

The Influence of Metallic Antioxidants on some Critical Properties of Magnesia-carbon Refractories

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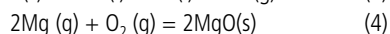
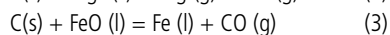
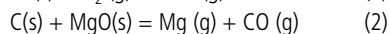
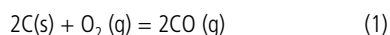
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MgO-C refractories received great attention in steel making process during the last decade. However, the oxidation of carbon at high temperature degrades its mechanical and corrosion resistance properties. Antioxidants like metal powder and carbides suppress carbon oxidation of MgO-C brick. Judicious selection of antioxidants optimizes the properties of MgO-C refractory. In the present work the effect of Al, Si and their combination in MgO-C refractory is studied. Phase development between 1100 °C to 1500 °C was evaluated through XRD analysis. The properties of the refractory were evaluated in terms of oxidation resistance, bulk density, apparent porosity, coked CCS, hot modulus of rupture and dynamic corrosion resistance test. Combined antioxidants develop forsterite and spinel phase and suppress oxidation of carbon. Both these phases are solid soluble with each other and refractory in nature. As a result the developed MgO-C brick leads to improved hot strength and corrosion resistance.

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 corrosion resistance and thermal shock resistance [1, 2]. Due to carbon's low wettability nature slag cannot wet MgO-C structure, for which it is able to give long service life. It is affirmed in some references that some properties of refractory materials, including thermal shock and chemical resistance, thermal conductivity and fracture toughness improve due to the presence of flake graphite [3]. Carbon in MgO-C refractories is oxidized in two ways: direct oxidation and indirect oxidation. Direct oxidation occurs below 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 [4]:



MgO-C refractories contain above 80 % MgO, 10–15 % graphite, a few percent of antioxidant and binders [5]. In this composite refractory the main problem is carbon's oxidizing behavior. Therefore to eradicate this problem various antioxidants are used. Al and Si powders are mostly used as antioxidants due to their low cost and effective protection from slag. Aluminium is one of the mostly used antioxidant, but it has hy-

dratation problems when Al_4C_3 forms, because this phase is easily hydrated even at room temperature [6, 7]. 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 [8]. B_4C , a carbide based antioxidant, reacts with CO to form B_2O_3 , which reacts with MgO to form low melting $3MgO \cdot B_2O_3$ (M_3B) [9]. M_3B is liquid at high temperature and blocks the open pores and/or covers the carbon surface to suppress its oxidation. Thermodynamic calculations predicted by Zhang *et al.* [10] show that between 1200–1500 °C B_4C reacts with CO from the atmosphere to form B_2O_3 which further reacts with MgO to create low melting (1350 °C) M_3B . The low temperature liquid formation due to M_3B will be detrimental to refractory corrosion resistance and hot strength. Yamaguchi *et al.* [11] investigated the effects of refractory oxides on the oxidation resistance of graphite. Al_2O_3 accelerates the

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Tab. 1 Granulometry composition of MgO-C refractory bricks

Granulometry [mass-%]	Compositions [mass-%]			
	0	A	S	AS
MgO -3+5 BS mesh	20	20	20	20
MgO -5+10 BS mesh	30	30	30	30
MgO -10+30 BS mesh	18	18	18	18
MgO -30+72 BS mesh	8	8	8	8
MgO -72 BS mesh	17	17	17	17
Graphite (99 % pure)	5	5	5	5
Al	-	2	-	1
Si	-	-	2	1
Binder (pitch)	4	4	4	4

Tab. 2 Slag composition for the rotary drum test

CaO	MgO	FeO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	MnO	C/S
49,6	10,3	17,5	17,4	0,9	1,7	1,1	2,9

oxidation of graphite. In contrast TiO₂, ZrO₂ and MgO inhibit the oxidation of graphite. According to them TiO₂ and ZrO₂ donate electrons to graphite and stabilize its structure. *Aneziris et al.* [12] depicted that the addition of TiO₂/Al in MgO-C refractory leads to formation of TiCN and TiC. These carbides improve the oxidation resistance, mechanical strength, abrasion resistance and thermal shock performance of the bonding matrix. SiC has been used to improve the corrosion resistance of MgO-C and it has been observed to retard the carbon oxidation although the mechanism has not been clearly specified [13]. The present study includes

high temperature phase evaluation of Al, Si and their combination in the MgO-C system. The final properties of MgO-C bricks with different antioxidants were correlated.

2 Experimental procedure

2.1 Preparation and characterization

MgO-C brick samples were developed from sea water magnesia. The MgO-C granulometry was selected on the basis of optimum packing density, which is given in Tab. 1. 5 % graphite, 2 % antioxidants along with 4 % pitch were added to the MgO composition.

The antioxidants used were Al [marked "A"], Si [marked "S"] and 1:1 combination of Al and Si [marked "AS"]. After the batch preparation proper mixing was done in a counter current *Eirich* mixer at 150 °C. The bricks of dimension 230 mm × 115 mm × 85 mm were fabricated in a hydraulic press at a pressure of 1400 kg/cm² and then tempered at 300 °C for 24 h.

2.2 Characterization of MgO-C bricks

The tempered bricks were cut into different shapes for characterization. For the oxidation resistance test samples were cut into 20 mm Ø × 20 mm height cylindrical shape and subjected to heat treatment in an electric muffle furnace at 1500 °C. The percent weight loss was calculated. For the physical testing like bulk density, apparent porosity and cold crushing strength samples were cut into 50 mm-cubes. For hot modulus of rupture (HMOR) test sample size was maintained at 25 mm × 25 mm × 150 mm and for corrosion testing the sample size was 40 mm × 40 mm × 160 mm. The bulk density (BD), apparent porosity (AP) and cold crushing strength (CCS) of the samples were performed both before and after coking. For coking, the samples were placed in alumina crucibles and covered with coke bed. Then they were subjected to firing at 1400 °C with a soaking period of 1 h. BD and AP of samples were measured by liquid displacement method in kerosene medium using *Archimedes* principle. HMOR test was done

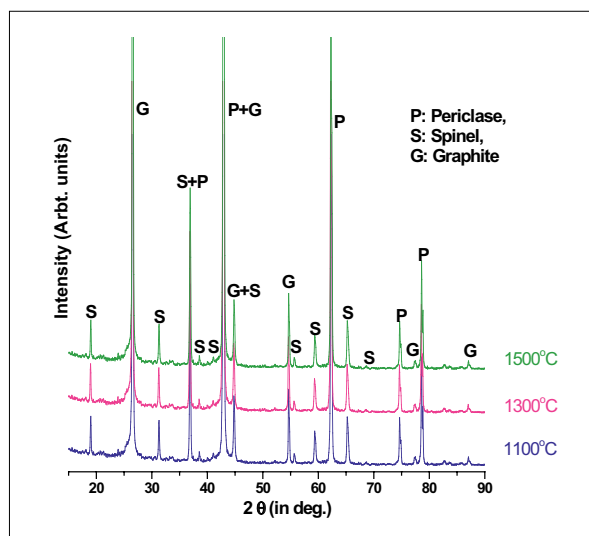


Fig. 1 XRD pattern of MgO-C sample with Al antioxidant after calcination at different temperatures

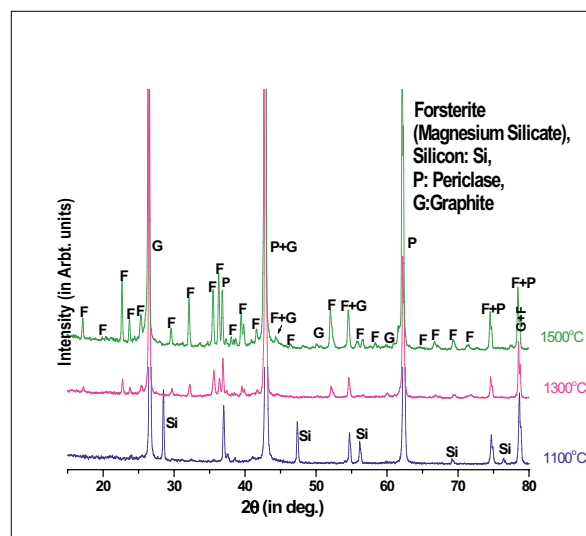


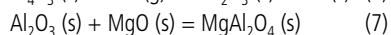
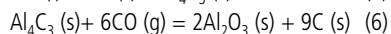
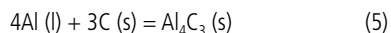
Fig. 2 XRD pattern of MgO-C sample with Si antioxidant after calcination at different temperatures

under three point loading after subjecting the samples to 1400 °C using an equipment of *Bysakh & Co/IN*. The corrosion resistance test was carried out by rotary drum dynamic method at 1650 °C for 30 min of each cycle. The slag used was highly basic in nature with a basicity (CaO : SiO₂) of 3. The slag composition is given in Tab. 2. The ratio of molten mild steel with synthetic slag was maintained at 10:1. After every cycle, the molten steel and slag was drained out. Total six cycles were performed for conducting the rotary drum test. The slag corrosion results were measured in terms of wear index and oxidizing layer in [mm]. This is a comparative test and the wear in [mm] was converted to an index system. The sample without any antioxidant was considered as 100. MgO-C comes in contact with slag an oxidized layer is formed. The layer thickness is measured in millimeter.

3 Results and discussion

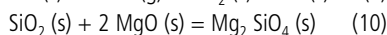
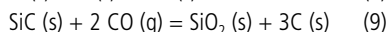
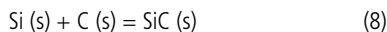
3.1 Phase development with antioxidants

The phase development with antioxidants estimated by XRD analysis is shown from Fig. 1 to Fig. 3. The XRD analysis of MgO-C sample with Al antioxidant (Fig. 1) shows that the main phases formed at high temperature are periclase and graphite along with spinel as minor constituent. The spinel formation takes place at 1100 °C and with rise of temperature the amount increases marginally. It has been indicated elsewhere [4] the spinel formation mechanism in MgO-C refractories. The Al oxidizes rapidly and forms a thin layer of Al₂O₃ layer. The Al melts at 660 °C and reacts with C to form Al₄C₃ which subsequently reacts with CO to form Al₂O₃ again. This Al₂O₃ further reacts with MgO to form MgAl₂O₄. All this reactions are given in the equations 5–7:



The XRD analysis of Si added MgO-C samples at different temperature between 1100–1500 °C is given in Fig. 2. It shows that apart from periclase and graphite the phase formed from the antioxidant is forsterite (Mg₂SiO₄). At 1100 °C significant amount of Si metal is present. The forsterite

formation starts at 1300 °C and increases significantly at 1500 °C. Si reacts with C to form SiC followed by formation of SiO₂ and subsequently MgSiO₄ as per the following reactions 8–10:



In case of both Al and Si added MgO-C samples, the phase formation at different temperature is given in Fig. 3. Here it is seen that both forsterite (Mg₂SiO₄) and spinel (MgAl₂O₄) phases are formed from the combined antioxidants. The occurred reactions were already described above for Si and Al antioxidants with MgO-C separately.

3.2 Oxidation resistance of MgO-C samples

The oxidation weight loss of MgO-C samples at 1500 °C is shown in Fig. 4. It shows that the weight loss for the sample without antioxidant is around 17 % where as the same for the antioxidants Al, Si, or their combination is between 13–14 %. The optimum oxidation resistance occurs for Si added MgO-C sample. It is assumed that for this sample, forsterite at high temperature fills up

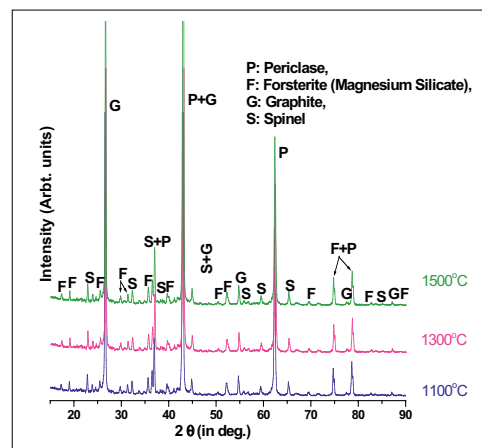


Fig. 3 XRD pattern of MgO-C sample with Al+Si antioxidant after calcination at different temperatures

the open pores and inhibits the oxygen ingress to the sample. Similarly for Al antioxidant, the in situ spinel formed blocks the pores and stops the penetration of oxygen. Thereby it improves the oxidation resistance.

3.3 Bulk density, apparent porosity and cold crushing strength

The bulk density and apparent porosity of tempered MgO-C samples are given in Fig. 5. It is seen that the bulk density of

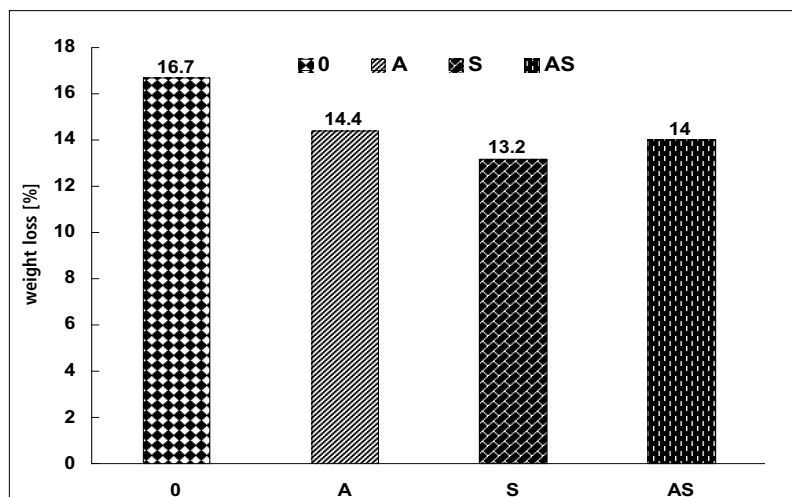


Fig. 4a Oxidation weight loss at 1500 °C of different MgO-C samples

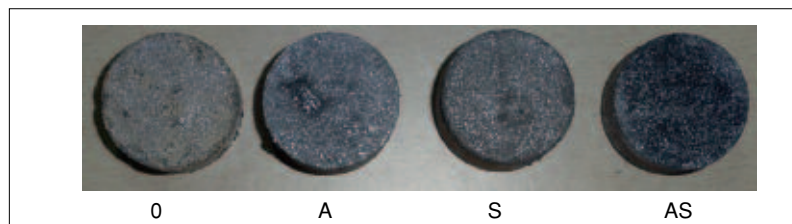


Fig. 4b MgO-C samples with different antioxidants after oxidation study at 1500 °C

all sample is between 3,0–3,05 g/cm³ and the apparent porosity is between 1,3–2,0 %. As such there is little variation of the BD and AP of the samples with and without antioxidants. However, when the samples were coked at 1400 °C there is a significant variation of coked porosity of

MgO-C samples (Fig. 6). The sample "0" without any antioxidant shows an apparent porosity of 18 %, whereas the samples with antioxidants (A, S, AS) show substantial drop of coked porosity between 10–12 %. It suggests that spinel and forsterite formation in antioxidant containing samples block the

pores and reduce the apparent porosity of the samples. The cold crushing strength (CCS) of the samples before and after coking is depicted in Fig. 7. The CCS ranges between 250–260 kg/cm² for all the samples. The sample "0" shows highest strength before coking. However the coked

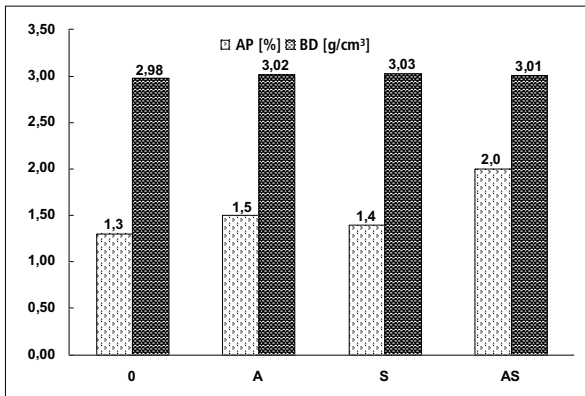


Fig. 5 Apparent porosity [%] and bulk density [g/cm³] of MgO-C samples with different antioxidants

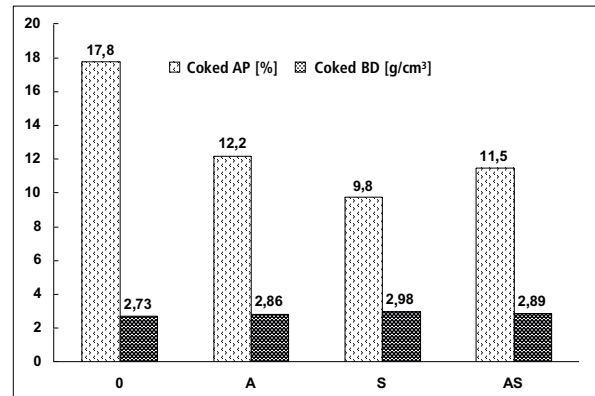


Fig. 6 Coked apparent porosity [%] and coked bulk density [g/cm³] of MgO-C samples with different antioxidants

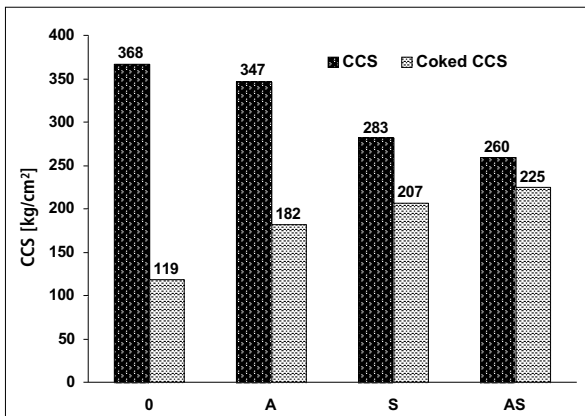


Fig. 7 CCS of MgO-C samples before and after coking at 1400 °C

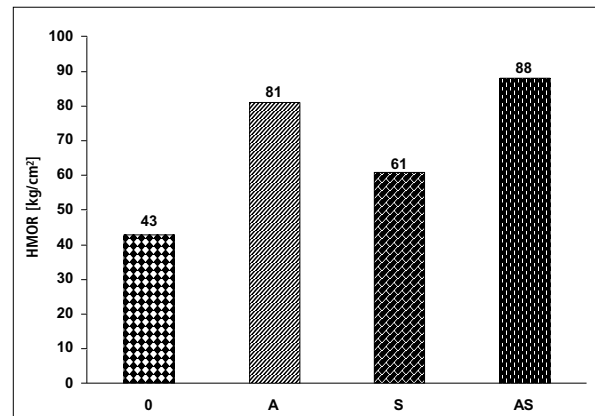


Fig. 8 HMOR of MgO-C samples at 1400 °C with different antioxidants

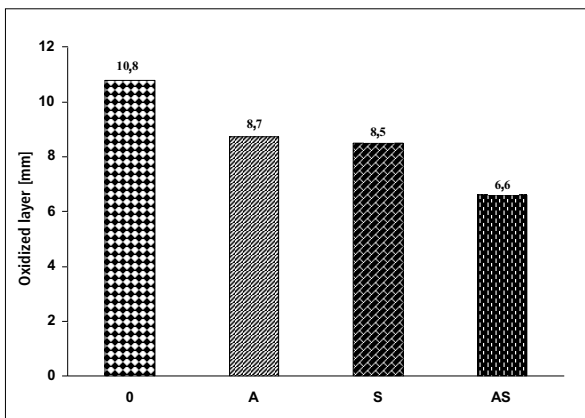


Fig. 9 Oxidized layer thickness of MgO-C samples with different antioxidants

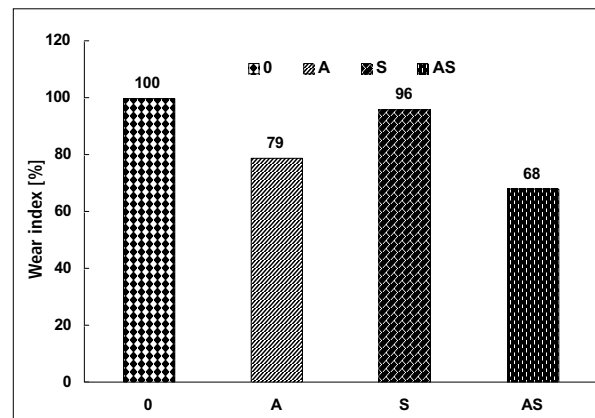


Fig. 10 Corrosion resistance of MgO-C sample with different antioxidants



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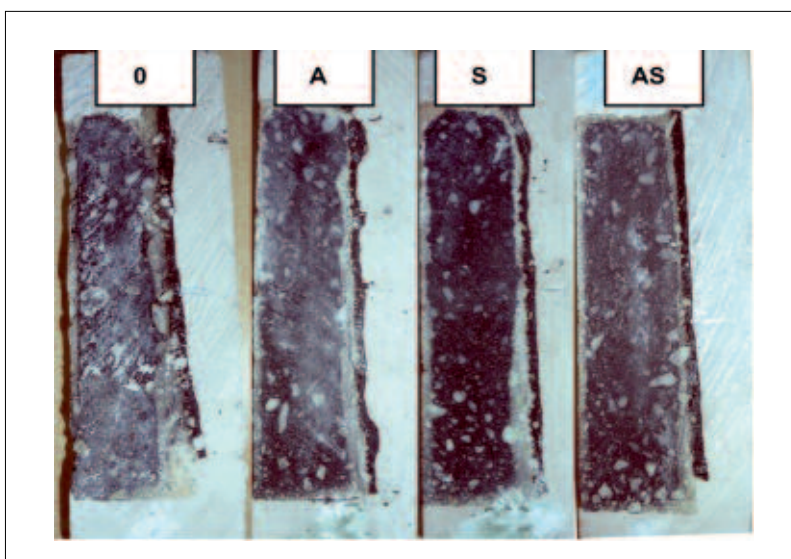


Fig. 11 Photos of MgO-C samples after corrosion test

CCS of sample "0" is minimum (119 kg/cm²) and for sample "AS" it is the highest (225 kg/cm²). The reduction in apparent porosity for the coked "AS" sample is responsible for improved strength. All the antioxidant containing samples show higher CCS than the "0" sample due to their lower coked porosity.

3.4 Hot modulus of rupture

The HMOR of MgO-C sample is given in Fig. 8. It reveals that the sample without antioxidants develops minimum strength. In this sample due to the absence of antioxidant carbon loss takes place at higher temperature and consequently the porosity increases at elevated temperature, which reduces the poor strength to 43 kg/cm². The HMOR of antioxidant containing MgO-C samples is between 60–88 kg/cm². In these samples the reason for good HMOR is due to formation of high melting bond phases like spinel (MgAl₂O₄) and forsterite (Mg₂SiO₄). These high melting phases remain in the matrix, act as a bond between the MgO grains and also reduce carbon loss by blocking the pores and lowering oxygen ingress. The sample "AS" shows highest HMOR of 88 kg/cm². In this sample, at high temperature both spinel and forsterite matrix phases form solid solution with each other [14] and improve the bond strength, which is responsible for highest HMOR of the MgO-C samples.

3.5 Slag corrosion resistance

Fig. 9–11 depict the slag corrosion test results conducted by the rotary drum method. They reveal sample "0" with minimum slag corrosion resistance with wear index of 100 % and 10,8 mm oxidized layer. Sample "AS" shows highest corrosion resistance with minimum wear index of 68 % and 6,6 mm oxidized layer. The additive suppresses the carbon oxidation through reducing oxygen ingress to the sample. Therefore due to non-wettability of carbon the slag infiltration is low and because magnesia is covered by carbon, minimum reaction with slag takes place.

4 Conclusions

MgO-C samples containing antioxidants like Al, Si and their combination cause better oxidation resistance compared to the samples without antioxidant. Spinel and/or forsterite formation at elevated temperature blocks the pores and is responsible for better oxidation resistance for "A", "S" and "AS" samples. The CCS for sample "0" is slightly better than for the antioxidants containing samples but the coked CCS and HMOR of sample "0" is considerably less compared to the other samples. The lower coked porosity of antioxidant containing samples along with high temperature melting bond phase formation is the reason for better coked CCS and HMOR of these samples. "AS" sample shows highest HMOR due to formation of

spinel and forsterite bond phases, which are soluble with each other and improve bond strength at elevated temperatures. Sample "AS" also shows maximum corrosion resistance because of minimum carbon loss and blocking of pores with the bond phases.

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