REVIEW PAPER

A Review on Recent Advances on Magnesia-Doloma Refractories by Nano-Technology

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ABSTRACT
Due to exhibiting an excellent chemical resistance against basic environments at high temperature, good thermal shock resistance, thermodynamic stability in the presence of carbon, and a suitable abrasion resistance, MgO-CaO refractories are widely used in argon-oxygen decarburization furnaces in the metallurgy industry and cement rotary kilns. 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. Also, MgO-CaO materials have become one of the attractive steelmaking refractories because of their low cost and high ore reserves. However, in spite of these primary advantages, the application of MgO-CaO refractories has not been popular due to its tendency to hydration when exposed to the atmosphere. In world most of MgO-CaO bricks producers used of organic components such as tar, pitch, and peck for produce MgO-CaO refractories. But during the application of these bricks in steel and cement and industrials, they released CO and CO_2 gases to air and pollute the atmosphere. For this reason, recently some researcher investigate the effect of additive nanoparticles on MgO-CaO refractories performance. They reported the used of Nano-additive have acceptable results and additive nanoparticles can replace by aforementioned environment contaminating organic compounds. In this study, we reviewed all effort that done for improving the hydration resistance of MgO-CaO refractories by application of Nano-additives with an emphasis on the beneficial the use of additives nanoparticle for reduction of environmental pollution by various industries which used of MgO-CaO refractory bricks.

Keywords: *MgO-CaO, Refractories, Nanoparticles, Additive, Hydration Resistance.*

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INTRODUCTION

Typically, MgO-CaO refractories are composed of50-80 wt. % of MgO. Different ways have been proposed to produce MgO-CaO refractories [1-5]. Due to exhibiting an excellent chemical resistance against basic environments (as slag and fluxes) at high-temperature, good thermal shock resistance, low vapor pressure, thermodynamic stability in the presence of carbon, and a suitable abrasion resistance, MgO-CaO refractories are widely used in ferrous, non-ferrous and cement industries. However, in spite of these advantageous properties, the application of MgO-CaO refractory bricks have not been popular due to their tendency to hydration when exposed to the atmosphere [5-10].

Recently Nano-technology was introduced to the MgO-CaO refractories industry, and nowadays it is an important tool included in many research

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projects [11]. In this study, all the efforts which donned for improvement the hydration resistance of MgO-CaO refractories were investigated and revealed that the use of nanoparticles has been the best results.

Refractories and Magnesia-Doloma Refractories

Refractories are in use since mankind began to develop metallurgical process, being clay the first refractory raw material ever used. This traces refractory development back to years 3500-3000 BC, and at around 1500 BC furnaces made of refractory bricks have started to be developed for the production of metals and glass. Up to the 19th century, refractories were composed of natural ores, such as dolomite stones and clay, because, the temperatures required for ore beneficiation, as well as the aggressiveness of the industrial slags, were not as demanding as those of modern industry. It was at the end of the 18th and the beginning of the 19th century that the foundations of modern metal beneficiation, the development of Portland cement and of modern glass processes started to impose higher requirements on the refractory industry. The new processes demanded higher quality refractory linings, which brought the need to use higher quality raw materials. Silica, zircon sand, chrome ore, magnesite, dolomite, and fireclay started to be used according to the particularities of the process for which the refractory was needed. Schaefer rediscovered monolithic linings at 1914, which were pliable in the beginning, but evolved to cement-bonded powdery concretes in the 1930's [12]. In the 1960's, calcium-aluminate cement, more specifically Cement Fondue started to be used for refractory applications, followed by higher-quality 70% and 80% cement at the end of 1970's and beginning of 1980's. Concomitantly, the difference between mechanical and corrosion resistance of castables, when compared to bricks, started to be diminished, due to the introduction of super-fine raw materials and dispersing aids to castables, which enabled the reduction of cement and water content, creating a more compact microstructure with enhanced properties. In the beginning of the 1990's, pumping was adapted from the building to the refractory industry, which enabled very high installation rates, and also reduced the material losses and environmental problems associated to dry gunning [13]. Refractories play an important role in metallurgical, glassmaking and ceramic industries, where they are formed into a variety of shapes to line the interiors of furnaces or kilns or other devices for processing the materials at high temperatures [14-16]. Many of the scientific and technological inventions and developments would not have been possible without refractory materials. Dreaming about producing one kilogram of any metal without the use of refractory is almost quite impossible. The ASTM C71 defines the refractories as "nonmetallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000 °F (538°C) [12, 14]. In tune with the changing trends in steelmaking, especially in ladle metallurgy, the high performing shaped refractories are on an increasing demand in recent years. The higher campaign lives and the variety of the newer steelmaking operations are decided by the availability and performance of such shaped refractories with superior high-temperature mechanical strength, erosion and corrosion resistance [17]. Initially, the ladles were used only to transport the steel from steel making unit to casting bay, but nowadays the refining process is also carried out in the same. Thus, steel producers throughout the world have been putting on a continuous effort to improve the ladle life in order to increase the performance of ladles as well as reduces the specific consumption of refractories so as to have a strong grip over the cost and quality of steel and also to increase the ladle availability with lesser number of ladles relining per day. Due to the above-said reasons, there had been a great technological evolution in ladle lining concept such as; Zonal lining concept, which deals with both selections of refractory quality and refractory lining thickness [17-19].The type of refractories to be used is often dictated by the conditions prevailing in the application area. Generally, refractories are classified into two different groups:

(a) Based on raw materials, the refractories are subdivided into three categories such as acidic (zircon, fireclay, and silica), basic (dolomite, magnesite, magnesia-carbon, chrome-magnesite and magnesite-chrome) and neutral (alumina, chromite, silicon carbide, carbon, and mullite).

(b) Based on the manufacturing process, the refractories are subdivided into two categories such as shaped refractories (available in the form of different brick shapes, and includes the oxide and non-oxide systems) and unshaped refractories (which includes mortars, castables and monolithic) [17, 20].

The MgO-CaO system is remarkable for the high liquidus and solidus temperatures over the complete range 100% MgO- 100% CaO, as the eutectic for the CaO–MgO binary system occurs at 2370 ºC [3, 21]. MgO–CaO bricks are high-value refractories composed of lime (CaO) and periclase (MgO). MgO –CaO refractories have some advantageous and disadvantageous compared to MgO and CaO refractories (Table 1). Typically, these refractories are composed of 50-80 wt. % of MgO. MgO-CaO refractories are considered as one type of chrome-free refractories that are suitable for substituting the MgO-Cr_2O_3. Different ways have been proposed to produce MgO-CaO refractories. 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. Another way is mixing magnesite and dolomite and calcination them at high temperature that let to in–situ MgO-CaO refractory brick [2, 6].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 advantageous 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[21, 22]. 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 [23]. 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 [24].However, in spite of these advantages properties, the application of MgO-CaO refractory bricks has not been popular due to their tendency to hydration when exposed to the atmosphere[1, 25-28]. The CaO and MgO phases react easily with moisture in the atmosphere and formation CaO $(OH)_2$ and Mg $(OH)_2$ phases (Eq. 1 and 2), the volume expansion of the resultant can cause severe damage to the materials [29, 32-36].

$$CaO + H_2O = Ca(OH)_2 \quad (1)\ [1, 2\ and\ 5]$$
$$MgO + H_2O = Mg(OH)_2 \quad (2)\ [1, 2\ and\ 5]$$

Much effort has been made to improve the performance of MgO-CaO bricks. It has been reported that physical properties of MgO-CaO refractory bricks could be improved by using pitch, tar, flake, and vein graphite minerals [22, 26, 68, and 38]. For example, multi-impregnated pitch-bonded dolomite refractory brick for ladle furnace was described by Rabahand Ewais [39]. Brick samples were prepared from a blend of calcined dolomite mineral and coal tar pitch. The blend was hotly mixed and pressed under a compression force up to 151 MPa. Green bricks were baked for 2 h at temperatures up to 1000◦C. Voids in the baked bodies were filled with carbon by multiple impregnations using low softening point coal tar pitch. Each impregnation step (30 min)was followed by calcination at 1000◦C. Brick samples containing8–12 wt.% coal tar pitch binder and

Table 1. Compare properties of MgO, CaO and MgO-CaO refractories [15]

Raw material	Expensive	Cheep	Cheep
Chemical character	Basic	strongly basic	strongly basic
Hydration resistance	good	very poor	poor
Fusion point	very high	very high	high
High–temperature stability			
-at oxidizing Atmosphere	Good	Good	Good
-at reducing atmosphere	moderate	good	moderate
Thermal Shock Resistance	Poor	moderate	moderate
Thermo-mechanical Behavior	good or very (good-strongly depending on impurity and texture)	good or very (good-strongly depending on impurity and texture)	good or very (good-strongly depending on impurity and texture)
Corrosion Resistance To:			
-Ferruginous Slags	good	poor	poor
-Ca-Silicates	moderate	very good	good
-Alkaline Slags	very good	very good	very good

pressed under 108–151 MPa acquired quantify crushing strength. However, multi-impregnating favored the mechanical strength of the baked brick samples and improved their hydration resistance (>45 days). Dolomite brick samples containing 10 wt. % coal tar pitch and pressed at 108 MPa gave high hydration resistance (more than 60 days in normal condition) compared to the hydration resistance of the commercial bricks (30 days). The prepared brick samples have acceptable density, chemical stability, outstanding resistance and good mechanical properties that would meet the requirements of ladle furnace (LF) for steelmaking industry. Although the aforementioned method (used of tar, coal, and pitch) have acceptable results, due to released CO and CO_2 gases into the atmosphere it can lead to polluting the air. Also, the hydration resistance of MgO-CaO refractories can be improved by treating in a CO_2atmosphere or by surface phosphate coating which leads to the formation of a dense layer on the surface of CaO and protects Cao grain from hydration [1].For example, Min Chen *et al.* [40] reported the effect of porosity on carbonation and hydration resistance of CaO materials. Cao pellets with different porosity were carbonated at 700 ◦C in the CO_2 atmosphere. The carbonation rate was controlled by the diffusion of CO_2, regardless of the difference in porosities. For the low-porosity pellet, carbonation reaction only occurred on the surface, with a dense $CaCO_3$ film thus formed, which combined well with the substrate material; while for the pellet of high-porosity, the carbonation reaction occurred simultaneously both on surface and inside pores, and each CaO grain was surrounded by $CaCO_3$ film that contained micro fissures. Hydration test results showed that carbonation treatment could effectively improve the hydration resistance of CaO materials regardless of porosity, but the carbonated high-porosity pellet was prone to breakage due to a poor combination between the carbonated CaO grains. Therefore, for the purpose to improve the hydration resistance by carbonation treatment, it is recommended that the CaO materials should be either with less appreciable apparent porosity or with a limited carbonation ratio for the high-porosity CaO material. Also, much effort has been made to improve the performance of MgO-CaO bricks through the addition of different additives [27, 37, and 41], such as V_2O_5 [42], CaF_2 [43], CuO [9], $FeTiO_3$ [44], ZrO_2 [45, 46], Ce_2O [23], NiO [47], BaO [48], Al_2O_3 [49], $ZrSiO_4$ [50], La_2O_3 [51, 52] and Fe_2O_3 [7, 53, 54, 55], For example; Min Chen *et al.*[56] investigated the slaking resistant of CaO aggregate from lightweight $CaCO_3$ with oxide addition. For this propose, CaO aggregate was sintered from reagent-grade lightweight $CaCO_3$ powder by the addition of 0–20% (molar ratio) MgO and ZrO_2, respectively. The results showed that the CaO derived from lightweight $CaCO_3$ was highly sinterable and compact CaO aggregate with relative density above 96% was obtained after sintering at 1400 °C for 2 h, but further increase of compactness was restrained due to the occurrence of abnormal grain growth. The densification of the aggregate was promoted due to the behavior of oxide addition on restraining the grain growth of CaO. With increasing the amount of oxide addition, the microstructure of CaO aggregate underwent a restructuration process. Homogeneous microstructure, with well -growing MgO grains occupying most of the boundary triple points of CaO grain, formed by the addition of 20% MgO. Especially when 20% ZrO_2 was added, a $CaZrO_3$ layer formed around CaO grains. The slaking resistance of the aggregate was appreciably improved due to the promotion of densification, the formation of CaO solid solution (while MgO added) and the modification of microstructure. In another study [78] the effect of NiO addition on the sintering properties of dolomite clinker was investigated. In this study, nature dolomite was carried out in the presence of NiO by two-step calcination process. The results showed that the doping of NiO to natural dolomite changed the lattice constants of CaO and MgO and made the MgO lattice distortion happen, which consequentially reduced the activation energy of the grain growth and promoted the sintering of the dolomite. Without additive the bulk density and the apparent porosity of dolomite clinker after the sintering at 1600°C were 3.30 g/cm^3 and 3.4%, the crystal size of MgO only was 3.26 μm. But when the addition of NiO accounted to 0.75%, the bulk density and the apparent porosity of dolomite clinker after the sintering at 1600°C were 3.33 g/cm^3 and 2.7%, respectively. At the same time, the crystal size of MgO reached to 3.54 μm [47]. Zhang Han *et al.* [43] studied the effect of CaF_2 on the sintering properties of MgO-CaO materials. The results show that with increasing the addition of CaF_2, the bulk density of the samples increased, while the apparent porosity decreased and the densification of MgO-CaO materials promoted. When the amount of CaF_2 exceeded 2wt. % the densification degree of samples decreased. The nature of CaF_2promoting densification of MgO-CaO materials could be concluded as follows: due to its thermal defects, F-entered into the octahedral voids that existed in CaF_2crystal structures and produced F-vacancies with positive charge, then combined with O_2-vacancies by electrostatic attraction during the migration process, which increased the diffusion speed of O_2-and enhanced the diffusion of MgO, then promoted the growth of periclase grains. In another study, A. Ghosh *et al.* [73] investigated the densification and properties of lime with V_2O_5 additions. For this propose, sintering of lime was carried out in the presence of V_2O_5 by a single firing process. A pure limestone was crushed, mixed with 1, 2 and 4 wt. % V_2O_5, pelletized and fired between 1550 and 1650 °C. The sintered lime was evaluated by bulk density, apparent porosity, microstructure, hydration resistance and hot modulus of rupture (HMOR) at 1300 °C. Incorporation of V_2O_5 forms liquid phase with lime at elevated temperature and influences the densification process by liquid phase sintering. As a result bulk density of sinters improved and they become more hydration resistant due to the larger grain size of the lime phase. The hot strength increased up to a certain temperature followed by deterioration because of the pressure of higher amount of liquid phase. Sintering behavior and hydration resistance of reactive dolomite was studied by Ghosh and Tripathi [24]. The hydroxide derived from dolomite was developed through pre-calcination of dolomite followed by its hydration. For hydroxide development, after pre-calcination, one sample was air quenched and the other powder was a furnace cooled before hydration. The air quenched samples showed better densification than that of the furnace cooling process at the same temperature. Fe_2O_3addition enhances sintering by liquid formation at higher temperature. The grain size of doloma with Fe_2O_3addition is bigger than that without additive. Hydration resistance was related to densification and grain size of sintered dolomite. H. A. Yeprem investigated the effect of iron oxide addition on the hydration resistance and bulk density of doloma. At his study, pure (with no additives) and mill scale (98.66 wt. % Fe_2O_3 content) added (up to 1.5 wt. %) natural dolomite of Selcuklu-Konya-Turkey fired at 1600–1700 ◦C for 2–6 h using the one-stage process. According to the results of experiments with 15 sintered samples, sintering temperature, soaking time and increase of the mill scale amount were found to increase the bulk density and thus decrease the observed apparent porosity. In hydration resistance tests, it seemed that the same characteristics also increased the resistance. Furthermore, EDX analysis of the dolomas that were sintered at three different temperatures each with 0.5 wt. % mill scale additions and also at 1700 °C/2 h with 0–1 wt. % mill scale additions were performed. Quantities of $Fe^{2+, 3+}$ inside the periclase (MgO) were examined [55, 57]. A.G.M. Othman *et al.* [37] studied The Hydration-resistant lime refractories with addition ilmenite raw materials. For this reason, the ferri-ilmenite ore existing at Abu Ghalaga, Eastern Desert was added as a dopant material in amounts of 0.5, 1.0, 2.0, and 3.0%. Densification parameters and hydration resistance of the fired grains were investigated. The densest hydration resistant grains were selected to assess their refractory quality by determining load-bearing capacity and thermal shock resistance. These results were interpreted in the light of phase composition and microstructure of the fired grains. It is concluded that dense and hydration resistant lime grains can be processed by doping the pure limestone powder with 2.0–3.0 wt. % of ferri-ilmenite before firing up to 1550C. Such level of ilmenite content has contributed in the densification of lime particles in the solid state and also by limited amount of the developed liquid phase. Hence, direct-bonded lime network is formed with partial interruption by a platey calcium–alumino–ferrite–titanate phase, which crystallized on cooling from the liquid phase at the grain boundaries of the lime–lime network. This improves the bulk density of fired grains to about 3.2–3.3 g/cm^3 and its rate of hydration to 4.15–3.80 g/h without significant deterioration of its load-bearing capacity and thermal shock resistance. A. Ghosh *et al.* [9] studied the effect of CuO addition on the sintering of lime. The result showed that Hydration resistance was measured at 50°C in 95% relative humidity through the weight gain after 3 h. Addition of CuO up to 2 wt.% improved the hydration resistance, but it was not significantly high in comparison to that of 1 wt.%CuO. The use of a higher level of CuO in lime did not show any further improvement in hydration resistance. The CaO forms a low melting compound (2CaO.CuO) with CuO which helps liquid phase sintering of lime. When the liquid content increased in the sintered lime grain growth takes place simultaneously along with pore growth. L. Liu *et al.*

[48] reported the effect of BaO addition on densification and mechanical properties of Al_2O_3-MgO-CaO refractories. Results indicated that the formation of calcium hex aluminate (CaO. $6Al_2O_3$, or CA_6) grains with a high aspect ratio in the alumina-rich zone depressed the densification of the sample without BaO addition, resulting in a higher apparent porosity of 21.2%. When 6 wt. % BaO was added, a new phase of $Ba_2Mg_6Al_{28}O_{50}$ (BAM) with a lower aspect ratio was formed and the densification of the sample with an apparent porosity of 5.52% was promoted. In addition, mechanical performance was significantly improved due to an increase in compactness and modification of the microstructure. The cold compressive strength increased from 348 MPa to569 MPa and the flexural strength increased from 178 MPa to 243 MPa by addition of 6 wt. % BaO. Meanwhile, the breadth of the widest crack after the thermal shock test decreased from 7 μm to 1 μm in the refractory. A. Miskufova *et al.* [49] reported the properties of CaO sintered with addition of active alumina. They evaluated the influence of active gama alumina addition on green and sintered CaO material properties, microstructures and mineralogical phase formation. Experimental results have shown the possibility to prepare more stable CaO with excellent properties by energy saving one-stage burning process of natural ground limestone with small addition of γ-Al_2O_3 (1 wt. %) at up to 1550°C for two hours. The additive caused increasing of the sintered density but especially significant decreasing of apparent porosity of CaO. X-ray diffraction and energy dispersive X-ray fluorescence analysis confirmed mainly the presence of $3CaO{\cdot}Al_2O_3$ on the grain boundaries. Formation of other phases during sintering, more specifically $12CaO{\cdot}7Al_2O_3$ and $CaO{\cdot}6Al_2O_3$ with lower tendency to hydration was also proved. In another research, CH. Hee Chao at al. [58] studied the effect of Al_2O_3, MgO and SiO_2 on sintering and hydration resistance of CaO ceramics. CaO ceramics were prepared by conventional sintering process and their hydration behaviors were evaluated by measuring weight increment on saturated water vapor pressure at ambient temperature. $CaCO_3$ and limestone were used as CaO source materials and Al_2O_3, MgO and SiO_2 were added as sintering agents. Al_2O_3 was as liquid phase sintering agent to increase densification and grain growth rates, whereas MgO and SiO_2, densification and grain growth inhibitors. Regardless of composition, all of the prepared CaO ceramics showed the improved hydration resistance as bulk density increased. Therefore, to decrease contact area between CaO and water vapor by increasing bulk density with the Al_2O_3 sintering additive was effective for the improvement of CaO hydration resistance.

Application of Nanotechnology in magnesia doloma refractories

Nano-technology is mainly defined by size and comprises the visualization, characterizations, production and manipulation of structures which are smaller than 100 nm [59, 60]. The structures the dimensions of which range from 100 nm down to approx. 0.1 nm exhibit special mechanical, optical, electrical, and magnetic properties which can differ substantially from the properties of the same materials at larger dimensions. Therefore, nanotechnology is a very active research field and has applications in a number of areas. Currently, significant attention has been paid to the application of nanotechnology in the development of refractories products [61-63]. Nanotechnology has been introduced to refractories. It has been reported that the performance of the refractories was appreciably improved for the good dispersion of nano-sized particles in the microstructure and reaction activity. Several efforts have been made by various researchers to improve the properties of refractories (bricks and castable) by using Nanoparticles (Table 2). The application of nanotechnology is aimed at obtaining the following unique properties of brick and castable refractories: ultra-high compressive strength, relatively high tensile strength and ductility, more efficient cement hydration, increased aggregate-paste bond strength, high corrosion resistance, control of cracks and self-healing. In the case of refractory materials, the same properties as well as, high resistance to thermal shock, abrasion, and chemical corrosion must be obtained [62, 106-108]. The first papers on nanotechnology in refractories causing a big interest appeared in UNITECR (The Unified International Technical Conference on Refractories) in 2003.The researchers of these as well as later published papers try to modify the matrix (binding phase) of advanced refractory materials with nano-sized additives[59, 107, 109, 110]. Recently Nano-technology was introduced to the Magnesai-Doloma refractories, and nowadays it is an important tool included in many research

Table 2. Published articles with title the use and application of nano-particles additives in the refractories since 2002 -2016

Research Team	Year of Publication	Title of Paper	Results
Z. Huizhong *et al.* [64]	2002	influences of Nano-alumina and Nano-silica on sintering and mechanical property of corundum refractories	The results show that both the two type Nano-materials can decrease the calcining temperature within 100 to 200 °C,and make the cold modulus of rupture and cold crushing strength of the samples increase within 100%～200% under the same calcination condition
L. Hong *et al.* [65]	2003	influence of nano-Fe_2O_3 on sintering and mechanical property of magnesia - chrome refractories	The results show that the nano-Fe_2O_3 can reduce the firing temperature about 150 °C, and can improve the cold modulus of rupture (CMOR) and cold crushing strength (CCS) of the specimens obviously under the same firing temperature condition
W. Hou *et al.* [61]	2005	application of nanotechnology in refractories	The study shows that the nanometer powder or precursor introduced into the refractory can compact the material, improve sintering, better the microstructure, and increase the reaction activity and catalyst functions. In other words, the nanometer powder or its precursor can enhance the refractory property
J. Dongmei *et al.* [63]	2006	research status and developing trend of Nano-technology in refractories	The characteristics of Nano-technology were summarized. The present status of research and application, disperse technologies and development trend of Nano-technology at home and abroad in refractories industry are also involved
L. Caiyun et al. [28]	2007	effects of Nano-ZrO2 addition on sintering and thermal shock resistance of MgO-CaO refractories	The results showed that the sintering and thermal shock resistance of MgO-CaO refractories were obviously improved by adding 2% nano-ZrO2.The optimum addition of nano-ZrO2 was 6%
M. Chen *et al.* [45]	2007	improvement in performance of MgO-CaO refractories by addition Nano-sized ZrO_2	The slaking resistance of the MgO–CaO refractories was appreciably improved by addition of ZrO_2 due to its effect on decreasing the amount of free CaO in the refractories; promotion of densification as well as modification of microstructure, the nano-sized ZrO_2 addition was more effective due to its higher activity.
S. Ghosh*et al.* [66]	2007	improvement of thermal characteristics of refractory castable by addition of gel-route spinel nanoparticles	Limited numbers of hydroxyl groups created around the spinel precursor helped to improve thermal shock resistance. Micrographic examination confirmed that retained nano-dimensional spinels firmly connected the hibonite and corundum grains in the castable, developing multiple interfaces after densification. Castable-containing spinel with excess alumina powder was found to have the best combination of bulk density, apparent porosity, and hot modulus of rupture.
S. Otroj *et al.* [67]	2008	behavior of alumina-spinel self-flowing castables with Nano-alumina particles addition	The results show that the Nano-alumina particles have great effect on the self-flow characteristics and mechanical strength. With increase of Nano-alumina particles in castable composition, the self-flow value and working time tends to decrease and cold crushing strength is enhanced at all temperatures. By use of 1.5 wt.% Nano-alumina contents in the castable composition, the alumina-spinel self-flowing castable with adequate working time and very high mechanical strength can be obtained.
W. Zhanmin *et al.* [68]	2008	effect of Nano-Al_2O_3 addition on the properties of Al_2O_3-SiC-C castables	The results show that as the nano-Al_2O_3 addition increases, water addition increases when the castables keeping the flow value at same level, and CMOR and CCS get no marked changes. Hot MOR climbs to the summit at 0.5%nano-Al_2O_3 addition and goes down slowly then. Slag tests show that the slag resistance is not improved so remarkably, but slag penetration resistance is enhanced by 1.0%nano-Al_2O_3 addition. Mullite phase can easily form by the introduction of Nano Al_2O_3.
A. Azhari *et al.* [69]	2009	effect of nano iron oxide as an additive on phase and microstructuralevolution of Mag-Chrome refractory matrix	It was found out that the formation of magnesioferrite spinel was encouraged at lower temperatures in the presence of nano iron oxide. The dissolution of iron oxide and ionic migration improved the sintering process in the matrix of the refractory. The presence of nano iron oxide also influenced the bonding structure in a way that direct bonding was enhanced while silicate bonding was hindered.
M. Amin *et al.* [70]	2009	the effect of nano-sized carbon black on the physical an thermo-mechanical properties of Al_2O_3–SiC–SiO_2–C composite	Nano-sized carbon black addition improved the relative heat resistance and oxidation resistance of composites.
G. Mingliang *et al.* [71]	2009	effect of nano-calcium carbonate addition on properties of corundum castable	The results show that: the platelet calcium hexaluminate(CA_6) formed from the reaction of nano-calcium carbonate and alumina in the matrix after thermal treatment affects the properties of the castable. After thermal treatment at 110 °C, with the increase of the nano-calcium carbonate content, the apparent porosity and bulk density have no obvious change and the cold crushing strength (CCS) and modulus of rupture in bending (MOR) have increased a bit. However, after thermal treatment at 1000, 1500 and 1600 °C,the apparent porosity increases gradually while the bulk density, CCS and MOR decrease simultaneously.
S. Badiee *et al.* [72]	2009	non-cement refractory castables containing nano-silica: performance, microstructure, properties	The results show that the proper nano-silica content for achieving self-flowing performance of such castables and sufficient strength is 10-11 %. By increasing of firing temperature up to 1000°C, porosity and pore sizesof castable tend to decrease, because of complete dehydration of reminder hydroxyl groups, which can lead to increasing of strength. Because of using nanometer-sized colloidal silica particles with high surface area, the solid phase sintering of the nano-sized particles and also, mullite formation can occurr in the low temperatures up to 1300°C.
B. Liu *et al.* [73]	2010	effects of nanometer carbon black on performance of low-carbon MgO-C composites	The results show that the mechanical properties, oxidation resistance and thermal shock resistance of the low-carbon samples are improved with the decrease of CB particle size. Thermal shock resistance of the low-carbon sample containing nanometer CB N220 is obviously better than that of other low-carbon samples, and reaches the level of the high-carbon samples.

Continued Table 2. Published articles with title the use and application of nano-particles additives in the refractories since 2002 -2016

Research Team	Year of Publication	Title of Paper	Results
S. Otroj *et al.* [74]	2010	the effect of nano-size additives on the electrical conductivity of matrix suspension and properties of self-flowing low-cement high alumina refractory castables	It was shown that if the electrical conductivity of matrix suspension is less than 0.71 mS/cm, high alumina low-cement self-flowing refractory castable can be obtained. The best self-flow, sufficient working time and adequate mechanical strength in the castables are obtained with 0.08 wt.% FS 20.
H.R. Zargar *et al.* [75]	2010	influence of nano boehmite on solid state reaction of alumina and magnesia	Nano boehmite also discouraged formation of hybonite (CA_6) phase. The results are explained with emphasis on the importance of low temperature spinel formation in refractory materials.
D. Kuznetsov *et al.* [60]	2010	Nano-materials in refractory technology	The possibility of controlling material properties at the atomic level makes it possible to create new innovative refractory materials and technology.
R. Rekha Das *et al.* [14]	2010	effect of micron and nano $MgAl_2O_4$ spinel addition on the properties of magnesia-carbon refractories	It was observed that with addition of 0.5 to 1 wt % nano $MgAl_2O_4$ spinel gives better HMOR and TSI as well as oxidation and slag corrosion resistance as compared to 10 wt % AR-78 spinel added MgO-C brick.
S.Otroj *et al.* [76]	2011	microstructure and phase evolution of alumina–spinel self-flow in refractory castables containing nano-alumina particles	The results show that the addition of nano-alumina has a great effect on the physical and mechanical properties of these refractory castables. With the increase of nano-alumina content in the castable composition, the mechanical strength is considerably increased at various temperatures. It is shown that nano-alumina particles can affect formed phases after firing. As a result of using nanometer-sized alumina particles with high surface area, the solid phase sintering of the nano-sized particles and CA_6 formation can occur at lower temperatures.
H. Shaobo *et al.* [77]	2011	Influences of Nano-Al_2O_3 and Nano-Cr_2O_3 on sintering and mechanical properties of magnesia-chrome refractories	It is found that:(1)adding an appropriate amount of nano-powder can accelerate the sintering and improve mechanical properties of magnesia-chrome refractories at both ambient temperature and high temperatures; and the effect is more significant at the lower firing temperatures;(2)the appropriate additions of nano-Al_2O_3 or nano-Cr_2O_3 powders are both 4% based on the particle size composition of magnesia-chrome refractories of this experiment;(3)The firing temperature of magnesia-chrome refractories can be reduced by adding nano-Al_2O_3 powder, down 100 °C with 4% nano-Al_2O_3 powder addition.
L. Akselrod *et al.* [78]	2011	development of refractory production in the world and in russia, new technologies	It is noted that under conditions of increasing competition among refractory producers there is a greater tendency of Russian refractory manufacturers to expand the production of oxide-carbon refractory objects, unmolded refractories, the production of high quality raw materials, and creation of the latest production processes, in particular the use of Nano-materials.
V.AntonoviČ *et al.* [62]	2011	a review of the possible applications of nanotechnology in refractory concrete	Applying nanotechnology in manufacturing refractory concretes creates a possibility that during the process of hardening binding material, nanostructure would be formed to determine a significant increase in compressive strength and thermal durability. When using the materials of nano-particle composition (sodium silicate solution, amorphous SiO_2) as binding materials for refractory concretes and in parallel with respectively selected deflocculates (super plasticizers), it is possible to increase the compressive strength and thermal durability of concrete up to 2–3 times.
S. Badiee *et al.* [79]	2011	effect of nano-titania addition on the properties of high-alumina low-cement self-flowing refractory castables	The results show that the addition of nano-titania particles has great effect on the self-flow characteristics, phase composition, physical and mechanical properties of these refractory castables. With increase of nano-titania particles in castable composition, the self-flow value and working time tend to decrease. With addition of 0.5 wt.% nano-titania in the castable composition, the mechanical strength of castable in all firing temperatures tends to increase. It is attributed to the formation of CA_6phase and enhanced ceramic bonding. Nano-titania particles can act as a nucleating agent for hibonite phase and decrease the formation temperature of hibonite. Because of perovskite phase formation, the addition of 1 wt.% nano-titania can decrease the mechanical strength of castable after firing
H. Yaghoubi *et al.* [80]	2012	influence of nano silica on properties and microstructure of high alumina ultra-low cement refractory castables	It's concluded that the castables containing the optimum amount of silica sol shows remarkable increase in both castable fluidity and mechanical strength (CCS and MOR) in dried and sintered state. It was also found that nanosilica particles increase the rate of needle-shaped mullite formation during sintering at 1400°C.
L. Zhigang *et al.* [81]	2012	effect of nano calcium carbonate on properties of corundum-spinel castables	The results show that nano calcium carbonate decomposes at high temperature and in-situ forms calcium aluminates, which can significantly increase the cold and hot modulus of rupture of the castables after treating at 800-1 400 °C; adding nano calcium carbonate obviously improves the thermal shock resistance of the castables, and has little influence on corrosion resistance to high basicity slag, however, significantly decreases the corrosion and penetration resistance to low basicity slag.
N.M .Khalil *et al.* [82]	2012	improvement of mullite and magnesia-based refractory castables through addition of nano-spinel powder	The castable sample mix containing 10 wt.% nano-MA spinel powder was chosen as an optimum composition according to its good sintering, mechanical as well as refractory properties
H.R. Zargar *et al.* [83]	2012	the effect of Nano-Cr_2O_3 on solid-solution assisted sintering of MgO refractories	It was shown that the densification of magnesia was enhanced by reducing the particle size of the added chromia to the range of 20 nm. According to the phase analysis results, the higher dissolution rate of Cr_2O_3 in MgO in the MgO–Cr_2O_3 system was responsible for the faster densification of nano-Cr_2O_3 containing mixes.
D. Kuznetsov *et al.* [84]	2012	development of a procedure for modifying nanomaterials of mullite-corundum mixes in equipment with a high-intensity rotating electromagnetic field	The possibility is demonstrated of a considerable improvement in mechanical properties of vibration-cast refractory objects by introducing nanosize fractions into thixotropic mullite-corundum mixes. It is established that the efficiency of using nano-additions is governed by its introduction technology into refractory material. The best method is mixing in vortex layer equipment with use of a high-intensity rotating magnetic field.

Continued Table 2. Published articles with title the use and application of nano-particles additives in the refractories since 2002 -2016

Research Team	Year of Publication	Title of Paper	Results
S. Mukhopadhyay *et al.* [85]	2012	nanostructured cementitious sol gel coating on graphite for application in monolithic refractory composites	The better oxidation resistance of coated graphite has been confirmed by thermo gravimetric analysis (TGA). Improved water-wettability of coated graphite's has been examined by the 'ball-in-hand' test for moisture requirement during installation of a high alumina based refractory castable composite containing that graphite. Green bulk density of castable cubes has been determined to corroborate the better performance of the graphite coated with calcium aluminate.
E.Y. Sako *et al.* [86]	2012	how effective is the addition of nanoscaled particles to alumina–magnesia refractory castables?	Although the addition of a nanoalumina and nanomagnesia mixture ensured the best results regarding to the expansive behavior, thermo-mechanical and thermo-chemical properties, its performance was only slightly superior to the castable containing micrometric alumina and magnesia particles. Therefore, as the cost–benefit ratio is one of the main requirements for the end users, the nanotechnology use in the refractory production must be previously carefully analyzed.
S. Dudczig *et al.* [87]	2012	nano- and micrometre additions of SiO_2, ZrO_2 And TiO_2 in fine grained alumina refractory ceramics for improved thermal shock performance	
C. Gogtas *et al.* [88]	2012	Development of Nano-ZrO_2 reinforced self-flowing low and ultra low cement refractory castables	The results indicate that the addition of Nano-ZrO_2 improves the flexural strength by 20% but it does not have an important effect on the K_{IC}. Apparently, the presence of a relatively high density of pores and cracks overrides the potential benefits associated with the Nano-ZrO_2 and YSZ reinforcement additions.
D. Zhang *et al.* [89]	2012	Influence of Nano-Al_2O_3 on properties of magnesia chrome refractories	The results indicate that the performance of brick with 4 mass% of nano-Al_2O_3 is greatly improved after firing at 1650° C.
Sh. Badiee *et al.* [90]	2012	effect of Nano-TiO_2 addition on the properties of mullite-zirconia composites prepared by slip casting	The results showed that the flexural strength of composite tends to increase with the addition of 0.5 wt.% nano–TiO_2. It is attributed to the formation of larger size rod–like ZrO_2 and enhanced ceramic bonding between them.
M. Bag *et al.* [91]	2012	nano carbon containing MgO-C refractory: effect of graphite content	Addition of 3 wt% of flake graphite in combination with 0.9 wt% of nano carbon black was found to be optimum and resulted in etter/comparable properties to that of conventional MgO-C refractory.
M. Bag *et al.* [92]	2012	study on low carbon containing MgO-C refractory: use of nano carbon	Different percentages of nano carbon are used in combination with graphite as carbon source and the total carbon is maintained below the half of the total carbon of the conventional MgO-C refractories. The compositions were processed as per the conventional manufacturing techniques and the properties were evaluated and compared against the conventional refractory prepared under exactly similar conditions. Also elemental mapping of carbon was done to study the distribution of the nano carbon in the matrix.
R.R.Das *et al.* [93]	2012	influence of nanocrystalline $MgAl_2O_4$ spinel addition on the properties of MgO-C refractories	Due to the lower pore size and higher concentration of fine pores as well as higher amount of carbon retention, nano-$MgAl_2O_4$ spinel-added MgO-C bricks show better physical as well as chemical properties and may have potential applications in both steel and refractory industries.
S. Mukhopadhyay *et al.* [94]	2013	Nano-scale calcium aluminate coated graphite for improved performance of alumina based monolithic refractory composite	It revealed that Nano-coating considerably improved matrix-aggregate bonding. Less porous simulated matrix upgraded slag resistance.
N. Farzadnia *et al.* [95]	2013	characterization of high strength mortars with nano alumina at elevated temperatures	Nano alumina enhanced compressive strength of samples up to 16% and improved residual compressive strength. An increase in the relative elastic modulus, higher energy absorption and lower permeability were also observed when 1% nano alumina was added.
S. Dutta *et al.* [96]	2014	significant improvement of refractoriness of Al_2O_3–C castables containing calcium aluminate nano-coatings on graphite	The sol–gel coating overcomes the pitfalls of including uncoated graphite's in castables and should be explored for commercial utilization.
S. Behera *et al.* [97]	2014	low-carbon magnesia-carbon refractory: use of N220 nano-carbon black	The coked strength, hot strength, corrosion resistance, and oxidation resistance were found to be improved for Nano-carbon-containing MgO-C refractory compared with the conventional refractory due to in situ formation of Al_4C_3. Higher amount of Nano-carbon black was found to deteriorate the refractory properties.
S. Otroj *et al.* [98]	2015	impact of Nano–Cr_2O_3 addition on the properties of aluminous cements containing spinel	The results showed that nano-Cr_2O_3 addition has effect on the increasing of spinel and CA_2 and decreasing of CA and $C_{12}A_7$ phases in the cement composition. The decreasing of $C_{12}A_7$ leads to increasing of setting times of cement. Besides, the slag resistance of refractory castables containing prepared cements is improved due to increasing of spinel and decreasing of $C_{12}A_7$ amount in the cement composition.
C. G. Rodríguez *et al.* [99]	2015	effect ofadditionofAl_2O_3 and Fe_2O_3 nanoparticles on the microstructural and physico-chemical evolution of dense magnesia composite	As a result, it was found that the presence of nano-iron oxide in the magnesia matrix induced magnesioferrite spinel formation, which improved the sintering process. Nano-iron oxide also influenced the bonding structure through a direct bonding enhancement. On the other hand, the presence of nano-alumina in the magnesia matrix induced magnesium-aluminate spinel formation, resulting in lower properties in comparison with those obtained by nano-iron oxide addition.
L. Lu *et al.* [100]	2015	effect of Nano-ZrO_2 addition on microstructure, mechanical property and thermal shock behavior of dense chromic oxide refractory material	Dense chromic oxide refractory material with 2~3 wt% nano-ZrO_2 possessed good densification, uniform microstructure, normal mechanical property and proper thermal shock resistance. The rupture strength retention ratio was nearly twice than that of chromic oxide material without ZrO_2 after three cycles of quenching test from 950°C to cold water.

Continued Table 2. Published articles with title the use and application of nano-particles additives in the refractories since 2002 -2016

Research Team	Year of Publication	Title of Paper	Results
E. Rodríguez *et al.* [101]	2016	effect of nano-titania content on thermo-physical properties of magnesia refractory composite	It was found that the presence of η-TiO_2 in the magnesia matrix induced titanates formation (Mg_2TiO_4 and $CaTiO_3$), which improved the sintering process. Nano-titania also produced a fine-grained microstructure with intergranular second phase particles, which remain at the boundary and exert a pinning effect. In general, the addition of 5 wt% of η-TiO_2 contributed to reach a maximum increment in physical and mechanical properties.
C. Gogtas *et al.* [102]	2016	Effect of Nano-YSZ and Nano-ZrO_2 additions on the strength and toughness behavior of self-flowing alumina castables	It is found that the addition of 3 wt% nano-ZrO_2 improves the MOR of self-flowing castables (SFCs) by 20% and 50% matrix and binding systems respectively due to stabilization of t-ZrO_2. Alternatively, there is no noticeable change in the exhibited K_{IC} of castables when aggregates are present. In contrast, the K_{IC} of aggregate-free binding systems can reach values of up to 2.277 0.21 MPa m1/2 with the addition of 1 wt% Y-ZrO_2. Consequently, the effect of nano-YSZ in promoting toughness is significantly reduced or eliminated due to the presence of high porosity and internal flaws in the SFCs.
A. K.Singh *et al.* [103]	2016	nano mullite bonded refractory castable composition for high temperature applications	Considerably improved hot strength, high corrosion resistance and flexural strength (hot modulus of rupture) are obtained for the mullite sol containing composition but with relatively lower thermal shock resistance.
S. Gh. Kahrizsangi *et al.* [21]	2016	densification and properties of ZrO_2 nanoparticles added magnesia–doloma refractories	Results show that with addition of ZrO_2 the bulk density and hydration resistance of the samples increased while apparent porosity decreased. Also the hydration resistance of the samples was appreciably improved by the addition of ZrO_2 due to its effect on decreasing the amount of free CaO in the refractories, promotion of densification as well as modification of the microstructure. Also it revealed that the nanoZrO_2 addition was more effective than microZrO_2 due to its higher activity.
S. Gh. Kahrizsangi *et al.* [7]	2016	densification and properties of Fe_2O_3 nanoparticles added CaO refractories	As a result, it was found that the presence of Nano-iron oxide in the CaO refractory matrix induced 2CaO.Fe_2O_3 (C_2F), CaO.Fe_2O_3 (CF) and 3CaO.Al_2O_3 (C_3A) phase's formation, which improved the sintering process. Nano-iron oxide also influenced the bonding structure through a direct bonding enhancement. On the Other hand, the presence of Nano-iron oxide resulting in improvement properties of CaO refractory matrix refractories such as bulk density, hydration resistance and cold crushing strength. The maximum flexural strength at 1200 °C is achieved by the samples containing 4 wt. % nano-Fe_2O_3.
S. Behera *et al.* [104]	2016	nano carbon containing low carbon magnesia carbon refractory: an overview	Use of nano carbon significantly improves the packing efficiency of the refractories, improves the quality of MgO-C refractories and results in better mechanical and thermo mechanical, oxidation, corrosion and thermal shock properties. As the nano carbon has higher surface area, reactivity and specific volume, it helps to form in situ ceramic phases resulting in better properties for MgO-C refractory compositions compared to that of the conventional MgO-C refractories.
S. Gh. Kahrizsangi *et al.* [1]	2016	effect of nano-sized Fe_2O_3 on microstructure and hydration resistance of MgO-CaO refractories	With the addition of Nano-sized Fe_2O_3, bulk density and hydration resistance of the samples increased while apparent porosity decreased. Densification of MgO-CaO refractories was promoted to increase of Nano-sized Fe_2O_3 content.
S._Behera *et al.* [105]	2016	Study on variation of graphite content in N220 nanocarbon containing low carbon MgO–C refractory	Graphite (3 wt-%) with 1 wt-% nanocarbon containing composition resulted in better density and strength values, and 5 wt-% graphite with 1 wt-% nanocarbon containing composition showed better hot strength and corrosion resistance.
S.Gh. Kahrizsangi *et al.* [46]	2016	the effect of nano-additives on the hydration resistance of materials synthesized from the MgO-CaO system	The use of both additives (nano Fe_2O_3 and nano ZrO_2) improved the hydration resistance.

projects. Several research groups have been working on the addition of different types of additives in Magnesai-Doloma refractories, and some of them have focused their investigations on the use of Nano-oxides, due to the reported benefits of adding these particles to ceramic bodies. In their research work, Salman Ghasemi-Kahrizsangie *et al.* [7] studied the densification and properties of Fe_2O_3 nanoparticles added CaO refractories. For this propose, up to 8wt. % of Nano-iron oxide was added to CaO refractory matrix. As a result, it was found that the presence of Nano-iron oxide in the CaO refractory matrix induced 2CaO.Fe_2O_3 (C_2F), CaO.Fe_2O_3 (CF) and 3CaO.Al_2O_3 (C_3A) phase's formation, which improved the sintering process. Nano-iron oxide also influenced the bonding structure through a direct bonding enhancement. On the Other hand, the presence of Nano-iron oxide was resulting in improved properties of CaO refractory matrix refractories such as bulk density, hydration resistance (Fig. 1) and cold crushing strength. The maximum flexural strength at 1200°C is achieved by the samples containing 4wt. % nano-Fe_2O_3. Also, they reported the effect of nano-TiO_2 additions on the densification and properties of the magnesite-dolomite ceramic composite. Nano-titania, up to 8 wt. %, was added to Magnesite-Dolomite refractory matrix. As a result, it was found that the presence of Nano-TiO_2 in the Magnesite-Dolomite matrix induced titanates formation (Mg_2TiO_4 and $CaTiO_3$), which improved the sintering process. Nano-titania influenced the bonding structure through a direct bonding enhancement. In general the addition of 6 wt. % of Nano-TiO_2 contributed to reaching a maximum increment in physical and mechanical properties. Also, the hydration resistance increase with addition Nano-TiO_2 up to 8 wt. %(Fig. 2) [2]. Another interesting report comes from Min Chen *et al* [28], who studied different sizes of zirconia (micro–nano-powders) added to MgO–CaO refractories sintered at 1600 °C. The results showed that the densification of the MgO–CaO refractories were appreciably promoted when a small amount of ZrO_2 was added owing to the formation of small size $CaZrO_3$ facilitated to sintering, and the densification was promoted further with increasing the amount of ZrO_2 due to the volume expansion caused by the reaction of the added ZrO_2 and CaO to form $CaZrO_3$ in the refractories, and the

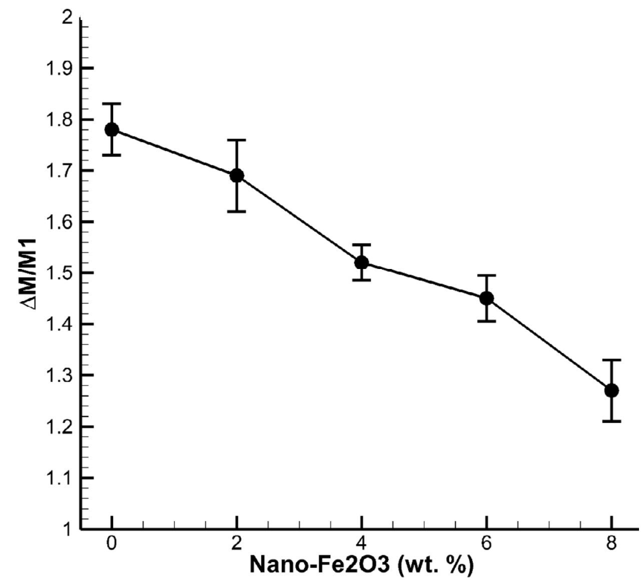

Fig. 1. Effect of Nano- Fe_2O_3 addition on improvement of hydration resistance of MgO-CaO refractories [7]

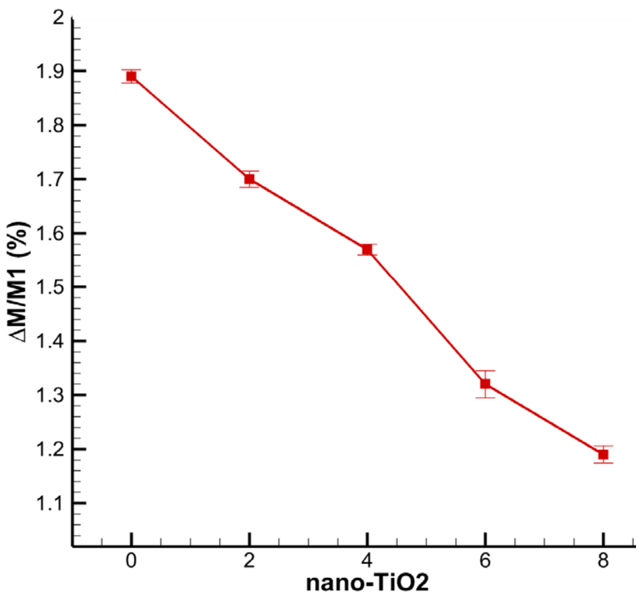

Fig. 2. Effect of nano-TiO_2 addition on improvement of hydration resistance of MgO-CaO refractories [2]

addition of nano-sized ZrO_2 was more effective. The thermal shock resistance of the MgO–CaO refractories was improved by modification of the microstructure due to the formed $CaZrO_3$ particles that predominately located on the grain boundaries and triple points in the whole microstructure, and the addition of nano-sized ZrO_2 was more effective attributed to its good dispersion and the critical addition amount was effectively decreased to 6%. The slaking resistance of the MgO–CaO refractories was appreciably improved by the addition of ZrO_2 due to its effect on decreasing the amount of free CaO in the refractories; promotion of densification as well as modification of microstructure, the nano-sized ZrO_2 addition was more effective due to its higher activity (Fig. 3). The slag corrosion resistance of the MgO–CaO refractories was enhanced by the addition of ZrO_2 due to the increase of the viscosity of the liquid phase and thus inhibited further penetration of slag at elevated temperatures. Also, the use of ZrO_2 nanoparticles on the densification and properties of ZrO_2 magnesia – doloma

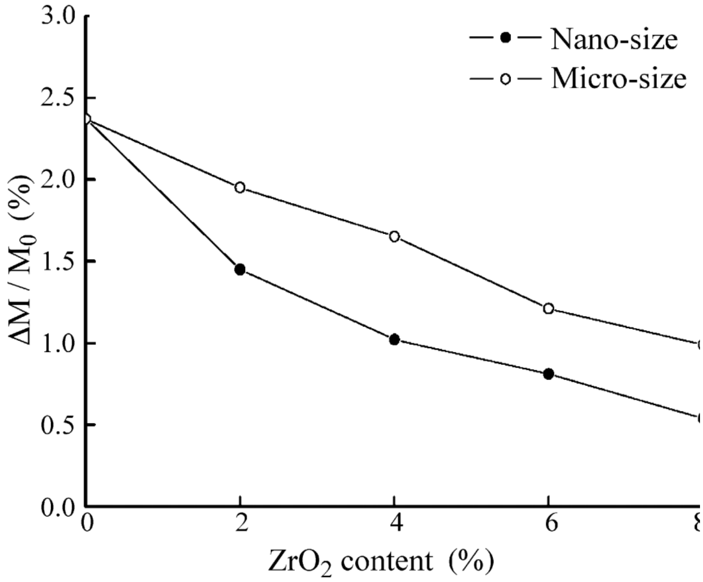

Fig. 3. Effect of ZrO_2 on improvement of slaking resistance of MgO-CaO refractories [45]

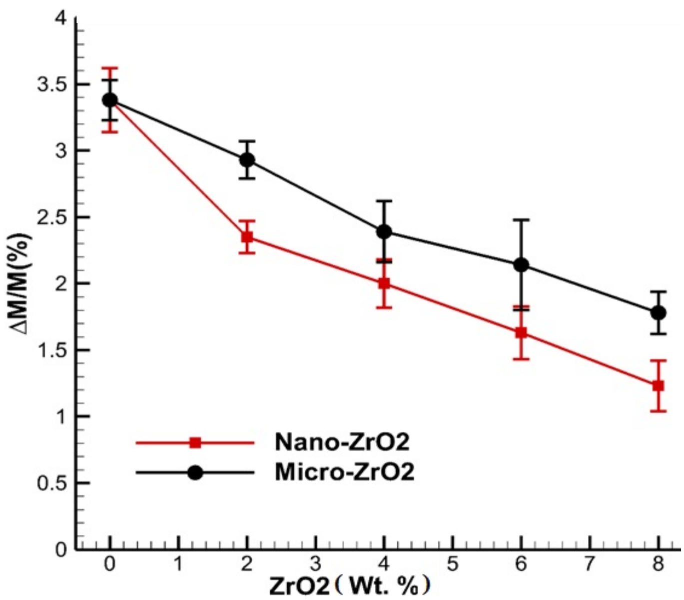

Fig. 4. The effect of nano and micro ZrO_2 addition on improvement of the hydration resistance of the MgO-CaO refractories [21]

refractories was investigated by Salman ghasemi-kahrizsangi *et al*. [21]. In their work, the effect of nano and micro ZrO_2 addition on the densification and hydration resistance of MgO-CaO refractories was investigated. 0,2,4,6 and 8 wt. % ZrO_2 was added to MgO-CaO refractories that contain 35 wt. % CaO. Results show that with the addition of ZrO_2 the bulk density and hydration resistance of the samples increased (Fig. 4) while apparent porosity decreased. Also, the hydration resistance of the samples was appreciably improved by the addition of ZrO_2 due to its effect on decreasing the amount of free CaO in the refractories, promotion of densification as well as modification of the microstructure. Also, it revealed that the nano ZrO_2 addition was more effective than micro ZrO_2 due to its higher activity. In another study, $MgAl_2O_4$ nanoparticles were added to MgO–CaO refractory ceramic composites in the range of 0–8 wt. %. Refractory specimens were obtained by sintering at 1650◦C for 3 h in an electric furnace. Results show that with additions of $MgAl_2O_4$ nanoparticles

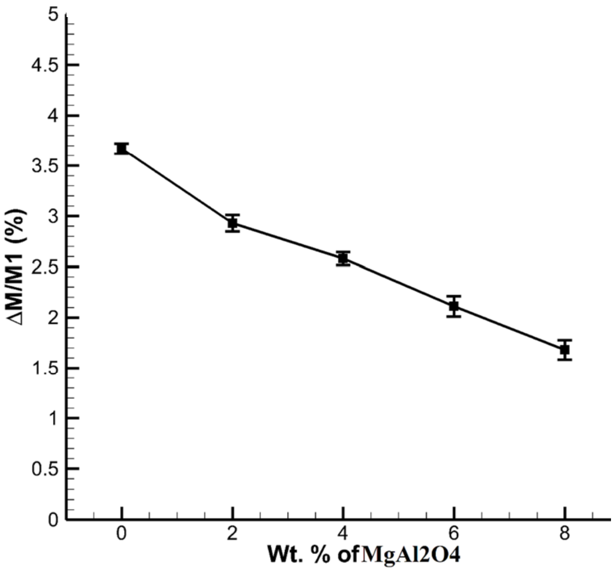

Fig. 5 Effect of Nano-spinel addition on improvement of hydration resistance of MgO-CaO refractories [111]

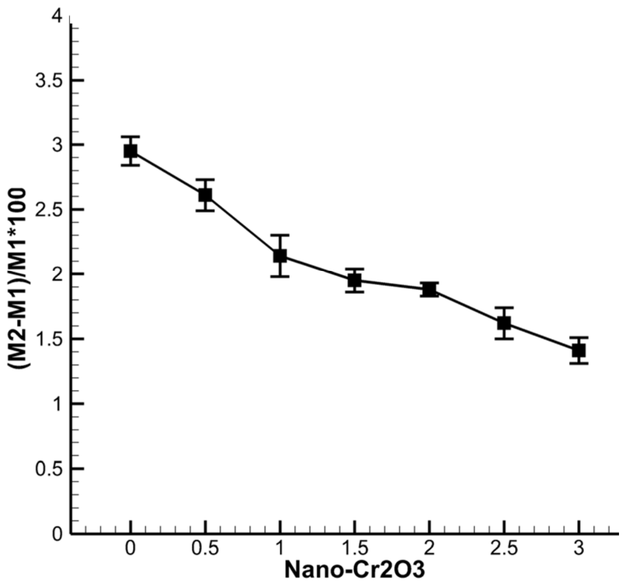

Fig. 6 Effect of Cr_2O_3 nanoparticles addition on the improvement of hydration resistance of MgO-CaO samples [112]

the bulk density of the samples increased. But the apparent porosity and cold crushing strength decreased and increased, respectively with addition $MgAl_2O_4$ nanoparticles up to 6 wt. % and for further $MgAl_2O_4$ nanoparticles, due to the thermal expansion mismatch, the results is reversed. Also, the hydration resistance of the samples was appreciably improved by the addition of $MgAl_2O_4$ nanoparticles due to its effect on decreasing the amount of free CaO in the refractory composite and promotion of densification by creating a dense microstructure (Fig. 5) [111].

Also, Up to 3wt. % of Cr_2O_3 nanoparticles were added to MgO-CaO refractory matrix. As a result, it was found that the presence of Cr_2O_3 nanoparticles in the MgO-CaO refractory matrix induced $CaCr_2O_4$ and $MgCr_2O_4$ phases formation, which improved the sintering process. Cr_2O_3 nanoparticles also influenced the bonding structure through a direct bonding enhancement. On the other hand, the presence of Cr_2O_3 nanoparticles resulted in improvement properties of MgO-CaO refractory matrix such as bulk density, hydration resistance (Fig. 6), and cold crushing strength. The optimum properties have been achieved by the samples containing 1.5wt. % Cr_2O_3 nanoparticles [112].

CONCLUSION

In this review paper, we mentioned all efforts done to improve the performance of MgO-CaO refractories and it was found that the use of Nano-additives has the best results compared to microparticles. Studies show that in the recent years, researchers strongly have been using Nano-additives and have achieved satisfactory results. The results show that in general the use of Nano-additives to improve the properties of magnetite-dolomite refractories through the following ways:

- Promotes densification of MgO-CaO by forming solid-solution and by creating cation or anion vacancies (solid –state sintering mechanism).
- Or by liquid phase sintering mechanism.

Generally, the improvement hydration resistance trend of nano additives is $MgAl_2O_4$< Fe_2O_3<TiO_2<Cr_2O_3<ZrO_2. Also, the use of nano-additives compared with other additives (micro) with smaller amounts, have better results. Which leads to cost savings, and subjected to the attention of refractories producers and consumers.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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