Effects of Ferrosilicon Addition and Formation of Insitu SiC Nano-whiskers on MgO-C Refractories

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Abstract

Nowadays, SiC is one of the refractory materials which is used widespread because of its unique properties like structural stability in high temperatures. SiC nano whiskers are important in reinforcement of different kinds of composites like ceramic base materials, thanks to their outstanding mechanical, thermal, and chemical properties like low expansion coefficient, high thermal resistant, high elastic coefficient, low density, and high resistant to oxidation. The most important problem of MgO-C refractories is carbon oxidation in high temperatures, resulting in the porosity and loss of strength. Using SiC as an antioxidant in such refractories also improves the behavior of MgO-C refractories. In this study ferrosilicon has been used to prepare insitu nano SiC whiskers and the effects of insitu SiC nano-whiskers on mechanical, physical and corrosion properties of MgO-C refractories during heat treatment have been investigated. The strength was measured by Cold crushing strength (CCS) according to ASTM C133-97 and Brazilian test. Also, bulk density (BD) and apparent porosity (AP) were studied according to ASTM C-20-92. XRD and SEM have been used to study phase composition and observing the structure, respectively. The results showed that by the formation of these nano-whiskers at high temperatures the strength was increased and corrosion and physical properties have been improved.

Keywords: MgO-C refractories; SiC nano-whiskers; Strength, Corrosion; Physical properties.

1. Introduction

MgO-C based refractories have been widely used in steel making industries, mainly in steel ladles, basic oxygen (LD) converters, electric arc furnaces and also in secondary steel making production, mainly because of its good compatibility, high refractivity, excellent corrosion resistance, thermal shock resistance, low thermal expansion, high slag penetration resistance and low wettability. These properties are due to low wettability and good thermal conductivity of graphite [1)]. The combination of MgO with graphite improves the corrosion resistance, increases the thermal shock resistance and decreases the wettability and thermal expansion [2- 6)]. The strength of these materials decreases during the in-service conditions, which stems from the carbon oxidation. High porosity and low density are the other disadvantages of Carbon. For solving these problems, antioxidants like silicon and aluminum are added [7)]. SiC is the other important additive. It has a lot of important properties such as excellent oxidation and corrosion resistance. Furthermore, SiC nano-whiskers which exhibit high strength, high elastic modulus, and high thermal-chemical stability, are widely used to strengthen ceramic composites [8)]. In this study, ferrosilicon has been added in order to produce insitu SiC nano-whiskers. Karamian et al. [7)] used ferrosilicon in bauxite–carbon composite materials and produced SiC-nano whiskers. Exposure to high temperature of composite refractory results in decomposition of SiC to Si and C. Si acts as an antioxidant and C has its beneficial effects on MgO-C refractories.

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2. Materials and Methods

2. 1. Sample preparation

In this paper, Chinese raw materials including fused magnesia with particle size of 3- 5 mm, 1- 3 mm and <1 mm, sintered magnesia with particle size of 0- 75 µm, natural graphite flakes and ferrosilicon (from Delminco Inter. Pars Company) in the range of 1–5 wt. % were used as the initial starting powder. Cylindrical samples, with the dimensions of 50 mm in diameter and 50 mm in height for mechanical and physical tests and 50 mm in diameter, and 20 mm in height and an inner hole (20 mm diameter and 20 mm height) for slag resistant, were prepared for the purpose of mechanical and resistant test, respectively. Novalac resin was used as a binder. The formulation and phase analysis of the raw materials and additives are given in Tables 1 and 2, respectively.

Starting materials were carefully mixed for about 10 minutes and then shaped by a hydraulic press under the pressure of 4 MPa. The green samples were tempered according to the following cycles:

• 24 hours in 100 °C
• 8 hours in 200 °C
• 24 hours in 250 °C

For surveying the mechanical and physical properties and slag resistant of the samples in practical situations, they were heated to 1650 ºC while embedded in coke bed to prevent oxidization. The properties of the samples were measured and compared after tempering and exposing to in-service situations. For measuring the strength of the samples, Brazilian test was used, leading to splitting the tensile strength measurement. The related equation is as follows:

$$\sigma = P / \pi RL \qquad \text{Eq. (1)}$$

, where P is the fracture force, R is the radius of the sample and L is the thickness. Also, Mechanical test of Cold Crushing Strength (CCS) according to ASTM C-133- 97 was evaluated.

For determination of physical properties, the specimens were characterized according to ASTM C-20- 92 for apparent porosity (AP) and bulk density (BD) tests.

Table 1. Formulation of raw materials (wt. %).

Fused magnesia	Sintered magnesia	Calcinated alumina	Flake graphite	Novalac resin	Hexametile tetra amen (additive of the resin)
65	25	3	7	6	0.6

Table 2. Phase analysis of raw materials and additives (XRF results).

Material	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	C	Si	Fe
Fused magnesia	97	1.2	0.5	0.2	0.4	-	-	-
Sintered magnesia	97.5	1	0.5	0.5	0.6	-	-	-
Flake graphite	0.13	0.13	1.6	0.45	0.75	96.5	-	-
Ferrosilicon metal	-	-	-	-	-	2	72	23

Bulk density was determined according to Archimedes method. BD and AP were determined by using the following equations:

$$AP(\%) = \left[(W_2 - W_1) / (W_2 - W_3) \right] \times 100 \quad \text{Eq. (2)}$$

$$BD\left(g/cm^3\right) = W_1 / \left(W_2 - W_3\right) \quad \text{Eq. (3)}$$

, where, W_1, W_2 and W_3 are the weight of the dried sample, saturated weight with water, and weight of the sample in water suspended by a thin thread without contacting the vessel walls, but fully inside the water, respectively.

For the slag resistant test, crucible method was carried out. Cylindrical samples with an inner hole were used. 2 g slag was put in these holes. The chemical composition of slag is shown in Table 3. After being heated to 1650 °C for 4 hours, the samples were cut vertically through the center of the hole. A thin section was put in a flat glass. The prepared samples were observed via a metallographic microscope.

An X-ray diffraction (XRD) instrument was used for analyzing the raw materials. 2 theta range between 0 ° and 80 ° was used for the XRD experiments (step size 0.04 ° and time step 1 second). XRD was performed in a Philips X'PERT MPD diffractometer (Cu Kα radiation, λ= 0.154056 nm at 20 kv and 20 mA). Scanning electron microscopy (SEM, Philips XL30) was used for microstructural investigation. SiC nano whiskers were determined by XRD and SEM.

3. Results and Discussion

3.1. SEM and XRD

Fig. 1 and 2 show the XRD pattern and SEM of the samples fired at 1650 °C, respectively. In figure 1(a) high peak of Carbon (Graphite) is clear because high carbon ferrosilicon was used. In addition, the new peaks of SiC are seen. Fig. 2a shows the microstructure of the specimens fired at 1650 °C without ferrosilicon which contains no nano whiskers. Fig. 2b represents the sample containing 5 wt. % ferrosilicon, which shows the formation of the whiskers.

SEM photomicrographs revealed that the whiskers of nano sized diameter developed in the specimens with 5 wt. % ferrosilicon. The sizes of these whiskers are measured by modified Scherer equation [9]. Formation of SiC by Ferrosilicon Alloys and Silicon at 1550 °C have been studied by J. Pedro et al. [10] The occurrence of some interfacial reactions during the wetting on graphite, and therefore, the formation of interfacial products are likely to occur, according to Eq. (4) and Eq. (5):

$$\text{Fe-Si} \rightarrow \text{Fe (l)} + \text{Si (l)} \quad \text{Eq. (4)}$$

$$\text{Si (l)} + \text{C(s)} \rightarrow \text{SiC (s)} \quad \text{Eq. (5)}$$

At 1650 ºC, the Gibbs free energy for SiC is negative (-41796 J), so the formation of this product is thermodynamically feasible at such a temperature.

3.2. Strength, Density and Apparent porosity

The effect of ferrosilicon on the strength (Brazilian test), CCS, BD and AP of the samples fired at 250 °C and 1650 °C are shown in Fig. 3, 4, 5 and 6, respectively.

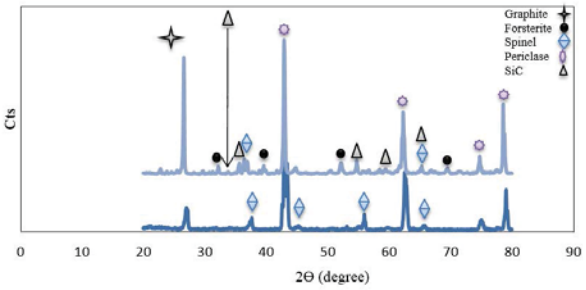

Fig. 1. XRD pattern of specimens fired at 1650 °C, *a)) without ferrosilicon, b) with 5 wt. % ferrosilicon. The new SiC peaks are observed in the sample containing ferrosilicon.*

Table 3. Chemical composition of slag.

Chemical composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	SrO	BaO	CuO	ZrO_2	MnO	TiO_2	MgO	LOI
wt. %	41.48	18.10	5.17	1.09	2.32	0.059	0.058	0.014	0.10	0.212	0.328	5.16	25.78

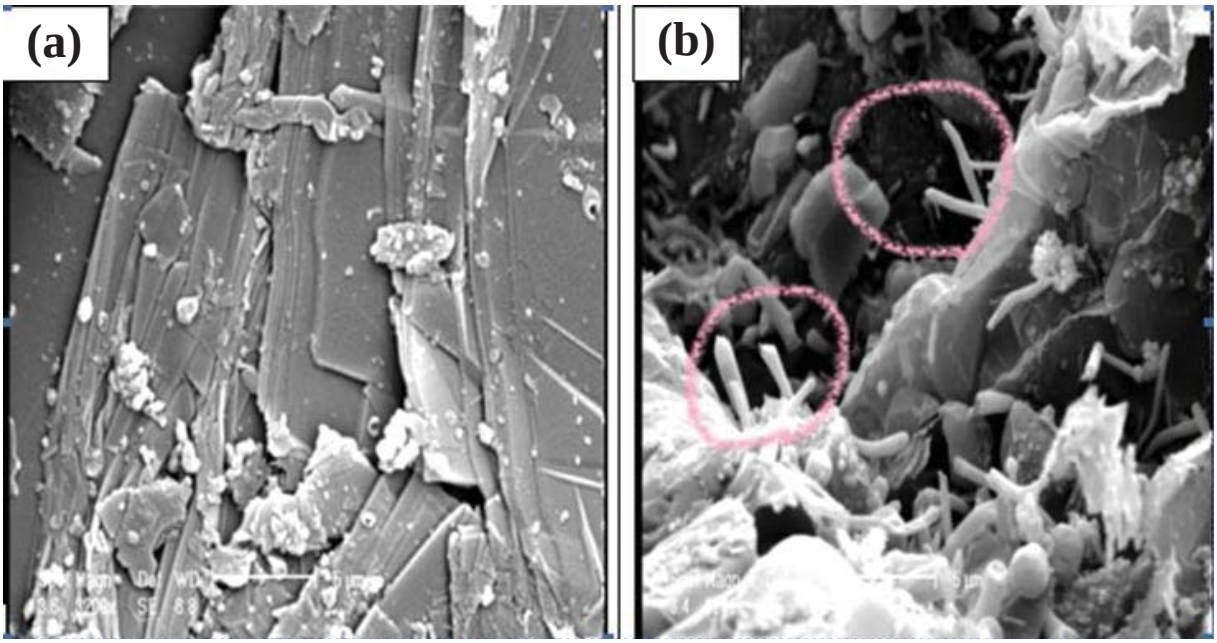

Fig. 2. SEM of MgO-C refractories fired at 1650 ºC. a) No ferrosilicon, b) containing 5 wt. % ferrosilicon. Nano-sized SiC whiskers developed in the microstructure (b).

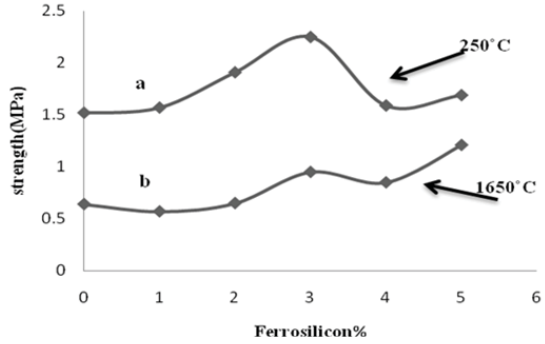

Fig. 3. Effect of adding ferrosilicon on the strength (Brazilian test) of the specimens fired at a) 250 ºC, b) 1650 ºC.

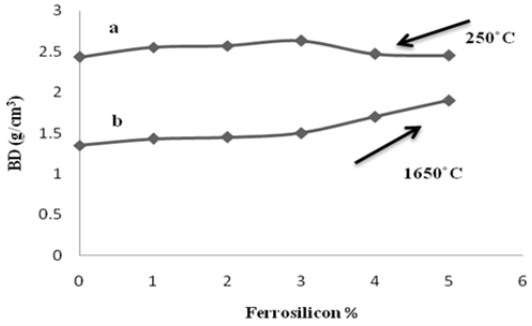

Fig. 5. Effect of adding ferrosilicon on BD of the specimens fired at a) 250 ºC, b) 1650 ºC.

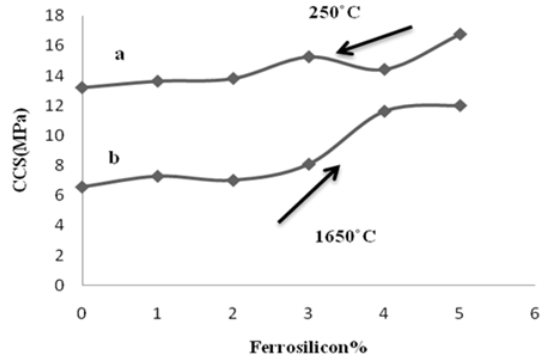

Fig. 4. Effect of adding ferrosilicon on cold crushing strength (CCS) of the specimens at a) 250 ºC, b) 1650 ºC.

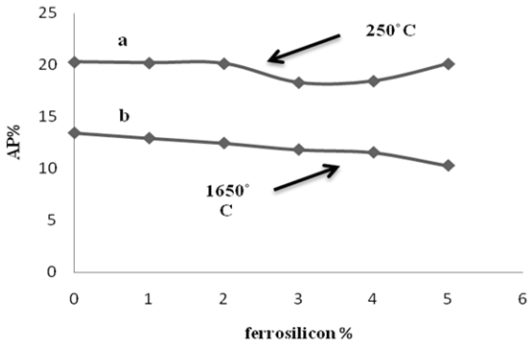

Fig. 6. Effect of adding ferrosilicon on AP of the specimens fired at a) 250 ºC, b) 1650 ºC.

The results show that by adding ferrosilicon to MgO-C refractory, the strength and BD have been increased. Also can be seen that AP has been decreased. The maximum strength and BD was observed at 3% ferrosilicon at 250 ºC, It seems ferrosilicon can be attributed to the formation of cross-linking structure of the resin binder. Therefore, there is a limit of 3 wt. % ferrosilicon for cross-linking at 250 ºC. The cross-linking improves the density and by blocking the porosity AP has been decreased.

Also in high temperatures (1650 ºC), the strength has been increased as a function of ferrosilicon which is due to the formation of SiC nano whiskers at this temperature. SiC whiskers facilitate the improvement of the strength of the refractory because of having high strength. Also the whiskers result in decreasing of AP by closing the porosity. It is seen that the maximum strength and BD, is at 5% ferrosilicon. The formation of β-SiC bond is due to the reaction of Si and C [11]. The sources of these carbon atoms are resin and graphite. This bonding provides a network structure which keeps the refractory aggregates firmly together, so increase the strength of the MgO-C refractory.

3. 3. Slag resistance

Fig. 7 shows the optical micrographs of the slag corroded and penetrated layers of crucible samples. According to Fig. 7a, the slag reacts with the grains and matrix of the sample seriously at the slag-refractories interface, and dissolving of particles into the slag. Additionally, there are many holes in the penetrated layer due to the serious reaction between penetrated slag and matrix of the sample, as shown in Fig. 7a. While the sample with 5 wt. % ferrosilicon has an excellent slag resistance (Fig. 7b).

4. Conclusions

• Adding ferrosilicon to the samples which were tempered at 250 ºC redounded the increase in the strength and bulk density, this increasing was due to occurrence of cross-linking. This bonding provides a network structure which keeps the refractory aggregates firmly together, leading to the increase in the strength of the MgO-C refractory.
• There is a limit of 3 wt.% ferrosilicon for cross-linking at 250 ºC. Fewer or higher than this amount resulted in the decrease of the strength at this temperature.
• In addition, adding ferrosilicon resulted in the increasing of the strength and bulk density of sintered sample in high temperature (1650 ºC) which is because of the formation of SiC nano whiskers and β-SiC bonds.
• Apparent porosity in the samples with 5 wt. % ferrosilicon, were decreased for both temperatures by adding ferrosilicon up to 5 wt. %.
• Specimen with 5 wt. % ferrosilicon has better slag resistant than the one without ferrosilicon.
• XRD and SEM, both reveal the presence of SiC Nano whiskers.
• Producing of insitu SiC nano whiskers in refractory materials is very economical for industries.

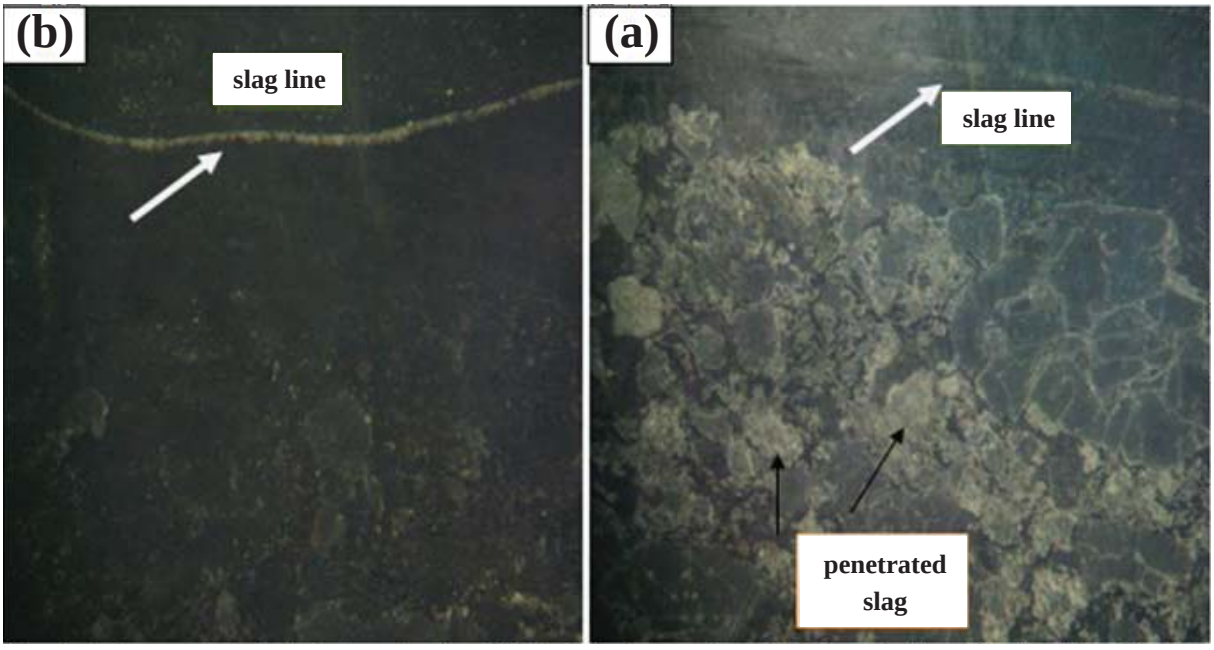

Fig. 7. Optical photos of slag corroded and penetrated layers after slag resistance test at 1650 ºC. (a) sample without ferrosilicon, (b) sample with 5 wt.% ferrosilicon. Slag has not penetrated to sample (b).

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