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The effect of antioxidants on the oxidation behaviour of magnesia–carbon refractory bricks

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Abstract

Oxidation of carbon is the main problem in magnesia–carbon refractories. The effects of various antioxidants, Al, Si, SiC and B_4C on the oxidation resistance of magnesia–carbon bricks were investigated at temperatures of 1300 °C and 1500 °C. Carbon losses as wt.% of the bricks were calculated and oxidized areas of the bricks were examined by XRD, SEM and EDS. B_4C was found to be the most effective antioxidant at both temperatures. Magnesium–borate ($Mg_3B_2O_6$) compound was determined to be present by characterization studies on B_4C added specimens. Magnesium–borate, which is in liquid state above 1360 °C, had an excellent effect on the oxidation resistance of the bricks by filling up the open pores and forming a protective layer on the surface. Forsterite (Mg_2SiO_4) and spinel ($MgAl_2O_4$) provided similar effects on the Si and Al added specimens respectively at both temperatures. The SiC added specimens had similar phases with Si added specimens, but SiC was the least effective antioxidant at both temperatures.

Keywords: D. Carbon; D. MgO; E. Refractories; Oxidation; Antioxidants

1. Introduction

Magnesia–carbon (MgO–C) refractories are widely used in basic oxygen furnaces, electric arc furnaces and steel ladles. These refractories have excellent slag resistance and thermal shock resistance due to the good properties of carbon. The slag cannot wet MgO–C structure because of the low wettability of carbon, so the service life of the MgO–C bricks increases. However, carbon tends to oxidize at high temperatures. After the oxidation of carbon, the structure of magnesia–carbon brick is destroyed and the slag can penetrate into the structure. Therefore, metals, compounds or alloys so-called antioxidants are added during fabrication to prevent oxidation of carbon [1–5].

Carbon, in MgO–C refractories, is oxidized in two ways: direct oxidation and indirect oxidation. Direct oxidation occurs under 1400 °C (reaction (1)), when carbon is oxidized directly by the oxygen from atmosphere. Indirect oxidation occurs above 1400 °C where carbon is oxidized by the oxygen from MgO (reaction (2)) or slag (reaction (3)). The resulting Mg gas (reaction (2)) oxidizes again and generates MgO (reaction (4)) which is called the secondary oxide phase or the dense layer. It is claimed that the secondary oxide phase protects the brick against oxidation by preventing oxygen ingress [6–8]

$$2C(s) + O_2(g) = 2CO(g) \tag{1}$$

$$C(s) + MgO(s) = Mg(g) + CO(g) \tag{2}$$

$$C(s) + FeO(l) = Fe(l) + CO(g) \tag{3}$$

$$2Mg(g) + O_2(g) = 2MgO(s) \tag{4}$$

Different researchers have studied the oxidation behaviour of antioxidants. The Al, Si and Mg powders are mostly used antioxidants due to their low cost and effective protection. Aluminium is one of the mostly used antioxidant, but it has hydration problems when Al_4C_3 forms, since this phase is easily hydrated, even at room temperature [9,10]. The hydration of Al_4C_3 causes volume expansion and cracks. Silicon is another widely used antioxidant. Ghosh et al. indicated that the oxidation resistance of MgO–C bricks containing Al is better than the bricks containing Si, at 1200–1550 °C [11].

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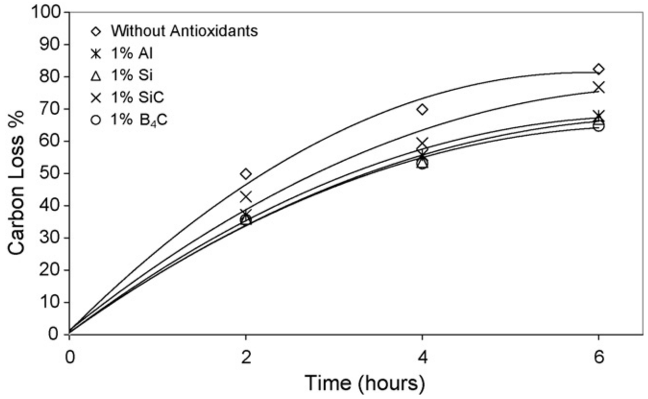

Fig. 1. Carbon losses % of MgO–C specimens with/without 1 wt.% antioxidant at 1300 °C.

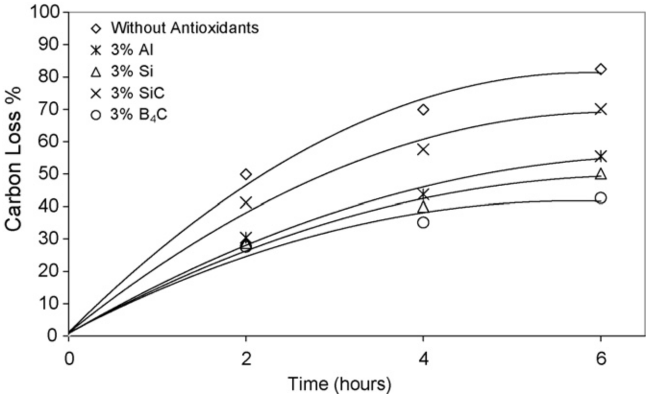

Fig. 2. Carbon losses % of MgO–C specimens with/without 3 wt.% antioxidant at 1300 °C.

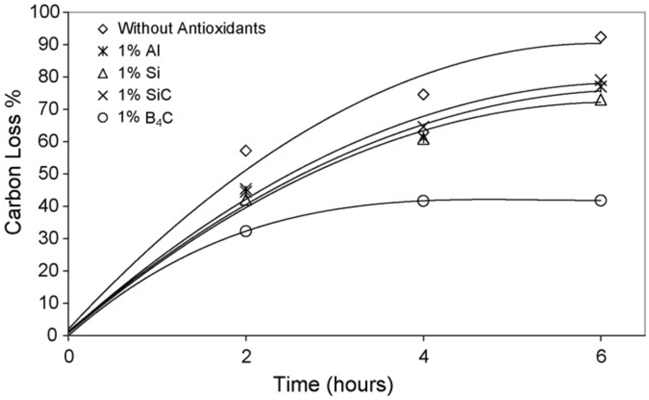

Fig. 3. Carbon losses % of MgO–C specimens with/without 1 wt.% antioxidant at 1500 °C.

Silicon and boron carbide are carbidic antioxidants. There have not been many studies on the oxidation behaviour of these compounds. Many researchers indicated that boron based antioxidants are very effective against oxidation. Wang and Rymon–Lipinski corroborated that boron carbide has excellent antioxidation properties [10,12]. The formation of low melting phases like magnesium borate increases oxidation resistance by filling up the open pores and forming a dense layer on the brick surface, thus oxidation ingress is restricted. Zhang and Lee indicated that the low melting phases cause extremely low corrosion resistance [13]. However, they showed that the presence of Al and B_4C together in the brick increased the corrosion resistance.

The aim of this study was to examine and compare the effects of different antioxidants on the oxidation resistance of magnesia–carbon refractory bricks.

2. Experimental procedure

The raw materials listed in Table 1 were used to prepare the experimental bricks. The Andreasen equation [$y = (d/D)^n \times 100$] was applied [14] to classify magnesia grains at eight different size distributions, between 0 mm and 6.3 mm. Here, y is the weight percentage of material of a size less than d, D is the maximum particle size and n is an empirical parameter, which was set as 0.4 to obtain optimum apparent porosity and bulk density. Novalac type liquid phenolic resin (Çukurova Chemical, Turkey) was selected as a binder and it was cured with hexamethylene tetramine powder (hexamine). Besides solid novalac, a resin powder (Çukurova Chemical, Turkey) was also added to the mixture, to increase the hot strength of the bricks. Total mixing time was 30 min, after which the powders were uniaxially pressed at 1550 kg/cm^2 to form a cylindrical

Table 1
Composition of the MgO–C refractory bricks

Raw materials	Purity (%)	wt.%	Particle size
MgO			
Fused magnesia	>98.0	82–85	0–6.3 mm
C			
Graphite	>97.0	15	<250 μm
Antioxidants			
Al	>98.0	1 and 3	<100 μm
Si	>98.0	1 and 3	<100 μm
SiC	>97	1 and 3	<100 μm
B_4C	>97	1 and 3	<100 μm
Binders			
Hexamine	>99	+0.23	<250 μm
Phenolic resin	–	+0.50	<63 μm
Phenolic resin	–	+2.30	Liquid

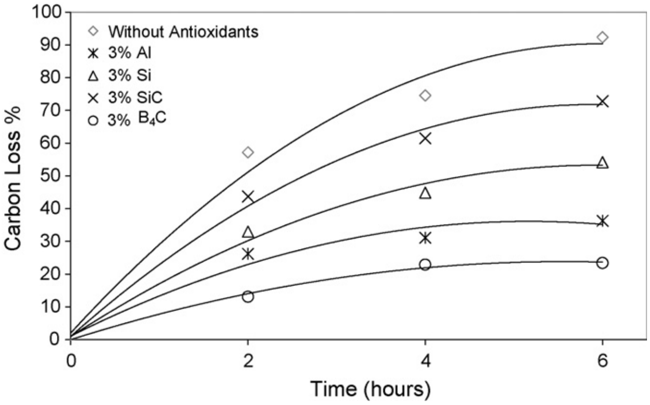

Fig. 4. Carbon losses % of MgO–C specimens with/without 3 wt.% antioxidant at 1500 °C.

compact measuring 50 mm × 50 mm. The specimens were then heat treated for 24 h at 200 °C to stabilize their structure. The apparent porosities and bulk densities of the MgO–C refractory compositions without antioxidants were ~4.82 vol.% and ~2.96 g/cm^3, respectively.

Oxidation tests were conducted in a box type electric furnace for 2 h, 4 h, 6 h at 1300 °C and 1500 °C. The oxidation resistance of magnesia–carbon refractories containing 1 and 3 wt.% antioxidants (Al, Si, SiC and B_4C) was compared in this study. In this study, the carbon loss as wt.% was determined for each specimen by using the formula below. A Jeol 5410 Scanning Electron Microscope with a Noran 2100 EDS analysis system and a Philips PW 3710 X-ray diffractometer (Cu Kα radiation) were used to determine the phase changes in the oxidized areas of the specimens

$$\text{carbon loss (wt.\%)} = \frac{m_1 - m_2}{m_3 \times (\%\text{G})} \times 100$$

where m_1 is the weight of the heat treated specimen (g), m_2 the weight of the oxidized specimen (g), m_3 the weight of the specimen without heat treatment (g) and G is the wt.% graphite.

3. Results and discussion

Changes in the carbon loss of MgO–C refractories with 0–3 wt.% antioxidant additions at 1300 °C are shown in Figs. 1 and 2. Carbon loss curves showed that all antioxidant added specimens had similar results at 1300 °C, excluding the specimen with SiC addition. Carbon losses of the specimens containing particularly Al, Si and B_4C were very similar to each other. The B_4C was the most effective antioxidant at this temperature and SiC was the least effective.

Changes in the carbon loss of MgO–C refractories with and without antioxidants at 1500 °C are shown in Figs. 3 and 4. It can be seen that the 1% B_4C addition had an excellent effect on the oxidation resistance at this temperature, followed by 1% Si,

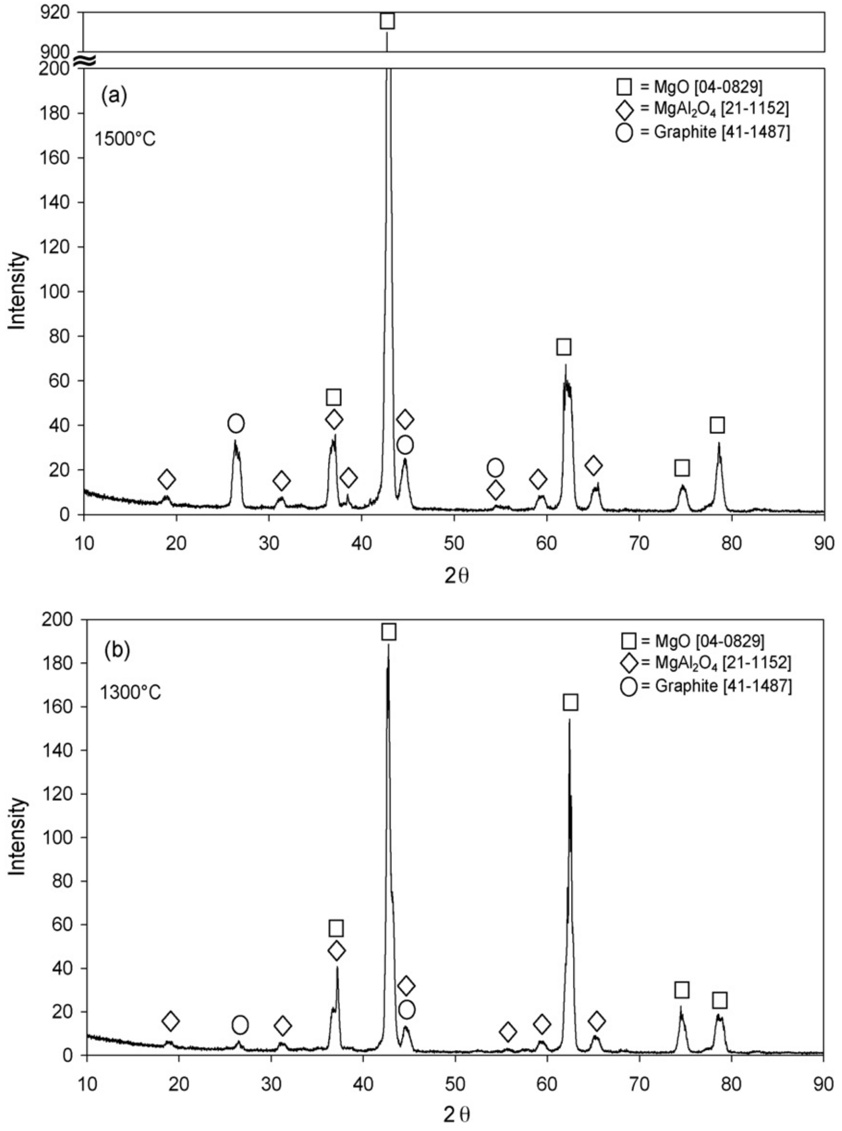

Fig. 5. XRD analysis of MgO–C refractory specimens containing 3 wt. % Al oxidized for 4 h at: (a) 1500 °C; (b) 1300 °C.

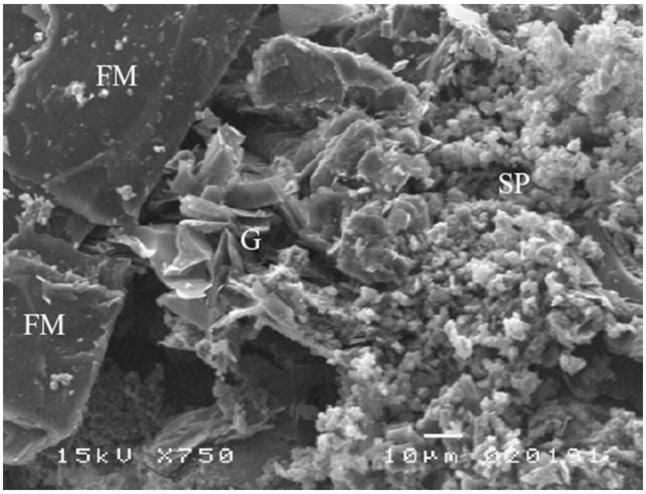

Fig. 6. SEM image of the oxidized area of the 3 wt.% Al added MgO–C refractory specimen oxidized for 6 h at 1500 °C; FM = fused magnesia, G = graphite, SP = spinel.

Al and SiC. The 3% B_4C addition had an excellent result on the oxidation resistance at 1500 °C and 3% Al addition was also effective, followed by 3% Si and 3% SiC, respectively. The degree of oxidation was considerably different between specimens at 1500 °C because the formation of the secondary phases was increased at this temperature. The amount and the behaviour of these phases in the MgO–C structure affected the carbon loss of the specimens.

The XRD analysis of 3% Al added MgO–C specimens, oxidized at 1300 °C and 1500 °C, are presented in Fig. 5. Spinel ($MgAl_2O_4$) phases were detected in the oxidized areas at both temperatures. Smaller amounts of spinel were found at 1300 °C (Fig. 5b) compared to 1500 °C (Fig. 5a). Graphite from the MgO–C structure was also present in the XRD patterns. No Al_4C_3 peaks were detected at either temperature.

The SEM micrograph of the oxidized area of the 3% Al added MgO–C refractory specimen, oxidized at 1500 °C, is shown in Fig. 6. Large fused magnesia grains can be seen on the left side, flake graphites in the middle and spinel phase on the right side of the image.

Taffin and Poirier indicated the spinel formation mechanism in MgO–C refractories [15]. The Al oxidizes rapidly after fabrication and forms a thin Al_2O_3 layer (reaction (5)). When the melting temperature of Al (660 °C) is reached, the thin Al_2O_3 layer can contain the liquid aluminium for a while, until it breaks and releases the molten aluminium. The released aluminium reacts with C to form Al_4C_3 (reaction (6)), Then the

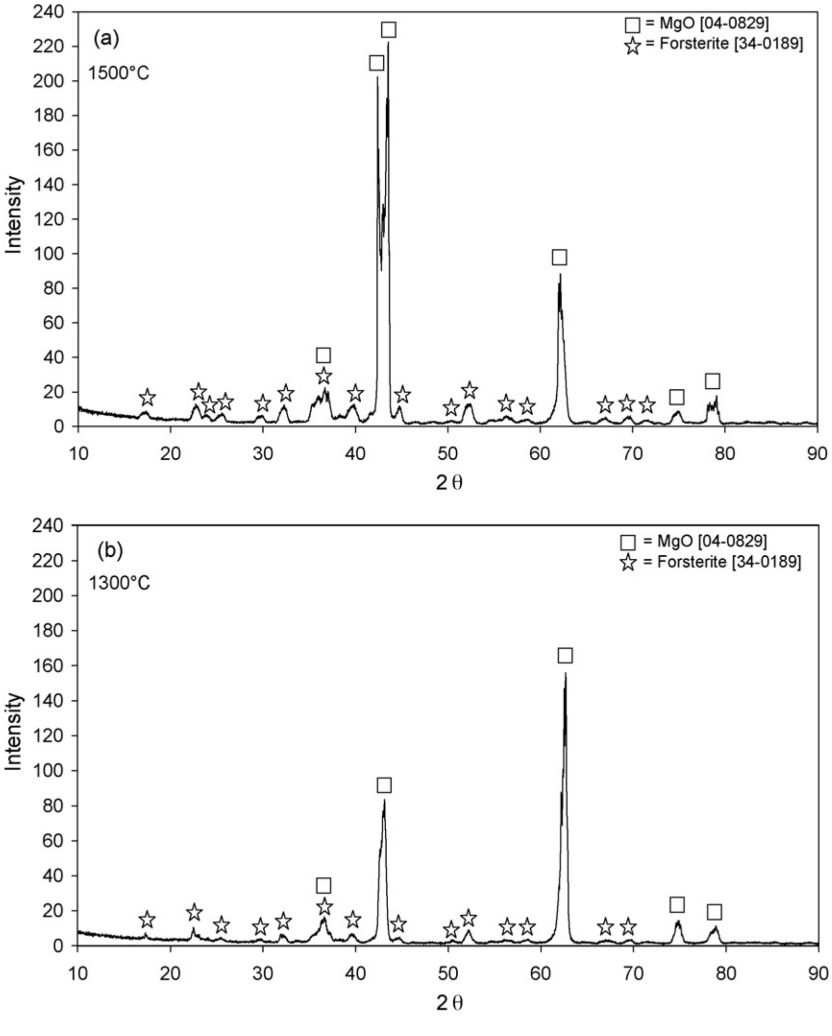

Fig. 7. XRD analysis of MgO–C refractory specimens containing 3 wt.% Si oxidized for 4 h at: (a) 1500 °C; (b) 1300 °C.

Al_4C_3 reacts with CO (carbon is oxidized by the air diffused into the brick) to form Al_2O_3 (reaction (7)), which further reacts with MgO to form $MgAl_2O_4$ (reaction (8))

$$4Al(s) + 3O_2(g) = 2Al_2O_3(s) \tag{5}$$

$$4Al(l) + 3C(s) = Al_4C_3(s) \tag{6}$$

$$Al_4C_3(s) + 6CO(g) = 2Al_2O_3(s) + 9C(s) \tag{7}$$

$$Al_2O_3(s) + MgO(s) = MgAl_2O_4(s) \tag{8}$$

$$Al_4C_3(s) + 12H_2O(g) = 3CH_4(g) + 4Al(OH)_3(s) \tag{9}$$

After 3–4 weeks volume expansion and cracks were observed on the 3% Al added specimens oxidized at 1300 °C. However, these physical changes were not seen in the specimens with 1% Al. Volume expansion and cracks were rarely observed in the 3% Al added specimens oxidized at 1500 °C. The volume expansions and cracks were found to be the results of Al_4C_3 hydration (reaction (9)), which might occur even at room temperature [10].

The XRD analysis of the 3% Si added MgO–C specimens oxidized at 1300 °C and 1500 °C are given in Fig. 7. Considerable amount of Mg_2SiO_4 (forsterite) was found in the oxidized area of the specimens at 1500 °C (Fig. 7a). Fewer forsterite peaks were observed for the specimens oxidized at 1300 °C (Fig. 7b). Forsterite was also observed in the specimens with SiC additions. Fig. 8 shows the XRD patterns of the specimens with 3% SiC additions. Fewer forsterite peaks were observed in the 3% SiC added specimens compared to the 3% Si added specimens, at both temperatures. A higher amount of forsterite was found to be present at 1500 °C than 1300 °C for Si and SiC added refractories. This is because of the higher amount of CO gas formation at 1500 °C which increases the SiO2 formation (reaction (11)). Silicon carbide, which is more stable than metallic Si, did not have a considerable effect on the oxidation resistance of MgO–C refractories at either temperature.

The Si addition had a positive effect on the oxidation resistance of the specimens owing to the occurrence of a high amount of forsterite (Mg_2SiO_4), as shown in Fig. 7. It is assumed that forsterite inhibits oxygen ingress by filling up the

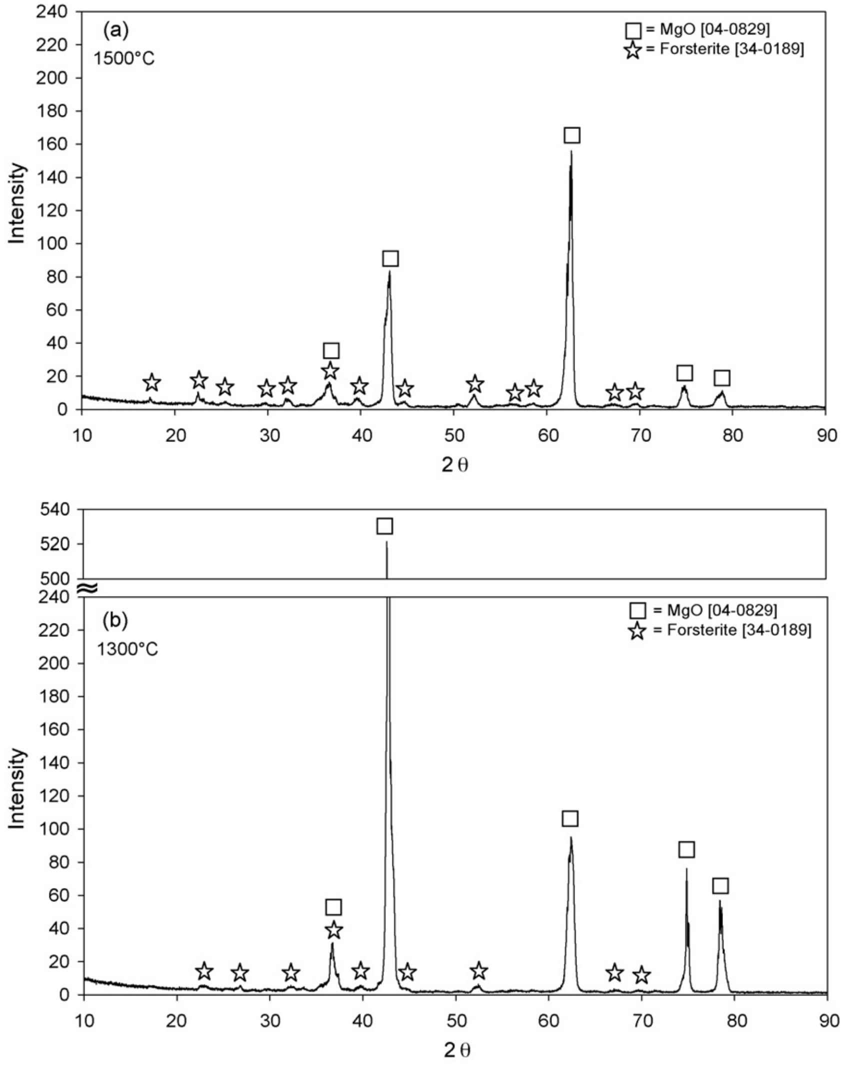

Fig. 8. XRD analysis of MgO–C refractory specimens containing 3 wt.% SiC oxidized for 4 h at: (a) 1500 °C; (b) 1300 °C.

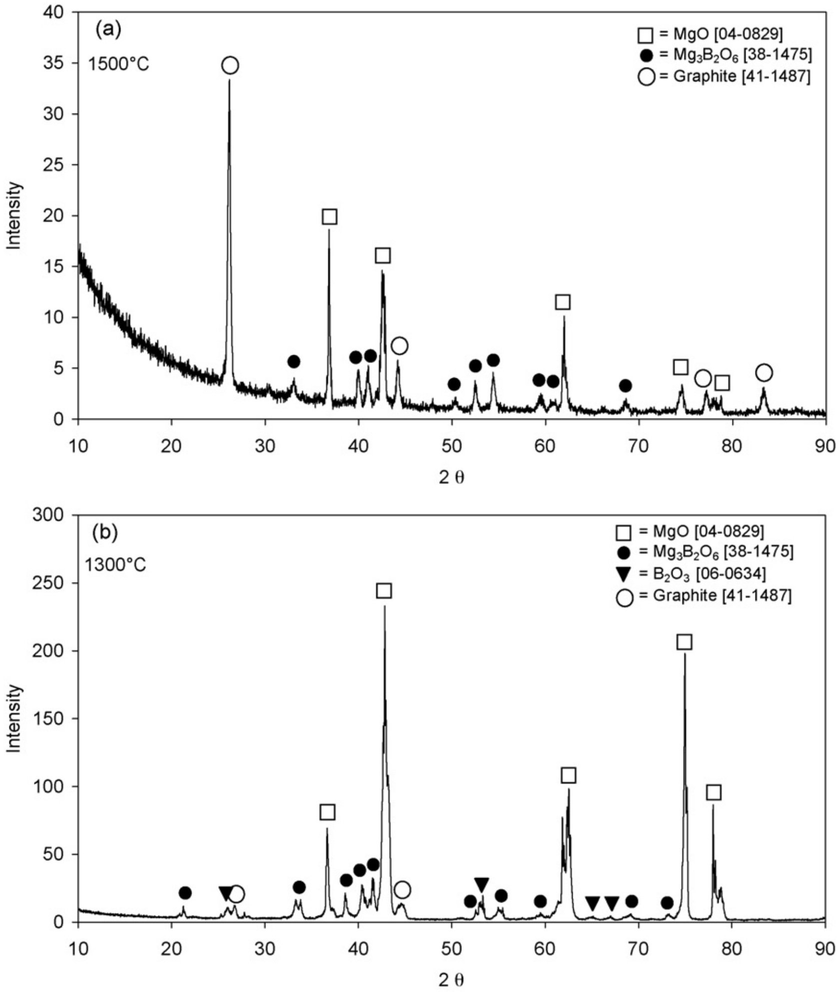

Fig. 9. XRD analysis of MgO–C refractory specimens containing 3 wt.% B_4C oxidized for 4 h at: (a) 1500 °C; (b) 1300 °C.

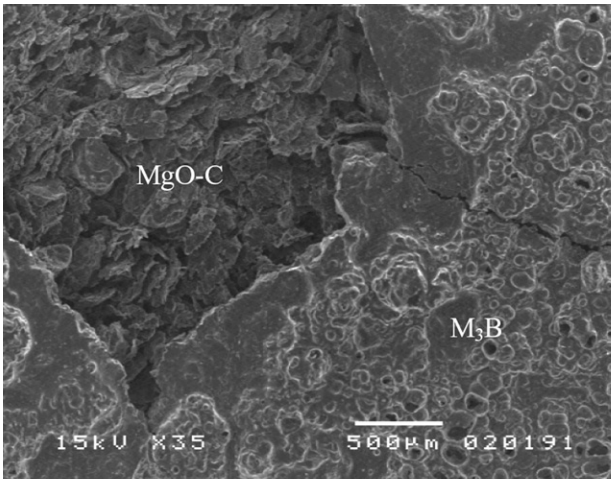

Fig. 10. SEM image of the M_3B layer which occurred on the surface of the 3 wt.% B_4C added MgO–C refractory specimen oxidized for 6 h at 1500 °C; M_3B = magnesium borate ($Mg_3B_2O_6$), MgO–C = magnesia–carbon structure.

open pores. Si first reacts with C to form SiC (reaction (10)) which then reacts with CO to form SiO_2(s) (reaction (11)). SiO_2 then reacts with MgO to form Mg_2SiO_4 (reaction (12))

$$Si(s) + C(s) = SiC(s) \tag{10}$$

$$SiC(s) + 2CO(g) = SiO_2(s) + 3C(s) \tag{11}$$

$$SiO_2(s) + 2MgO(s) = Mg_2SiO_4(s) \tag{12}$$

Fig. 9 shows the XRD patterns of oxidized areas of 3% B_4C containing MgO–C refractory specimens. B_2O_3 and $Mg_3B_2O_6$ phases were found in the oxidized areas of MgO–C specimens oxidized at 1300 °C (Fig. 9b). The 3% B_4C added MgO–C specimens oxidized at 1500 °C were found to have a very thin oxidized layer on the surface, which was analysed by XRD, as shown in Fig. 9a. Many magnesium–borate ($Mg_3B_2O_6$) peaks were seen by XRD analyses on the surface of MgO–C specimens oxidized at 1500 °C. No other boron based compounds or impurities have been found on the surface. The $Mg_3B_2O_6$ layer on the surface, as observed by SEM, can be seen in Fig. 10. The B_4C oxidizes and forms B_2O_3 (reaction (13)) which further reacts with MgO to form $Mg_3B_2O_6$

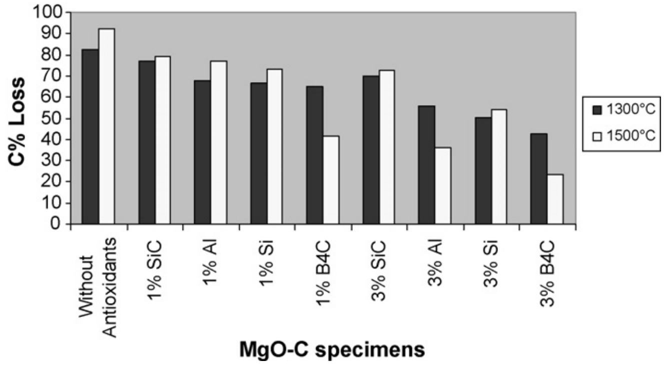

Fig. 11. Carbon losses % of MgO–C refractory specimens with/without antioxidants, oxidized for 6 h at 1300 °C and 1500 °C.

(reaction (14))

$$B_4C(s) + 6CO(g) = 2B_2O_3(l) + 7C(s) \qquad (13)$$

$$B_2O_3(l) + 3MgO(s) = Mg_3B_2O_6(s) \qquad (14)$$

It was observed that the B_4C was a much more effective antioxidant at 1500 °C, compared to 1300 °C. Because the $Mg_3B_2O_6$ is a very good oxygen barrier above its melting temperature (∼1360 °C). It is assumed that the liquid magnesium–borate fills up the open pores and forms a thin film layer on the brick surface at 1500 °C (Fig. 10), so that oxygen cannot diffuse into the refractory.

The changes in carbon loss for all types of specimens oxidized at 1300 °C and 1500 °C for 6 h are shown in Fig. 11.

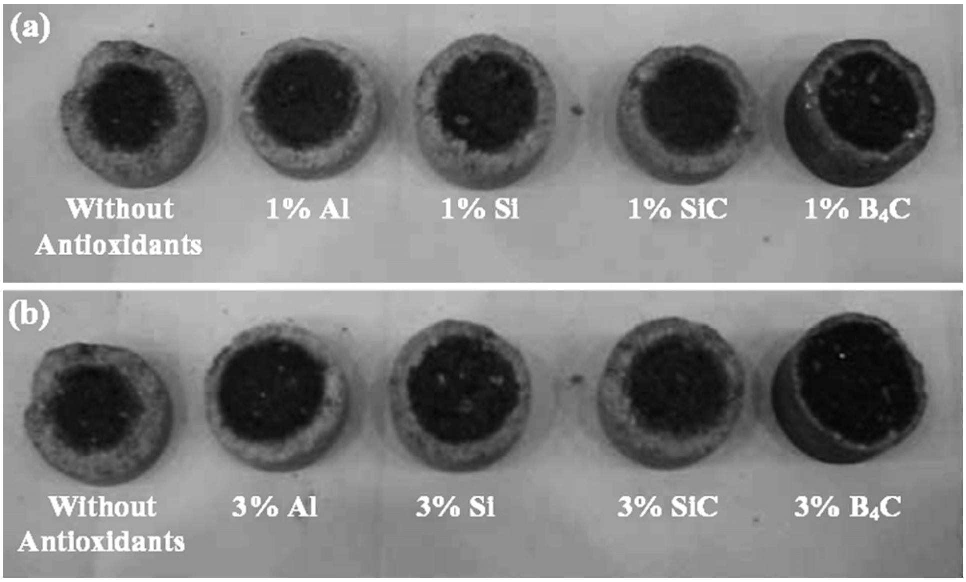

Fig. 12. Oxidized areas of MgO–C specimens after 6 h oxidation at 1300 °C: (a) with/without 1 wt.% antioxidant; (b) with/without 3 wt.% antioxidant.

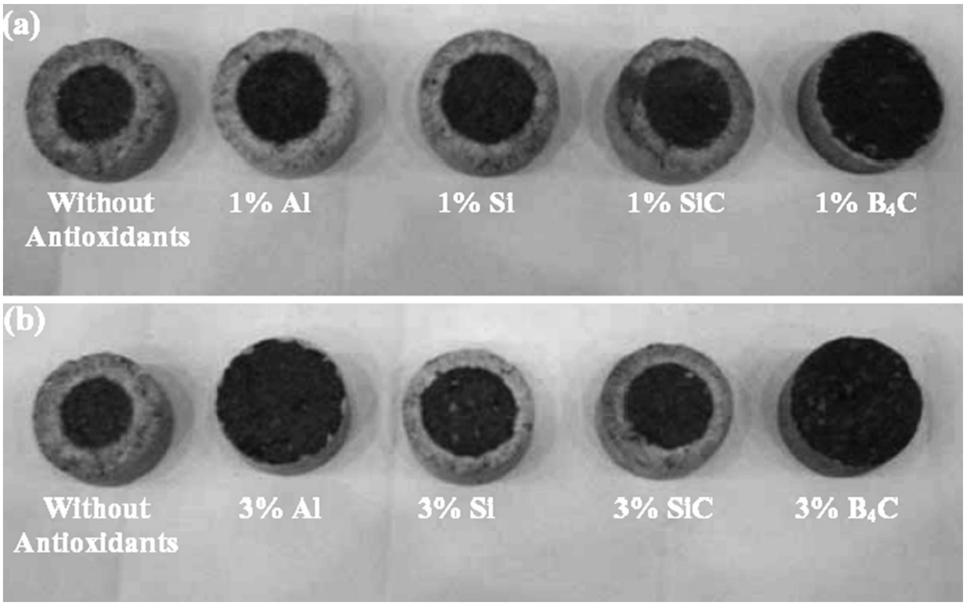

Fig. 13. Oxidized areas of MgO–C specimens after 6 h oxidation at 1500 °C: (a) with/without 1 wt.% antioxidant; (b) with/without 3 wt.% antioxidant.

Carbon losses of a number of specimens increased when the temperature was increased from 1300 °C to 1500 °C. On the other hand, carbon losses of the specimens with 1% and 3% B_4C addition and 3% Al addition considerably decreased at 1500 °C. The reason for this was that more spinel phase formed in the Al added specimens and the $Mg_3B_2O_6$ layer melted above 1360 °C in the B_4C added specimens. These phases slowed down the oxygen ingress by filling up the open pores and creating impermeable dense layers on the brick surface (Figs. 6 and 10). It can be seen that increasing the SiC content did not cause a decrease of carbon loss, as shown in Fig. 11. It was found that the oxidation resistance of the specimens with 3% Al addition was higher than for 3% Si addition at 1500 °C. However, the oxidation resistance of the specimens with 1% Si was higher than for specimens with 1% Al at 1500 °C. Similar results for 2–3% Si and Al additions at 1550 °C were found in a previous study [11].

Photographs of the cut section of the oxidized area of MgO–C specimens with and without antioxidants after 6 h oxidation test at 1300 °C and 1500 °C are shown in Figs. 12 and 13, respectively. The thickness of the oxidized areas supported the results given in Fig. 11. It can be seen that the 3% B_4C added MgO–C specimen oxidized at 1500 °C for 6 h had a very thin grey layer on the surface. This layer is the solidified $Mg_3B_2O_6$ phase which protected the brick structure from oxidation.

4. Conclusions

The oxidation resistances of MgO–C refractory bricks with 0%, 1% and 3% antioxidant (Al, Si, SiC and B_4C) additions have been compared by determining the carbon loss % of the brick specimens as a function of temperature (1300 °C and 1500 °C) and time (2 h, 4 h and 6 h). Phase changes and microstructural modifications were also investigated in the oxidized areas of the bricks and the main results are as follows:

1. The B_4C addition improved the oxidation resistances of the bricks and B_4C was the most effective antioxidant both at 1300 °C and 1500 °C. The carbon loss of the bricks containing other antioxidants was not much higher than for the B_4C added bricks at 1300 °C. The oxidation resistance values of Al, Si and B_4C containing bricks were similar at 1300 °C. However, there were considerable differences in the oxidation resistance at 1500 °C. The C loss of B_4C added bricks was very low, compared to other bricks. The B_4C had an excellent effect on the oxidation resistance of the MgO–C specimens oxidized at 1500 °C. The increase in the temperature from 1300 °C to considerably increased the oxidation resistance of B_4C containing refractory bricks because of the formation of the impermeable dense $Mg_3B_2O_6$ layer on the brick surface at 1500 °C.
2. The second most effective antioxidant was the Al. In the case of Al addition, spinel phases formed in the oxidized areas, which restricted the further oxygen ingress into the bricks. The 3% Al added bricks oxidized at 1500 °C showed the best results among the Al, Si and SiC containing bricks. The increase in the temperature and the metallic Al content caused a considerable increase of the spinel phase, protected the brick against oxidation, by filling up the open pores and forming a dense zone in the oxidized areas. Volume expansion and cracks were observed in MgO–C refractories containing 3% Al, oxidized at 1300 °C, but were rarely seen in the Al added specimens oxidized at 1500 °C. These physical changes were the results of hydration of Al_4C_3.
3. The Si addition was not as effective as B_4C at both temperatures. Besides, at 1300 °C the carbon loss of Si added bricks was lower than of the Al added bricks, so the Si added brick was better protected against oxidation compared to the Al added brick at 1300 °C. This was due to more forsterite phase formation at 1300 °C compared to the spinel formation at this temperature.
4. The SiC addition improved the oxidation resistances of the bricks compared to the bricks containing no antioxidants. The SiC was the least effective antioxidant at both temperatures because of the formation of a lower amount of forsterite phase in the SiC added bricks compared to the Si added bricks.

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