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A comparative study of the influence of trivalent and tetravalent nano-sized oxides on the performance and microstructure of dolomite refractories

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ABSTRACT

Contrary to the many benefits of dolomite refractories, their usage has been limited due to poor hydration resistance. For this reason, the aim of this research work is a comparative study of the influence of trivalent and tetravalent nano-sized oxides [iron (Fe_2O_3), alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2)] on the performance and microstructure of dolomite refractories with an affirmation their hydration resistance improvement. After preparation and firing the specimen's, physical properties such as bulk density, apparent porosity, and hydration resistance tests were examined. Furthermore, XRD and SEM/EDX analysis were used to evaluate the ceramic phases and their microstructure, respectively. Results revealed that specimens with trivalent and tetravalent nano-sized oxides have improved densification and hydration resistance of the specimens through the liquid phase mechanism and solid state firing mechanism, respectively. Also, the specimens with tetravalent nano-sized oxides have higher hydration resistance than the specimens with trivalent nano-sized oxides. Generally, the hydration resistance improvement trend of specimens with various nano-sized oxides presence is $Al_2O_3 < Fe_2O_3 < TiO_2 < ZrO_2$.

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Estudio comparativo de la influencia de óxidos nano-dimensionados trivalentes y tetravalentes sobre el rendimiento y la microestructura de los refractarios de dolomías

Palabras clave:
Dolomite
Resistencia a la hidratación
Trivalentes y tetravalentes
Oxidos de tamaño nanométrico

RESUMEN

Contrariamente a los muchos beneficios de los refractarios de dolomita, su uso ha sido limitado debido a la mala resistencia a la hidratación. Por esta razón, el objetivo de este trabajo de investigación es un estudio comparativo de la influencia de óxidos nano-dimensionales trivalentes y tetravalentes [Hierro (Fe_2O_3), Alúmina (Al_2O_3), Zirconia (ZrO_2) y Titania (TiO_2)] en el rendimiento Y la microestructura de refractarios de dolomita con una afirmación de su mejora de la resistencia a la hidratación. Después de la preparación y la cocción de la muestra, se examinaron las propiedades físicas tales como la densidad aparente, la porosidad aparente y los ensayos de resistencia a la hidratación. Además, se utilizaron

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análisis XRD y SEM/EDX para evaluar las fases cerámicas y su microestructura, respectivamente. Los resultados revelaron que los especímenes con óxidos nano-dimensionados trivalentes y tetravalentes han mejorado la densidad y la resistencia a la hidratación de los especímenes a través del mecanismo de fase líquida y el mecanismo de disparo en estado sólido, respectivamente. Además, los especímenes con óxidos nano-dimensionados tetravalentes tienen mayor resistencia a la hidratación que los especímenes con óxidos nano-dimensionados trivalentes. En general, la tendencia de mejora de la resistencia a la hidratación de especímenes con diversos óxidos nano-tamaño presencia es $Al_2O_3 < Fe_2O_3 < TiO_2 < ZrO_2$.

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Introduction

Dolomite refractories are considered as one kind of Cr_2O_3-free refractories that are appropriate for replacement the magnesia-chrome and magnesia-spinel bricks [1–4]. Due to represent an outstanding properties such as high chemical resistance against alkaline environments at high-temperature, good thermal shock resistance, slight vapor pressure, thermodynamic durability in the existences of carbon, high refractoriness, and an appropriate abrasion resistance, dolomite refractories are extensively consumed in argon oxygen decarburization (AOD) furnaces in the metallurgy industry and cement rotary kilns [1,5–7]. Furthermore, dolomite refractories are useful to eliminate impurities such as sulfur, phosphorus, etc. from molten steels; thus, they have been considered to be one of the impressive refractory kinds for processing clean steel products [3,5,8,9]. However, notwithstanding these primary advantageous properties, the utilization of dolomite refractories has not been prevalent due to its high tendency to moisture absorption when subject to the atmosphere [10–12]. This tendency led to lime (CaO) and magnesia (MgO) phases change to $Ca(OH)_2$ and $MgO(OH)_2$ phases according to following reactions:

$$CaO_{(g)} + H_2O_{(g)} = CaO(OH)_{2(g)} \quad (1)$$

$$MgO_{(g)} + H_2O_{(g)} = Mg(OH)_{2(g)} \quad (2)$$

These reactions causes to a volume expansion and generation many cracks in the structure. Lately, much attempt has been done by several researcher to ameliorate the efficiency of dolomite bricks by the addition of various additives such as V_2O_5 [8], CuO [9], $FeTiO_3$ [10], ZrO_2 [4,7,11], Fe_2O_3 [1,3,4,12], NiO [13], BaO [14], Cr_2O_3 [15], and CaF_2 [16]. It has also been mentioned that physical properties of these bricks could be improved by using pitch, tar, flake, and vein graphite minerals [1,3,12]. Also, the hydration resistance of dolomite refractories can be enhanced by treating in a CO_2 atmosphere which results in the generation of the dense layer on the surface of calcia (CaO) and protect CaO grains from contact with moisture [17]. On the other hand, nano-technology was offered to the refractory industry some year ago, and nowadays it is a significant tool subjected in many research projects [18–20]. The aim of this research work is to offer a comparative study of the impact of trivalent and tetravalent nano-sized oxides addition (Fe_2O_3, Al_2O_3, ZrO_2, and TiO_2) on the performance and microstructure of dolomite refractories with an affirmation of enhancement on the hydration resistance of dolomite refractories and determination of the most effective nano-sized oxide. This research work can be a useful guide for producer of these type refractory bricks in choosing the best additives according to their function.

Table 1 – Chemical composition and properties of dolomite.

Oxide	Dolomite
SiO_2	0.7
Al_2O_3	2.8
Fe_2O_3	0.8
TiO_2	0.2
CaO	57.2
MgO	37.2
Alkalis	0.44
Physical properties	
Bulk density(g/cm^3)	2.85–3.1
Apparent porosity (%)	3.80–3.85

Table 2 – Properties of liquid paraffin.

Properties	Value
Viscosity (CPS) at 25 °C	8500–9000
Specific gravity at 25 °C	1.25
Fixed carbon (%)	48.2
Non-volatile matter (%)	81.12
Moisture (%)	<0.5

Experimental procedure

Starting materials (raw material, binder, and additives)

The raw materials used for create the batches composition of the dolomite refractories was dolomite (Table 1). The liquid paraffin was utilized as a binder (Table 2). Also, trivalent and tetravalentn-sized oxides (Supplier: US Research Nanomaterials, Inc., Fig. 1, Table 3) such as iron (Fe_2O_3), alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2) were used as additives.

Specimens preparation

Firstly, dolomite materials were calcined at 900 °C for 1 h and after it crushed to micro, 0–1, 1–3, and 3–5 mm particles. Composition comprise 0, 2, 4, 6, and 8 wt.% nano-sized oxides were made according to Table 4. Micro-sized dolomite is substituted

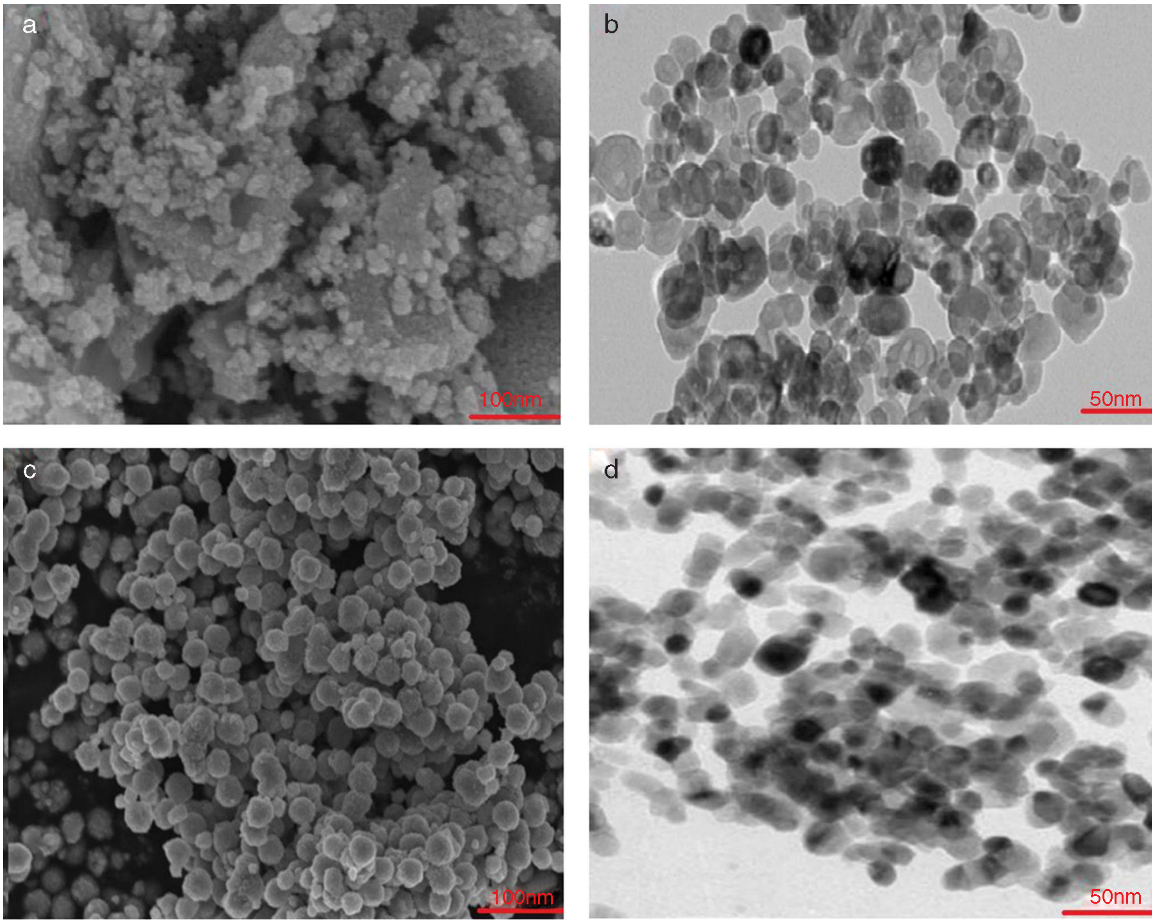

Fig. 1 – Transmission electron microscopy images of (a) Fe_2O_3, (b) Al_2O_3, (c) TiO_2, and (d) ZrO_2 nano-sized particles.

Table 3 – Properties of the nano-sized oxides.

Oxide	Purity (%)	Size (nm)	Density (g/cm^3)	SSA (m^2/g)	Color
Fe_2O_3	>98	40–50	5.24	115	Red
Al_2O_3	>99	55± 50	2.9	90	White
ZrO_2	>99.9	45± 40	5.89	160	White
TiO_2	>99	40–60	3.9	60>	White

Table 4 – Batch composition with specimen's code.

Specimens code	Liquid paraffin (wt.%)	Fe_2O_3 (wt.%)	Al_2O_3 (wt.%)	TiO_2 (wt.%)	ZrO_2 (wt.%)	Micro sized dolomite (wt.%)
MD	3	0	0	0	0	12
MDF_2	3	2	0	0	0	10
MDF_4	3	4	0	0	0	8
MDF_6	3	6	0	0	0	6
MDF_8	3	8	0	0	0	4
MDA_2	3	0	2	0	0	10
MDA_4	3	0	4	0	0	8
MDA_6	3	0	6	0	0	6
MDA_8	3	0	8	0	0	4
MDT_2	3	0	0	2	0	10
MDT_4	3	0	0	4	0	8
MDT_6	3	0	0	6	0	6
MDT_8	3	0	0	8	0	4
MDZ_2	3	0	0	0	2	10
MDZ_4	3	0	0	0	4	8
MCZ_6	3	0	0	0	6	6
MCZ_8	3	0	0	0	8	4

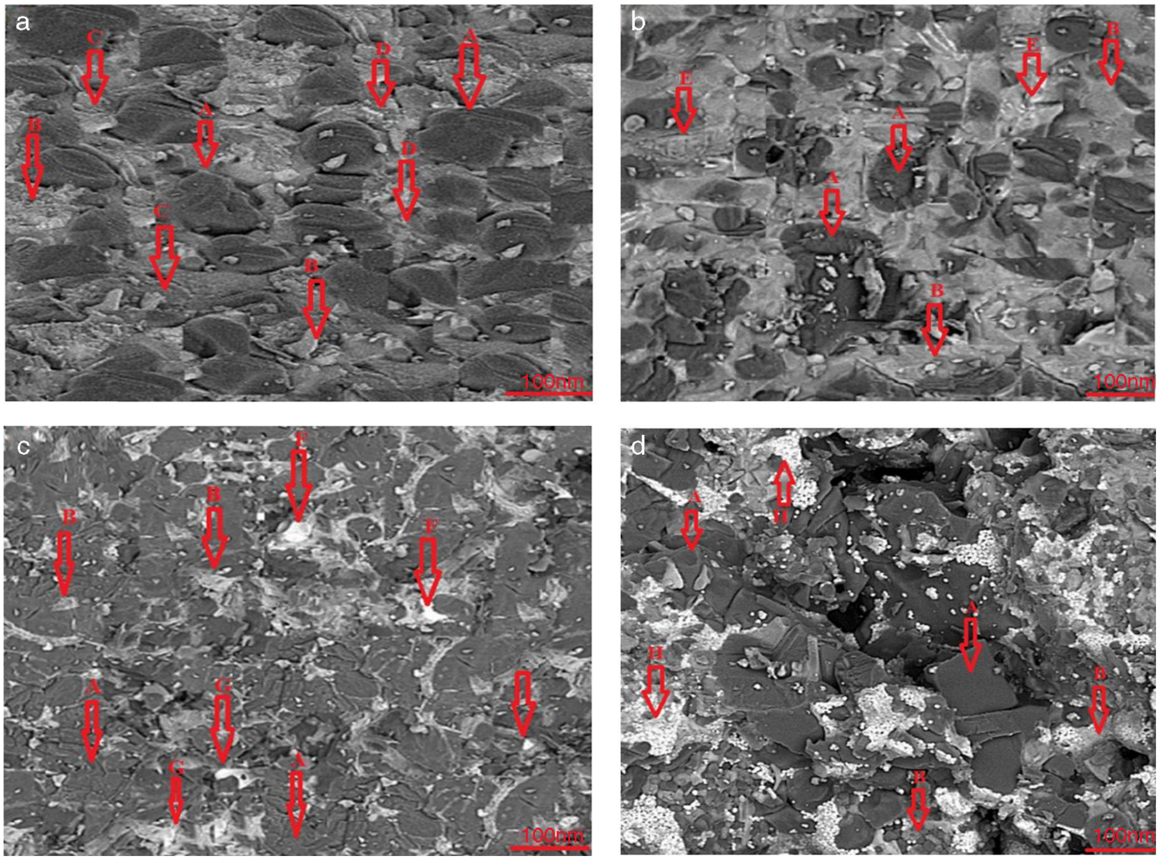

Fig. 2 – Scanning electron microcopy images of the specimens possess 8 wt.% (a) Fe_2O_3, (b) Al_2O_3, (c) TiO_2, and (d) ZrO_2 nano-sized oxides.

Table 5 – Mixing steps of dolomite compositions.

Steps	Mixing steps	Mixing time (min)
1	Coarse and medium (dolomite)	3
2	Addition of liquid paraffin	7
3	Addition of nano-sized oxide, and fine particles (dolomite)	12

by aforementioned nano-sized oxides (Table 5). Then all specimens pressed at 100 MPa. Green briquettes were dried at 110 ± 5 °C for 24 h and after it fired at 1600 °C with 4 h soaking at peak temperature.

Physical properties measurements

Apparent porosity (AP) and bulk density (BD)

The bulk density and apparent porosity were examined by a liquid displacement approach using Archimedes principle in a Kerosene medium (ASTM C-20). Three specimens were tested for each composition.

Hydration resistance

For determine the hydration resistance of the specimens, each specimen was grinded to gain a particle size finer than sieve no. 40 (425 μm) and after weighing, located in Petri dish in a climate room with 25 °C and 95% relative moisture. The specimens then were weighed at various times to 72 h. The percentage mass gains before and after hydration was the measures of hydration resistance (Eq. (3)).

$$\text{Hydration} \quad (\%) = \frac{M_2 - M_1}{M_1} * 100 \qquad (3)$$

where $M_{2(g)}$ = weigh gain after hydration test, $M_{1(g)}$ = initial weigh of the samples.

Phase and microstructure analysis

The existence of ceramic phases was determined by X-ray diffraction method (XRD) with Cu K_α radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA. Also, the microstructure analysis was evaluated using SEM 200 scanning electron microscope equipped with an electron dispersive X-ray spectroscopy (EDX) detector.

Results and discussion

Microstructure analysis

Fig. 2 demonstrate the Scanning Electron Microscopy (SEM) images related to the polished fractured surfaces of specimens possesses 8 wt.% of trivalent and tetravalent Nano-sized oxides. For specimens own trivalent nano-sized oxides, it

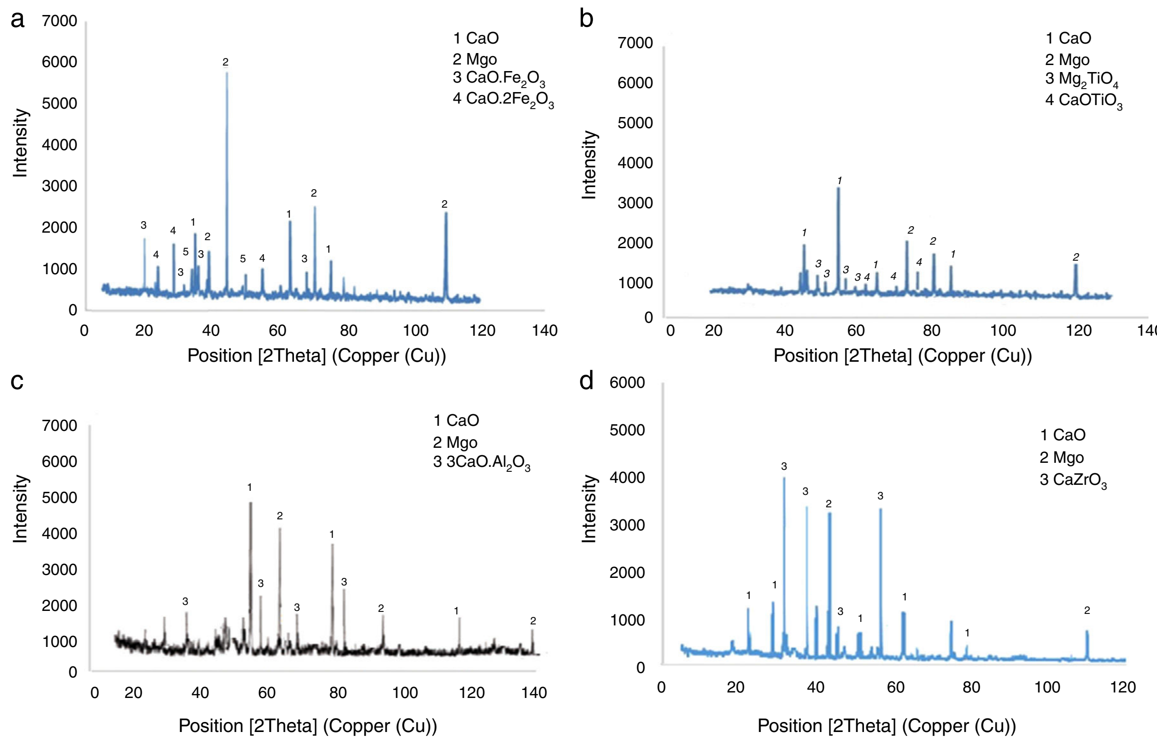

Fig. 3 – X-ray diffraction patterns relate to specimens possesses 8 wt.% (a) Fe_2O_3, (b) Al_2O_3, (c) TiO_2, and (d) ZrO2 nano-sized oxides.

Table 6 – EDX analyses of (A) MgO, (B) CaO, (C) CaO·Al_2O_3, (D) CaO·$2Fe_2O_3$, (E) 3CaO·Al_2O_3, (F) $CaTiO_3$, (G) Mg_2TiO_4, and (H) $CaZrO_3$ points.

Element	Point A (wt.%)	Point B (wt.%)	Point C (wt.%)	Point D (wt.%)	Point E (wt.%)	Point F (wt.%)	Point G (wt.%)	Point H (wt.%)
O	35.58	35.58	41.12	38.74	41.21	49.1	44.62	42.21
Mg	64.42	–	–	–	–	–	26.27	–
Ca	–	71.71	32.17	28.45	37.81	23.12	–	32.65
Ti	–	–	–	–	-	27.78	29.11	–
Al	–	–	–	–	20.98	–	–	–
Zr	–	–	–	–	–	–	–	25.23
Fe	–	–	26.71	32.81	–	–	–	–

was apperceived that direct-bonding among magnesia (MgO) and calcia(CaO) grains was evident, due to generation some low melting point phases such as 3CaO·Al_2O_3 (1524 °C), CaO·Fe_2O_3 (1449 °C, and CaO·$2Fe_2O_3$ (<1350 °C phases at the grain boundaries and triple points of matrix. For specimens own tetravalent nano-sized oxides more than dark gray and white gray particles recognized as magnesia and calcia phases. Also, there are phases besieged by the MgO and CaO ground mass. From the EDX and XRD analysis (Fig. 3, Table 6), these phases identified as $CaTiO_3$ (1975 °C, Mg_2TiO_4 (1732 °C, and $CaZrO_3$ (2345 °C. Aforementioned phases have high melting point.

Densification

Fig. 4 demonstrate the influence of trivalent and tetravalent nano-sized oxides on the bulk density and apparent porosity of the specimens after firing at 1600 for 4 h. It is observed that the bulk density increased and the apparent porosity decreased with additions nano-sized oxides, respectively. Also, it is observed that this trend, for specimens possesses tetravalent nano-sized oxides is higher than specimens containing trivalent nano-sized oxides. Densification improvement of the fired specimens with the incorporation of nano-sized oxides may be associated with the following theories:

(i) Further firing procedure of the refractory matrix owning to the attendance of nano-sized particles.
(ii) A better compression of the matrix on filling up of the intergranular porosities among magnesia (MgO) and calcia (CaO).
(iii) A better mass relocation due to nano-sized oxides can operate as a ceramic bond (abridge) among the MgO and CaO grains.
(iv) Generation phases with low melting point such as 3CaO·Al_2O_3, CaO·Fe_2O_3 and CaO_2·Fe_2O_3 to diminish the porosity and density is increased.

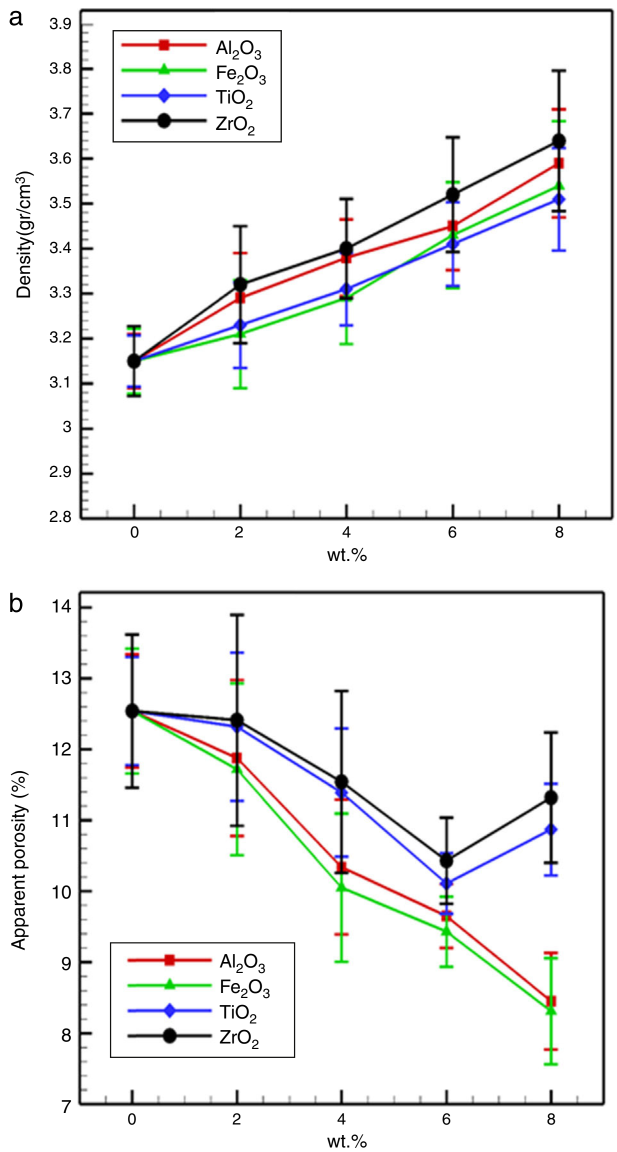

Fig. 4 – Change of the (a) bulk density and (b) apparent porosity of dolomite refractory specimens with various content of nano-sized oxides.

(v) The higher density of Fe_2O_3 (5.24 g/cm^3), Al_2O_3 (3.95 g/cm^3), TiO_2 (4.23 g/cm^3) and ZrO_2 (5.68 g/cm^3), compared to the dolomite (2.87 g/cm^3) and magnetite (3 g/cm^3).

(vi) Also, increasing in apparent porosity at high TiO_2 and ZrO_2 nanoparticles concentrations is due to large diversity in thermal expansion coefficients between MgO ($\sim 13.5 \times 10^{-6}$ °C^{-1}), CaO ($\sim 13.8 \times 10^{-6}$ °C^{-1}) $CaTiO_3$ ($\sim 12.2 \times 10^{-6}$ °C^{-1}), Mg_2TiO_4 ($\sim 10.1 \times 10^{-6}$ °C^{-1}), and ZrO_2 (7.5×10^{-6} °C^{-1}), it can generate extreme micro-cracks in the microstructure, stimulate a porosity enhancement.

Hydration resistance

From Fig. 5 it is illustrated that the mass gain of the dolomite specimens reduced extremely with nano-sized oxides addition. For the MD, the mass gain after 72 h was 3.49%. For specimens with Fe_2O_3 and Al_2O_3 nano-sized, with increasing the amount of additives reduces the weight gain, due to more grain growth and decreased grain boundary and porosity. The surface area was reduces along with grain growth with due to generation low melting phases, which is another contribution for improved hydration resistance. It is reported that the hydration resistance of lime (CaO) systems, strongly relies on the content of free CaO [1,3,4]. When ZrO_2 and TiO_2 nano-sized were added, the enhancement of the hydration resistance of the specimens is due to the following reasons:

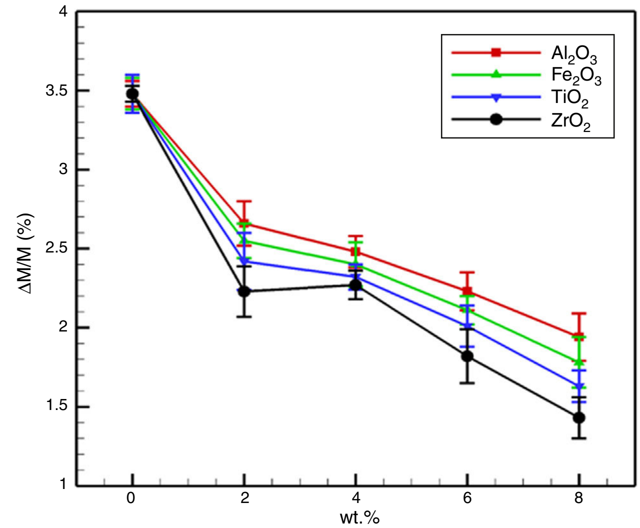

Fig. 5 – Influence of nano-sized oxides addition on hydration resistance improvement trend of dolomite specimens.

- Transition of partial free CaO to high hydration resistance phases such as $CaZrO_3$, Mg_2TiO_4 and $CaTiO_3$.
- The densification enhancement of dolomite bricks by nano-sized oxides can be rationalized on the basis of cation vacancy generation as follows, which increase the hydration resistance of dolomite specimens.

$$TiO_2 \xrightarrow{CaO} Ti^{00}_{Ca} + V''_{Ca} + 2O_O \quad (4)$$

$$ZrO_2 \xrightarrow{CaO} Zr^{00}_{Ca} + V''_{Ca} + 2O_O \quad (5)$$

Generally, the use of trivalent nano-sized oxides leading to the generation of some low melting phases that crated a protective layer on free-CaO and MgO surfaces which increases the hydration resistance of the specimens. But the application of tetravalent nano-sized oxides leading to the Zr^{4+} and Ti^{4+} cations create a solid solution with CaO, which diminish the Ca^{2+} concentration and results in the improved hydration resistance of specimens.

Summary

- The application of trivalent and tetravalent nano-sized oxides lead to improved densification and therewith an increase hydration resistance of dolomite specimens by the liquid phase firing mechanism and solid phase firing mechanism, respectively.

- The improvement trend of hydration resistance of specimens possesses various nano-sized oxides is $Al_2O_3 < Fe_2O_3 < TiO_2 < ZrO_2$.

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