phases and elongated and intertwined structures. The surfaces at the grain boundaries showed terraced substructures, forming prominent ridges with shallow grooves and small voids that were filled with the sulfate products. The magnesia aggregates disintegrated into fine particles of a porous material of sulfates with varying ratios of Mg to Si to Ca to S. The porosity was affected as the sulfates filled the pores.

Figures 6a and 7a show the microstructure of magnesite-chrome D60/100 and chrome-magnesite A, respectively, after exposure to SO₂-O₂ gas mixtures for 7 days and two weeks at 700°C. In magnesite-chrome D60/100 (Figure 6a) the angular structures (C3) occur as small grains that appear to have been excluded from the large spinel grains to the grain boundaries leaving uniformly

distributed Cr_2O_3 sesquioxide (C2). In the microstructure of chrome-magnesite A (Figure 7a) the phase separation was pronounced with the angular structures (C3) coalescing at grain boundaries. When exposed to $\text{SO}_2\text{-O}_2$ gas mixtures the phases identified were MgSO_4 , CaSO_4 and $\text{CaMg}_3(\text{SO}_4)_4$. These occurred with the refractory matrix and comprised various composition ratios of Fe to Cr to Al as remnant sesquioxides from the deteriorated and sulfated magnesia spinel. After 7 days, the phases formed with the refractory aggregates along grain boundaries and filled the pores. After two weeks of exposure (Figure 6b), the sulfate attack extended to the grain peripheries of magnesia spinel and microstructural disintegration resulted in terraced substructures having ridges.

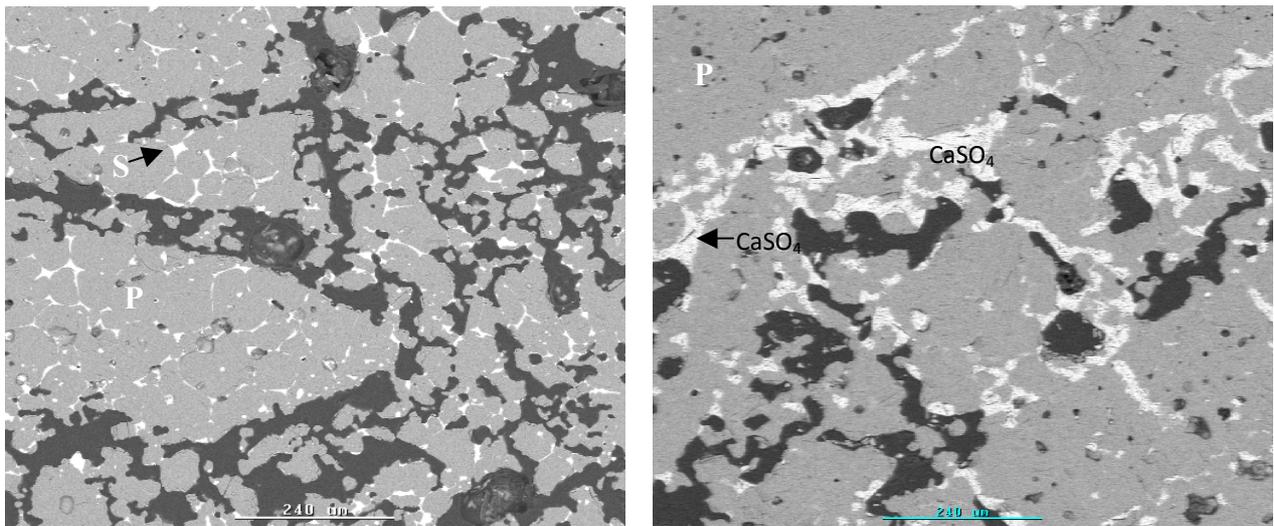


Figure 2: SEM-BSE micrograph of magnesite refractory (a) original (b) reacted in $\text{SO}_2\text{-O}_2$ gas mixture at 1350°C

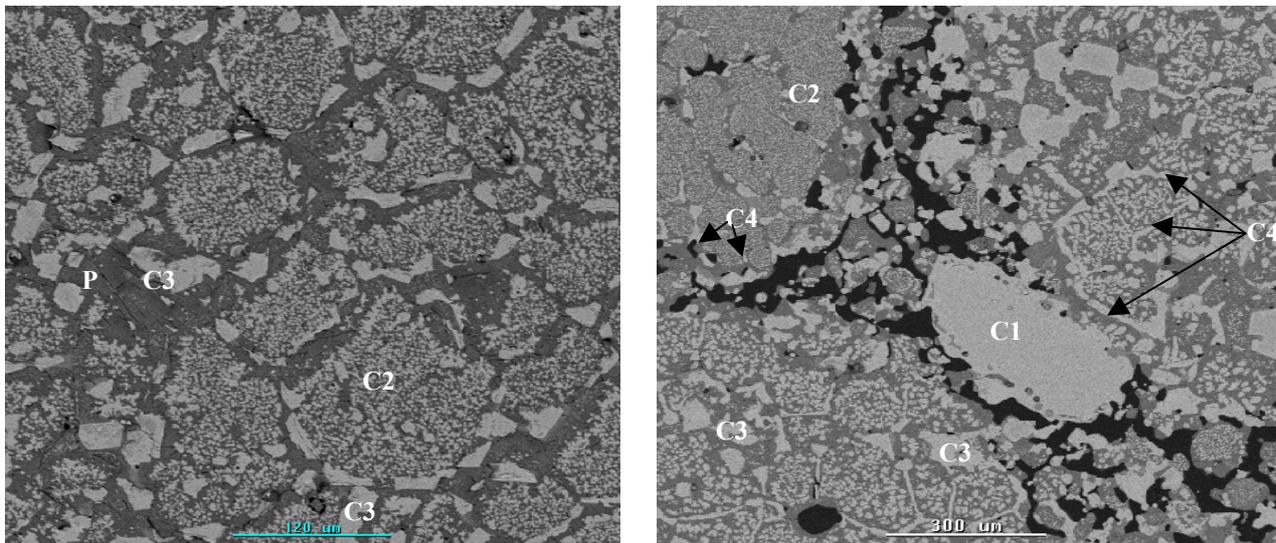


Figure 3: SEM-BSE micrograph of magnesite-chrome D60/100 (a) original (b) in O_2 at 1350°C

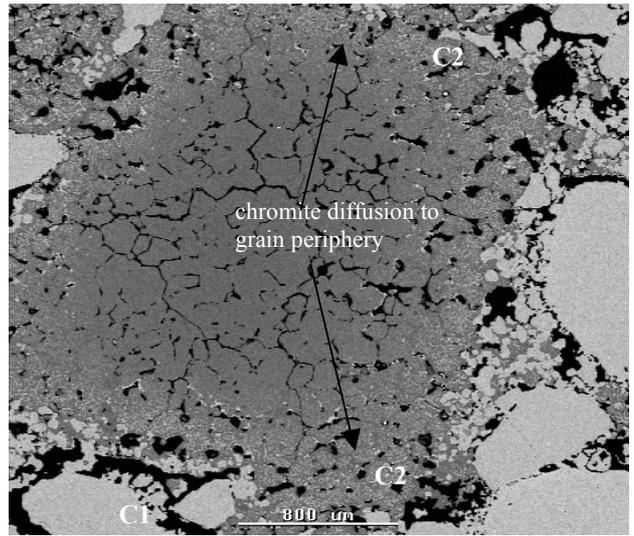
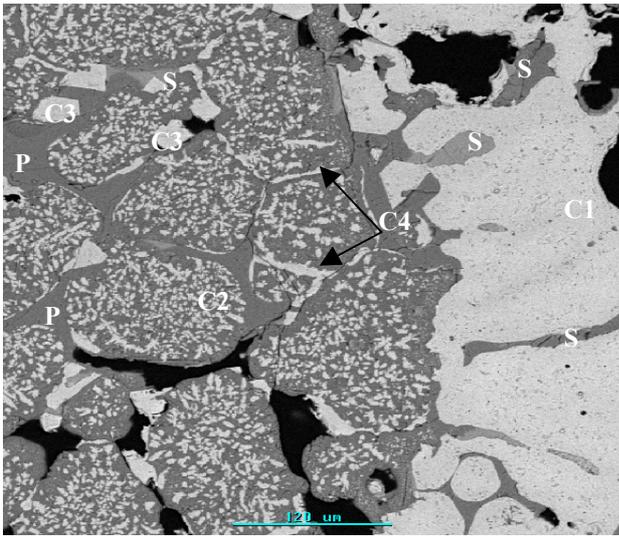


Figure 4: SEM-BSE micrograph of chrome-magnesite A (a) original (b) reacted in O₂ at 1350°C

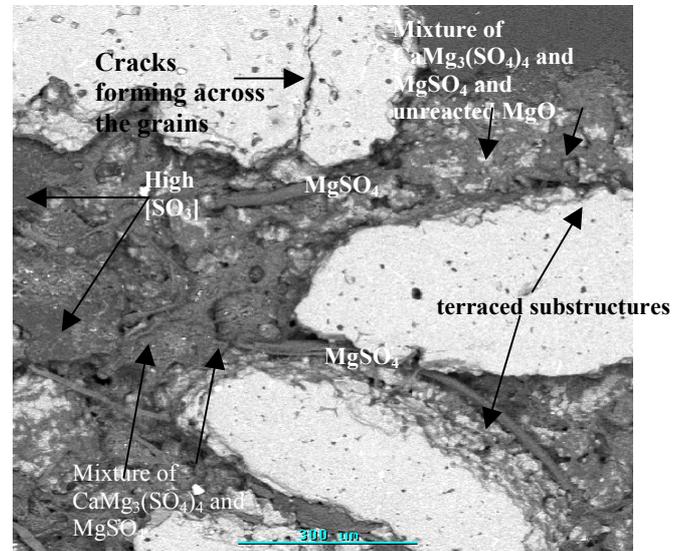
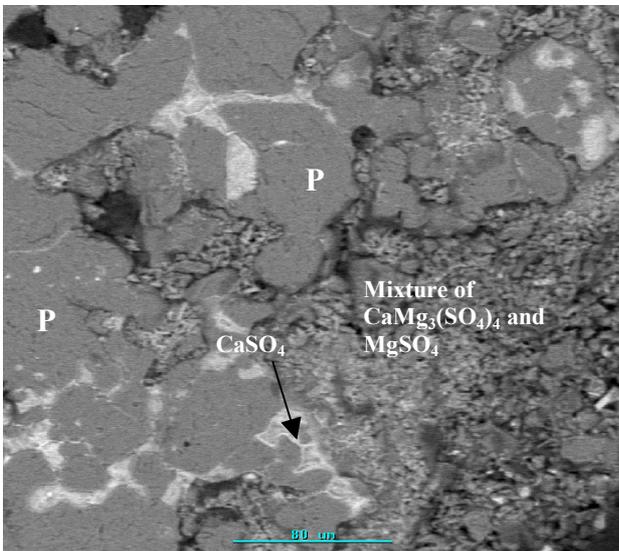


Figure 5: SEM-BSE micrograph of magnesite refractory exposed to SO₂-O₂ gases at 700°C (a) 1 week (b) 2 weeks.

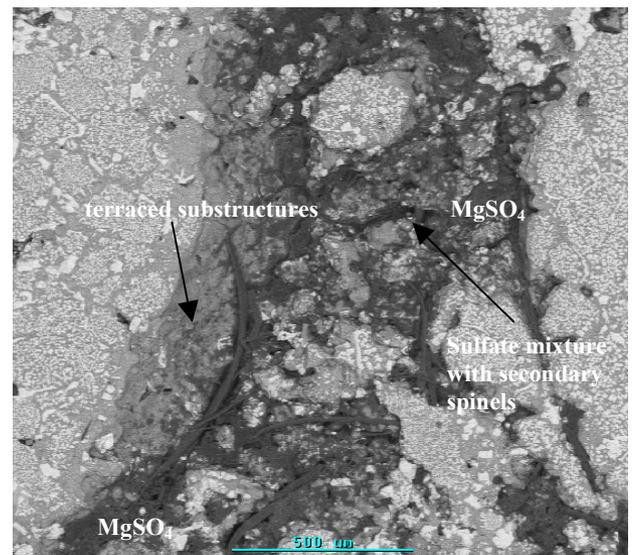
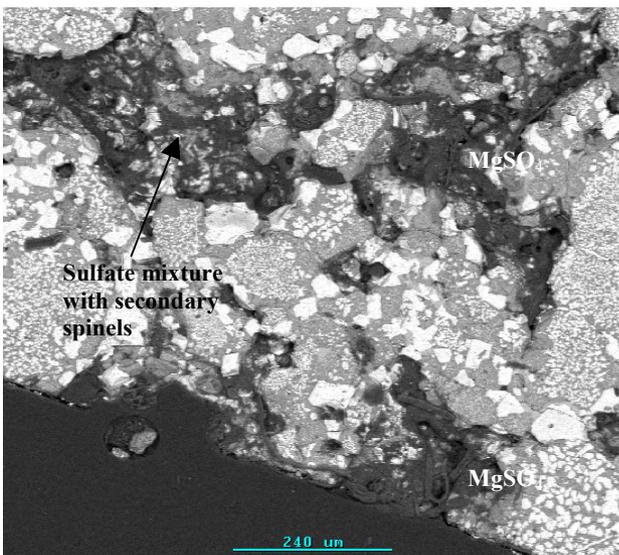


Figure 6: SEM-BSE micrograph of magnesite-chrome D60/100 exposed to SO₂-O₂ gases at 700°C (a) 1 week (b) 2 weeks

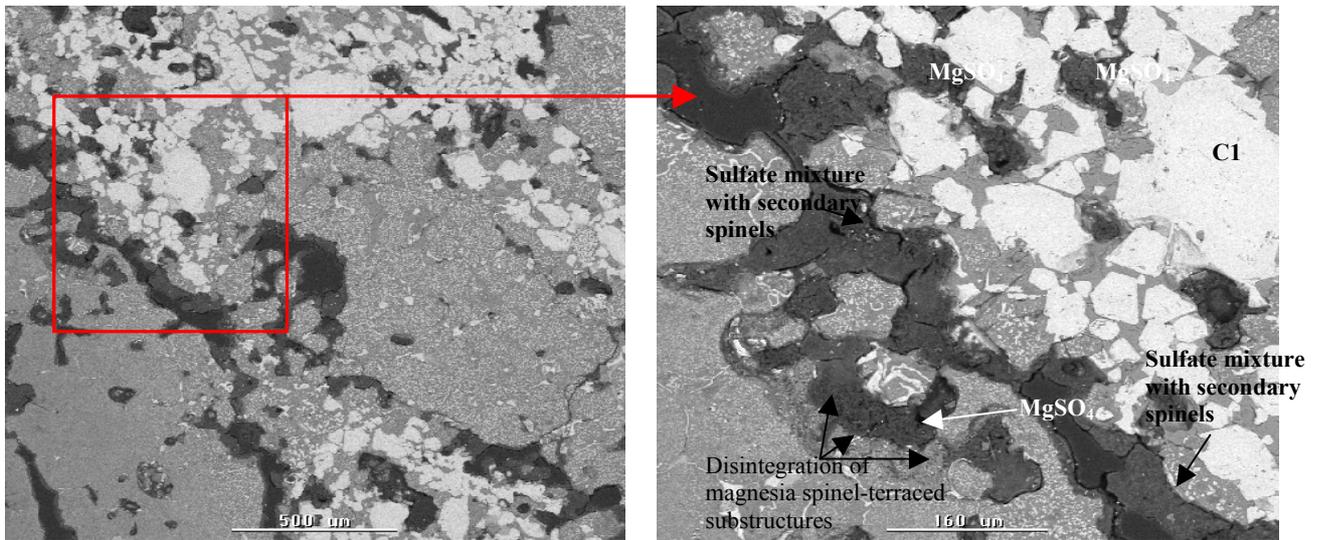


Figure 7: SEM-BSE micrograph of chrome-magnesite A exposed to SO₂-O₂ gases at 700°C for 1 week

Phase characterization by XRD

The analysis of phases and compounds in the refractories before and after exposure to SO₂-containing gases for 7 days is listed in Table II. Also tabulated are the amounts of sulfates (SO₄) determined by chemistry (gravimetric analysis) and by mass change (SO₃) in the refractories. The sulfate compounds identified are CaMg₃(SO₄)₄, MgSO₄, CaSO₄ for temperatures in the range 700–1000°C. In the magnesite sample MgSO₄·H₂O (1.6%) was detected at 700°C, and Ca₂SiO₄ was identified at 800°C. No sulfates were identified in CrMg A at 1350°C, whereas CaSO₄ formed in the magnesite refractory and in the MgCr D60/100.

Extent of MgO sulfation

The conversion percentages in the refractories with time were determined from mass-change calculations for “sulfate formed (wt%)”. The proportion of MgO in the refractories that was converted to sulfate was calculated from the change in actual mass and theoretical mass:

$$\%MgO = \frac{Actual\Delta m}{Theoretical\Delta m} \times 100 \quad [1]$$

Where *Actual Δm* is the measured mass change of the sample
Theoretical Δm is the calculated mass change based on complete sulfation of MgO to MgSO₄.

The relationship between the relative proportions converted to sulfate at temperatures between 700°C and 1200°C are plotted against time in figures 8–11. The relationships indicate that reaction extent increases with temperature, and for chrome-magnesite A and magnesite-chrome the conversions were highest at 900°C and 1000°C, respectively, and lowest at 1200°C. The magnesite refractory was investigated for temperatures up to 1000°C which resulted in the highest conversion. The amount of sulfate (conversion to SO₄) in the refractories reacted at 700°C, determined by gravimetric analysis and mass-gain

calculations, is shown in Figure 8. The amount of sulfate determined by chemical analysis is higher than that obtained from mass-gain calculations.

Table II: Phase formed after exposure to SO₂-O₂ gas mixtures at temperature

Test conditions	Magnesite	MgCr D60/100	CrMg A
Before reaction	MgO, Ca ₃ SiO ₅	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , CaMgSiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , Mg ₂ SiO ₄
700°C	MgO, CaMg ₃ (SO ₄) ₄ , MgSO ₄ , MgSO ₄ ·H ₂ O	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , CaMgSiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , MgSO ₄ , CaSO ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , MgSO ₄ , CaSO ₄
mass gained (g)	0.479	0.149	0.151
"Sulfate formed (wt%)"	12.72 [†] 4.15 [‡]	4.36 [†] 3.6 [‡]	6.14 [†] 3.52 [‡]
800°C	MgO, CaMgSiO ₄ , Ca ₂ SiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , CaMgSiO ₄ , Ca ₂ SiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , MgSO ₄ , CaSO ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , CaMgSiO ₄ , Ca ₂ SiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , MgSO ₄ , CaSO ₄
mass gained (g)	0.348	0.255	0.171
"Sulfate formed (wt%)"	15.74 [†]	10.32 [†]	13.24 [†]
1000°C	MgO, CaMgSiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , CaSO ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , CaMgSiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , MgSO ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , CaMgSiO ₄ , Mg ₂ SiO ₄ , CaMg ₃ (SO ₄) ₄ , MgSO ₄ , CaSO ₄
mass gained (g)	0.529	0.419	0.524
"Sulfate formed (wt%)"	19.08 [*]	12.24 [*]	21.6 [*]
1350°C	MgO, CaSO ₄ , Mg ₂ SiO ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , Mg ₂ SiO ₄ , CaSO ₄	MgO, (Mg,Fe)(Cr,Al) ₂ O ₄ , Mg ₂ SiO ₄
mass gained (g)	0.237	-0.1	-0.017
"Sulfate formed (wt%)"	5.14 [*]	0.42 [*]	0.2 [*]

[†]As measured by chemical technique

[‡]Based on the mass-gain calculation

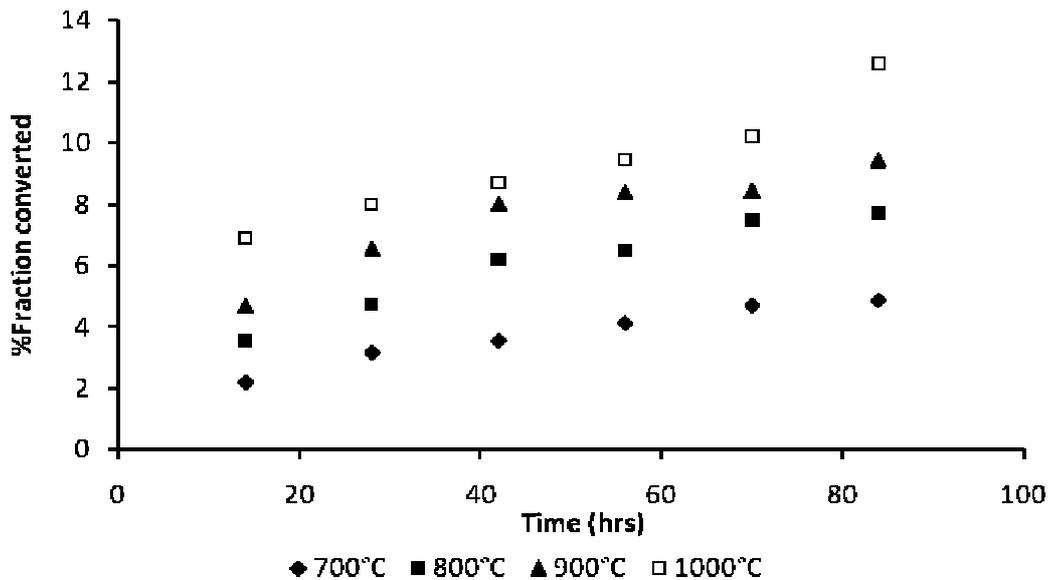


Figure 8: Fraction converted (%) in magnesite as a function of time

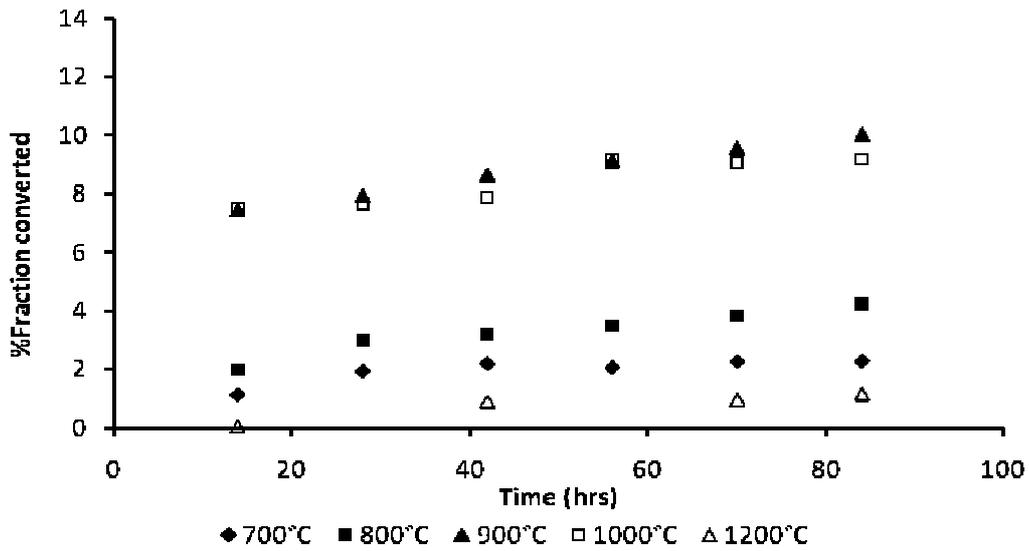


Figure 9: Fraction converted (%) in magnesite-chrome D60/100 as a function of time

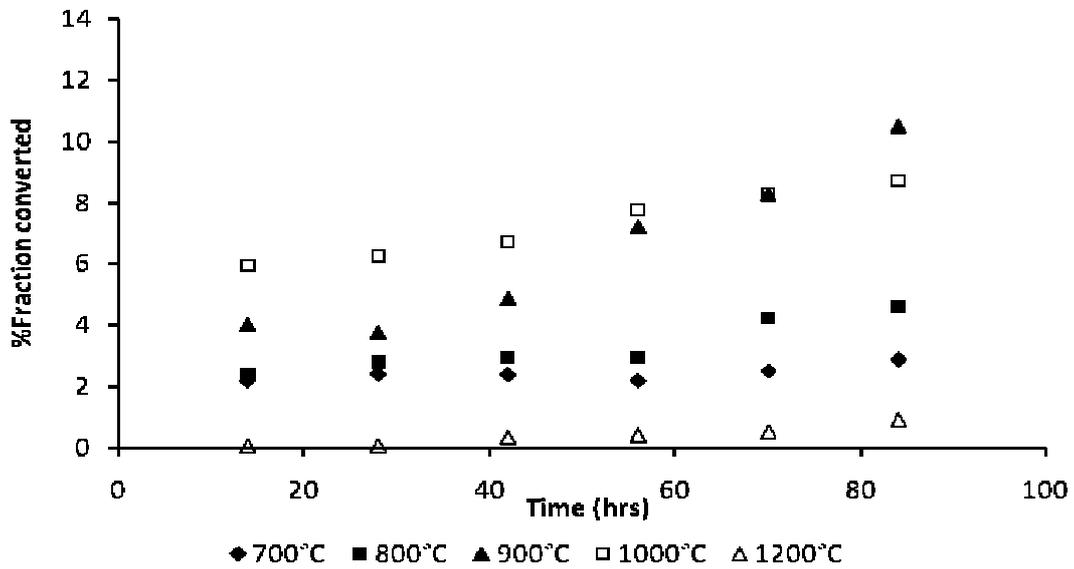


Figure 10: Fraction converted (%) in chrome-magnesite A as a function of time

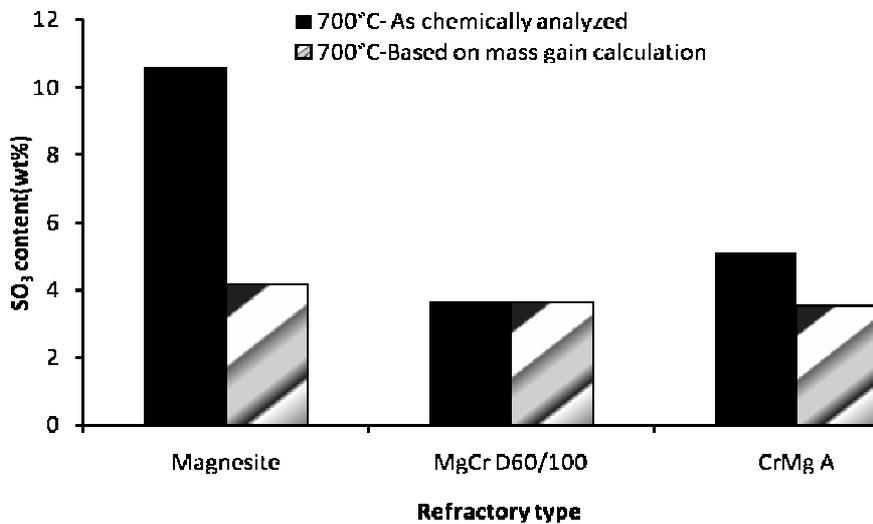


Figure 11: Sulfate (%SO₃) content in refractories after 7 days

DISCUSSIONS

Macroscopic observations

In all the refractories investigated heating at high temperatures changes microstructural and phase-chemical compositions. In magnesite-chrome and chrome-magnesite refractories diffusion results from the dissociation of Fe^{3+} and Al^{3+} in chromite spinel and the presence of Cr^{3+} and Mg^{2+} in chromite and magnesia grains.¹⁶⁻¹⁹ In the grains, sesquioxides forming spinels are redistributed within the magnesia matrix and change the phase-chemical composition as they grow, resulting in grain growth (due to unequal diffusion) at higher temperature. The dissociation¹⁶⁻¹⁹ begins gradually at low temperatures and minimal diffusion of sesquioxides within the grains is evident, where at 700°C phases exist mainly as $\text{Fe}_2\text{O}_3\text{-MgFe}_2\text{O}_4$ and $\text{Fe}_2\text{O}_3\cdot 2\text{Cr}_2\text{O}_3$ and there are no major structural changes. At high temperatures complete series of solid solutions form and at 1350°C major structural changes with phases existing as Fe , $\text{MgO}\cdot\text{FeO}$, FeCr_2O_4 and MgCr_2O_4 occurs. Such changes were observed in chrome-magnesite (Figure 8b), and dissociation resulted in physical separation of the Cr^{3+} from magnesia spinel forming FeCr_2O_4 (ferrochromite) grains. At grain boundaries, partial precipitation of Cr^{3+} diffused from chromite spinel resulted in MgCr_2O_4 , possibly during cooling, leaving magnesioferrite within the grains. In the presence of silicates the diffusion of sesquioxides excludes them to the grain boundaries and the grain surface arrangement and porosity are affected as small pores coalesce at grain boundaries. This effect has been reported as a wetting behavior of silicates in refractories.¹⁹ In the magnesite refractory, because of homogeneous diffusion of Mg^{2+} in magnesia grains, the grain growth is accelerated by diffusion of silicates to the grain boundaries.

The challenge, however, was that the changes observed in the refractories did not arise either from phase-chemical changes promoted by diffusion or the chemical attack of SO_2 -containing gases, rather the physical characteristics of the refractory matrix determined the volume of porosity in the refractory and the amount of gas infiltrating for chemical attack. The refractory matrix character is critical during chemical attack from the gases, and disintegration of the sulfate product causing cracks accelerates the deterioration mechanism in the refractory. The porosity promotes gas diffusion and the dispersed character of the refractory matrix creates reaction sites for sulfate formation and the progressive diffusion of the oxides promotes sulfation.

At 700°C , SO_2 -containing gases not only diffuse through the pores of the refractory, but also into the MgO grains, whereby CaSO_4 forms at the interfaces (Figure 5a) in magnesite and MgSO_4 forms with disintegrated spinels in magnesite-chrome and chrome-magnesite refractories. The elongated phases (Figures 5b and 6b) indicate structures formed as a result of gas condensation. The presence of water vapour (H_2O) in the gas could have accelerated the reaction of MgO and CaO with SO_2 -containing gases. Since the sulfates have a tendency to expand on formation, up to 400% expansion in MgSO_4 ,⁸ equilibrium partial pressures of SO_2 and O_2 in the pores could vary depending on the amount of gases diffused and product formed. Assuming that this

occurred in the refractories, at the same temperatures reactions will occur with the prevailing equilibrium partial pressures resulting in a non-stoichiometric relation between the oxides and total sulfur as observed in dark sulfate structures.^{20, 22-23} The sulfate structures having irregular surfaces of nodular particles with undulations and voids also prevented attainment of local equilibrium, which promoted precipitation of crystals of sulfates that coalesced and grew in the localized saturated gas atmosphere.

The terraced substructures (figures 5b, 6b and 7b) with shallow grooves were attributed to the differences in mass transfer across the interfaces, whereby the rapid growth of sulfates along the boundary interface, due to increased sulfur and oxygen reactivity,⁹⁻¹⁰ impeded the outward diffusion of oxides from the grains, which then accumulated towards the grain boundaries, forming grooves. The observed process formation through coalescence and growth into porous and spongy sulfates resulted in the incorporation of some unreacted MgO (Figure 5b) and sesquioxides of Fe₂O₃, Al₂O₃ and Cr₂O₃ from the disintegrated phases (figures 6b and 7b). The microstructural analysis indicates that structural changes played a role in transporting the reactive oxides without taking a real part in the reactions.

Reaction with SO₂-O₂ gas mixtures

When basic refractories are exposed to SO₂-O₂ gas mixtures the phases identified were MgSO₄, CaSO₄ and CaMg₃(SO₄)₄ and this agrees with the thermodynamic equilibrium of the oxides.²⁴⁻²⁵

Reaction at high temperatures at 1350°C

At 1350°C (Figure 6b) the Ca₃SiO₅ dissociated and the recrystallized CaO product reacted with infiltrated SO₂-containing gases to form CaSO₄, while the SiO₂ reacted with MgO and formed a Mg₂SiO₄ (forsterite). Formation of CaSO₄ from dissolved refractory phases has been reported to occur at temperatures up to 1550°C.¹⁵ The reaction agrees with the thermodynamic equilibrium of CaSO₄ with SO₂-containing gases in the following reaction mechanism,²⁵



In the magnesite-chrome refractory, the CaSO₄ identified was attributed to the dissociation of CaMg₃(SO₄)₄ found in the original brick (1.6%) and the change in mass indicates that no new sulfate was formed in reactions with SO₂-containing gases. The absence of CaSO₄ in the chrome-magnesite refractory was attributed to the limited accessibility of CaO present in refractory, which was controlled within the occasional Ca(Mg,Fe)SiO₄ (monticellite) found in the spinel grains. This suggests that spinels in chrome-magnesite and magnesite-chrome refractories are resistant to sulfate attack at 1350°C. The decomposition of sulfates at high temperatures possibly caused the changes in sulfate identified in MgCr D60/100, from CaMg₃(SO₄)₄ present before reaction to CaSO₄ identified after reaction.

Reaction at 700°C

The phases identified in basic refractories exposed to SO₂-containing gases at 700°C are listed in Table 2. The XRD confirmed the phases identified from

microstructural analyses by SEM. At 700°C, the diffused gases in the pores react with MgO at the grain surfaces and within the refractory matrix to form MgSO₄ by the following reaction mechanism,



This agrees with the thermodynamic equilibrium of MgO in SO₂-containing gases for temperatures below 1000°C.^{14, 25} MgSO₄ has been reported in basic refractories for temperatures up to 850–1050°C.^{8, 15} In the magnesite refractory, gases diffuse into the MgO grains and react with CaO from the partially dissociated Ca₃SiO₅ to form CaSO₄. Therefore, the presence of SiO₂ maintains the access of gases that react with oxide. The sulfates interconnect possibly by diffusion of oxides through the porous products from the grains to the reaction sites and form CaMg₃(SO₄)₄, that could be presented as CaSO₄·3MgSO₄.

Mechanism of sulfate formation

During a diffusion process, the grain boundaries act as barriers and the difference in mass transfer across the interfaces prevents an outward diffusion to and from the M_xSO₄/SO₂-O₂ gas interface in a mechanism proposed by Hsia *et al.*²⁶⁻²⁸ It can be proposed that initially at the MgO/gas interface equilibrium gas partial pressures were higher than in the gas phase and sulfation occurred. The porous spongy material of MgSO₄ structure acted as an inward diffusion path for gases and increased the concentration gradient across the product layer. At the MgO/MgSO₄ interface the reactions that are determined by the prevailing equilibrium partial pressure of SO₂ and O₂ progress until equilibrium is reached.²⁶⁻²⁸ The solid-state diffusion of MgO from the grains and that of gases through MgSO₄ to the reaction sites is very slow. This results in an increased gas concentration at the MgSO₄/gas interface, and the formation of a protective sulfate layer around the magnesia grains, one that appears to be elongated when examined under SEM.

The presence of CaO and sesquioxides of Al, Cr, Fe in magnesite-chrome and chrome-magnesite refractories might prevent the protective layer around the magnesia spinel grains from forming. The mechanism of CaSO₄ formation was attributed to lattice distortion controlled by differences in ionic radius of Ca²⁺ (1.08 Å), Si²⁺ (0.34 Å) and O²⁻ (1.32 Å) in the Ca₃SiO₅ structure, and to SO₄²⁻ (4.5 Å) in the CaSO₄ structure. This increased the amount and the distribution of free volume which increased outward diffusion and subsequent reaction of Ca²⁺ and O²⁻ from the structures through to the M_xSO₄/gas interface. The Si²⁺ diffusion would have been limited by the tetrahedral bond strength. The porous CaSO₄ indicates that sulfation proceeded at both the CaO/CaSO₄, and CaSO₄/gas interface. The thermodynamic stability and accessibility were the determining factors, and not chemical reaction and diffusivity of the gases. This agrees with previous studies.²⁶⁻²⁸

Kinetics of sulfation

To establish the relative conversions with time at different temperatures (figures 8–11) the refractories were exposed to SO₂-containing gases for varying periods of time. The amount of MgO converted was calculated by mass-change and indicated to be affected by temperatures up to 1000°C. The conversion

reached 12% and 10% at 900°C and 1000°C and 4% and 6% at 700°C and 800°C for magnesia and magnesia-spinel refractories. At 900°C and 1000°C, the conversions are similar as well as at 700°C and 800°C. This is related to structural changes that occur at 900°C and 1000°C and those that happen at 700°C and 800°C. At 800°C, a new phase Ca_2SiO_4 is identified in refractories and this promoted sulfation through the dissociation of silicates. The increasing solid-state diffusion kinetics with temperature promotes sulfation and the amount of MgO converted increased with time and temperature. The structural changes at high temperatures promote gas and oxide diffusion through the formation of pores and make the reagents available at reaction sites. In reactions conducted at the same temperatures, over time the solid-state diffusion allows more oxides to diffuse through to the reaction sites and the amount of MgO converted increases with time. This could be that the short period does not allow the diffusing oxides from the grains through the product formed to reach the reaction site for sulfation. At 1200°C, the fraction converted decreased because of decomposition and CaSO_4 is the only thermodynamically favoured reaction.

In Figure 5, the amount of sulfate (SO_3) determined in the magnesite refractory was found to be higher by chemical analysis than by mass-gain calculation. This is because of a tendency of MgO and CaO to absorb moisture and possibly CO_2 . It is important to note that, although the conversions to sulfate in figures 2–4 calculated based on the mass gained, in chromite-containing refractories these results show that the mass gained is proportional to the sulfate but the amount of sulfate formed could be different as shown in tables 2 and 3 and Figure 11.

CONCLUSIONS

Three basic refractory types, namely, magnesite, chrome-magnesite and magnesite-chrome, were exposed to SO_2 -containing gases and examined for phase-chemical changes, characteristic microstructure, and mineralogical constitutions. The reaction mechanisms in MgO-MgR₂O₃ refractories exposed to SO_2 -containing gases progress through a combination of structural disintegration and chemical attack. Upon heating, dissolution of spinels result in phase-chemical changes that cause loosening of the structures and this serves as a path for gas diffusion and chemical attack. The chemical reactions occur along the phase grain boundaries and in the pores, and lead to disintegration of various phase structures. Consequently, the incorporation of sesquioxides of Al, Cr and Fe in the sulfate products promotes the erosion of the refractory structures. The stable sulfate phases identified as MgSO_4 , CaSO_4 , and $\text{CaMg}_3(\text{SO}_4)_4$ formed reactions controlled by thermodynamic equilibrium. The magnesite-chrome refractory that comprised fine-grained and re-constituted fused-grain material showed a compact refractory matrix and limited chemical attack by SO_2 -containing gases.

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Ncuthukazi Ziyanda Fotoyi

Engineer, Mintek

Ncuthukazi Ziyanda Fotoyi, formerly a graduate student from the University of Cape Town and the University of the Witwatersrand, holds a B.Sc. in biochemistry, a B.Sc. (honours) in materials science, and an M.Sc. in engineering. She is currently employed in the Pyrometallurgy Division of Mintek, where she enjoys working in the Commercial Applications Group.
