

The influence of *in situ* spinel formation on microstructure and phase evolution of MgO–C refractories

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Abstract

The influence of *in situ* spinel formation on microstructure and strength of MgO–C refractories containing reactive alumina is investigated as a function of coking temperature. XRD, SEM, MOR techniques and rotary slag testing were employed to evaluate the microstructure and properties. The improvement of refractory properties was found to be related to the *in situ* spinel formation in the matrix. The microstructural evolution of the matrix was also influenced by the spinel formation from reactive alumina and MgO fine grains. It was also clarified that the spinel stoichiometric was varied from normal type to alumina rich depending upon the firing temperature and atmosphere.

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1. Introduction

The interest on MgO–C refractories for steelmaking application has been resumed and the improvement of their thermochemical properties is of great concern.^{1,2} In recent years, these refractories have been developed due to their excellent thermal shock and slag corrosion resistance for application in steel industries such as converters, electric arc furnaces and steel treatment ladles.³ These refractories usually consist of more than 80 wt.% MgO, 10–15 wt.% graphite and few percent resin and antioxidant materials.⁴ In order to develop a better microstructure and improve the property of MgO–C refractories, the effect of different additives on microstructural evolution has been investigated.⁵

The magnesium aluminate spinel, MgAl₂O₄ (MA), due to a good combination of physical and chemical properties has been reported to enhance the chemical and the thermal shock resistances.⁶ These improvements in properties of refractory

materials are mainly gained when the spinel phase is involved via a reaction of Al₂O₃ and MgO during the heat-up process in application. This so called *in situ* spinel formation is accompanied by volumetric expansion, which leads to a significant reduction in pore volume.^{7,8} The better corrosion and thermal shock resistance of refractories have been reported to be influenced positively by presence of *in situ* spinel.^{9,10} Researchers also have reported some other advantages in spinel bearing refractories mainly in steelmaking applications.¹¹

Recently, a new type of magnesia–carbon refractories has been developed by using pre-synthesis MA spinel as a raw material or *in situ* phase that formed by addition of aluminium oxide to these MgO base refractories. Ganesh et al.¹¹ indicated the addition of magnesium–aluminat spinel to MgO–C refractories for application in steelmaking ladles. They found that refractories containing spinel phase exhibited higher resistance to slag erosion and corrosion compared to MgO–C refractories.

Despite of the benefits of *in situ* spinel in MgO–C refractories, the microstructural evolution of formed spinel is not clearly understood. Particularly the effect of sever reduction atmosphere in MgO–C refractories on structural variation and phase analysis of *in situ* formed spinel has not been reported.

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Table 1
Chemical composition of basic raw materials (wt.%)

	MgO	C	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃
Fused magnesia	97	–	1.2	0.5	0.2	–	0.4
Sintered magnesia	97.5	–	1	0.5	0.5	–	0.6
Graphite flake	0.13	96.5	0.13	1.6	0.45	–	0.75
Reactive alumina	–	–	150 ppm	800 ppm	99.5	350 ppm	150 ppm

This paper will address the phase development during the spinel formation in MgO–C refractories containing fine alumina powder. Also the influence of *in situ* spinel on mechanical and corrosion resistance will be reported.

2. Experimental procedure

High quality commercial fused magnesia, sintered magnesia and Chinese natural flake graphite with chemical composition shown in Table 1 were used as raw materials. Fine aluminium powder with $d_{50} = 45 \mu\text{m}$, as antioxidant (Bahrain Atomizers B.S.C., Bahrain), reactive alumina powder ($d_{50} = 2.5 \mu\text{m}$), as an additive and phenolic resin (Cukurova Kimya Endustris, Turkey) as a binder were employ in sample formulations. Table 2 shows the sample compositions with (MCR) and without reactive alumina powder (MC).

All raw materials were mixed at room temperature following the standard commercial practice. After mixing, bricks with 150 Mpa pressure were shaped with a hydraulic press and made samples were then cured following the standard temperature–time curve up to 200 °C. Coking was carried out at 1000–1600 °C under reducing atmosphere (carbon bed) and then the mechanical properties were determined following Japanese (JIS) standards taking three samples from each firing temperature. Corrosion resistance of the samples were studied by a conventional gas-fired rotary slag testing furnace using a synthesized model EAF slag with chemical composition shown in Table 3. Air and propane (C₃H₈) were used as the fuel and the corrosion test was carried out at 1650 °C for 10 h. The reacted

Table 2
Composition of samples

Material	Sample code	
	MC	MCR
MgO (wt.%)		
1–5 mm	27	27
0–1 mm	27	27
Powder (0.075 mm)	35	27.8
Graphite (wt.%)	10	10
Novalak (resin) (+wt.%)	2	2
Hexa (additive of resin) (+wt.%)	0.2	0.2
Al ($d_{50} = 45 \mu\text{m}$) (wt.%)	1	1
Reactive alumina ($d_{50} = 2.5 \mu\text{m}$) (wt.%)	–	7.2

Table 3
Chemical composition of model slag (wt.%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	CaO/SiO ₂
25.07	12.78	13.85	36.17	5.82	3.52	1.44

slag was refreshed every 30 min by charging 300 g of new slag to ensure constant slag composition during the test. After the corrosion test, the furnace was cooled naturally to room temperature and corrosion index was calculated in terms of percentage by measurement of eroded area of samples.

Similar matrix model compositions (below 200 μm) of samples were prepared for phase analysis. Powders were hand-mixed and small cylindrical samples (15 mm in diameter and 20 mm in height) shaped and placed in alumina crucibles for coking. The crucibles were filled with carbon powder in order to inhibit the oxidation of carbon in samples.

The phase compositions and lattice parameters were determined by XRD using Cu K α radiation. Also, Microstructural observations were carried out on gold-coated samples by SEM employing standard sample preparation routs.

3. Results and discussion

3.1. As-cured samples

A typical microstructure of MCR sample after being cured at 200 °C is presented in Fig. 1(a and b). As shown in micrograph (Fig. 1(a)) both fused (FM) and sinter (SM) magnesia grains are surrounded by a matrix comprising graphite flakes (G). The white aluminium antioxidant particles (Al) are also distributed homogeneously in the matrix with a particle size of 20–75 μm . Also, one may notice another phase on magnesia and its grain boundaries with white contrast (IP) which was clarified by EDS have a calcium silicate nature and therefore, might be attributed to original magnesia raw materials.¹² The reactive alumina (RA) could be identified at higher magnifications (Fig. 1(b)). As revealed from this micrograph, the gaps between MgO grains and graphite flakes were filled by the reactive alumina powders, which well dispersed in the matrix. The microstructure of MC sample shown in Fig. 2(a and b) revealed that the above-mentioned components existed in the texture (Fig. 2(a)) with difference which the gaps between MgO grains and flakes of graphite were filled only by MgO powder and Al antioxidants (Fig. 2(b)).

Comparing the texture of MC and MCR samples that look similar in macroscale, we may expect significant differences in properties of fired samples, which originate from the differences in microscale texture.

3.2. Fired samples

The XRD patterns of the MCR matrix compositions heated at 1000–1600 °C in carbon bed are shown in Fig. 3. The differ-

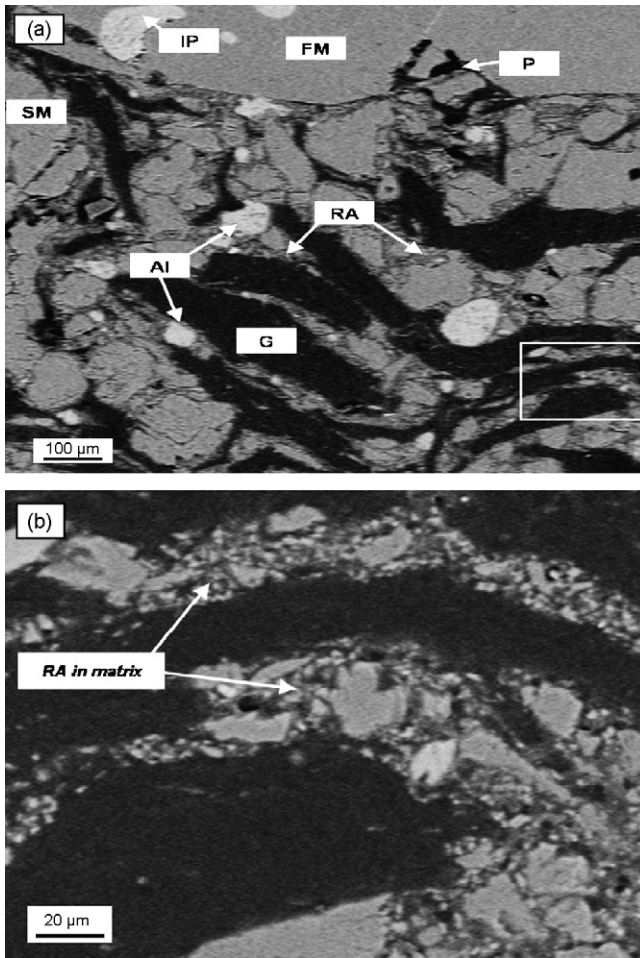


Fig. 1. (a) As-cured microstructure (BSE) of MCR sample. (b) Detail of reactive alumina distribution between graphite and MgO grains demarcated area (a), FM, fused magnesia; SM, sinter magnesia; G, graphite; RA, reactive alumina; AI, aluminium; P, pore; IP, impurity phases.

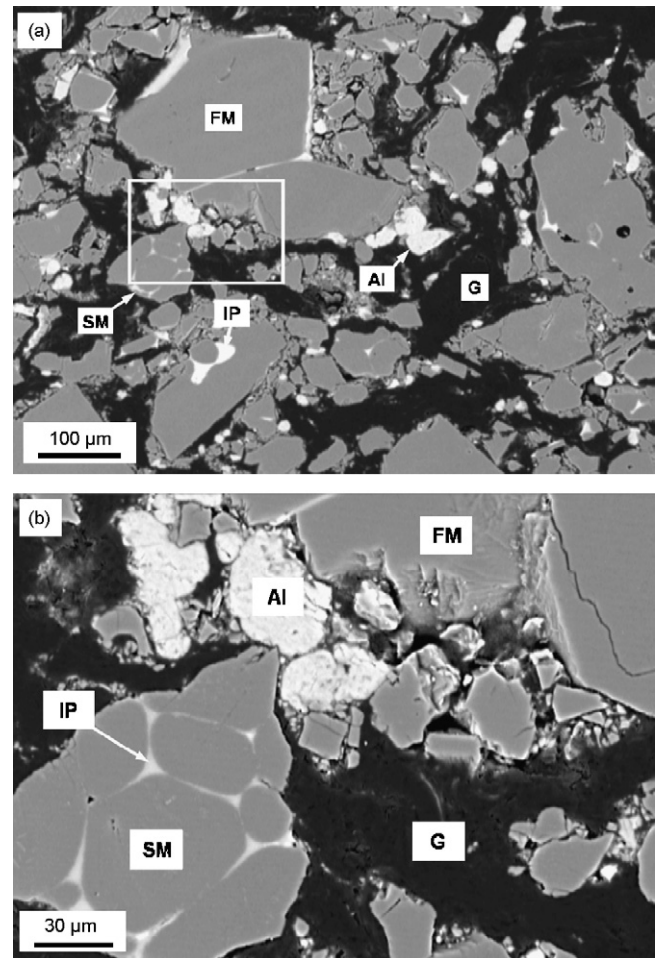


Fig. 2. (a) As-cured microstructure (BSE) of MC sample. (b) Detail of Al metal presence between graphite and MgO grains demarcated area (a), FM, fused magnesia; SM, sinter magnesia; G, graphite; RA, reactive alumina; AI, aluminium; P, pore; IP, impurity phases.

ent phases were formed by reaction of aluminium antioxidant and reactive alumina in the presence of MgO and carbon on firing. MgO and spinel are the principal crystalline phases above 1150 °C. Magnesium aluminate spinel is detected from initial temperature (1000 °C) in the matrix of MCR sample and its content increases at higher firing temperatures as seen from XRD peak at $2\theta = 36.85$. The intensity of corundum peaks in contrary to spinel is decreasing so that in XRD pattern of 1450 °C there is no sign of corundum peak at $2\theta = 35.15$. Therefore, we may conclude that the spinel formation initiates around 1000 °C and accomplished above 1300 °C.

Small peaks related to the aluminium carbide and nitride phases could be identified in XRD patterns of samples fired at 1000–1450 °C. These phases completely disappeared at 1600 °C as shown in XRD pattern. The phase analysis in the matrix of sample without reactive alumina (MC), also, showed corundum as well as aluminium carbide and nitride phases at 1000 °C. In addition, very small amount of spinel ($MgAl_2O_4$) was detected at 1300 °C that increased in higher temperatures and aluminum carbide and oxide phases disappeared up to 1450 °C. These are all could be attributed to Al antioxidant phase transformations in

the matrix of MgO–C refractories and finally the *in situ* formed spinel in Al sites is the stable phase at higher temperatures (Fig. 4).^{13–15}

It is well known that the Al antioxidant in MgO–C refractories causes the formation of carbide (Al_4C_3) and nitride (AlN) compositions below 1000 °C.^{13,14} Zhang et al.¹⁵ studied thermochemistry and microstructure of MgO–C refractories containing

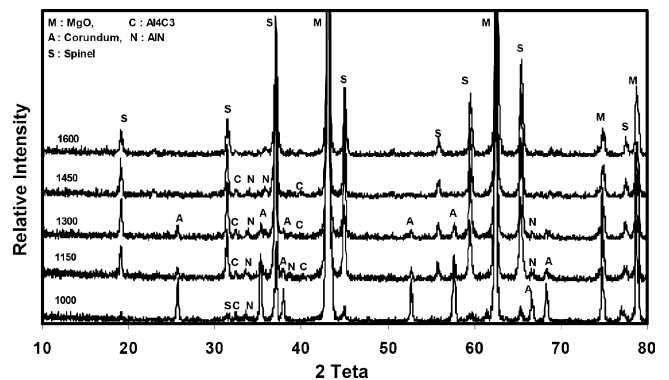


Fig. 3. XRD patterns of MCR samples coked in different temperatures.

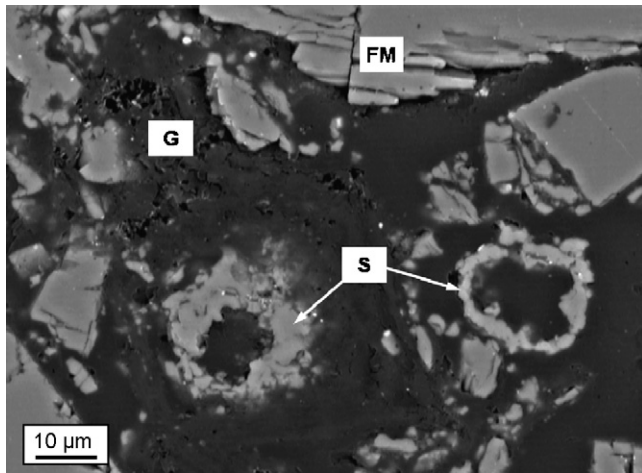


Fig. 4. BEI of the MC sample fired at 1600 °C, showing the formation of spinel shell at Al original site. FM, fused magnesia; G, graphite; S, spinel.

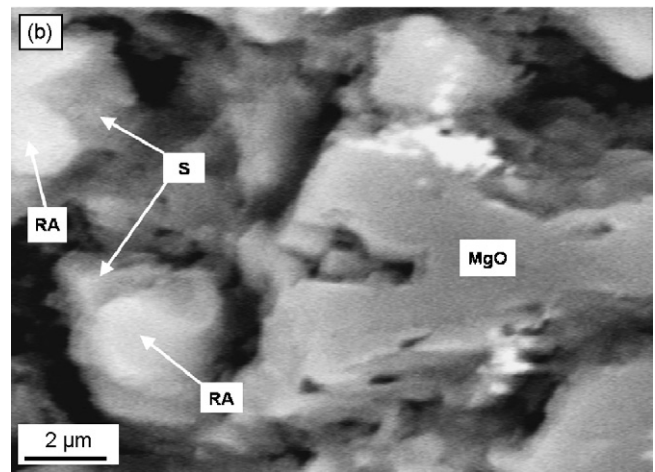
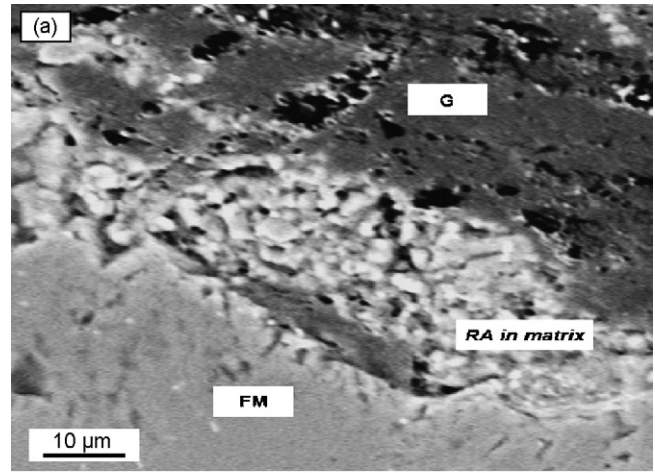


Fig. 5. BSE of the MCR sample after coking at 1150 °C in two magnifications, FM, fused magnesia; G, graphite; S, spinel; RA, reactive alumina.

Al metal and found that this antioxidant reacts with surrounding carbons forming an Al_4C_3 in the matrix. The formation of AlN was also found to proceed through Al and N_2 . Al and Al_4C_3 converted to alumina through the reaction with CO, which could further react with MgO for *in situ* spinel formation. They also investigated the stability of Al_4C_3 and AlN phases at 1500 °C where they coexisted with spinel in the matrix. Yamaguchi¹⁶ has studied the thermochemistry of Al–C–O–N system and extended the results to MgO–C–Al refractories. He found similar reaction mechanism on the behavior of Al metal antioxidant in carbon containing refractories. However, he believes that the partial pressure of $\text{Al}_{(g)}$ is responsible for the formation of Al_2O_3 and AlN whiskers. Spinel phase could then be formed via reaction of aluminium gas, CO and MgO.¹⁶ Also, AlN phase in MgO–C–Al form below 1000 °C and is a stable phase coexist with spinel at temperatures as high as 1550 °C. In another study, Aneziris et al.¹³ found that the Al_4C_3 crystals would grow in the position of Al antioxidant and different amorphous whiskers containing Al, C and O formed at higher coking temperature. They also clarified the Al_4C_3 remained stable up to 1500 °C in argon atmosphere.

Therefore, this fact was confirmed that the *in situ* spinel was formed due to reaction of Al antioxidant in the matrix of MgO–C refractories via Al_4C_3 oxidation or direct reaction of $\text{Al}_{(l,g)}$ with MgO and $\text{CO}_{(g)}$ atmosphere. Thus, in the present system it is well understand that the *in situ* spinel phase originate from Al reactions and form in Al sites in the matrix of MC sample (Fig. 4), while the reaction of reactive alumina with MgO fine grains is the main source for spinel formation in the matrix of MCR sample which further discussed in follow.

Fig. 5(a) shows the microstructure of MCR sample after being fired at 1150 °C. This figure particularly shows the area where reactive alumina (RA) settles in the gap between graphite flakes (G) and fused magnesia (FM). In higher magnification (Fig. 5(b)) reacted area as a core shell around the reactive alumina particles are distinguished. The detailed EDS analysis on this surface (labeled S in Fig. 5(b)) and center of reactive alumina particles (labeled RA in Fig. 5(b)) revealed the presence of Mg and Al on the surface of reactive alumina (Fig. 6) that could be attributed

to spinel phase formation on the surface of reactive alumina grains.

The spinel formation in the mixture of alumina and magnesia could be understood by the Wagner theory^{17,18} which solid-state reaction between alumina and magnesia grains occurs further on the surface of alumina grains. In fact, when fine reactive alumina powders react with MgO grains in the refractory matrix, a spinel texture will formed due to solid-state reaction between alumina and magnesia.¹⁹ It has been clarified that this reaction was proceed and controlled by counterdiffusion of Mg^{2+} and Al^{3+} ions through the formed spinel layer so that spinel formation by this process is particularly slow because low diffusivity of Mg^{2+} and Al^{3+} ions.^{5,18} Therefore, extended firing to 1300 °C, lead to a microstructure with a continuous spinel texture (Fig. 7) and no significant difference could be specified in the microstructures up to 1450 °C. But, the spinel formation was completed by firing at 1600 °C in MCR sample and developed a remarkably ceramic bonding in the microstructure by junction between MgO grains and graphite flakes (Fig. 8). However, as discussed before the *in situ* spinel phase formation due to reaction of Al antioxidant in the matrix of MC sample only occurred in original site of Al (Fig. 9). Therefore, spinel bonding could not be completely developed in the matrix of MC compared to MCR sample. This

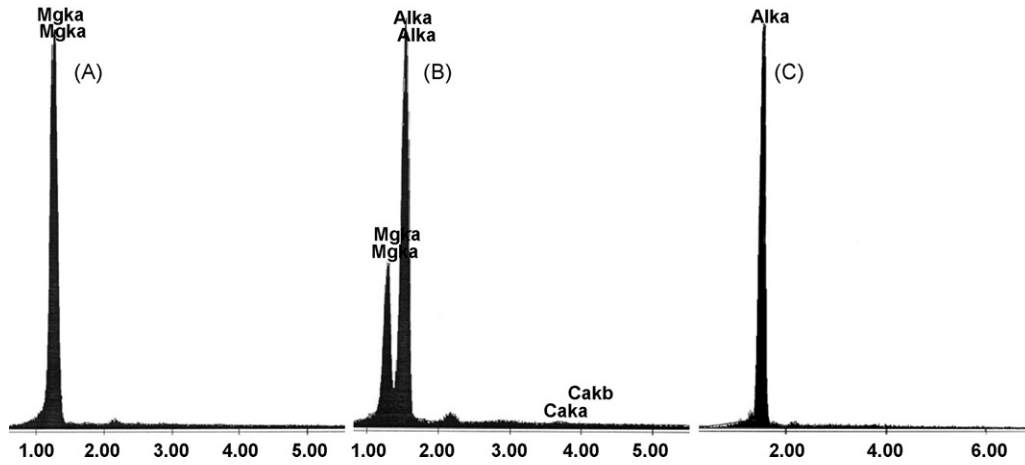


Fig. 6. EDS analysis of (A) MgO grains, (B) spinel rim (s) and (C) center of reactive alumina grains (RA) in Fig. 5(b).

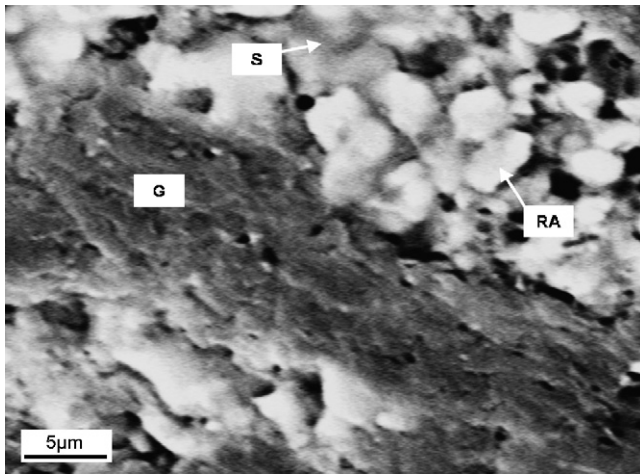


Fig. 7. BSE of the MCR sample coked at 1300 °C, showing the similar microstructure of MCR sample fired at 1150 °C. RA, reactive alumina; S, spinel; FM, fused magnesia; G, graphite.

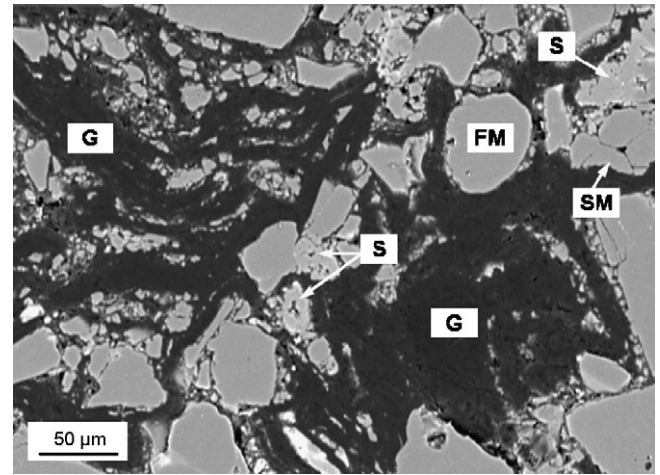


Fig. 9. BSE of the MC sample fired at 1600 °C, showing the formation of spinel in Al site. FM, fused magnesia; G, graphite; S, spinel.

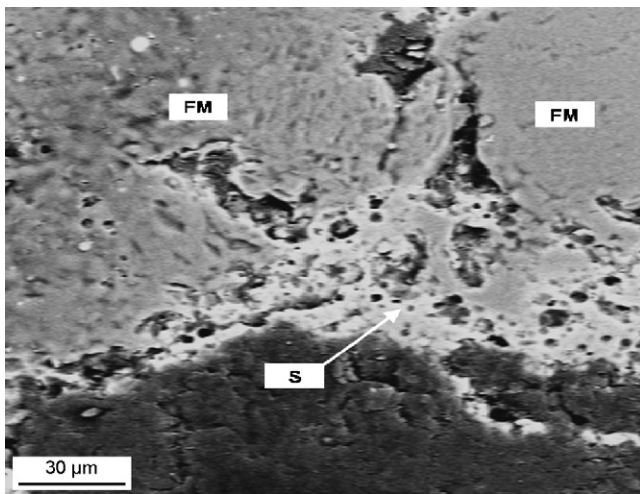


Fig. 8. BSE of the MCR sample fired at 1600 °C, showing the formation of spinel bond between graphite and magnesia grains. FM, fused magnesia; G, graphite; S, spinel.

judgment was supported by strength measurement at different temperatures in Fig. 10.

The presence of spinel phase, as has been reported before, improves the performance of steelmaking refractories, particularly, where thermal stress and chemical corrosion are the main wear mechanisms.^{6,11} Furthermore, it is well known that the presence of carbon in oxide refractories reduces the material's wettability by molten slags and metals.^{1,19} Fig. 11 illustrates

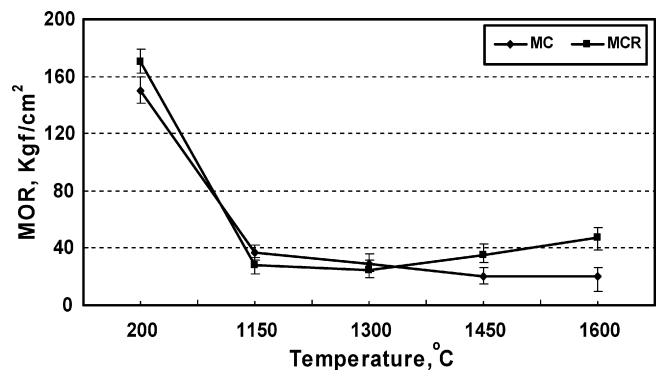


Fig. 10. Change of the MOR vs. coking temperature for MC and MCR samples.

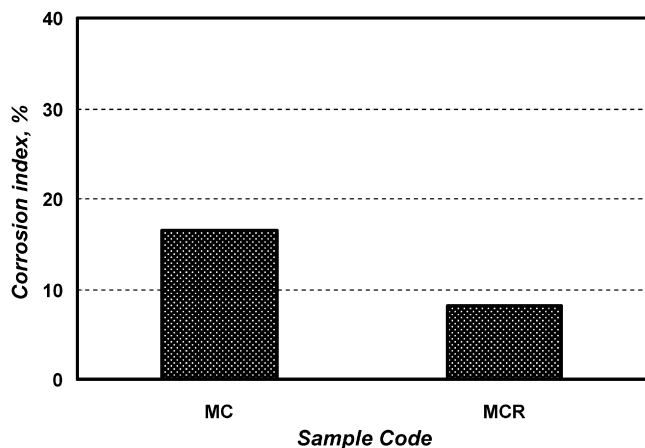


Fig. 11. Relative corrosion rate of MC and MCR samples.

the relative corrosion resistance (corrosion index) of the MC and MCR samples. As shown, the addition of reactive alumina has remarkably improved the corrosion resistance of MgO–C refractories. Zhang et al.¹⁵ reported that the spinel in the matrix of MgO–C refractory could effectively protect the graphite against oxidation, also bond together the flakes, and subsequently increase the erosion resistance. This also maintained the integrity of the refractory texture and thus inhibited further slag penetration and subsequent corrosion. Therefore, the refractory containing reactive alumina (MCR) demonstrates a better corrosion resistance compared to the bricks without reactive alumina (MC).

Interesting results were observed in the texture of bodies coked at 1600 °C in reducing atmosphere (Fig. 12). The evolution of porous and spongy microstructure, which forms at high firing temperatures, has been observed before.²⁰ The thermochemical studies on oxide/nonoxide refractory showed the reducing atmosphere caused the reduction and volatilization of oxide components at higher temperatures.²¹ It was also reported that the reduction could be severe due to the presence of car-

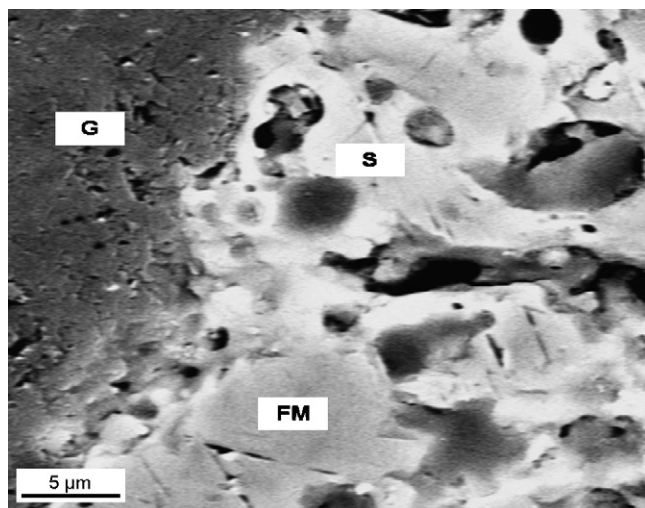


Fig. 12. BSE of the MCR sample fired at 1600 °C, showing formation of porous spinel in matrix. FM, fused magnesia; G, graphite; S, spinel.

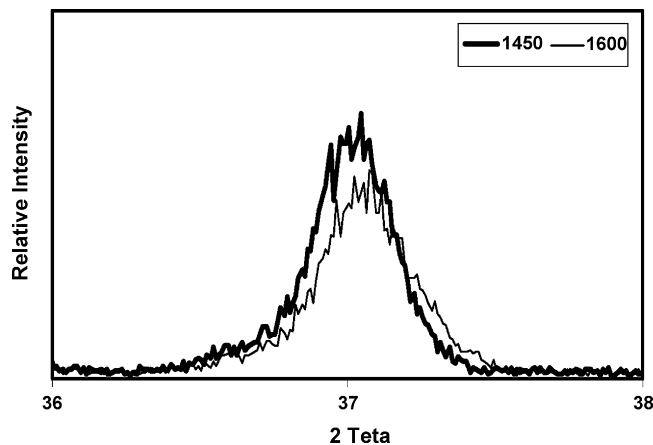


Fig. 13. Displacement of basic spinel peak (3 1 1) in MCR sample coked in 1450 and 1600 °C.

bon as a component of carbon containing refractories.^{22,23} In addition, Sainz et al.²² found that the spinel structure and its thermochemical stability could be influenced by atmosphere and oxygen partial pressure. In fact, magnesium evaporation and its escape from the system in severe reducing atmospheres, leads to alumina–spinel solid solution and this effect is accompanied by formation of microporous structure. Also, increasing the Al³⁺ ions in the spinel structure forms vacant sites for electroneutrality.²³ It has been clarified the MA spinel structure changes at high temperature and severe reducing atmosphere (similar to internal atmosphere of MgO–C refractories with $P_{CO} = 1$ atm)^{15,16} and show a slight shift from stoichiometric composition toward an alumina rich spinel (ARS). This process is accompanied by a decrease in the spinel lattice parameter and subsequent shifting of spinel peaks to higher 2θ in XRD patterns.^{22,24} This effect can be seen in Fig. 3 where the spinel peaks at high coking temperature (1600 °C) are lower in intensity and wider in comparison to low firing temperature (1450 °C).

Fig. 13 shows the details of XRD peak shift in (3 1 1) spinel planes in MCR matrix samples fired at 1450 and 1600 °C. On the basis of 2θ shift, the lattice parameters were calculated and presented in Table 4. The shift in XRD peak indicates the change in lattice parameter from 0.806 to 0.803 nm, which is believed to be imposed by increasing the Al³⁺ ions in spinel structure and formation of spinel–alumina solid solution.

Therefore, it may be concluded that the alumina rich spinel is preferred phase at high working temperatures in MgO–C refractories containing reactive alumina. This may lead to better thermal shock resistance in refractory applications.²⁵ The improvement in thermal shock resistance originates from lower thermal expansion coefficient of ARS matrix. Also, the vacant cation sites were formed by doping of excess Al³⁺ and formation

Table 4
 2θ measured and a_0 calculated from XRD patterns

	Stoichiometric spinel	1450 °C	1600 °C
2θ	36.85	36.945	37.075
d_{311} (nm)	0.2437	0.2431	0.242
a_0 (nm)	0.8083	0.806	0.803

of ARS matrix which becomes cation deficient with a smaller unit cell volume.⁵ Therefore, the corrosion resistance enhancement in ARS matrix compositions may also be attributed to the accommodation of Fe and Mn ions from corrosive slag in steelmaking process.²⁵

Finally, along with the carbon/graphite component the formation of matrix with better thermal shock resistance and traps of Fe and Mn ions are the main reasons causing improved slag corrosion resistance in MgO–C refractories containing reactive alumina.

4. Conclusions

1. The microstructural evolution and properties of MgO–C refractories with and without fine reactive alumina powders were investigated systematically. It was established that reactive alumina proved to be an effective additives in terms of improvements in the textural integrity of MgO–C refractories.
2. The formation of *in situ* spinel via reaction of reactive alumina and MgO fine grains was found to commence at 1000 °C and accomplish at 1300 °C. Also, despite the presence of aluminium carbide and nitride via reaction of Al antioxidant in the matrix the Al originated spinel was detected as the stable phase at high temperatures (>1450 °C).
3. The reaction of reactive alumina in the matrix of MgO–C was found to be accompanied by an improvement in ceramic bonding and corrosion resistance. This was attributed to an *in situ* spinel matrix development.
4. At high coking temperature, a micro-porous spinel texture was observed in the matrix, which was clarified to be an aluminium rich spinel by XRD and SEM.

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