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An Investigation of the Effect of Pyrolytic Liquid Obtained From Waste Tire on the Corrosion Behaviours of MgO-C Refractories

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ABSTRACT

In this study, corrosion behaviours of MgO-C refractories by incorporating different binders as phenolic resin and pyrolytic liquid obtained by waste tire pyrolysis were investigated. Moreover, the effect of porosity on the corrosion resistance of those refractories according to types of binders was examined. The microstructures of corroded MgO-C refractories were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analyser (EDX). The results showed that K1 refractory produced with only phenolic resin had the lowest amount of porosity (1.37%) and K2 refractory produced by the use of pyrolytic liquid had the highest amount of porosity (5.37%) due to lower binder effect of pyrolytic liquid. According to the results, the refractories produced by the use of pyrolytic liquid had higher porosity and lower corrosion resistance than that of refractories produced by incorporation of phenolic resin as a binder.

Keywords:
Waste tire; Pyrolytic liquid; Binder; MgO-C refractory; Corrosion

INTRODUCTION

Magnesia-carbon (MgO-C) refractories contain about 12–18% total carbon. The primary source of carbon in magnesia-carbon refractories is graphite. Magnesia–carbon (MgO–C) refractory is extensively used in basic furnace and electric arc furnace due to its desirable properties that are obtained by the presence of graphite used as a carbon source. Some of the desirable properties of MgO-C refractories are: high refractoriness, no low melting phase occurs between MgO and C, high melting point, the excellent thermal shock resistance, low thermal expansion, high thermal conductivity, low elasticity, high corrosion resistance by less slag penetration and wettability with a molten metal. However, the spalling and pore generation by the oxidiation of graphite caused deteriorations in mechanical and thermal properties of the MgO–C refractories [1-3].

These refractories have excellent corrosion resistance due to the low wettability of carbon by the slag, so the service life of the MgO–C bricks increases. However, after the oxidation of carbon at high temperatures, the slag can penetrate into the structure of magnesia–carbon brick because it is destroyed. Therefore, antioxidants such as metals, compounds or alloys are added to prevent oxidation of carbon [4].

Corrosion can be identified as debonding and the destruction of the bond liquid glass together with the chemical dissolution of all phases of the refractory, subsequent physical fragmentation [5].

The vast quantity of waste tires is a serious environmental problem of our age. In the European Union countries, the amount of used tyres was estimated at 3.6 million tonnes in 2013 and about 4 million tonnes of used tyres were generated in the U.S. in 2015. A systematic approach for the recycling and reuse of waste tyres should be handled around the world because they are a source of great potential for valuable chemicals, materials, and fuels [6-7].

Waste tyres are primarily made up of carbon black, natural rubber (NR), and synthetic rubber (SR) [8]. Pyrolysis is a useful method for the recovery of waste tyres to produce three potentially useful products (oil, gas, and char) [9]. The pyrolytic oil can be used directly or added to fuels. The gas has enough energy for the pyrolysis process itself, and the solid product (char) can be used as a solid fuel, carbon black or upgraded to produce activated carbon or other carbon products [10].

Although phenolic resin binder is used in very low amounts, it is a very important ingredient for the refractory body. Due to its sticky structure, it holds raw materials together. Through the curing process which is usually below 300 °C, the binder in the shaped refractory is transformed into a solid state with a macromolcular network structure. In higher temperatures at which refractory is fired, the cured phenolic resin binder is transformed into a rigid carbon skeleton [11]. Waste tyre derived pyrolytic liquid is a complex mixture of aromatic and aliphatic compounds and it can be a carbon source for the refractory body.

In the present study, the effect of pyrolytic liquid obtained by waste tire pyrolysis on corrosion behaviours of the MgO-C refractories was investigated. The refractory samples were produced by incorporating two different binders as phenolic resin and pyrolytic liquid. The effect of porosity on the corrosion resistance of those refractories according to types of binders was examined. The microstructures of corroded MgO-C refractories were characterized by Scanning Electron Microscopy (SEM- FEI NOVANANOSEM 650) and Energy Dispersive X-Ray Analyser (EDX - FEI NOVANANOSEM 650).

MATERIAL AND EXPERIMENTAL PROCEDURE

In this study, MgO-C refractories were produced by incorporating flake graphite (10% by weight) into fused MgO. Moreover, phenolic resin and pyroytic liquid were used as binders. Pyrolytic liquid was produced by pyrolysis of waste tire whose particle sizes were between about 70 µm and 850 µm, at 500°C with 15°C/min heating rate, and 0,5 litre/min N_2 flow rate. Density, viscosity, pH, and sulphur content values of that liquid were measured as 0.95 g/ml, 45.2 cST, 6.7, and 1.56%, respectively. After pyrolysis, this liquid product was extracted twice by 10% H_2SO_4 acid in order to provide sulphur removal. After this improvement, the density, viscosity, pH, and sulphur values were measured as 0.98 g/ml, 351.4 cST, 5.8, and %1.08, respectively.

Raw materials, antioxidant (metallic Al) , novalac (phenolfomaldehyde resin), hexamine ($(CH_2)_6N_4$), and binder solutions (totally 2 wt.%) were mixed, square prism shaped refractories (50 mm×50 mm×50 mm) were produced by applying ~ 100 MPa pressure. Graphite was used as a carbon source in all refractories. Phenolic resin in K1, only pyrolytic liquid in K2, and either phenolic resin or pyrolytic liquid in K3 were used as binder(s). Then those shaped samples were tempered in Nabertherm N11/R ash furnace at 250 °C for 3 hours with of 5°C/min heating rate.

Table 1. XRF analysis of blast furnace slag

Oxide	(%)
SiO_2	37.92
CaO	34.90
Al_2O_3	11.75
MgO	7.92
MnO	2.06
Fe_2O_3	1.58
SO_3	1.20
TiO_2	0.85
K_2O	0.76
BaO	0.38
Na_2O	0.33
ZrO_2	0.06
SrO	0.06
CuO	0.03
P_2O_5	0.02
Loss of ignition	0.18

Three parts were cut and, waited in water about 24 hours in room temperature for each in order to determine the density and open porosity values by Archimedes principles.

In order to determine the interaction of the blast furnace slag with MgO-C composite refractory materials, corrosion tests were performed in two ways according to the ASTM C621-09 standard:

- In the first one, the hole (diameter: ~ 20 mm, depth: ~ 20 mm) was drilled on top of 50 mm×50 mm×50 mm square prism shaped refractories. Then, 4 g (D100 < 63 µm) blast furnace slag was put into those holes and, static corrosion tests were performed for 3 hours at 1450 °C under argon atmosphere using 10 °C/min of heating and cooling rates.

Using the SEM-Mapping analysis with backscattered electron images at 1000x magnification, characterization of the microstructures of those corroded samples was performed in the regions including: i) Zone 1 (close to slag) where the blast furnace slag started to penetrate into refractories, ii) Zone 2 that was the middle region between the slag and refractory, and iii) Zone 3 (close to refractory) where the blast furnace slag penetration into refractories was finished. Furthermore, elemental analysis was examined by Energy Dispersive X-Ray Analysis (EDX).

- Secondly, 4 g blast furnace slag was placed at the

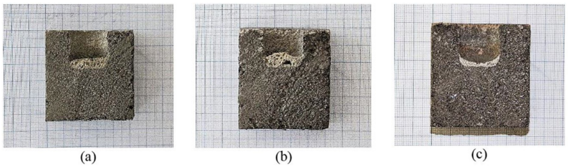

Figure 1. The cross-sectional view of 5cm×5cm×5cm square prism shaped and corroded MgO-C refractories: a) K1, b) K2 and c) K3

centre of the surfaces of refractory materials whose dimensions were 10cm×10cm×2cm (length×width×height) in order to determine the spreading area of slag on the refractory surfaces. Then, the static corrosion tests were conducted at 1450 °C for 3 hours with 10 °C/min heating and cooling rates under argon atmosphere. The measurements of spreading areas were carried out by Image J program [12].

XRF chemical analysis of the blast furnace slag used in this study were given in Table 1.

RESULTS AND DISCUSSION

Images of 5cm×5cm×5cm square prism shaped and corroded MgO-C refractory samples at 1450 °C in argon atmosphere are given in Figure. I. Different binder types were used in MgO-C refractories: only phenolic resin in the K1, only pyrolytic liquid in K2 and either phenolic resin or pyrolytic liquid in K3. Graphite was used as a carbon source in all refractory samples. The light coloured area seen in the cross-sectional view of all refractory materials indicated the slag material (Fig. 1).

The penetration distance of the blast furnace slag into the refractory could not be measured due to the lack of colour contrast in the images (Fig. 1).

Microstructures of those materials were analyzed by the SEM, and also, the corrosion effects were interpreted according to EDX analysis, elemental distributions, and microstructural changes (Fig.2).

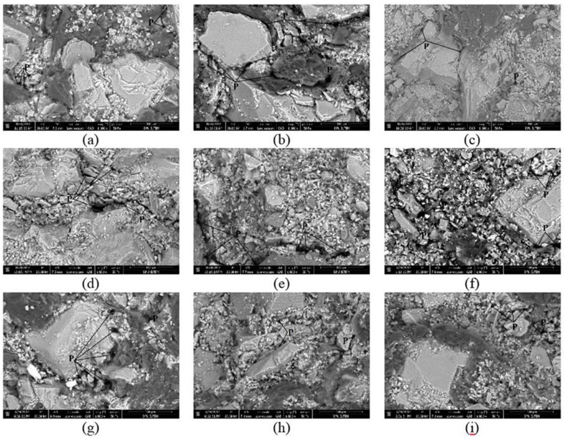

Figure 2. Back scattered electron images of corroded MgO-C refractories (1000×) a)K1-Zone1, b)K1- Zone 2, c)K1- Zone 3, d)K2- Zone 1, e)K2- Zone 2, f)K2- Zone 3, g)K3- Zone 1, h)K3- Zone 2, i)K3- Zone 3, P:Pores

Table 2. SEM/EDX analysis of MgO-C refractories

Composition		Mg	C	O	Ca	Si	Al	Fe
K1	Zone 1	45	25	7	10	6	3	3
	Zone 2	51	21	8	8	5	4	3
	Zone 3	62	13	9	6	3	5	2
K2	Zone 1	35	13	11	14	21	5	1
	Zone 2	43	11	12	13	16	4	1
	Zone 3	69	9	11	3	3	4	1
K3	Zone 1	43	23	7	13	9	4	0
	Zone 2	50	17	11	9	7	3	2
	Zone 3	59	15	9	5	3	7	2

According to EDX analysis results (Table 2), for K1 refractory material generally the amounts of Ca, Si, and Al were higher in Zone1 than other zones. More amount of carbon and less amount of magnesia in the regions near the slag were observed in K2 than K1. It was thought that magnesite material more and more dissolved in the slag for K2 refractory material and also, it was more affected by the slag due to slag penetration into the porosities. Also, similar to K1, in general, the amounts of Ca, Si, and Al were high in Zone1 according to EDX analysis results (Table 2) for K2 and K3 refractories. Those results confirmed the result of the chemical analysis of the slag (Table 1).

When going to the Zone3, which was close the refractory, from Zone1, which was close to slag, the amount of Mg was generally increased and the amounts of C, Ca and Si were generally decreased for the K1 sample (Figure 2 and Table 2). Ca could be either impurity in MgO or at high amount in the slag. Mg element referred to the periclase phase which was the main matrix of refractories. It was thought that more magnesite grains were dissolved by the influence of the slag than carbon grains, and then the amount of carbon increased in percentage in Zone1. Furthermore, it was seen that the slag concentrated especially on the thin and medium sized MgO grains and affected those grains (Fig. 2a-2c).

In the microstructure images of K1, little amounts of Ca, Si, and Al elements, which were at high amount in the slag, located in regions where the dark gray carbon grains were present. It was also seen that there were more amounts of porosities in the structure due to the dissolution of the magnesite grains into the slag for Zone1 (close to slag) and Zone2 (between refractory and slag) than the Zone3 (close to refractory).

K2 refractory material that was produced by incorporation of pyrolytic liquid as a binder had more porosities and microcracks because the pyrolytic liquid could not bind the structure as the resin did. Also, Ca and Si elements (indicated with light colour), which were at high amount in slag, were also observed in the graphite regions meaning that refractory was affected by slag more than K1 (Fig. 2d-2f). The slag concentration especially on the thin and medium sized MgO grains and its influence on those grains were observed.

Generally MgO contents decreased whereas slag phase content increased similar to results of the work of Zhang and Lee. Oxidation of carbon and dissolution of MgO in the slag were the main factors for corrosion of MgO–C refractories. [13].

According to SEM microstructure images of K3 after corrosion test (Fig. 2g-2i), either thin or medium sized or bigger sized magnesia grains were affected by slag, and also microcracks were observed. The slag located in porosities and grain boundaries of magnesite and carbon grains in the structure.

When K2 and K3 materials were examined after corrosion test, from Zone1, which was close to slag, to Zone3, which was close the refractory, the amounts of Mg was generally increased, and the amounts of C, Ca, and Si were generally decreased. In this case, when the graphite was used as a carbon source, the slag mainly affected the magnesite grains.

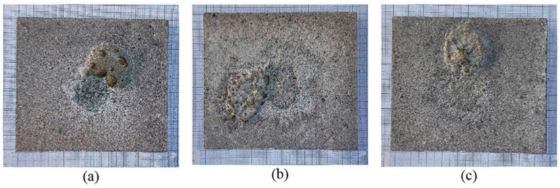
(a) (b) (c)

Figure 3. Images of spreading area of slag on the surfaces of 10cm×10cm×2cm (length×width×height) shaped and corroded refractory materials a) K1, b) K2 and c) K3

Images of refractory materials subjected to corrosion tests in argon atmosphere in order to determine the spreading areas of blast furnace slag on refractory surfaces are given in Fig. 3.

In general, the spreading area values of slag on the refractory surfaces decreased as the amount of porosities in the refractory materials decreased (Fig. 3 and Fig. 4). As the decrease of the amount of porosity and the pore size leaded to the increase of the corrosion resistance, and it was determined that porosity was an important parameter affecting the corrosion resistance. Also, for refractory materials, which were produced by incorporation of phenolic resin as a binder, more dense structure was formed due to better binding property of phenolic resin.

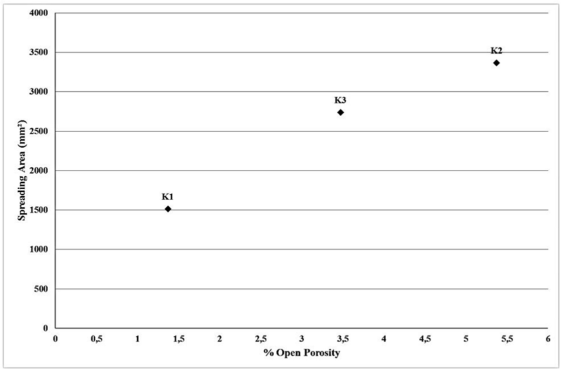

Figure 4. The spreading area of slag on the surfaces of the corroded refractory materials as a function of open porosities

CONCLUSION

When pyrolytic liquid was used in MgO-C refractories as a binder, microcracks and porosities were formed in the structure because of its less binding property than that of resin.

When the spreading areas of slag on the refractory surfaces were examined, it was found that as the amount of porosity in the refractory materials decreased, the spreading area values of the slag on the refractory surfaces decreased, as well.

In the present study, the use of pyrolytic liquid product alone could not show a sufficient effect on corrosion resistance of MgO-C refractories. Therefore, it was suggested to use pyrolytic liquid by mixing it with phenolic resin at different ratios.

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