Effect of MgO on the Properties of Alumina-Graphite Based Refractory Including 20 wt% Non-Stabilized ZrO₂

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Research Article

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Abstract

In this study the effect of magnesium oxide in the range of 0 to 10 wt. % on the mechanical properties, corrosion rate, preventing carbon bond oxidation and microstructure of alumina-graphite (coarse-grained) refractory bodies including 20 wt. % of non-stabilized zirconia is investigated. The refractories were fabricated by mixing raw materials, where phenolic resin in the form of liquid was used as binder, and then granulation, cold isostatic pressing and firing at 1400 °C for 8 hours in a reducing atmosphere. Mechanical, physical and chemical properties of the fabricated refractories were evaluated by determining cold compressive strength, modulus of rupture and thermal shock resistance, bulk density, molten shock resistance, permeant linear change, oxidation and corrosion resistance. The results showed that in the presence of MgO, the zirconia grain size increases and it results in a decrease in bulk density that leads in more slag penetration and decreasing corrosion resistance. It has also revealed that addition of MgO to the base refractory leads to decreasing in cold crushing strength, modulus of rupture, and thermal shock resistance. It has been also proved that it causes an expansion during sintering process and results in positive permeant linear change.

1. Introduction

Refractories are one of the most important industrial materials so that growth in all high temperature and metallurgical industries are depend on these vital materials. Refractories mainly are made of different oxide materials having low evaporation rate and stable at high temperature, which in their advanced forms they are used in combination with carbon as a well know high temperature resistance material [1-2]. These type of advanced refractories include nonferrous element oxides and carbon, such as $\text{ZrO}_2\text{-C}$, MgO-C and $\text{Al}_2\text{O}_3\text{-C}$, and are mainly used in the steel sector in different areas [3]. One of the most important application of these types of refractories in steel industries is in fabrication of stoppers, that are mainly made of $\text{Al}_2\text{O}_3\text{-C}$ based refractories and their chemical composition mainly consists of 55 wt% Al_2O_3 and 25 wt% C. These types of refractories are proved to show high modules of rupture, high cold crushing strength, low thermal expansion coefficient, high thermal conductivity, high thermal shock resistance, and slag and molten metal resistance, therefore are suitable to be used for fabricating stoppers. Despite the aforementioned advantages of using alumina-carbon refractories, they have a few problems. One of the most important issue is carbon oxidation at high temperatures, which by increasing the amount of porosity leads in decreasing strength and corrosion resistance. The second problem is erosion (chemical and physical) caused by the penetration of molten metal or slag into the pores due to dissolution of alumina by slag or carbon oxidation by iron oxide in liquid slag and ambient gas. The third problem is direct wear with liquid iron flow and thermal or mechanical impacts. These problems may be overcome by using antioxidants that play an important role in reducing oxidation of carbon [4].

LIU Qing-cai and his coworkers studied the corrosion resistance and microstructure of $\text{Al}_2\text{O}_3\text{-C}$ -based refractories in reducing melt. They evaluated performance of the refractories by submerging in a quasi-steady state and also in a rotating state. They show that the corrosion rate of $\text{Al}_2\text{O}_3\text{-C}$ based refractories

is reduced by adding carbon and zirconia [5]. In other research W.S. Resende and his coworkers studied the properties of alumina-magnesia-graphite refractory with resin bonds. They proved that this new class of refractories demonstrate excellent chemical and thermodynamic stability and excellent thermal and mechanical properties [6]. A. Mustafa Al Bakri et al. investigated the effects of using uniaxial and cold isostatic pressing methods on the mechanical properties of alumina-zirconia composites with different compositions sintered at different temperatures in the range of 1500 ° C and 1650 ° C. They showed that the composites produced by cold isostatic press have better mechanical properties at lower sintering temperature [7]. B. Rand and his coworkers have investigated the role of carbon and graphite in composite refractories. They emphasized that the main reason for the use of carbon is not wettability but its ability of carbon in modifying the thermal shock properties of the composite resulting from its unique thermal and mechanical properties [8].

In the present work the effect of MgO addition in the range of 0 to 10 wt% on the chemical, physical and mechanical properties of Al₂O₃-C based refractories including 20 wt % non-stabilized zirconia has been studied.

2. Experimental Procedure

In the present work chemical composition of the samples including different amount of magnesia were adjusted according to Table 1. As it can be recognized all the samples include the same amount of three different types of alumina (Tubular alumina, white fuse alumina, and brown fuse alumina), fused silica, coarse grained sheet graphite (Specification according to Table 2), non- stabilized zirconia, silicon and phenolic resin in the form of powder and liquid, respectively, that the later additive was used as binder. All the raw materials used in this study were analytically pure. Particle sizes and morphology of the raw powders were determined by using laser particle size analyzer and by preparing scanning electron microscopic images, respectively. To prepare green samples, the raw materials were weighted according to the required chemical composition (Table 1) and were mixed in different stages. For better mixing and distributing the liquid resin between the particles of the used powders, the liquid resin was first dissolved in analytically pure methanol alcohol and then added to the raw material mixture (every three grams of resin was dissolved in 12 grams of methanol). After mixing, that was carried out by using a laboratory impeller mixer, the mixture was dispensed into a large container and placed under a batch for half an hour to remove the remained alcohol. In this stage it was paid attention to keep the temperature enough low to prevent any loss of resin. After removing of at least 80 wt% of alcohol, the mixture powders were passed through 60 mesh sieve to obtain uniform granulated powder. For fabricating green body, the powders were first poured into a latex mold and after placing in a vacuum machine for 5 minutes, they were consolidated by using a cold isostatic pressing machine, where the applied pressure was around 50 bars in the first step and then went up to 850 bars. The green samples fabricated in this study were in the shape of solid cylinders with 50 mm diameter and 50 mm height and also hollow cylinders with outer diameter of 45 mm, inner diameter of 18 mm and height of 100 mm. Solid cylinders were used for determining the modulus of rupture, thermal shock resistance, melt shock resistance, and hollow and

solid cylinder specimens were used in all other tests. The fabricated green samples were dried at 80 ° C for 12 hours, then at 110 ° C for 12 hours and finally at 250 ° C for another 12 hours. The samples were sintered at 1400 ° C for 8 hours in a reducing atmosphere. To carry out sintering process, the samples were pre-incubated at 700 ° C for 48 hours before being placed in the baking oven at 1400 ° C to prevent the samples from disintegrating at high temperature.

Bulk density of the fired samples were measured according to ASTM C-20 standard, their modulus of rupture (MOR) according to ASTM C-133, thermal shock resistance (TSR) according to ASTM C-1171, cold crushing strength (CRS) according to ASTM C-133, thermal expansion coefficient (TEC) according to ASTM C-133 -823, oxidation resistance according to ASTM G-83 standard, corrosion test according to ASTM G-74 standard, linear permeant changes according to ASTM C-210-95. It is worthy to note that in this study three samples were prepared for each experiment.

3. Results And Discussions

The result of particle size analysis of the ceramic powders used as raw materials are presented in Fig. 1. The size characteristics of all six different oxides raw materials are also reported in Table 3. As it can be seen, for the tubular alumina, white fused alumina, fused silica and magnesia powders the size of the particles are less than 100 microns and the average size is around 10 micrometers. For the brown alumina, size of the particles is larger and the average size is around 150 microns, while the size of zirconium oxide used in this study is lower than 10 mm and the average size is around 4 mm. The SEM image of the powders that not presented in this report, shows that all the powders used in this study have irregular shape and for the powders with smaller size, the particles are to some extent agglomerated. For the graphite powder, as it can be seen in Fig. 2, the particles are in planar shape and the average size is around 150 mm.

Effect of MgO addition on the physical and chemical properties of the fabricated refractory is shown in Fig. 3 and is also presented in Table 4. As it can be seen, addition of MgO led to decrease in bulk density, MOR, CRS and TSR of the base material. Decrease in bulk density that may be as a result of increase in zirconia grain size due to the presence of magnesia, can be considered as a reason for decreasing MOR, CRS and TSR of the fabricated refractories including magnesium oxide. Furthermore, modulus of rupture and the other mentioned physical properties also depend on the grain size, grain shape, apparent porosity, nature and the percentage of different phases present in the fired refractory that in turn are mainly influenced by the used chemical composition [9].

For the refractories not included magnesia, the grain size is finer and therefore showed higher cold crushing strength and modulus of rupture [1]. Moreover, magnesium oxide although has good refractive index, but its expansion coefficient is high, as a result, with increasing magnesium oxide, thermal shock resistance decreases.

Based on the data presented in Fig. 3b, it can be seen that the permanent linear changes for the sample does not include magnesia is negative, which it means that the sample shrinks during baking, and cause

a negative value for the permanent linear change. For the other samples including 5 to 10 wt% magnesia an expansion during baking process were observed and therefore the permanent linear changes were positive that can be due to spinel formation in the presence of magnesia (it can form spinel with alumina).

The effect of magnesia addition on the oxidation resistance of the fabricated refractories is also shown in Fig. 3b. As it can be seen, the sample contains 5 wt. % of magnesia has the least reduction in thickness and thus the highest oxidation resistance. In fact, the oxidation of carbon-carbon bands depends on texture, grain size distribution, purity and chemical composition of the raw materials used, and it also depends on the amount of remained porosities and size distribution of the pores. Using alumina as a basic raw material in fabrication of C-Alumina refractories leads in higher oxidation of graphite. In fact, Al^{3+} ions in the alumina acts as an electron acceptor against C^{4+} and weakens the C-C bond, thus alumina greatly accelerates graphite oxidation. On the other hand, TiO_2 and MgO inhibit oxidation, these compounds act as electron donor to graphite and can stabilize its structure [9]. As a result, by addition of magnesia up to 5 wt. %, oxidation resistance increases. More increase in using magnesia caused decreasing in oxidation resistance, which is due to increasing in remained porosities by more using of magnesium oxide. The large amount of remained porosities in the samples containing carbon leads to irreversible expansion of graphite at high temperature, which can affect the oxidation resistance.

For the samples containing magnesia, two phenomena control oxidation resistance and act in reverse ways. Magnesium oxide acts as an oxidation inhibitor but it also results in more growth of zirconia grains that leads in decreasing the density, which in return causes the structure to become more open and decreasing in structure integrity and therefore accelerates oxidation. By increasing the amount of used magnesia, the effect of decreasing the density on lowering oxidation resistance is more pronounce than its effect as oxidation inhibitor, so that by addition of MgO , oxidation resistance increases and after reaching a maximum it starts to decrease.

The effect of MgO addition on the thermal expansion of fabricated refractory is shown in Fig. 4 and Table 5. As it can be seen, for the sample does not include MgO , at around 1100 °C a significant change in the slope (from positive to negative value) of the expansion versus temperature graph can be observed, where it changed again to positive value after the temperature increased to more than 1200 °C. For the sample includes 5 weight percent of MgO also nearly the same trend can be recognized but when the amount of used MgO reached to 10 weight percent, mostly no significant change in the slope was recorded. Change in the slope is probably mainly due to the phase transformation of zirconia from monoclinic to tetragonal phase that is expected to occur in the temperature range of 1100 to 1200 °C. For the sample includes 10 wt.% of magnesium oxide, according to the XRD pattern shown in Fig. 5, cordierite and zirconium silicate phases have been formed and as a result, the sample containing 10 wt% MgO does not undergo any transformation, and no change in the slope were observed. Based on the thermal expansion coefficients data presented in Table 5, it can be seen that, for the sample includes 10 wt% MgO , for the temperatures in the range of 100 to 1200 °C, TEC value is the highest.

X-ray diffraction pattern for the sample not included magnesium oxide and also for the one included 5 wt.% of MgO are also presented in Fig. 5. As it can be seen, just peaks related to raw materials are observable and no significant reaction can be supposed to occur between the raw materials. For the sample containing 5 wt.% magnesia, in addition to the peaks of the raw materials, it also includes ZrSiO_4 (zirconium silicate) and $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (cordierite) peaks. It means that in this case some reaction between raw materials must be expected. And finally for the sample containing 10 wt.% magnesia it is clear that in addition to the peaks of the raw materials, the same as the sample includes 5 wt.% MgO, it also includes some amount of ZrSiO_4 (zirconium silicate) and $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (cordierite), as the most important phase in the SiO_2 -MgO- Al_2O_3 ternary system [10]. Creation of cordierite phase is due to the solid state reaction between three mentioned oxides phase during sintering process [11], can influence physical and chemical properties of the refractory included it. Based on the pure cordierite phase properties such as low TEC, high refractive index and high chemical resistance to corrosion, low dielectric coefficient and high heat shock resistance [10, 12], properties of the refractory, which included this phase, it is expected to be modified.

The SEM images of the refractories microstructures including 0, 5 and 10 wt% of MgO, before and after corrosion test, which carried out in molten metal at 1600 °C, is shown in Fig. 6 to 8. As it can be seen, the microstructure integrity in the samples containing zero percent magnesia is greater than that of the samples containing 5 and 10 wt.% of magnesia. This results are consistent with the results obtained by density measurement where proved that the sample containing 0 wt.% MgO has higher density. Considering the SEM images presented in Figures 6, 7 and 8 in part b, which are for the samples corroded by the melt at 1600 °C, it is clear that the samples containing 5 and 10 wt% of magnesia, are more corroded by the melt. This is mainly due to lower density of these samples and more melt penetration, in comparison with the sample not included MgO.

4. Conclusions

Refractories based on Al_2O_3 -C including 20 wt% non-stabilized zirconia were fabricated to investigate the effect of addition of MgO in the range of 0 to 10 wt. % on the physical, chemical and mechanical properties of the base refractory. It has been shown that addition of MgO to the based refractory leads to decrease in bulk density, cold crushing strength, modulus of rupture, and thermal shock resistance. It has been also proved that it causes an expansion during baking process and shows positive permeant linear change. The highest thermal expansion coefficient was measured for the sample included 10 wt% of MgO. Samples containing 5 and 10 wt% of magnesium oxide have shown lower corrosion resistance than the sample not included magnesium oxide, due to their lower fired densities.

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Tables

Table 1: Formulation of Samples

Analysis (wt%) Sample	Tubular Alumina	Brown Fuse Alumina	White Fuse Alumina	Fused Silica	Coarse- Grained Sheet Graphite	Zirconia Not Stabilized	Magnesia	Metallic Si	Phenolic Resin	
									Powder	Liquid
0% MgO	25	10	10	10	20	10	0	5	3	3
5% MgO	25	10	10	10	20	10	5	5	3	3
10% MgO	25	10	10	10	20	10	10	5	3	3

*Due to the withdrawal of phenolic resin during baking, The percentage used in the formula cannot be calculated.

Table 2: Coarse grained sheet graphite Specification

Analysis	Fixed carbon	Ash	Volatile	Moisture	Particle Size (µm)
(wt%)	Min 95	Min 4. 00	Max 1.50	Max 0.50	(50) 100-200 (50) 200-350

Table 3: Size and size distribution characteristics of the used raw ceramic materials

Characteristics size	D (0.1)	D (0.5)	D (0.9)
Compound	mm	mm	mm
Tabular Alumina	0.726	6.968	42.374
Brown Alumina	38.319	126.927	246.672
White Fused Alumina	0.996	13.205	62.939
Magnesia	1.037	13.973	67.681
Zirconia	0.544	2.605	7.293
Fused Silica	1.363	24.208	99.051

Table 4, Bulk density, cold crushing strength, modulus of rupture, thermal shock resistance, permeant linear changes and oxidation resistance

Sample	Al ₂ O ₃ - C 0% MgO	Al ₂ O ₃ - C 5% MgO	Al ₂ O ₃ - C 10% MgO
Bulk density (g/Cm ³)	2.25	2.10	2.15
Cold crushing strength (Kg/Cm ²)	287.95	174.7	182.02
Modulus of Rupture (Kg/Cm ²)	122.21	109.72	72.69
Thermal shock resistance (Kg/Cm ²)	67.05	47.75	36.2
Permanent linear changes (mm)	- 0.69	0.59	1.86
Oxidation resistance (reduce of thickness (mm))	5	2.6	3.6

Table 5: Thermal expansion coefficient results

Temperature (°C)	$\alpha \times 10^{-6}$ Al ₂ O ₃ - C 0% MgO	$\alpha \times 10^{-6}$ Al ₂ O ₃ - C 5% MgO	$\alpha \times 10^{-6}$ Al ₂ O ₃ - C 10% MgO
145	3.57	2.74	3.71
500	4.59	4.50	5.93
800	5.92	5.79	7.98
900	6.20	6.05	8.09
1000	4.19	4.01	7.60
1125	-1.10	2.47	2.56
1200	4.51	3.12	5.86

Figures

Figure 1

Particle size Distributions of different ceramic powders used as raw materials.

Figure 2

SEM image of coarse grained sheet graphite.

(a)

(b)

(c)

Figure 3

(a) Bulk density and Modulus of Rupture, (b) Permanent linear changes and oxidation resistance (c) Cold crushing strength, and thermal shock resistance.

(a)

(b)

(c)

Figure 4

Thermal expansion coefficient of the samples containing a) 0, b) 5 and c) 10 wt.% of magnesia.

Figure 5

X-ray diffraction for the sample containing 0, 5 and 10 wt.% of magnesium oxide.

(a)

(b)

Figure 6

SEM image of sample surface containing 0% Magnesia at three magnifications a) before corrosion, and b) after corrosion.

(a)

(b)

Figure 7

SEM image of sample surface containing 5% Magnesia at three magnifications a) before corrosion, and b) after corrosion.

(a)

(b)

Figure 8

SEM image of sample surface containing 10% Magnesia at three magnifications a) before corrosion, and b) after corrosion.