The Effect of Carbon Sources on the Thermal Shock Properties of MgO-C Refractories

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Abstract Thermal shock resistance of MgO-C refractories, which were used in the iron and steel industry, by incorporation of pyrolytic carbon black obtained by waste tire pyrolysis was investigated. The effect of porosity on the thermal shock resistance of those refractories as a function of carbon source (graphite or pyrolytic carbon black) was also examined in the current study. The microstructure and fracture surfaces were characterized using the Scanning Electron Microscopy (SEM). Experimental studies showed that refractories produced by the use of pyrolytic carbon black had higher amount of porosity and lower thermal shock resistance than refractories containing flake graphite.

Keywords Pyrolysis, Carbon Black, Waste Tire, MgO-C refractories, Thermal Shock

1. Introduction

Refractories are materials that are resistant to high temperature, and used as furnace linings for elevated temperature materials processing [1]. Although refractories are used in the glass melting, cement, and ceramic industries, the greatest user is the iron and steel industry [1].

The MgO-C (magnesia-carbon) bricks are widely used in the steel industry, electric arc furnaces, and basic furnaces because of its excellent resistance to erosion, corrosion and thermal shock, and hot strength [2-4].

Generally, carbon refractories contain a high amount of carbon content up to 12–20 wt%, and the main carbon source is flaky graphite due to its non-wetting nature and anisotropic properties, excellent corrosion resistance from molten metal and slag attack [4, 5]. The smaller the graphite flake size, the higher the strength of the body due

to the smaller defect size. Bending strength increases with increasing the graphite content in a carbon-bonded system [1].

However, the mechanical and thermal properties of the MgO-C are deteriorated due to the spalling and pore generation by the oxidation of graphite. Therefore, antioxidants are added into the MgO-C batches during fabrication in order to improve high temperature behavior and oxidation resistance [6]. Thus, various additives such as Si, Al, SiC, MgAl₂O₄, TiO₂, and B₄C powders are incorporated into MgO-C bricks to improve their resistance to oxidation. Among these additives, Si powder is the most important and widely used one [7].

In carbon-bonded oxide refractories, the aggregate phases, typically MgO, are held together by a complicated bond system derived from decomposition of tar/pitch or phenolic resin binders [1]. The phenolic resin phase remains as a three-dimensional network containing the refractory ingredients and imparts cold strength to the refractory body. This also reduces the elastic modulus of the refractory which is required for better thermal shock resistance [4].

Thermal shock can be defined as serious cracking in components subject to rapid changes in temperature. Carbon-bonded oxides have good thermal shock resistance due to the high thermal conductivity of carbon leading to reduced thermal gradients and a microstructure which is resistant to crack propagation [1].

Mechanical and thermal properties of MgO-C determined at room temperature emphasize that:

- these properties are mainly governed by the carbonaceous materials at room temperature
- the carbon content presents in both the binder and the graphite and contributes to achieve a higher resistance to initiation of cracks due to thermal shock.
- higher content of graphite presents greater deformation at the fracture level.

- higher porosity and a higher percentage of sintered magnesia with the quality of the binder could reduce the firebrick's fracture strength at room temperature [8].

Waste tires are increasingly becoming an important environmental problem. The current main routes for the management of waste tires are energy recovery, material recycling, retreading, and export. Pyrolysis is an alternative method with the possibility for the recovery of valuable products from used tires [9]. The pyrolysis or thermal degradation under inert conditions of waste tyres gives away to three main products; gases, tyre pyrolysis oil (TPO), and residual pyrolysis char [10]. The inorganic components (mainly steel) and mineral fillers remain as relatively unaltered solid residues which are referred as Pyrolytic Carbon Black [11].

In the present study, thermal shock resistance of MgO-C refractories produced by either flake graphite or pyrolytic carbon black obtained from the waste tire pyrolysis and used as carbon sources for MgO-C refractories were investigated as a function of their porosities and densities.

2. Materials and Methods

In this study, commercially fused Magnesia and flake graphite were used as a raw materials. Also, the other raw material used as a carbon source for magnesia-carbon (MgO-C) refractories was pyrolytic carbon black.

Pyrolytic carbon black was produced by pyrolysis of waste tire at 500°C with 15°C/min heating rate and 0.5 litre/min N₂ flow rate. The particle size of waste tire was between about 70 µm and 850 µm. After pyrolysis, that solid product was extracted twice by 37% HCl and 65% HNO₃ acid mixtures with 1:1 volume percentage at 175°C in order to provide sulphur removal. After these steps, the carbon black was extracted by 1N H₂SO₄ and 10N NaOH solutions at 60°C with 1:1 volume percentage in order to decrease the ash content. After the improvement, the amount of sulphur was reduced from 8.16 to 2.02 and the amount of ash decreased from 0.64 to 0.49.

Phenolic resin as binder, antioxidant, Novalac, and Hexamine were also used in refractory prescriptions given in Table 1. Either 50mm×50mm×50mm

(width×length×height) square prism samples or 25mm×25mm×150mm (width×thickness×length) in the form of bar samples were shaped by applying pressure of 100 MPa. The shaped samples were tempered in Nabertherm N11/R ash furnace at 250 °C for 3 hours with of 5°C/min heating rate.

The amount of porosity in a material affects the mechanical properties as strength and elasticity, thermal properties, and corrosion resistance. Porosity and density measurements were based on the Archimedes principle in the current study.

For the thermal shock tests, five pieces for each composition produced in the forms of either 50mm×50mm×50mm or 25mm×25mm×150mm square prisms were used. Before the test, those samples were put into chamotte refractory container in order to prevent oxidation and closed with graphite. Then they were heated up to 1000°C with 10°C/min heating rate in Nabertherm N11/R ash furnace and held at 1000°C for 10 minutes, thrown into cold water, and quenched.

Before and after the thermal shock test at 1000 °C:

- Cold crushing strength (CCS) test was applied to five pieces of 50mm×50mm×50mm square prism samples for each material by Liya compression testing machine. 200-ton loads were applied with 4 kN/sec rate, and CCS (MPa) was calculated by dividing the load (N) by the cross-sectional area (mm²).
- 3-point bending test was performed on five pieces of 25mm×25mm×150mm bar samples by Shimadzu AGS-X device according to ASTM C1161-90, L=125 mm and the loading speed was set to be 0,15 MPa/s. The 3-point bending strength and elastic modulus were determined using the following equations where P is the fracture load (N), L is the distance between supports (m), W is the width of the sample (m), D is the thickness of the sample (m), and m is the slope of the stress-strain (σ-E) curve (N / m) [12]:

$$\text{Strength: } \sigma = \frac{3}{2} * \frac{P.L}{WD^2}$$

$$\text{Elastic Modulus: } E = \frac{L^3}{4 * W * D^3} * m$$

Table 1. Prescriptions of MgO-C refractories

Composition	1-4 mm MgO(%)	0-1 mm MgO (%)	Powder (<63µ) MgO (%)	Flake Graphite (%)	Pyrolytic Carbon Black (%)
C1	50	30	10	10	0
C2	50	30	10	0	10
C3	50	30	10	6.66	3.33

Then the strength ratio values for each material which means the percentage of retained strength were calculated by dividing the strengths after the thermal shock test by the strengths before thermal shock test.

In order to examine the microstructure by the Scanning Electron Microscopy (SEM), the samples were cut into 20mm×20mm×20mm for each refractory composition given in Table 1 with the MAC Allister ceramic cutting device. The cut samples were cold molded. 20 ml of polyester were mixed with 1 ml of curing agent for a minute, then 1 ml of accelerator was added, and the mixture was stirred for another minute. The resin was poured onto the sample in a mold and cold molded for 30 minutes. Then samples were polished with Metkon polishing machine using 150, 300, 600, and 1200 grits for five minutes, respectively.

Characterization microstructures of those polished samples were performed by the SEM-Mapping analysis with backscattered electron images at 1000x magnification. Also, elemental analysis of those refractories was examined by Energy Dispersive X-Ray Analysis (EDX).

For fracture surface characterization before and after thermal shock, the 25mm×25mm×150mm bar samples subjected to 3-point bending test were cut and cold molded as mentioned above. Fracture surfaces of samples were characterized by the SEM with secondary electron images at 1000x magnification.

3. Results and Discussion

3.1. Porosities and Densities of MgO-C Refractories

(a)

(b)

Figure 1. a) Porosity and b) density values of MgO-C refractories

The density and porosity graphs of MgO-C refractories produced by incorporation of graphite and pyrolytic carbon black are given in Figure 1.

As the amount of porosity in those MgO-C refractories decreased, the density values increased. The C1 sample obtained with graphite and phenolic resin had the highest density value. The increase in the amount of pyrolytic carbon black reduced the density values of the produced compositions. The lowest density and the highest porosity were observed in the C2 composition produced by only pyrolytic carbon black as a carbon source.

3.2. Mechanical Behaviours of MgO-C Refractories before Thermal Shock Test

The Cold Crushing Strength (CCS) graphs for the square prism shaped compositions are given in Figure 2.

Figure 2. Cold Crushing Strength (CCS) for MgO-C refractories before thermal shock test

It was observed that the higher strength values of C1 composition were produced by incorporation of graphite and phenolic resin. When the CCS values were compared, the CCS value decreased as the amount of pyrolytic solids increased and graphite decreased. Increasing the density value and decreasing the porosity value caused an increase in the CCS, and thus it was observed that the porosity had a negative effect on the CCS.

Figure 3. 3-point bending strength values of MgO-C refractories

The 3-point bending strength graphs for the bar shaped compositions are given in Figure 3.

Similar results were obtained with CCS. While the bending strength of K1 composition produced with resin and graphite admixtures had the highest bending strength

value as similar to the CCS value, 3-point bending strength values decreased with pyrolytic carbon black addition.

Elastic modulus of those MgO-C refractories obtained by the 3-point bending test are given in Figure 4.

Figure 4. Elastic Modulus of MgO-C refractories obtained by 3-point bending test

While the elastic modulus values of the MgO-C materials including graphite were high, the elastic modulus values of the MgO-C refractory compositions produced with the pyrolytic solid were lower. The highest elastic modulus value was reached in the C1 composition and the lowest elastic modulus was determined in the C2 material.

It is thought that the plate structure of graphite and therefore the void in the structure of the pyrolytic carbon black reduced the density of the refractories. The C1 refractory which had a higher packing density and higher strength values than other compositions was produced using graphite and resin. The C1 specimen had better bonding due to the larger surface area of flake graphite, together with good wetting of the resin entering between the flake graphite plates. As a result, higher energy was required to break those plates.

3.3. The Results of Thermal Shock Test

CCS (Figure 5) and 3-point bending test (Figure 6, 7) were applied to MgO-C refractories after thermal shock test. Then for each specimen strength ratios, which means that how much its strength could be protected, were calculated by dividing those strengths by the strengths before thermal shock test (Figure 8, 9).

Figure 5. CCS of MgO-C refractories after thermal shock test

Figure 6. 3-point bending strength of MgO-C refractories after thermal shock test

Figure 7. Elastic modulus of MgO-C refractories after thermal shock test

The C1 composition produced by the resin and graphite among the MgO-C refractory specimens subjected to the thermal shock test had the highest CCS, 3-point bending strength, and elastic modulus values as a result of both the compression and 3-point bending tests. It was observed that both strength values of all compositions decreased after thermal shock test. It is thought that pre-existing cracks and newly formed cracks after thermal shock reduced the strength values.

When the strength ratio values of MgO-C refractory materials in different compositions were examined (Figure 8, 9), the C1 refractory material with the highest initial strength values either before or after thermal shock test at 1000°C maintained approximately 50% of its strength after thermal shock. Although the initial strength values were lower than the C1, it was observed that the C2 and the C3 refractories by incorporation of pyrolytic carbon black had generally higher strength ratio values.

Figure 8. According to CCS test, the strength ratio values of thermally shocked MgO-C refractories

Figure 9. According to 3-point bending test, the strength ratio values of thermally shocked MgO-C refractories

3.4. Microstructure and Fracture Surface Characterizations

According to microstructural image of the C1 refractory material produced by adding graphite and resin, graphite (dark gray) and MgO grains (gray) were well-bonded together, created a more dense structure than refractories produced by pyrolytic carbon addition. Black regions indicated porosities, and white regions indicated the compounds of Al, Si, and Ca coming as impurities in magnesia (Figure 10).

Figure 10. a) Microstructural image recorded with backscattered electrons (1000x), b) EDX analysis and c) colorized BSE image of R1 refractory material and the element distributions of C1 refractory material d) Mg, e) C, f) O, g) Fe, h) Al, i) Si, j) Ca

In C2 refractory material produced by only pyrolytic carbon black as a carbon source had the highest amount of porosity, therefore the lowest density was reached in this material (Figure 11). In the C3 refractory material in which either flake graphite or pyrolytic carbon

black was used, number of porosities was higher than the C1 and lower than the C2 refractory materials (Figure 12).

According to the results of the EDX analysis (Figure 10-b, 11-b, and 12-b), it was observed that the amounts of MgO and C were high in the C1 sample. For the C2 and C3, the amount of carbon became to increase due to incorporation of pyrolytic carbon black. Moreover, the proportions of impurities in MgO such as Si, Al, and Ca increased while the amount of MgO decreased.

Figure 11. a) Microstructural image recorded with backscattered electrons (1000x), b) EDX analysis and c) colorized BSE image of R1 refractory material and the element distributions of C2 refractory material d) Mg, e) C, f) O, g) Fe, h) Al, i) Si, and j) Ca

Figure 12. a) Microstructural image recorded with backscattered electrons (1000x), b) EDX analysis and c) colorized BSE image of R1 refractory material and the element distributions of C3 refractory material d) Mg, e) C, f) O, g) Fe, h) Al, i) Si, and j) Ca

According to the fracture surface images of the C1 refractory materials given in Figure 13, either before or after the thermal shock test, the C1 refractory material had predominantly transgranular and also intergranular cracks in its structure. Due to this type of fracture character, the C1 material had relatively high resistance to crack initiation while it had lower resistance to cracking propagation.

In the C2 and C3 materials, predominantly transgranular cracks were obtained before the thermal shock test (Figure 14, 15). After the thermal shock test, fracture type turned into either intergranular or

transgranular crack types for the C2 and C3 refractories (Figure 14, 15).

The change in crack types as transgranular to either transgranular or intergranular types in the C2 and C3 refractory materials produced by incorporation of pyrolytic carbon black indicated higher strength ratios (Figure 8, 9). The presence of porosities, intergranular fracture type as well as transgranular fracture, is considered to be an important factor affecting the change in mechanical properties obtained as a function of thermal shock at high temperature.

Figure 13. Fracture surface images of C1 recorded by secondary electrons (1000x): a) before, b) after thermal shock test

Figure 14. Fracture surface images of C2 recorded by secondary electrons (1000x): a) before, b) after thermal shock test

Figure 15. Fracture surface images of C3 recorded by secondary electrons (1000x): a) before, b) after thermal shock test

Properties of the MgO-C refractory samples either before or after the thermal shock test at 1000 °C are given in Table 2. The C1 had the highest density, CCS, bending strength, and elastic modulus values before and after thermal shock test.

Moreover, the C1 had the highest strength values obtained by either CCS or 3-point bending tests.

Table 2. Properties of MgO-C refractory samples either before or after thermal shock test at 1000 °C

Properties		Compositions		
		C1	C2	C3
Before Thermal Shock	Density (g/cm ³)	2.89	2.43	2.74
	Porosity (%)	1.37	13.13	4.18
	CCS(MPa)	102.5	1.,85	39.99
	Elastic Modulus (GPa)	13.12	0.38	3.52
	3 Point Bending Strenght (MPa)	28.62	1.76	5.77
After Thermal Shock	Density (g/cm ³)	2.83	2.36	2.61
	Porosity (%)	7.23	19.83	14.32
	CCS(MPa)	51.59	10.67	30.48
	Elastic Modulus (GPa)	2.97	0.25	1.42
	3 Point Bending Strenght (MPa)	14.48	0.67	2.86
CCS Strength Ratio (%)		0.5	0.6	0.76
3 Point Strength Ratio (%)		0.47	0.38	0.5

4. Conclusions

The C1 sample obtained by graphite and resin had the highest density, CCS, 3-point bending strength, and elastic modulus values. The density values began to decrease, and open porosities increased in the compositions by the pyrolytic carbon black addition. Before the thermal shock test, it was observed that CCS and 3-bending strength values increased as the open porosity values decreased, and thus strength was affected inversely by the porosity for all compositions. It was observed that both strength values of all compositions decreased after the thermal shock test. It was thought that pre-existing cracks and newly formed cracks after thermal shock reduced the strength values. The C2 and C3 refractories had a higher strength ratio due to the presence of either intergranular fracture or transgranular crack types after thermal shock test. Strength was also affected by the carbon source for all compositions.

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