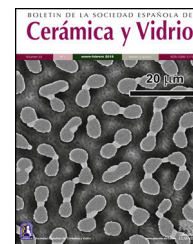




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MgO–CaO–Cr₂O₃ composition as a novel refractory brick: Use of Cr₂O₃ nanoparticles



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ARTICLE INFO

Article history:

Received 7 September 2016

Accepted 3 November 2016

Available online 15 December 2016

Keywords:

Cr₂O₃ nanoparticles

Hydration resistance

MgO–CaO refractory densification

ABSTRACT

At this study the effect of Cr₂O₃ nanoparticles (up to 3 wt.%) on the physical and mechanical properties of MgO–CaO refractory composition with emphasis on the hydration resistance improvement have been investigated. Specimens pressed at 90 MPa then were sintered at 1650 °C for 5 h in an electric furnace. Properties such as bulk density, apparent porosity, cold crushing strength and hydration resistance were examined. The crystalline phases and microstructure characteristics of sintered specimens were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDS), respectively. Results shown that add of the 1.5 wt.% Cr₂O₃ nanoparticles have the best results i.e. increased the bulk density (3.41 g/cm³), cold crushing strength (848 kg/cm²), hydration resistance (1.5%) and decreased apparent porosity (5.58%), respectively. The mechanism of specimens hydration resistance improvement are: (i) decreasing the amount of free CaO and MgO with converted to high hydration resistance phases such as CaCr₂O₄ and MgCr₂O₄ phases, (ii) promotion of the densification as well as (iii) modification of the microstructure.

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Nuevos ladrillos refractarios de MgO–CaO–Cr₂O₃: uso de nanopartículas de Cr₂O₃

RESUMEN

En este trabajo se ha estudiado el efecto de la adición de nanopartículas de Cr₂O₃ (hasta un 3% en peso) en las propiedades físicas y mecánicas de refractarios de MgO–CaO, poniendo especial énfasis en la mejora de la resistencia a la hidratación. Las muestras fueron prensadas a 90 MPa y posteriormente sinterizadas a 1.650 °C durante 5 h en un horno eléctrico. Se han evaluado propiedades tales como la densidad y la porosidad aparente, la resistencia a la compresión en frío y la resistencia a la hidratación. Las fases cristalinas y las características microestructurales de las muestras sinterizadas se han estudiado mediante difracción de rayos-X (DRX) y microscopía electrónica de barrido (MEB/EDS), respectivamente.

Los mejores resultados se han obtenido con una adición del 1,5% en peso de nanopartículas de Cr₂O₃, lo cual incrementa la densidad aparente (3,41 g/cm³), la resistencia a la compresión en frío (848 kg/cm²) y la resistencia a la hidratación (1,5%), y disminuye la porosidad aparente (5,58%), respectivamente.

Palabras clave:

Nanopartículas de Cr₂O₃

Resistencia a la hidratación

Densificación de refractarios de MgO–CaO

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<http://dx.doi.org/10.1016/j.bsecev.2016.11.002>

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Los mecanismos de mejora de la resistencia a la hidratación son: 1) disminución de la cantidad de CaO y MgO libre mediante la conversión a fases altamente resistentes a la hidratación, como son las fases CaCr_2O_4 y MgCr_2O_4 ; 2) fomento de la densificación, y 3) modificación de la microestructura.

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Introduction

Magnesia-Doloma or Mag-Dol (MgO - CaO) refractory bricks have been considered as one type of chrome free refractories that are suitable for substituting the MgO - Cr_2O_3 refractories [1]. Typically, MgO - CaO refractory bricks composed by 50–80 wt.% of MgO [2]. Different ways have been proposed to produce MgO - CaO refractory bricks. A new approach is using sintered and fused co-clinker of magnesite and dolomite as a starting material for the MgO - CaO refractories which would lead to more homogenous products with more desirable properties [3]. Another way is mixing magnesite and dolomite and calcination them at high temperature that let to in-situ MgO - CaO refractory brick [4]. These refractory bricks have been playing a crucial role as a refractory material in various industries such as secondary metallurgy (AOD, VOD, etc.), non-ferrous furnaces (copper converter) and cement making (rotary kiln) because of their great advantages such as high temperature stability, low thermal expansion, excellent thermal shock resistance, outstanding erosion-corrosion performance at high temperatures, wide availability of raw materials, low vapor pressure, and thermodynamic stability in the presence of carbon in a composite oxide/carbon refractory [1–8]. Furthermore, MgO - CaO refractories are beneficial to removing inclusions from molten steels; thus, they have been considered to be one of the effective refractory types for processing clean steel products [2,4,9]. In recent years, with the increasing demands of molten steel purity, the awareness of environmental protection and resource shortage grows, MgO - CaO materials have become one of the attractive steelmaking refractories [3–6]. However, in spite of these advantageous properties, the application of MgO - CaO refractory bricks has not been popular due to their tendency to hydration when exposed to the atmosphere [1–5,10].

Recently, much effort has been made to improve the performance of MgO - CaO refractory bricks through the addition of different additives, such as V_2O_5 [11], CuO [12], FeTiO_3 [13], La_2O_3 [14], Ce_2O_3 [15], ZrO_2 [16], and Fe_2O_3 [17]. It has also been reported that physical properties of MgO - CaO refractory bricks could be improved by using pitch, tar, flake, and vein graphite minerals [2–6]. Also the hydration resistance of MgO - CaO refractories can be improved by treating in a CO_2 atmosphere or by surface phosphate coating which leads to the formation of a dense layer on the surface of CaO , and protect CaO grain from hydration [18,19]. Nanotechnology was introduced to the refractory industry some year ago, and nowadays it is an important tool included in many research projects [16,20–22]. Several research groups have been working on the addition of different types of additives in ceramic bodies, and some of them have focused their investigations on the use of

Table 1 – Physic-chemical of raw materials.

Oxide	Magnesite	Dolomite
SiO_2	0.95	0.7
Al_2O_3	1.6	2.8
Fe_2O_3	0.6	0.8
TiO_2	0.2	0.2
CaO	2.7	57.2
MgO	93.2	37.2
Alkalis	0.3	0.44
<i>Physical properties</i>		
Bulk density (g/cm^3)	3.28–3.3	2.85–3.1
(%) Apparent porosity	3.75–3.80	3.80–3.85

nano-oxides, due to the reported benefits of adding these particles to ceramic bodies [23–26]. On the other hand, it is known that the fine fraction is considered to be the weakest constituent of a refractory matrix. Therefore, it has to be reinforced by the development of a strong bond. The bonding strength represents one of the main microstructural characteristics that contributes to the development of a reliable refractory matrix. Increasing the bonding strength, the resistance against many kinds of stresses during performance and structural spalling would be improved [25]. Taking the above into account, in the present research work, the effect of nanoparticles of Cr_2O_3 as structural bonding on the microstructure, sintering process and properties of MgO - CaO refractory matrix was investigated.

Experimental procedure

The raw materials used for preparation the batch composition of the MgO - CaO refractories specimens were calcined magnesite and dolomite (derived from Birjand and Zefreh mines in Iran, respectively), and the details of them are provided in Table 1. High-grade nano- Cr_2O_3 (supplier: US Research Nanomaterials, Inc. CAS Number: 1308-38-9) with an average particle size in the range of 50–60 nm was used as additive (Fig. 1, Table 2). Also a liquid resin was used as binder and the details of it are provided in Table 3. Different compositions of MgO - CaO refractories specimens were formulated by varying nano- Cr_2O_3 content between 0 and 3 wt.% with fixed CaO content of 35 wt.%. Conventionally used MgO - CaO refractory (Batch MC) has also been prepared under similar conditions for comparison purpose and details of all the batches are provided in Table 4.

In order to obtain a suitable and stable suspension of nano oxides, a dispersion process was carried out using an acrylic copolymer (Zephrym PD3315) as a dispersant agent and acetone as a dispersion medium. The ultrasonic agitation method

Table 2 – Properties of the high-purity nano-Cr₂O₃.

Powder	Purity (%)	Size (nm)	SSA (m ² /g)	Density (g/cm ³)	Color
Cr ₂ O ₃	>99	50–60	>80	5.22	Green

Table 3 – Physico-chemical of liquid resin.

Properties	Content
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

Table 4 – Batch composition with sample code.

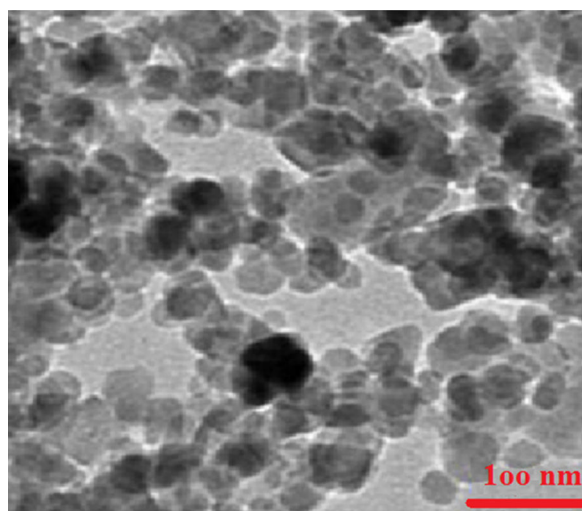
Sample code	Cr ₂ O ₃ nanoparticle (wt.%)	Liquid paraffin (wt.%)
MC	0	2.5
MCCr _{0.5}	0.5	2.5
MCCr ₁	1	2.5
MCCr _{1.5}	1.5	2.5
MCCr ₂	2	2.5
MCCr _{2.5}	2.5	2.5
MCCr ₃	3	2.5

Table 5 – Mixing sequence of MgO–CaO refractory samples.

Steps	Mixing sequence	Mixing time(min)
1	Coarse and medium magnesite and dolomite	2
2	Addition of liquid paraffin	5
3	Addition of nano-Cr ₂ O ₃ and fine magnesite and dolomite	10

(Aqua sonic TM 75T model) was carried out for 1 h for homogenization.

All the raw materials, additives and binders were thoroughly mixed in a pan mixer as per the batch composition and following the mixing sequences, as mentioned in Table 5, to

**Fig. 1 – TEM image of Cr₂O₃ nanoparticles.**

obtain a homogeneous mixture. Mixed batches were aged for 1 h and specimens with a diameter of 50 mm and a height of 50 mm were obtained using uniaxial press at 90 MPa. Pressed refractory specimens were sintered in an electric furnace at 1650 °C at a rate of 3 °C/min for 5 h, which removes volatiles, polymerizes the organic binders and imparts strength to the shapes. Different physical and mechanical properties of the sintered samples were evaluated. An average of five different individual test results is represented here in different plots as data point and discussed in the results and discussion portion. Apparent porosity (AP), bulk density (BD), and cold crushing strength (CCS) were measured as per the standard of is: 1528, part-8 (2002), is: 1528, part-12 (2002) and is: 1528, part-4 (2002), respectively. In order to determine the hydration resistance of the refractory specimens, each sample was powdered to gain a particle size finer than sieve no. 40 (425 μm) and after weighing, placed in Petri dish in a climate room with 25 °C temperature and 95% relative humidity. The samples then were weighed at different times to 72 h. The percentage weight gains before and after hydration was the measures of hydration resistance Eq. (1).

$$\text{Hydration resistance (\%)} = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

M_2 , weight gain after hydration test; M_1 , weight of sample before hydration test.

The presence of ceramic phases was determined by X-ray diffraction technique (XRD; Bruker D8 Advance model) with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA. The scans were performed in the 2θ range from 10 to 110 with a step scan of 0.05 and 1.5 s per step in a continuous mode. The microstructure analysis was performed using an FEI Nova Nano SEM 200 scanning electron microscope equipped with an electron dispersive X-ray spectroscopy (EDX) detector (EDAX, Apollo XP model, 2930 serial number).

Results and discussion

Phase analysis

Figs. 2 and 3 Shows the XRD patterns of the samples with and without Cr₂O₃ nanoparticles. Periclase (MgO) and lime (CaO) were the main crystalline phases in all the samples. Also, in the sample with 1.5% and 3 wt.% Cr₂O₃ nanoparticles; MgO, CaO, CaCr₂O₄ and MgCr₂O₄ were the main crystalline phases. CaO and MgO reacted with Cr₂O₃ nanoparticles and formed CaCr₂O₄ and MgCr₂O₄, with melting point 2170 °C and 2350 °C respectively [26]. The aforementioned phases at the sintering temperature (1650 °C) are in solid state. Also Cr₂O₃ phase peaks not exist. It indicates that all added Cr₂O₃ had reacted with CaO and MgO to form CaCr₂O₄ and MgCr₂O₄ phases which preferred to locate on intragranular and intergranular sites of MgO and CaO grains. The intensity of the CaCr₂O₄

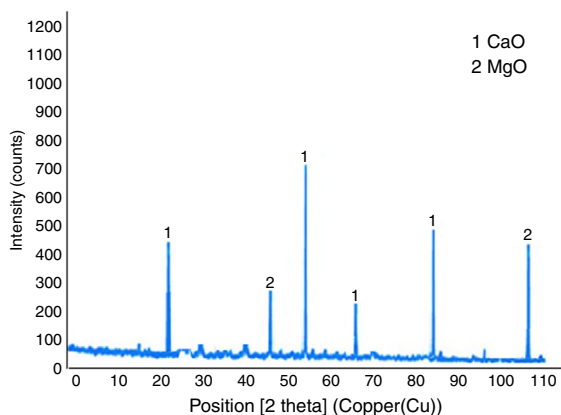


Fig. 2 – XRD pattern of the MC sample.

and MgCr_2O_4 phases peaks for samples contain more Cr_2O_3 nanoparticles (MCCr_3) are higher than samples without (MC) or contain lower amount of the Cr_2O_3 nanoparticles.

Microstructure analysis

Fig. 4a shows the microstructure corresponding to the specimen without the addition of Cr_2O_3 nanoparticles. From the analysis, the typical microstructure of an MgO – CaO fractured surface is observed. In addition, porosity and a white gray phase corresponding to CaO (calcia) were identified as well as MgO (magnesia) particles (dark phase), identified by energy dispersive X-ray (EDX) (Table 6). The microstructure analysis by SEM corresponding to specimens with Cr_2O_3 nanoparticles additions is shown in Fig. 4b and c. A homogeneous microstructure composed mainly of a well-distributed phases is observed. Using energy dispersive X-ray spectroscopy analysis (EDX), dark gray phase was identified as MgO (magnesia) and white gray phase was identified as CaO (calcia). As a second phase, there are two phases surrounded by the periclase and calcia ground mass. The first one corresponds to light gray particles composed by Ca and Cr elements, as it was identified by EDS. This phase is a spinel compound found in the XRD analysis and identified as CaCr_2O_4 . The last phase corresponds to bright gray particles composed by Mg and Cr elements (identified by the EDS technique), (Table 6). From the EDS and XRD analysis, this phase was confirmed as a spinel MgCr_2O_4 . During the microstructural analysis, it was observed that CaCr_2O_4 and MgCr_2O_4 are homogeneously dispersed through

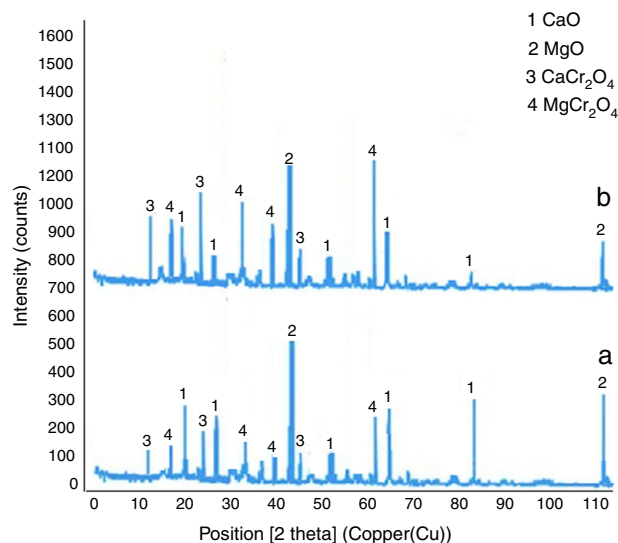


Fig. 3 – XRD pattern of the (a) $\text{MCCr}_{1.5}$ and (b) MCCr_3 samples.

the entire matrix. As the Cr_2O_3 nanoparticles content was increased, some coarse agglomerations composed by CaCr_2O_4 and MgCr_2O_4 were formed. This microstructural characteristic described above can be correlated to the diminished mechanical resistance at higher Cr_2O_3 nanoparticles content since CaCr_2O_4 and MgCr_2O_4 agglomerates could be acting as stress concentrates, thus making the matrix weaker.

Densification

Bulk density and apparent porosity are the two important indicative parameters to ascertain the densification of a ceramic system [2]. The variation in bulk density and apparent porosity of the sintered samples fired at 1650°C for 5 h with different amount of Cr_2O_3 nanoparticles have been shown in Fig. 5. It is observed that the bulk density begins to increase gradually starting from 0.5 wt.% of Cr_2O_3 nanoparticles (3.1 g/cm^3), and finding its higher value at 3 wt.% (3.41 g/cm^3). This behavior can be attributed to:

- A better compaction of the body on filling up of the intergranular voids between MgO and CaO grains.
- A better sintering of the refractory body due to the presence of fine/reactive nano- Cr_2O_3 phase.

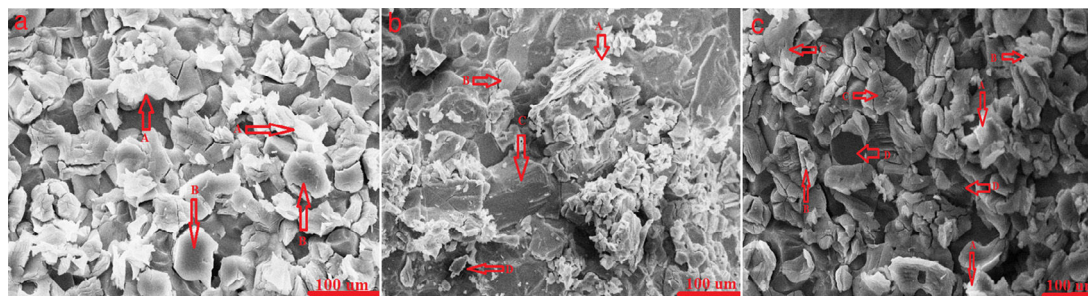
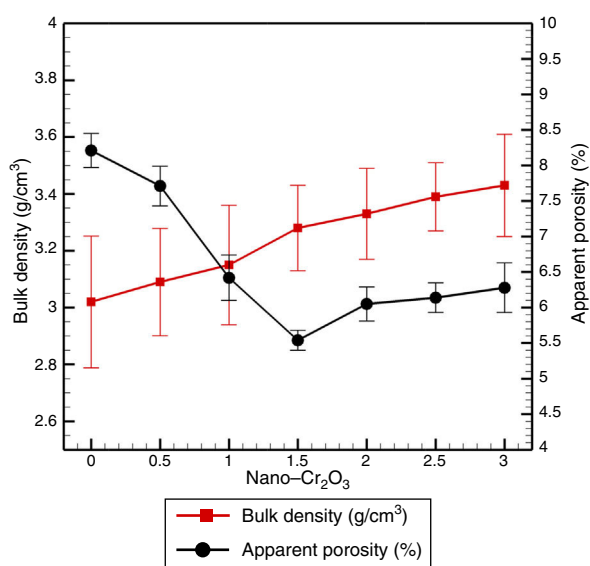


Fig. 4 – SEM images of fractured surfaces of the samples with various Cr_2O_3 nanoparticles additions: (a) MC, (b) $\text{MCCr}_{1.5}$ and (c) MCCr_3 samples (A = CaO , B = MgO , C = CaCr_2O_4 and D = MgCr_2O_4 phases).

Table 6 – EDX analyses of (1) A (CaO), (2) B (MgO), (3) C (CaCr₂O₃) and (4) D (MgCr₂O₄) points.

Element	Point A (wt.%)	Point B (wt.%)	Point C (wt.%)	Point D (wt.%)
O	37.19	38.54	43.73	45.65
Mg	62.64	–	0.52	15.30
Si	–	–	0.41	0.11
Ca	–	61.36	18.15	0.8
Cr	–	–	34.46	32.60
Al	–	–	2.60	5.42
Au	0.17	0.19	0.13	0.12

**Fig. 5 – Variation of the densification of MgO–CaO refractory samples with addition Cr₂O₃ nanoparticles.**

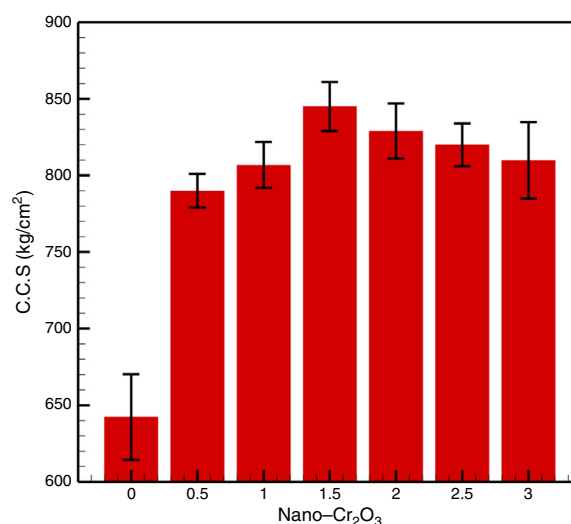
- (iii) The higher true density of Cr₂O₃ (5.22 g/cm³) [26], in comparison to the CaO (3.35 g/cm³) and MgO (3.58) [3–5] or maybe because of a possible new phases formation [such as MgCr₂O₄ (4.43 g/cm³) and CaCr₂O₄ (4.43 g/cm³)] [26,27].
- (iv) And Cr₂O₃ nanoparticles alter the grain boundary between assemblage and the morphology of the grains, changing the dihedral angle (θ). The lowering of the dihedral angle means γ_{ss} will be smaller, which will facilitate grain-to-grain contact and ultimately direct bond formation. This tendency increases the densification [2].

But the apparent porosity tendency shows that its values decrease with increasing Cr₂O₃ nanoparticles content up to 1.5 wt.% and for further spinel Cr₂O₃ nanoparticles (2 up to 3 wt.%), the apparent porosity increased. The reason is:

- (i) Due to large differences in thermal expansion coefficients between MgO ($\sim 13.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) [5], CaO ($\sim 13.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) [5] and MgCr₂O₄ ($\sim 8.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) [26], it can generate excessive micro-cracks formation in the microstructure, provoking a porosity increment.

Cold crushing strength

Fig. 6 shows the variation of the cold crushing strength of the MgO–CaO refractory compositions with addition Cr₂O₃ nanoparticles. The values of the CCS, registered by the

**Fig. 6 – Variation of C.C.S of the MgO–CaO refractory samples with different amount of Cr₂O₃ nanoparticles.**

refractory specimens containing Cr₂O₃ nanoparticles, were much higher than those determined by the specimens without nanoparticles addition. A sharp increase in the strength value is obtained with addition Cr₂O₃ nanoparticles up to 1.5 wt.%. The maximum CCS was found for the MCCr_{1.5} specimen (348 kg/cm²). It was observed that higher Cr₂O₃ nanoparticles concentrations (from 2 to 3 wt.%) decreased the CCS of the MgO–CaO refractory compositions.

This mechanical tendency may be attributed to the following phenomenons:

- (i) A good compactness induced by the Cr₂O₃ nanoparticles.
- (ii) The low apparent porosity registered (for MCCr_{0.5}, MCCr₁ and MCCr_{1.5} samples).

For MCCr₃ formulation corresponding to 2 up to 3 wt.% of Cr₂O₃ nanoparticles, there is a gradually decline in mechanical properties. This phenomenon can be explained due to the formation of coarse agglomerates and a large thermal expansion coefficient (MgO = $\sim 13.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, CaO = $\sim 13.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, MgCr₂O₄ = $\sim 8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) mismatch between different phases presented in the refractory bodies. The different thermal expansion coefficient between phases leads to the formation of peripheral micro-cracks around agglomerates; these micro-cracks could be a detriment to mechanical performance, as can be observed in the plot of Fig. 6.

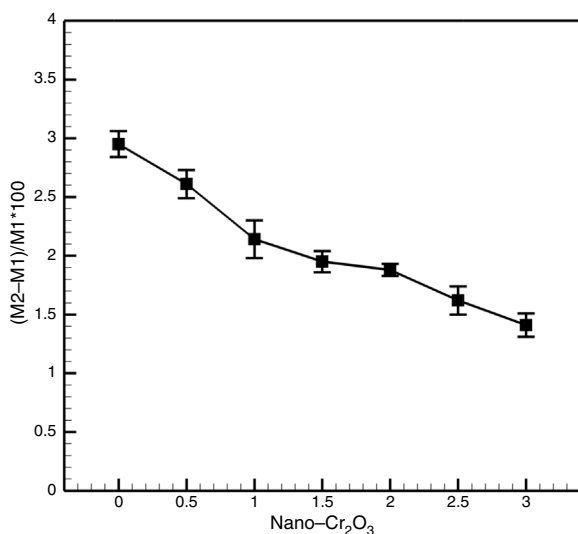


Fig. 7 – Effect of Cr₂O₃ nanoparticles addition on the improvement of hydration resistance of MgO–CaO samples.

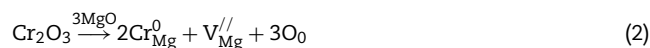
Hydration resistance

Refractories based on MgO and CaO can undergo hydration in humid atmosphere. In this case the powder grains break, the material is pulverized, and particles crack [8,11,13,14]. Several methods have been tested to control this phenomenon, including methods through which CaO and MgO grains are covered by phases grow in the grain boundaries and those through which the porosity of the system decreases; all methods lead the accession of CaO and MgO to the moisture to decrease [1–4,7,11,14]. From Fig. 7 it is observed that the mass gain of MgO–CaO specimens decreased appreciably with Cr₂O₃ nanoparticles addition. For sample without addition, the mass gain after 72 h was 2.95, which was gradually decreased with increasing the amount of Cr₂O₃ nanoparticles. The degree of hydration is related to the absorption of water on the grain boundary surface. It is known that the hydration resistance of CaO contains materials, both rich-CaO and rich-MgO materials, which is strongly dependent on the content of free CaO in materials and its microstructure [5,16]. When Cr₂O₃ nanoparticles were added, the promotion of the hydration resistance of the refractories is considered due to the following reasons:

- The promotion of densification by the addition of Cr₂O₃ nanoparticles decreased the porosity of the refractories and thus its active specific area was decreased while the refractories were exposed to a humid environment.
- by increasing the addition of Cr₂O₃ nanoparticles, the content of free CaO and MgO in refractories decreased further (because of convert free CaO and MgO to CaCr₂O₄ and MgCr₂O₄ phases that are better hydration resistance rather than CaO and MgO) and thus the hydration resistance of refractories was improved.
- It is well known that the hydration reaction always begins from the sites with crystal defects [2,5,16]. Thus, the grain boundaries, especially the triple points, are the poor hydration resistance sites. When Cr₂O₃ nanoparticles was

added, they formed phases such as CaCr₂O₄ and MgCr₂O₄ located at grain boundaries and the triple point of CaO and MgO grains, thus preventing the hydration resistance of the MgO–CaO specimens.

a possible explanation for the effect of Cr₂O₃ nanoparticles on the improve the densification and hydration resistance of MgO–CaO refractories involves a solution process in which Cr³⁺ cations are added to CaO (MgO) to form a solid solution:



The main notice in reactions (2) and (3) is the formation of calcium or magnesium vacancies. In reactions (2) and (3) these vacancies formation affects the calcined powders by forming new surfaces, because of the role of the electrostatic repulsion force between anions in vacancies, thus increasing the surface energy and promoting solid reactions and the sintering process. These effects increase the powder density, so as to increase the hydration resistance of MgO–CaO refractories. In terms of a preference of cations to form a solid solution with CaO and MgO, improvement of the hydration resistance of the CaO–MgO via a reduction of the Ca²⁺ and Mg²⁺ concentration in the solid of CaO and MgO with Cr³⁺ cations was favored.

Conclusion

- The addition of Cr₂O₃ nanoparticles helps in improvement of the densification process by solid state sintering mechanism. A maximum density of 3.41 g/cm³ is achieved at 1650 °C in presence of 3 wt.% nano-Cr₂O₃.
- The high cold crushing strength of Cr₂O₃ nanoparticles doped CaO–MgO specimens is due to the development of a strong and continuous bonding structure.
- The addition of Cr₂O₃ nanoparticles leads to the high solubility of chrome oxide (Cr₂O₃) in calcia (CaO) and magnesia (MgO) that leads to the formation of cationic vacancies in calcia and magnesia, resulting in a high atomic mobility, encouraging the precipitation and enhancing the direct bond formation.
- The addition of 1.5 wt.% of Cr₂O₃ nanoparticles contributed to reach a maximum increment in physical and mechanical properties.
- In general, for the purpose to improvement the hydration resistance of the MgO–CaO refractories, the addition of Cr₂O₃ could be more effective by nano-technology due to its intrinsic properties such as significant surface effect, size effect and higher activity.

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