THE EFFECT OF NANO METER SIZE ZrO_2 PARTICLES ADDITION ON THE DENSIFICATION AND HYDRATION RESISTANCE OF MAGNESITE–DOLOMITE REFRACTORIES

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Abstract: *In this study the effect of nano meter size ZrO_2 particles on the microstructure, densification and hydration resistance of magnesite –dolomite refractories was investigated. 0, 2, 4, 6 and 8 wt. % ZrO_2 particles that were added to magnesite –dolomite refractories containing 35 wt. % CaO. The Hydration resistance was measured by change in the weight of specimens after 72 h at 25℃ and 95% relative humidity. The results showed with addition of nano meter size ZrO_2 particles, the lattice constant of CaO increased, and the bulk density and hydration resistance of the specimens increased while apparent porosity decreased. With the addition of small amount ZrO_2 the formation of $CaZrO_3$ phase facilitated the sintering and the densification process. The mechanism of the nano meter size ZrO_2 particles promoting densification and hydration resistance is decreasing the amount of free CaO in the specimens.*

Keywords: *Magnesite-Dolomite Refractories, Nano Meter Size ZrO_2, Hydration resistance, Densification.*

1. INTRODUCTION

Magnesite-dolomite refractories have attracted widespread attention because of their high refractoriness, wide availability of raw materials, excellent resistance to alkalinity slag and ability to remove inclusions from molten steel [1-5]. However, the hydration susceptibility of these refractories is a major disadvantage limiting their practical applications [1-7]. The methods to improve the hydration resistance of magnesite-dolomite refractories include densification by the addition of sintering aids such as Fe_2O_3 [3, 7-9], Al_2O_3 [10], CuO [11], V_2O_5 [12] and TiO_2 [4]. The use of F_2O_3, Al_2O_3, CuO and V_2O_5 as liquid forming aids can improve the sintering of lime and subsequently the hydration-resistance of magnesite-dolomite refractories [3, 5-7, 10, 11, and 12]. However, the liquids formed may significantly reduce the refractoriness and slag resistance of refractory [3-5]. The other approach is by surface carbonation and phosphate coating [13]. It has been reported that addition of ZrO_2 can improve the hydration resistance of MgO-CaO refractories by enhancing solid state sintering without sacrificing refractoriness via formation of hydration resistant solid solutions, but it causes the rise in the production cost [5, 7, 14, and 15]. Therefore, it is important to decrease the amount of ZrO_2 for the purpose to improve the properties of the magnesite-dolomite refractories. It has been reported that the hydration resistance of the refractories was appreciably improved with well dispersion of nano-sized particles in the microstructure [5, 7]. The purpose of the current work is to study the effect of nano-size ZrO_2 particles addition on the properties of magnesite-dolomite refractories and show the possibility of improving the properties of the magnesite-dolomite refractories with less amounts nano meter size ZrO_2 particles.

2. EXPERIMENTAL PROCEDURE

Chemical analyses of sintered (at 1700℃) dolomite and magnesite (derived from Zefreh and Birjand mines, respectively) are shown in Table 1. Composition contains 35 wt. % CaO with 2, 4, 6, and 8 wt. % nano ZrO_2 (Table 2 and Fig. 1) mixed and subsequently uniaxial pressed, product of Inframat Advanced Materials Co) at 90MPa. Green briquettes were dried at 110 ±5℃ for 24 h and sintered at 1650℃ temperature with 3 h soaking at peak temperature. Sintering was done in an electric furnace and the heating rate was maintained at 5℃/min up to 1100℃, followed by 3℃/min up to final sintering temperature. Bulk density (BD) and apparent

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Table 1. Chemical analysis of magnesite and dolomite used in this study

Oxide	magnesite (wt.%)	dolomite (wt. %)
MgO	93.2	37.2
CaO	2.7	57.7
TiO_2	0.2	0.2
MnO	0.45	0.18
Fe_2O_3	0.6	0.6
Al_2O_3	1.6	2.8
SiO_2	0.8	0.7
L.O.I	0.3	0.44
Size(μm)	<80	<75

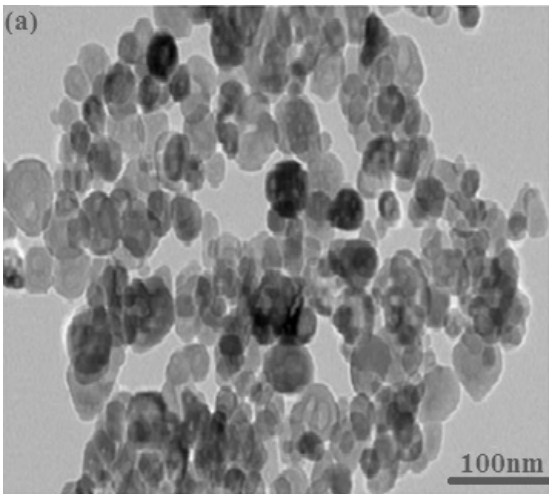

Fig. 1. TEM image of ZrO2 nanoparticles.

porosity (AP) of the samples were determined by a liquid displacement method using Archimedes principle in a xylene medium. Hydration resistance was determined as follows: each specimen was powdered to obtain a particle size finer than sieve no.40 (425μm). After weighing they were placed at a Petri dish in autoclave with 95% humidity at 25℃. The samples were then weighed at different time up to 72 h. Microstructure was investigated by using a scanning electron microscopy (SEM, Cambridge, S360) with an EDS unit of system 5480 IXRF. The phases present in the sintered product was done by X-ray diffraction (XRD) study (Jeol-8030, Cu-Kα, and 25 Kv).

3. RESULTS AND DISCUSSION

3. 1. Densification

Chemical analysis of the dolomite and magnesite used as starting material shown in Table 1. As it indicated the dolomite and magnesite used in this study have impurities such as SiO_2, TiO_2, Al_2O_3, and Fe_2O_3. The amount of Al_2O_3 is higher than other impurities. Fig. 2 shows the effect of nano size ZrO_2 addition on the bulk density and apparent porosity of the samples sintered at 1650℃ for 3h.

It is observed that the bulk density increased gradually and the apparent porosity decreased with the addition of nano ZrO_2. The bulk density increased to 3.16 g/cm3 and apparent porosity decreased to 16.8 % when the amount of nano ZrO_2 increased to 8 wt. %. From these results, it is known that the addition of nano ZrO_2 promoted the densification of magnesite-dolomite refractories. The addition of nano ZrO_2 promoted densification due to the formation of $CaZrO_3$ particles that is a volume expanding phase and decreased the porosity in matrix.

Table 2. characterizes of the nano size ZrO_2.

Particle	Average particle size	specific surface area (m^2/g)	purity (%)
Nano-ZrO_2	30±35(nm)	160	> 99.9

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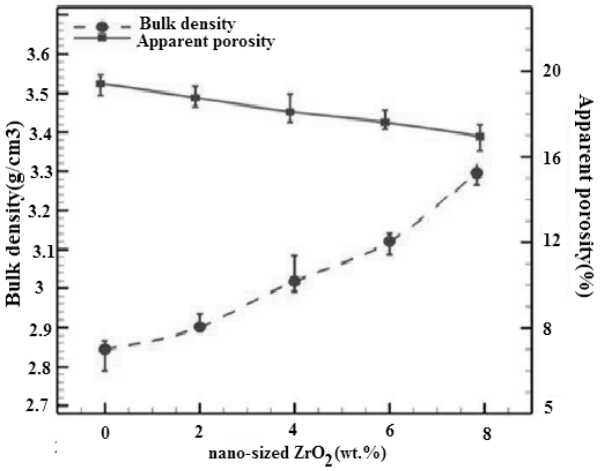

Fig. 2. The effect of nano size ZrO_2 particles addition on densification of the magnesite-dolomite refractories.

3. 2. XRD Analysis

Fig. 3 and 4 shows the XRD patterns of samples with and without nano ZrO_2 additions. Periclase (MgO) and lime (CaO) were the main crystalline phases in all the samples and the presence of Al_2O_3, as an impurity in starting materials, caused the formation of $Ca_3Al_2O_6$ phase.

In the sample with 2 and 8 wt. % nano ZrO_2, MgO, CaO and $CaZrO_3$ were the main crystalline phases, and there was no sign of nano ZrO_2

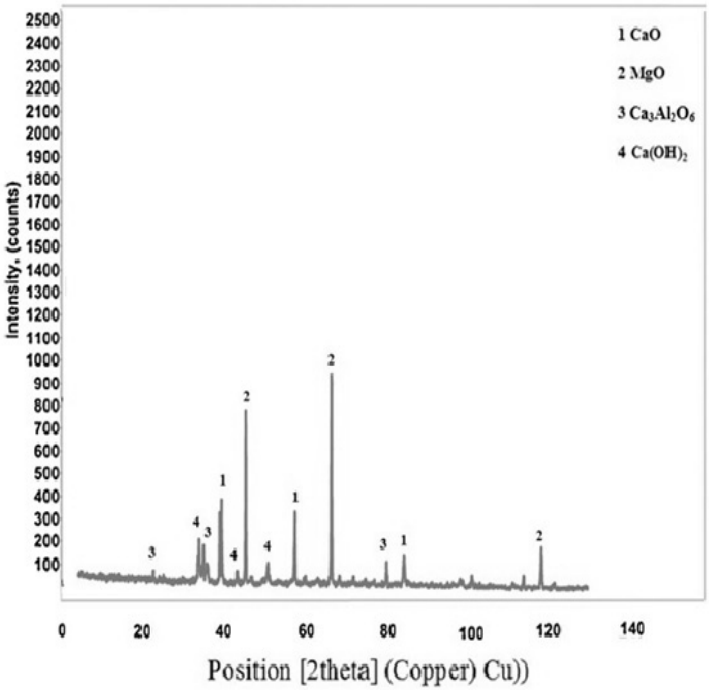

Fig. 3. XRD patterns of sample without ZrO_2.

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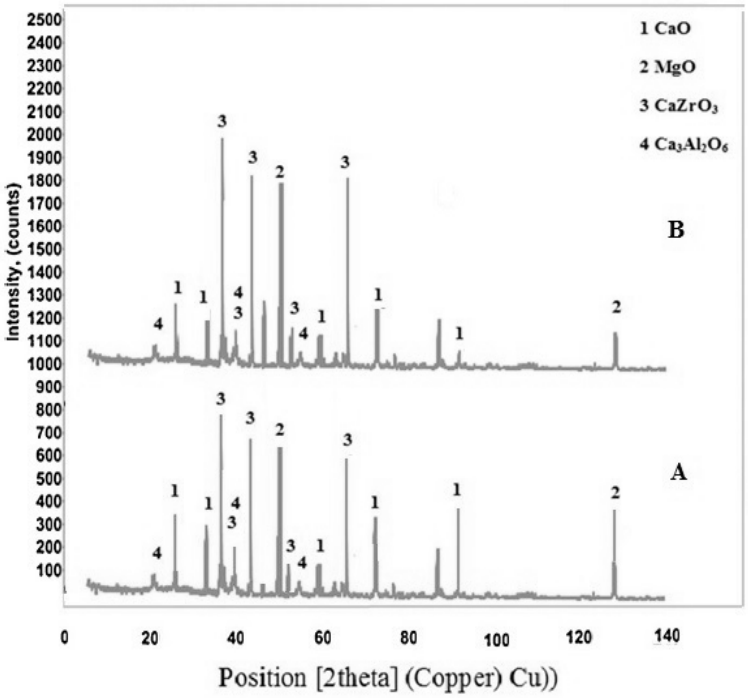

Fig. 4. XRD patterns of samples contain A) 2 wt. % and B) 8 wt. % ZrO_2.

Table 3. Calculated lattice constant for sintered samples.

Sample	Parameters	(111)	(200)	(220)	(311)	(222)	a(A ˚)
Absence ZrO_2	2θ(°)	31.31	37.51	53.4	63.54	67.08	4.7978
	d(A ˚)	1.654	2.382	1.678	1.457	1.387	
2wt.% ZrO_2	2θ(°)	31.45	37.45	53.39	64.37	67.45	4.8023
	d(A ˚)	2.674	2.3842	1.674	1.457	1.347	
4wt.% ZrO_2	2θ(°)	31.47	37.39	54.06	64.62	67.47	4.8544
	d(A ˚)	2.745	2.377	1.701	1.444	1.358	
6wt.% ZrO_2	2θ(°)	32.37	37.89	54.09	64.66	67.54	4.8871
	d(A ˚)	2.761	2.387	1.712	1.478	1.384	
8wt.% ZrO_2	2θ(°)	32.88	37.92	54.12	64.87	67.66	4.8972
	d(A ˚)	2.774	2.701	1.725	1.502	1.398	

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phase. It indicates that all added nano ZrO_2 reacted with CaO to form $CaZrO_3$ phase. No change in lattice parameter of MgO phase was measured when nano ZrO_2 was added. It indicates that nano ZrO_2 did not formed solid solution with MgO phase. The position of the diffraction peaks relates to the CaO was shifted as a result of adding nano ZrO_2, suggesting that Zr^{4+} entered in to the CaO lattice, changing the lattice parameter of CaO. However, there was no change in the positions of MgO. The CaO lattice constant of the samples was determined (Table 3) by comparing the peak positions (2θ) of the XRD patterns using the least square method.

The lattice constant of CaO in the samples without ZrO_2 was found to be 4.7978 a˚ [7, 14, 16], which was in accordance with the lattice constants of pure CaO [7]. Adding nano ZrO_2 increased the lattice constant of CaO. When the amount of added ZrO_2 was 8 wt. %, the lattice constant of CaO reached the highest point at α_{CaO}= 4.8972 A˚. Generally, the solid solution of metal oxides forms mainly by the replacement of positive ions in the solvent. Radius of positive ions directly affects the binding energy of positive and negative ions in ionic crystals and hence influences the solid solubility. When the difference in the radius of positive ions is less than 15%, it is easy to form a solid solution; when the difference is larger than 30%, it is not possible to form a solid solution [7]. In this study, the difference in radius between Ca^{2+} (0.099 nm) and Zr^{4+} (0.098 nm) [2, 7] was about 1%, but the difference in radius between Mg^{2+} (0.072 nm) [7] and Zr^{4+} was nearly 36%. Therefore, nano ZrO_2 is expected to dissolve easily in CaO but not in MgO, which is confirmed by the results of XRD analysis.

3. 3. Hydration Resistance

Fig. 5 shows the effect of nano ZrO_2 addition on hydration resistance of magnesite-dolomite refractories. It is observed that the mass gain of the magnesite-dolomite samples decreased appreciably with nano ZrO_2 addition. For the sample without addition, the mass gain after 72 h was 1.82 %, which was sharply decreased with the increase in the amount of ZrO_2. The mass gain was decreased to 1.42% when 8% nano ZrO_2 was added, indicating that the improvement of hydration resistance by nano ZrO_2 addition. It is known that the hydration resistance of CaO containing materials, both rich-CaO and rich-

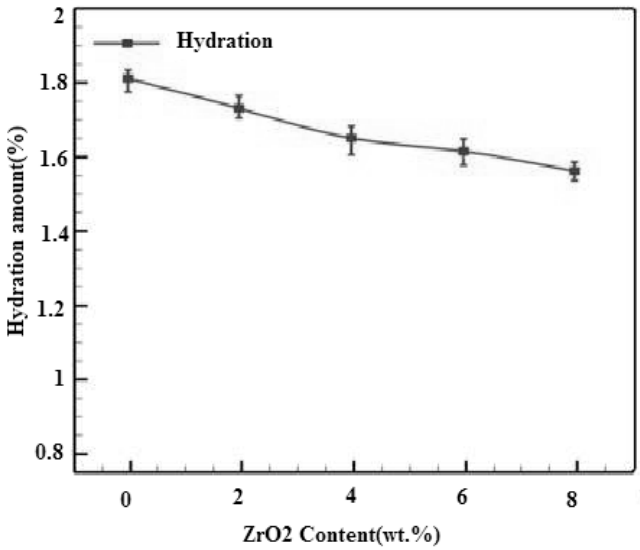

Fig. 5. Effect of nano ZrO_2 addition on improvement of hydration resistance of samples.

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MgO materials, is strongly dependent on the CaO content and the microstructure. When nano ZrO_2 was added, the increase in hydration resistance of the refractories is considered to be due to the following reasons: First, by converting part of free CaO to anhydrate $CaZrO_3$. With increasing the addition of nano ZrO_2, the content of free CaO in the refractories decreased further and thus the hydration resistance of the refractories was improved. Second, the promotion of densification by addition of nano ZrO_2 decreased the porosity of the refractories. Third, the hydration resistance of the refractories was improved by modification of the microstructure. It is well-known that the hydration reaction always begins from the sites with crystal defects. Thus, the grain boundaries, especially the triple points, are the poor hydration resistant sites. The addition of ZrO_2, lead to the formation of $CaZrO_3$ at grains boundaries and triple points in the microstructure. Thus, the hydration resistance of the magnesite-dolomite refractories was appreciably improved by addition of ZrO_2.

3. 4. SEM Analysis

Fig. 6 Shows the typical microstructure of samples without and containing various amounts of nano ZrO_2. The sintered sample without nano ZrO_2 addition has more pores and the grains are larger in size compared with the samples with nano ZrO_2 addition. Formation of $CaZrO_3$ phase (Table 4) with inhibits the grain growth in CaO and MgO. The CaO grain growth was hindered by the difficulty for Ca^{2+} to diffuse across the matrix during the sintering process. It can be seen

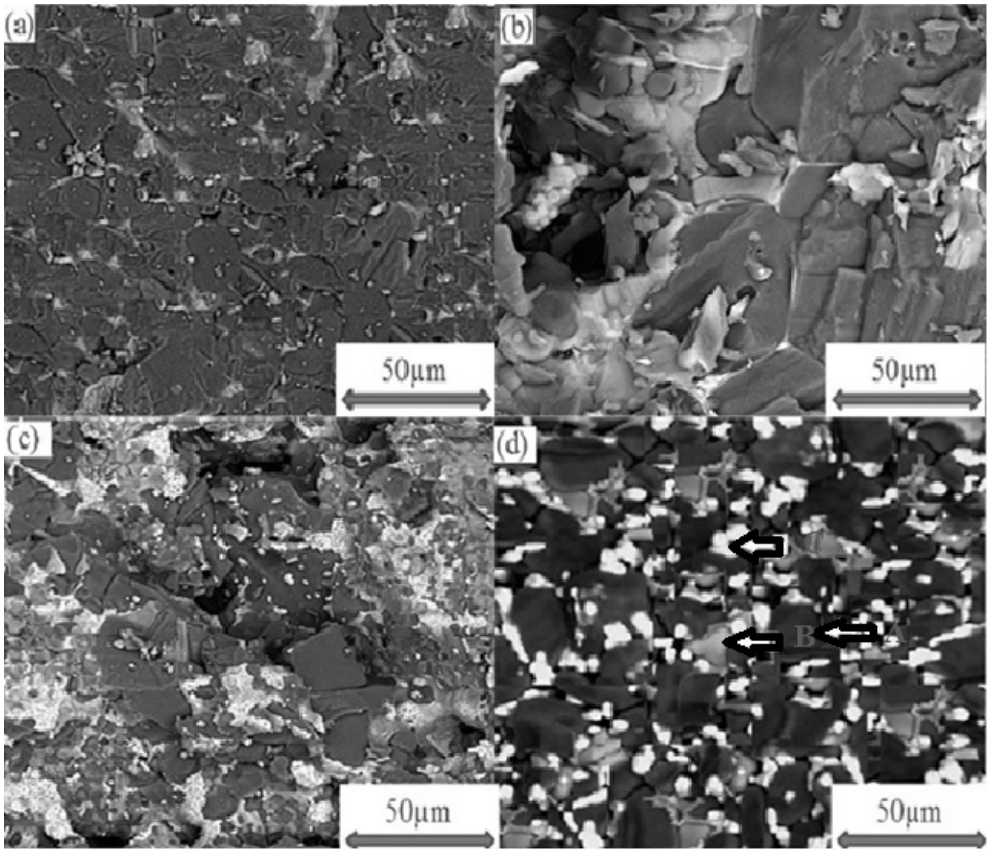

Fig. 6. SEM images of fractured surfaces of the samples with a) without, b) 2%, c) 6% and d) 8wt. % nano ZrO_2.

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Table 4. EDS analysis of A) MgO B) CaO and C) CaZrO3.

Element (wt. %)	Point A (wt.%)	Point B (wt%)	Point C (wt.%)
Mg	57.19	-	-
Ca	-	55.56	3.15
O	42.2	44.20	36.54
Zr	-	-	59.72
Au	0.61	0.24	0.59

that the number of pores decreased progressively as the nano ZrO_2 content was increased to 8 wt%. It can be also noted that the pores were present at the boundaries between MgO and CaO grains. The number of pores at grain boundaries will decrease during the sintering process as a result of grain boundary migration, leading to the formation of bigger pores on crystal surface, which may be eliminated as the sintering process progresses. A possible explanation for the effect of nano ZrO_2 on the densification and hydration resistance of MgO-CaO refractories involves a solution process in which Zr^{4+} cations are added to CaO (MgO) to form a solid solution according to Eq. 1:

$$ZrO_2 \xrightarrow{CaO} Zr_{Ca}^{00} + V_{Ca\,(Mg)}^{//} + 2\,O_o \qquad (1)$$

The main point in reaction (1) is the formation of calcium or magnesium vacancies in reaction (1). The formation of vacancies can have a positive effect on densification process.

These effects increase the powder density, and increase the hydration resistance of magnesite-doomite refractories. The preference of Zr4+ cations to form a solid solution with CaO could be explained from the crystal structure. Although MgO and CaO crystallize in the same cubic rock-salt structure, the Mg-O bond has higher single bond strength (1.55* 105 j/mol) than the Ca-O bond (1.33*105 j/mol) which is due to smaller radius of the Mg2+ cation (0.078nm) compared to that of Ca2+ cation(0.100nm)[2, 7 ,and14].

4. CONCLUSIONS

The addition of nano meter size ZrO_2 promoted densification due to the formation of $CaZrO_3$ particles which is a volume expanding phase caused by the reaction of the added ZrO_2 with CaO in the magnesite-dolomite refractories Zr^{4+} cations prefer to form a solid solution with CaO; improvement of the hydration resistance of the CaO-MgO via a reduction of the Ca^{2+} concentration in CaO.

The hydration resistance of magnesite-dolomite refractories was improved by converting part of free CaO to unhydrated $CaZrO_3$.

The promotion of densification by addition of ZrO_2 decreased the porosity of the refractories and thus its reaction specific area was decreased when were exposed to humidity environment.

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