

REVIEW PAPER

Recent Advancement in monolithic refractories via application of Nanotechnology “A review Paper”

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ABSTRACT

In recent years, the use of nanotechnology (nano-particles, nanomaterial, nano-additives and nano-structured materials) has attracted attention of scholars, engineers and scientists in all scientific fields such as chemistry, medicine, material, agriculture, electronic etc. The use of nanotechnology has also become widespread in the refractory products (which mainly used in various industries such as steel, casting, cement, glass etc.). Therefore, the effect of using different types and contents of nanomaterials (oxides and non-oxides) as well as the control of microstructure has been evaluated by many researchers on the properties of shapes (bricks) and un-shaped (monolithic) refractory products. The obtained results were very promising and satisfactory. One of the most consumable refractory products in various industries is monolithic refractories, which has been widely used because of their great benefits to the other refractory products (bricks). In this paper, recent advances in monolithic refractories by using the finding of nanotechnology are presented. This article can be considered as guidance for researchers, students gain easy access to experimental results obtained by different research group using nanotechnology and nano materials in monolithic refractories.

Keywords: Monolithic; Nano Materials; Nano-Particles; Nanotechnology; Refractory

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INTRODUCTION

Nanotechnology (basic introduction and application)

The nanotechnology phrase originating from two words consists of the Greek numerical prefix nano referring to a billionth and the technology world [1-3]. As an outcome, nanotechnology or nano-scaled technology is commonly considered to be at a size under 100 nm (a nano-meter is 10^{-9} m) [1-2]. Nano-scale sciences (or nano-science) evaluate the phenomena, properties, and responses of materials at atomic, molecular, and macro-molecular scales, and generally at sizes in limited 1-100nm [1, 4-6]. Nanotechnology is considered as an emerging

technology because of the feasibility to development of well-established products and to generate new products with totally new properties and functions with great potential in a wide range of applications [1, 7-8]. Remarkable applications of nano-sciences and nano-engineering lie in the fields of pharmaceuticals, processed food, cosmetics, chemical engineering, high-performance materials, electronics, material science, precision mechanics, optics, energy production, and environmental sciences. Over 50,000 articles and more than 2,500 patents have been published annually about the nanotechnology and its application and progress in the different fields. Nano-materials with unique properties such as: carbon

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nano-particles, nano-tubes, nano-fibers, and nano-composites allow completely new applications to be found. The range of commercial products available today is very wide, including metals, ceramics, polymers, smart textiles, cosmetics, sunscreens, electronics, paints and varnishes. However new methodologies and instrumentation have to be developed for increase our knowledge [1- 2 and 7-10]. Another important term is known as nano-structured materials in which at least on constituent must be in nano-scale. In the field of advanced materials both terms are being employed to develop new generation of advanced materials and composites. One of the sub-groups of advanced materials is refractory materials used in different industries [8-10].

Refractories

According to the ASTM C-71, the refractories are a “non-metallic materials having those physical and chemical properties that lead to them applicable for structures or as components of systems that are exposed to environments above 1000 °F (538°C) [11-14]. Also, some references mentioned that refractories are in-organic non-metallic material which can withstand high temperature without changing in their chemical or physical properties while remaining in contact with molten slag, metal and gases [11-13 and 14-18]. As well as, based on the operating condition, they should to have high resistant thermal shock, be chemically inert, and/or have specific ranges of thermal conductivity and of the thermal expansion coefficient[18- 22]. It is

clear that refractories have an important role in glassmaking, metallurgical, and ceramic industries, where they are generated into a variety of shapes to line the interiors of furnaces or kilns or other devices for processing the materials at high temperatures [23-25]. Some of the technological and scientific inventions and progresses would not have been possible without refractory materials. Producing 1Kg of any metal without utilize of refractory is almost quite impracticable [26-27]. The history of using refractory materials dates back to since mankind start to develop metallurgical process. The first refractor raw material was clay. Up to the nineteenth century, refractory products were made of natural ores, such as magnesite, dolomite stones and clay. It was at the end of the eighteenth century and beginning of nineteenth century that the basis of modern metal beneficiation, the development of Portland cement and of modern glass processes started to inflict higher requirements to the refractory industry [11-17]. The most important materials used in the manufacturing of refractories are according to Fig. 1 [11-18].

In recent years, with the changing trends in steelmaking, the high performing shaped refractories are on an increasing demand. The higher campaign lives and the mutability of the newer steelmaking operations are decided by the accessibility and performance of such shaped refractories with superior high-temperature mechanical strength, erosion and corrosion resistance. The selection of refractories is often being utilized according to the

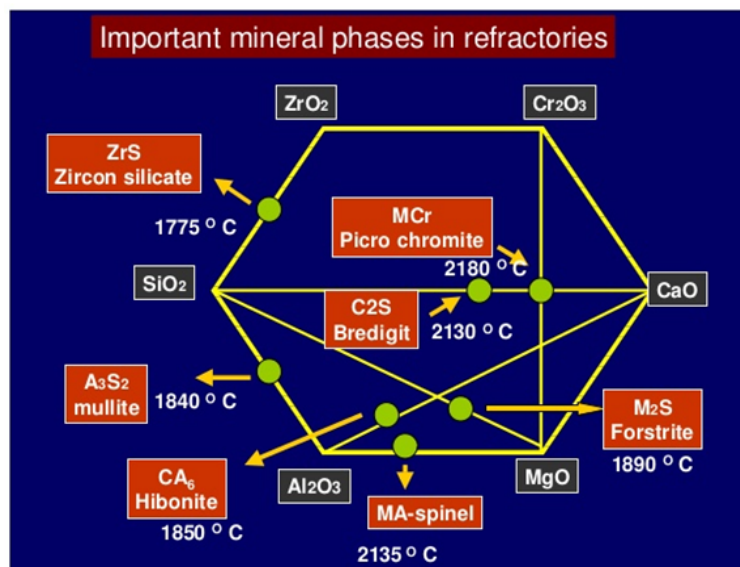


Fig. 1. The most important materials used in the manufacturing of refractories.

conditions dominating in the application zone [22-32]. According to Fig. 2, it is observed that attention to improving the performance of refractories materials as well as the production of new refractory products, as a strategic product in various industries, has been highly respected by researchers.

Classification

Generally, refractories are classified according the basis of chemical composition, method of manufacture, physical form or according to their applications (Fig. 3) [14-20].

Classification based on Chemical composition

a) Acidic refractories

These types of refractories are used in region

that slag and atmosphere are acidic. They have high resistance to acids but corroded by alkalis. The main raw materials belong to the RO_2 category, such as SiO_2 , ZrO_2 and etc.

b) Neutral refractories

These types of refractories are used in region that slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases. The main raw materials belongs to, but not confined to, R_2O_3 category. The common examples of these materials are Al_2O_3 , Cr_2O_3 and carbon(C).

c) Basic refractories

These types of refractories are used in region that slags and atmosphere are basic; they have high

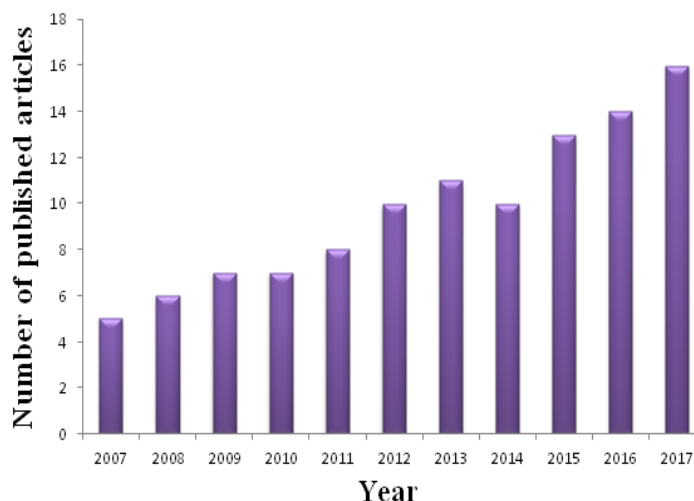


Fig. 2. Published articles in refractories material filed (since 2007 -2017).

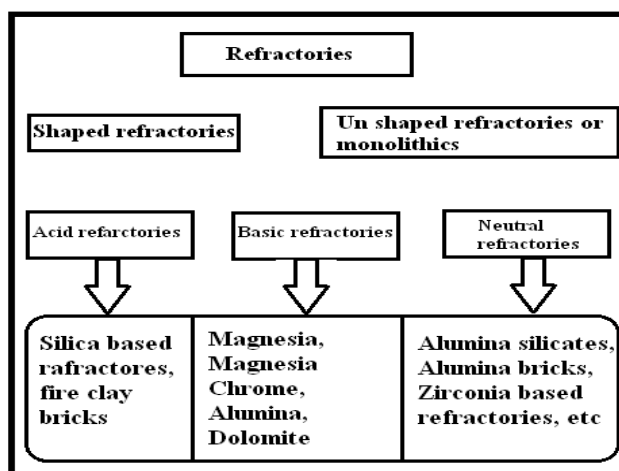


Fig. 3. Classification of refractories.

resistance to alkaline materials but corroded by acids.

The main raw materials belong to the RO category to which magnesia (MgO) is a very common example. Other examples include (Mg.Ca (CO₃)₂ and (MgO-Cr₂O₃).

Classification based on manufacturing methods

- a) Dry press process.
- b) Fused cast.
- c) Hand molded.
- d) Formed (normal, fired or chemically bonded).
- e) Un-formed (monolithic- plastic, ramming and gunning mass, castables).

Classification based on physical form

a) Shaped

These types have determined shapes and size. These divided into standard shapes and special shapes. Standard shapes have dimension that are conformed by most refractory producer and are usually appropriate to furnaces or kilns of the same types. Special shapes are specifically made for special furnaces or kilns.

b) Unshaped

These types are without clear form and are only given shape upon application. These types are known as monolithic refractories. The common examples castables are, plastic masses, gunning masses, ramming masses, fettling mix, mortars and etc.

Monolithic refractories

Monolithic refractory phrase is the name usually given to all un-shaped refractory products, the word “monolithic” extracted from the

word monolith which means ‘big stone’[33-35]. Monolithic refractories are specific batches or blends of dry granular or cohesive plastic materials utilized to form nearly joint free linings. These materials are un-shaped refractory products which are installed as some form of suspension that finally harden to create a solid shape. Most monolithic formulations are made of three constituent such as: large refractory particulates (an aggregate), fine filler materials (which fill the inter particle voids) and a binder phase (that gels the particulates together in the green state), Fig. 4 [33, 35-38]. Monolithic refractories display a great range of mineral compositions and vary greatly in their physical and chemical properties. Some of them have low melting point (low refractoriness) whereas others approach high purity brick compositions in their ability to tolerate severe environments. Monolithic refractories are replacing the conventional type fired refractories at a much faster rate in many applications including those of industrial furnaces [33-33, 39-40].

These refractories are used to advantage compare to brick construction in different type of furnaces. Their use enhanced fast installation. Utilize of monolithic refractories often eliminates difficult brick laying tasks, which may be accompanied with looseness in construction. Protect of furnaces is very importance because substantial repairs can be made with a minimum loss of time [35-39]. Sometimes, monolithic refractories linings of the same composition as firebrick provide better insulation, lower diffusion and enhanced spalling resistance to the effects of repetitive thermal shock. Other major benefits of monolithic refractory linings are as follows [33-42]:

- Removing joints which is an inherent weakness.

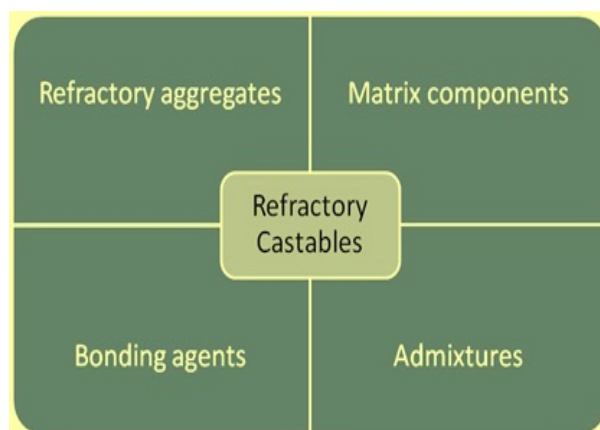


Fig. 4. refractory castables contents.

- Easier and faster application.
- Better properties than pressed (sintered or tempered) bricks.
- Simpler transportation and handling.
- Better volume stability.
- Possibility to install in hot standby state.
- Higher mechanical resistance to vibration and impact.
- Matching shrinkage and expansion to the application.

Different methods are used in the placement of monolithic refractories such as ramming casting, spraying, gunning, sand slinging and etc. Heat setting monolithic refractories have a very low cold strength values and rely on relatively high temperatures to progress a ceramic bond [81-83]. Furnaces wall having the usual temperature drop across its thickness, the temperature in the cooler part is generally not enough to progress a ceramic bond. However with the use of a proper insulating material as backup, the temperature of the lining can be high enough to progress a ceramic bond throughout its entire thickness. To the installation and curing, monolithic refractories need a carefully controlled dry-out program. This causes the filler, binder and aggregate to fire creating a strong material [34, 41-43].

Types of monolithic refractories

Usually the monolithic refractories are divided according to Fig. 5 [33, 36-38].

a) Castable refractories

Materials with hydraulic setting in nature are

name of castables. These refractories are containing cement binder (commonly aluminate cement), which creates hydraulic setting properties when blended with water. By heat-up temperature, the material and binder either transforms or volatilizes simplifying the generation of a ceramic bond. The most common binder used in castables is high alumina cement. Other binders are consisting of hydrate able alumina and colloidal silica. These materials are installed by casting and are also known as refractory concretes. Insulating castables are specialized monolithic refractories that are used on the cold surfaces of applications. These monolithic castables are composed of lightweight aggregates such as vermiculite, bubble alumina, perlite and expanded clay. The main function of castables is to create thermal insulation. Also, they are generally had low density and low thermal conductivity. The castables are classified according to following [33-37]:

- ✓ Conventional Castable.
- ✓ Low Cement Castables (LCC).
- ✓ Ultra Low Cement Castable (ULCC).
- ✓ No Cement Castable (NCC).
- ✓ Light weight Castables.
- ✓ Self-Flowing Castables (SFC).
- ✓ Insulating Castable.

b) Plastic refractories

Plastic refractories are used to form refractory monolithic linings in different types of furnaces. These refractories are suitable for making quick, economical emergency repairs and they are easily rammed to any shape or contour. Plastic refractories

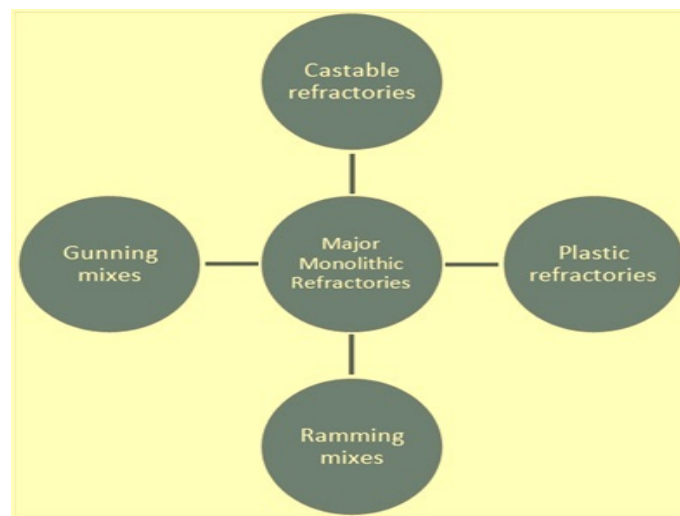


Fig .5. Main monolithic refractory categories

are consisting of refractory aggregates and adhesive clays which are prepared in stiff plastic condition at the proper consistency for use without more preparation. During utilization, the blocks are tasked into pieces and are rammed or casted into place with pneumatic rammer. These refractories can also be poured into place with a mallet. These refractories suitable for many important applications due to the high melting point (high refractoriness), the range of compositions, and the ease with which plastic refractories are rammed into place make them. Also, they have often highly spalling resistant. Plastic refractories can consist of all the, clay-graphite, fireclay, high alumina, high alumina graphite and chrome types adapted for many various operating situations. Specific gunning types are also accessible. These are in granulated shape and are produced at the proper consistency, ready to use. Some examples of plastic refractories are [33, 36-41]:

- ✓ Heat setting super duty fireclay plastic,
- ✓ Super duty heat setting plastics with graphite,
- ✓ Plastics in the 50 % alumina class,
- ✓ Heat setting 60 % alumina class plastics,
- ✓ Air setting high alumina plastics in 80 % alumina class,
- ✓ Phosphate bonded high alumina plastics with alumina content ranging from 70 % to 90 %,
- ✓ Phosphate bonded alumina chrome plastics,
- ✓ And silicon carbide based phosphate bonded plastics.

c) Ramming mixes

Ramming mixes composed essentially of ground refractory aggregates, with a semi-plastic bonding matrix. These refractory materials are like to plastic refractories but are much harder. They need some sort of form to maintenance them when formed. The grain sizes are carefully classified and the final product is usually rendered dry and then mixed with a little content of water just before utilization. Other ramming products are rendered in wet state and are ready for use immediately upon opening. Ramming mixes are placed with pneumatic rammer in layers of 25 mm to 40 mm. Steel making, burner blocks, ports and similar applications used of High purity ramming mixes based on mullite grain. Ramming mixes consist of 80wt. % alumina content have good shrinkage resistance and thermal spalling at high temperatures. Some ramming mixed such as, stabilized high alumina air setting, have good thermal spalling resistance at high temperatures

and volume stability up to their temperature limit. Also, phosphate-bonded alumina-chrome ramming mixes typically have very high strength at high temperatures and very good resistance to acid and neutral slags consist of coal ash slags. Alumina-graphite ramming mixes have mixture of high alumina grain and slag inhibitors which give them well slag resistance to acidic and slightly basic slags. In steel making industry, the dry ramming mixes based on high purity MgO and a sintering aid are useful. magnesite ramming mixes of exceptional purity and stability are used firstly as lining materials for coreless type induction kilns. Magnesia-Chrome fused grain ramming mixes can create special strength and density [33, 32-37].

d) Gunning mixes

The install method of more monolithic refractories is gunning. The constitution material of gunning mixes are different particles sized of refractory aggregate, a bonding compound, and may contain plasticizing agent to enhance their stickiness when pneumatically placed onto a kiln surface. These refractory materials are sprayed on application surfaces using a gun device. Usually gunning refractory mixes are supplied dry. In order to application, they are pre-damped in a batch mixer, and then continuously poured into a gun device. Water is added to the mix at the nozzle to achieve the proper consistency. Typically, gun mixes are including high alumina, siliceous, fireclay, dead burned magnesite and chrome types. Magnesite and hot gun mixes are not pre-damped and are placed in a batch pressure gun. Gun mixes should provide good coverage in a variety of applications [33, 34-40]. Some types of gunning mixes are:

- ✓ Fireclay gunning mixes of multipurpose hard fired fireclay and standard calcium-aluminate cement compositions.
- ✓ Fire clay gunning mixes with high purity calcium-aluminate bonding system.
- ✓ Gunning mixes based on vitreous silica.
- ✓ High purity alumina mixes which combine high fired alumina aggregate.
- ✓ High purity calcium aluminate binder.
- ✓ Basic refractory gunning mixes with magnesia content ranging from 60 % to 95 % with or without a phosphate bond.

e) Patching refractories

These type refractories materials are like to plastic refractories though have a very soft plasticity

let them to be casted into place [33-39].

f) Coating refractories

These types of refractories materials are used to maintain refractory linings usually against chemical attack. Coating refractories are usually intended to coat just the working surface of a lining. They tend to be justly thin layers [33-39].

g) Mortars

Generally, mortars are neither classified as refractory brick nor monolithic refractories. They are very fine refractory materials, which become plastic when mixed with water. These are used to bond the brickwork into solid unit, to provide cushion among the slightly irregular surfaces of the brick, to fill up spaces created by a deformed shell, and to make a wall gas-tight to prevent penetration of slag into the joints. Mortars should have good water keeping properties and must not foul. In this way, premature penetration of water in the refractory bricks after draying, causing the mortar to dry out can be avoided. Different types of refractory mortars are consisting of [33, 38-42]:

- Mortars with ceramic bonding (bonding starting at 800 °C)
- Mortars With chemical bonding
- Mortars with hydraulic bonding (bonding starting at 20 °C)

Also, the important properties of the mortars are consisting of:

- ✓ Composition and characteristics of the mortar materials
- ✓ Grain size
- ✓ Consistency

h) Fettling mixes

Fettling mixes are also granular refractory materials, with function like to gunning mixes, but are applied by shoveling into the kilns needing patching [33-36].

i) Tap-hole mixes

Tap-hole mixes are resin bonded. In these mixes the higher strength which is normally desired for monolithic refractory products, is not that important. Some criteria are necessary for all tap-hole mixes. These criteria are consisting of: correct consistency, setting and carbonization at the right time, precisely controllable PLC, and above all drilling capability [33-37]. Therefore, today, the use of monolithic refractories has become widespread because of their great benefits to shaped products. Therefore, research on the selection of raw materials, additives and formulations of this type of refractories has been considered as an important issue in recent researches (Fig. 6)

APPLICATION OF NANOTECHNOLOGY IN REFRACTORIES

Nanotechnology is mainly defined by size and comprises the visualization, characterizations, production and manipulation of structures which are smaller than 100 nm [1-3]. 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 [1-

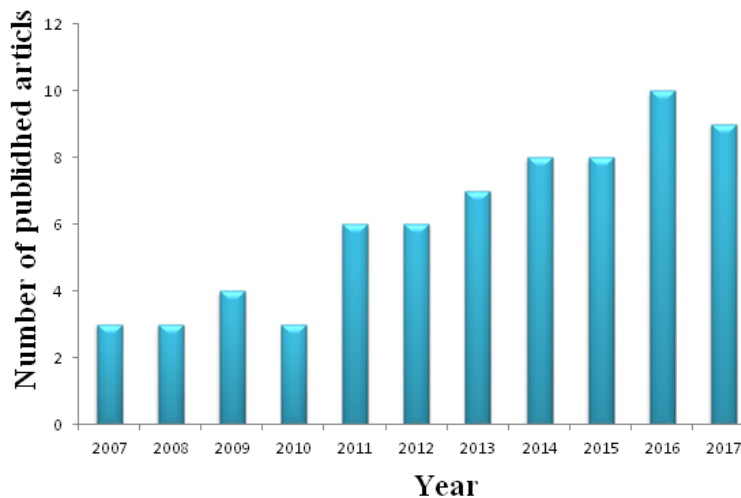


Fig. 6. Published articles in monolithic refractories filed (2007 -2017).



6]. The advancements in nanotechnology have an impact almost in all fields such as materials, instrumentation, electronics, healthcare, defense, sensors, energy, manufacturing, environments etc. Up to recently, the application of nanotechnology in refractory material was very limited. Currently, significant attention has been paid to the application of nanotechnology in the development of refractories products [44-55]. Nanotechnology has been introduced to refractories. It has been reported that the performance of the refractories was appreciably improved for the well 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 Nano-particles. The application of nanotechnology is aimed at obtaining the following unique properties of brick and castable refractories [52-56]:

- 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 past fifty years, refractories research and development based on conventional technical concepts and techniques seem to have had outstanding outcome for industries. If refinement of refractory technology is to be expected, the introduction of new technologies is indispensable. Nano materials as well Nano-structured materials improve several properties of refractory materials like mechanical resistance, thermal conductive,

and carbon oxidation protection.

The first papers on nanotechnology in refractories causing a big interest appeared in UNITECR (The Unified International Technical Conference on Refractories) in 2003 [56]. The first attempt by researchers was to modify the matrix (binding phase) of advanced refractory materials with nano-sized additives (Fig. 7) [56-74]. There have many articles in the field of application of nanotechnology in refractories [75-110]. Tamura and his co-worker from Nippon steel company published a technical report about technological philosophy and perspective on nanotech refractories [104]. P.R. Rauta and N. Sahoo [105] presented a paper titled: Properties enhancement of refractory bricks by incorporation of nano materials. Kuznetsov *et al* [98] studied the application of Nanomaterials in refractory technology in a short review in 2010. In this short review they presented of prospects for using nanomaterials in various refractories and future directions of their use for improving the operating properties of refractories. They suggested that the possibility of controlling material properties at the atomic level makes it possible to create new innovative refractory materials and technology. There are much more publications in this field, but our focus will be on monolithic refractories [75-110].

APPLICATION OF NANOTECHNOLOGY IN MONOLITHIC REFRACTORIES

Recently Nanotechnology was introduced to the monolithic refractories, and nowadays it is an

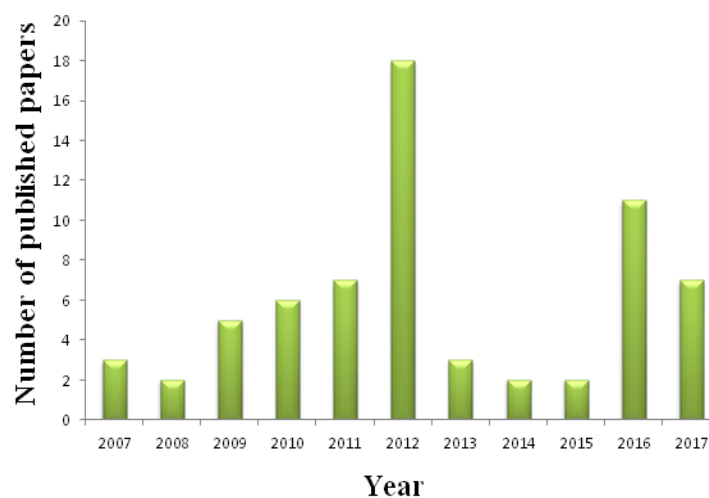


Fig. 7. Published papers in refractories field by application of nanotechnology (since 2007 -2017)

important tool included in many research projects. Several research groups have been working on the addition of different types and content of additives in monolithic 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. According to the above, in this section, the results of carried out activities by various researchers using nanotechnology in monolithic refractories have been expressed. It is observed that the use of nanotechnology has been heavily used by researchers in recent years and they have achieved very interesting results. V.C. Pandolfelli group studied and published many papers in this regards [99-103], Nouri-Khezrabad *et al.* published a few papers about nano-bonded refractory castables [99-101]. They indicated that Calcium aluminates cement (CAC) contents higher

than 3 wt% in refractory castables could have some drawbacks in the various processing steps (mainly drying) and also in their refractoriness when in contact with SiO₂. A comparison of different binding systems for refractory castables was shown (Table 1) [99]. The benefits of replacing CAC or hydratable alumina by colloidal binders were also discussed. The advantages of colloidal silica/alumina as a refractory binder were also highlighted [99-101].

Finally, the challenges for suitable use of colloidal binders were discussed and the future direction of nano-structured refractory castables was outlined [99-101 and 109-110]. They also studied development of nano-bonded refractory castables with enhanced green mechanical properties as well as rheological performance of high alumina nano-bonded refractory castables containing carboxylic

Table1. Properties of some available colloidal binders (alumina or silica) in comparison with calcium aluminate cement and hydrate able alumina [99]

Binder type	Chemical specification (wt%)	Surface area (m ² /g)	Aggregate size	Surface charge	pH range	Stabilizer	BD (g/cm ³)
Colloidal alumina [51]	Al ₂ O ₃ : 40	100	80 nm	Anionic	6-9	Citric acid	1.5
Colloidal silica [52]	SiO ₂ : 40 Na ₂ O < 0.4	200	15 nm	Anionic	10	Na-stabilized	1.3 >
Calcium aluminate cement [53]	Al ₂ O ₃ : > 69 CaO: < 30 SiO ₂ > 0.3 Fe ₂ O ₃ < 0.3	0.4	- 45 μm: 82 wt% D ₅₀ =13 μm	-	-	-	2.9-3.05
Hydratable alumina [21]	Al ₂ O ₃ : 90 Na ₂ O: 0.5 LOI: 6.5	270	D ₅₀ =2.5 μm	-	-	-	3.2

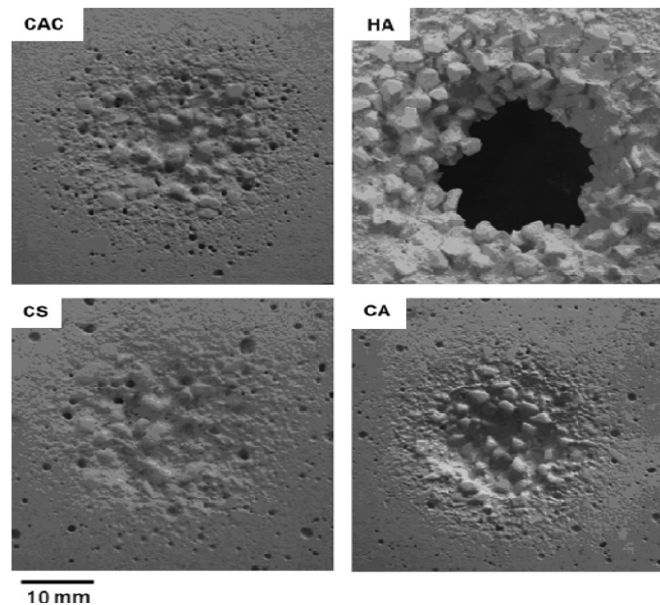


Fig. 8. Erosion profile for constables containing 4 wt.% of calcium aluminate cement(CAC), hydrate able alumina(ha), colloidal silica(CS) or colloidal alumina (CA), previously fired at 800 [99].

acids and other materials as additives [100-101, 109-110]. They showed that applying colloidal silica suspensions as a binder source for refractory castables has been of great interest in recent years. Nevertheless, the resultant low green mechanical strength of these castables has hindered their application in relevant areas. The current paper provides a novel engineering route to improve the mechanical properties of colloidal silica bonded castables before firing. In order to attain this target, small amounts of calcium aluminate cement (CAC) and/or hydratable alumina (HA) were used as gelling agents. A splitting tensile test showed that although using HA resulted in a more significant increase in the modulus of rupture of the samples when compared to CAC, mixing both (CAC+HA) had the most positive impact on the green mechanical properties of the castables, leading to strength levels as high as the reference cement-bonded system. The results indicated that CAC enhanced the hydration of HA based on the accelerated dissolution of the gel layer formed on HA particles. The dual additive system (HA+CAC) on the siloxane bond formation showed that improved green strength was mainly related to a more effective hydration of HA. This paper evaluated the role played by citric acid and gallic acid in high alumina colloidal silica-bonded castables. The addition of citric acid to three different types of colloidal silica-containing compositions led to distinct flow behavior. Vibrating flow measurements were carried out in order to define the castables' workability. The use of the mentioned carboxylic acids is required to provide enough workability to the system due to a

retarding effect on the setting agent (Fig. 9) [101, 109-110].

Besides the activities of this group, there have been other studies in the field of application of nano materials in monolithic refractories by other researchers, as well. The summary of few published data is presented in Table 2. Ghosh *et al.* [75] studied the improvement of thermal characteristics of refractory castable by addition of gel-route spinel nanoparticles. They used nano spinel as an additive. They found that castable containing nano spinel with excess alumina powder had the best combination of bulk density, apparent porosity, and hot modulus of rupture [Fig. 10]

Zhanmin *et al.* [76-77] studied the effect of nano- Al_2O_3 and nano SiC addition on the properties of Al_2O_3 -SiC-C castables. They showed that by adding 1.0% nano- Al_2O_3 the slag penetration resistance was enhanced. They also report that introduction of nano SiC to the castables by premixing with fines makes the castables denser; under the certain condition of flow ability, content of nano SiC addition increases to 2%, the water addition increases from 3.83% to 4.67%, by 22%, indicating that introduction of nano SiC has great effect on the flow ability, while it does not influence the cold MOR and hot MOR obviously, and hot MOR is the highest with 0.5% nano SiC addition, increased by 4%, phase composition analysis shows that the mullite form 1.0% nano SiC addition, while SiC residual content is more than that of samples without nano-SiC. M. Amin *et al.* [78] reported the effect of nano-sized carbon black on the physical thermo-mechanical properties of Al_2O_3 -SiC-

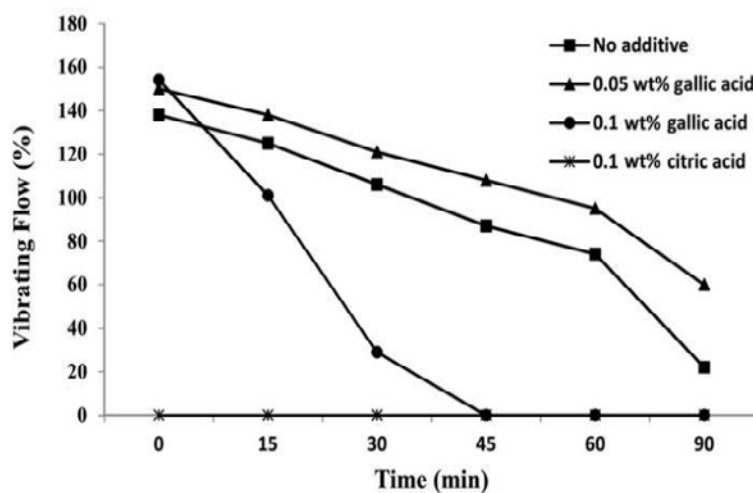


Fig. 9. vibrating flow curves of high alumina castables containing Bindzil 1440 with different additive content [101].

Table 2. Some of the published papers in monolithic refractories by application of nanotechnology and nano materials (2007 -2018)

Author(s)	Year	Topic	Nano additive(s)
S. Ghosh <i>et al.</i> [75]	2007	improvement of thermal characteristics of refractory castable by addition of gel-route spinel nanoparticles	spinel
W. Zhanmin <i>et al.</i> [76]	2008	effect of Nano-Al ₂ O ₃ addition on the properties of Al ₂ O ₃ -SiC-C castables	alumina
W. Zhanmin <i>et al.</i> [77]	2009	Effect of Nano SiC Addition on Properties of Al ₂ O ₃ -SiC-C Castables	SiC
M. Amin <i>et al.</i> [78]	2009	the effect of nano-sized carbon black on the physical and thermo-mechanical properties of Al ₂ O ₃ -SiC-SiO ₂ -C composite	carbon black
L. Zhigang <i>et al.</i> [79]	2009	effect of nano-calcium carbonate addition on properties of corundum castable	calcium carbonate
S. Otraj <i>et al.</i> [80]	2009	behavior of alumina-spinel self-flowing castables with Nano-alumina particles addition	alumina
S. Badiie <i>et al.</i> [81]	2009	non-cement refractory castables containing nano-silica: performance, microstructure, properties	silica
S. Otraj <i>et al.</i> [82]	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	FS10 FS20
S.Otraj <i>et al.</i> [83]	2011	microstructure and phase evolution of alumina-spinel self-flow in refractory castables containing nano-alumina particles	alumina
S. Badiie <i>et al.</i> [84]	2011	effect of nano-titania addition on the properties of high-alumina low-cement self-flowing refractory castables	titania
H. Yaghoubi <i>et al.</i> [85]	2012	influence of nano silica on properties and microstructure of high alumina ultra-low cement refractory castables	silica
L. Zhigang <i>et al.</i> [86]	2012	effect of nano calcium carbonate on properties of corundum-spinel castables	calcium carbonate
N.M. Khalil <i>et al.</i> [87]	2012	improvement of mullite and magnesia-based refractory castables through addition of nano-spinel powder	spinel
S. Mukhopadhyay <i>et al.</i> [88]	2012	nanostructured cementitious sol gel coating on graphite for application in monolithic refractory composites	calcium aluminate
E.Y. Sako <i>et al.</i> [89]	2012	how effective is the addition of nanoscaled particles to alumina-magnesia refractory castables	alumina magnesia
C. Gogtas <i>et al.</i> [90]	2012	Development of Nano-ZrO ₂ reinforced self-flowing low and ultra-low cement refractory castables	zirconia
S. Mukhopadhyay <i>et al.</i> [91]	2013	Nano-scale calcium aluminate coated graphite for improved performance of alumina based monolithic refractory composite	calcium aluminate
N. Farzadnia <i>et al.</i> [92]	2013	characterization of high strength mortars with nano alumina at elevated temperatures	alumina
S. Dutta <i>et al.</i> [93]	2014	significant improvement of refractoriness of Al ₂ O ₃ -C castables containing calcium aluminate nano-coatings on graphite	calcium aluminate
S. Otraj <i>et al.</i> [94]	2015	impact of Nano-Cr ₂ O ₃ addition on the properties of aluminous cements containing spinel	chrome
C. Gogtas <i>et al.</i> [95]	2016	Effect of Nano-YSZ and Nano-ZrO ₂ additions on the strength and toughness behavior of self-flowing alumina castables	YSZ ZrO ₂
Salman Ghasemi-Kahrizangi <i>et al.</i> [96]	2017	The influence of Al ₂ O ₃ nanoparticles addition on the microstructure and properties of bauxite self-flowing low-cement castables	alumina
H. Rastegar <i>et al.</i> [97]	2018	The influence of Iron nanoparticles	Iron nitride
M. Nouri-Khezrabad and <i>et al.</i> [99-101]	2013	Nano-bonded refractory castables	Nano materials
Nouri-Khezrabad <i>et al.</i> [99-101]	2014	Citric acid role and its migration effects in nano-bonded refractory castables	Citric acid
Nouri-Khezrabad <i>et al.</i> [109-110]	2015	high alumina nano-bonded refractory castables containing carboxylic acids as additives	carboxylic acids
T.M. Souza A.P.Luz V.C. Pandolfelli, [102]	2014	Magnesium fluoride role on alumina-magnesia cement-bonded castables	Magnesium fluoride
A.P. Luz, [103]	2018	Sintering effect of calcium carbonate in high-alumina refractory castables	calcium carbonate

SiO₂-C composite. They showed that nano-sized carbon black addition improved the relative heat resistance and oxidation resistance of composites (as shown in Fig. 11).

Zhigang *et al.* [79 and 86] studied the effect of nano-calcium carbonate addition on properties of

corundum castables. Their funding showed that after thermal treatment at 1000, 1500 and 1600 °C, the apparent porosity was increased gradually while the bulk density, CCS and MOR were decreased, simultaneously. They also indicated that after treating at 800-1400 °C; adding nano calcium

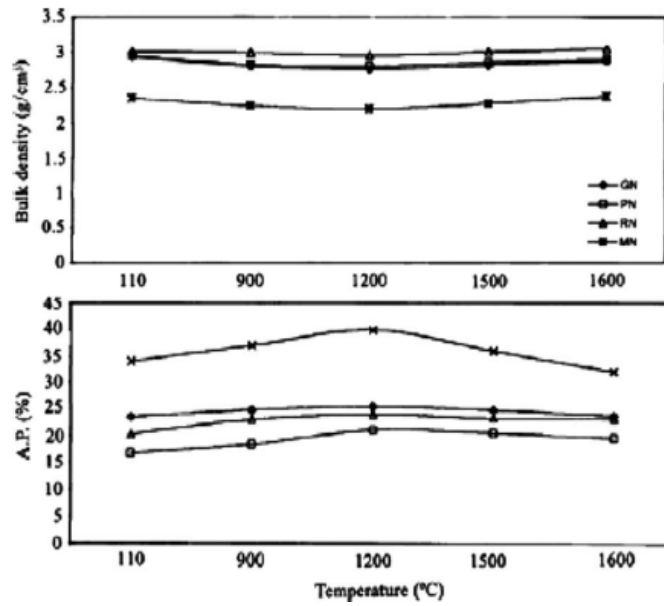


Fig. 10. Variation of bulk density and apparent porosity with temperature for GN, PN, RN AND MN types of castables [75]

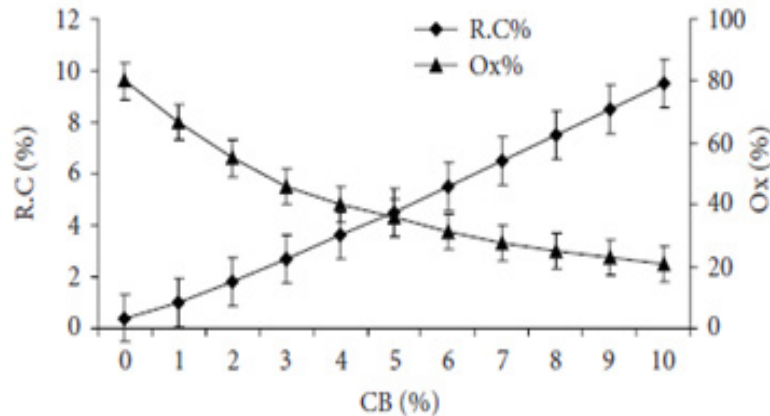


Fig. 11. The residual carbon content (R.C) of composite (wt %) and Ox% versus CB% as additives [78].

carbonate obviously improved the thermal shock resistance of the castables, and have little influence on corrosion resistance to high basic slag. Badiie *et al.* [81] made a research on the performance, microstructure, and properties of non-cement refractory castables containing nano-silica. He showed that by increasing of firing temperature up to 1000°C, porosity and pore sizes of castables tended to decrease (Fig. 12).

Otroj *et al.* [80, 94] studied the behavior of alumina-spinel self-flowing castables with nano-alumina particles addition and the impact of nano-Cr₂O₃ addition on the properties of aluminous cement containing spinel. They reported that 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 (Fig. 13).

They also reported that the slag resistance of refractory castables containing prepared cements was improved due to increasing of spinel and decreasing of C₁₂A₇ amount in the cement composition containing nano-Cr₂O₃ (Figs. 14 and 15).

Khalil *et al.* [87] reported the improvement of mullite and magnesia-based refractory castables through addition of nano-spinel powder. They showed that castable sample mix containing 10 wt. % nano-MA spinel powders was chosen as an optimum composition according to its good

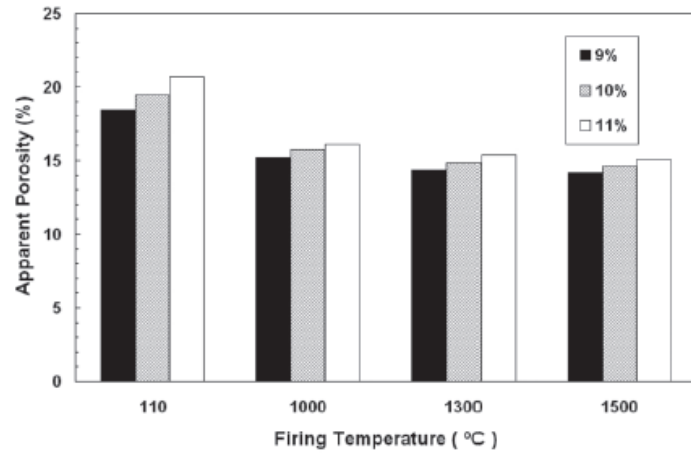


Fig. 12. The effect of sol content on the apparent porosity of castable after firing various temperatures [81]

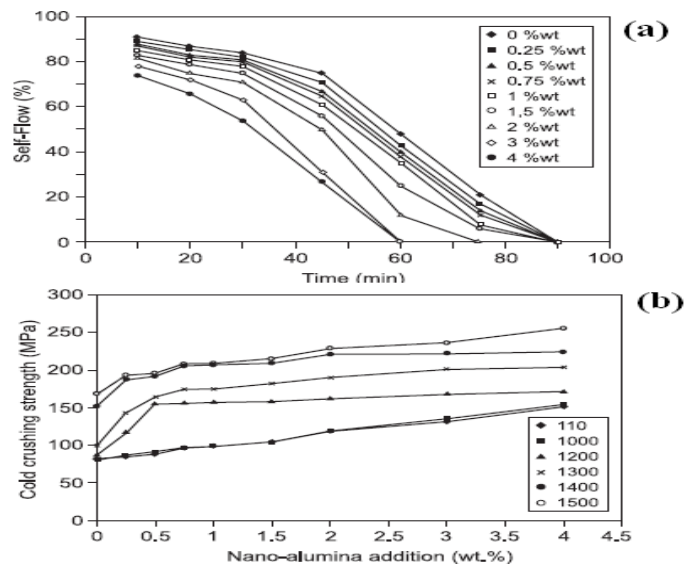


Fig. 13. the influence of nano-alumina particles on a) self-flow value and b) C.C.S of alumina spinel castable [80]

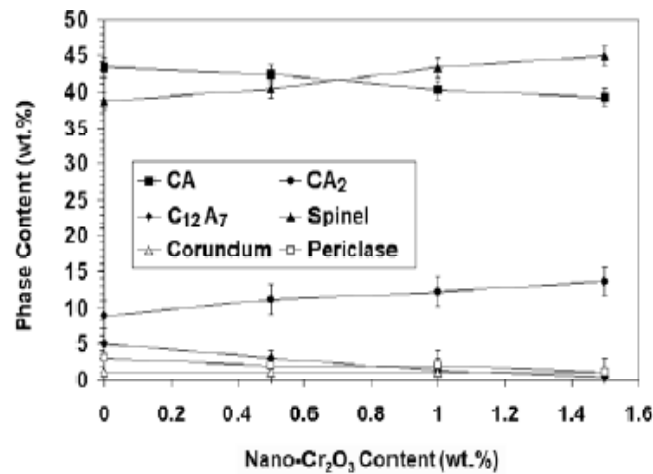


Fig. 14. The effect of nano-Cr₂O₃ content on the content of formed phases in the cement composition after firing [94]

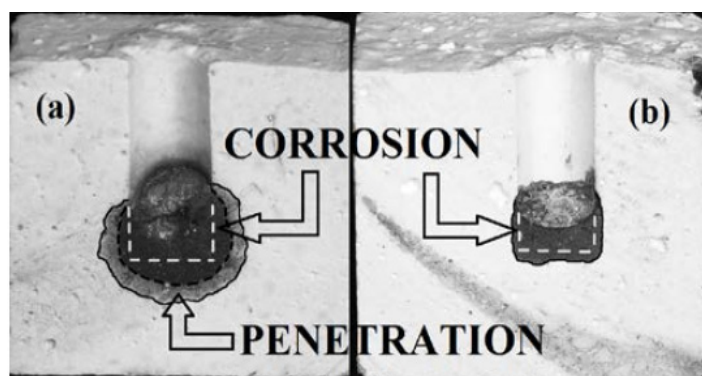


Fig. 15. Schematic diagram of the interior of the crucibles showing the extent of corrosion and penetration slag; a) without nano-Cr₂O₃ b) containing 1.5wt% nano-Cr₂O₃ [94]

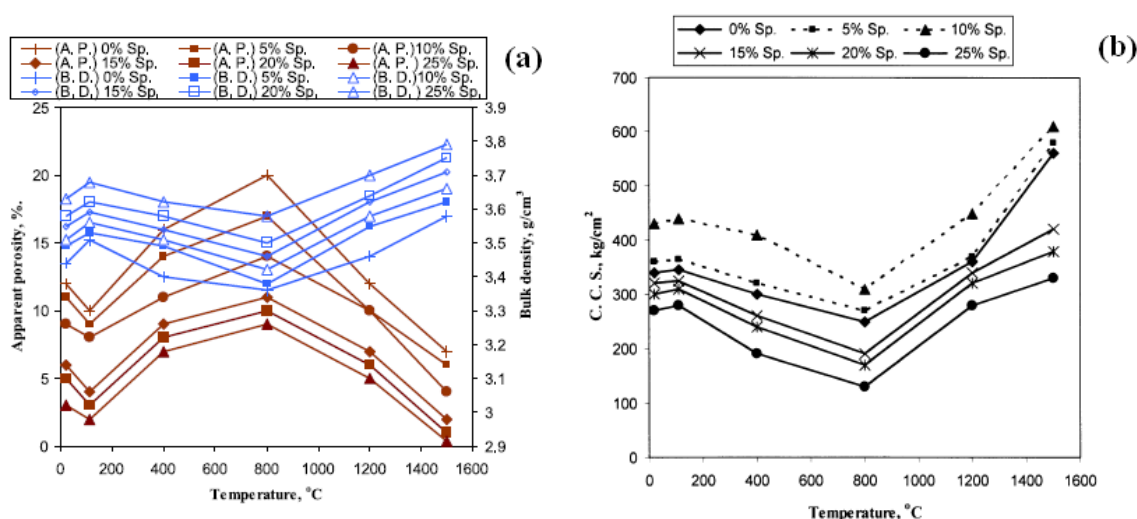


Fig. 16. a) Bulk density and apparent porosity and b) cold crushing strength of the nonmodified and modified mullite-based refractory castable sample [87]

sintering behavior, mechanical and refractory properties (Fig. 16).

Mukhopadhyay *et al.* [88, 91] made a few researches on the effects of nano materials in refractories, such as nano-scale calcium aluminate coated graphite for improved performance of alumina based monolithic refractory composite and nano-structured cementitious sol gel coating on graphite for application in monolithic refractory composites. They reported that the green bulk density of castable cubes has been determined to corroborate the better performance of the graphite coated with calcium aluminate (Fig.17) [88]. They also reported that nano-coating considerably improved matrix-aggregate bonding. Less porous simulated matrix upgraded slag resistance (Fig. 18) [91].

Sako *et al.* [89] studied how effective is the addition of nano-scaled particles (nano alumina

and nano magnesia) to alumina–magnesia refractory castables. They showed that although the addition of a nano alumina and nano magnesia 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 (Table 3).

Gogtas *et al.* [90] studied the development of nano-ZrO₂ reinforced self-flowing low and ultra-low cement refractory castables. They showed that nano-ZrO₂ improved the flexural strength by 20% but it did not have significant effect on the K_{IC}. They also investigated the effect of Nano-YSZ and Nano-ZrO₂ additions on the strength and toughness behavior of self-flowing alumina castables [95]. It was found that the addition of 3 wt% nano-ZrO₂

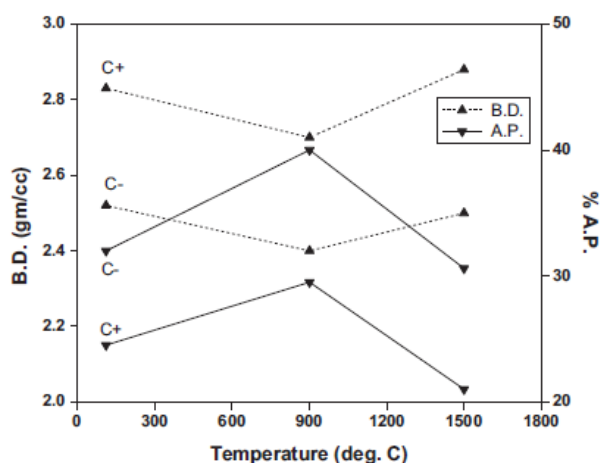


Fig. 17. Comparison of changes in bulk density and apparent porosity of C+ and C- type castable at 110, 500 and 1500°C [88]

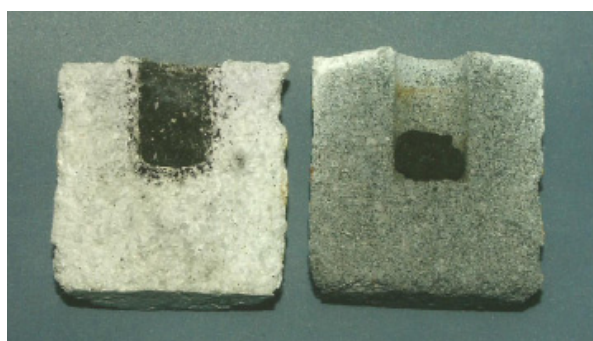


Fig. 18. Slag corrosion/ cut section photographs of C+ (right) and C- (left) castable[91].

Table 3. Overall expansion, initial spinel expansion temperature and apparent porosity after firing at 1500 for 5 h of the alumina–magnesia castables containing different alumina and magnesia grain size [89]

	Overall expansion (%)		Initial spinel expansion temperature (°C)		Apparent porosity (%)	
	A1	A2	A1	A2	A1	A2
M13	2.2	1.9	1050	1105	20.4 ± 0.7	18.5 ± 0.9
M45	3.6	2.9	1065	1130	22.9 ± 0.4	20.4 ± 0.3
M100	5.3	4.5	1210	1370	31.3 ± 1.1	28.6 ± 0.7

improved the MOR of self-flowing castables (SFCs) by 20% and 50% matrix and binding systems respectively. Their results indicated that 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 (Fig. 19).

Dutta *et al.* [93] reported a significant improvement of refractoriness of Al₂O₃–C castables containing calcium aluminate nano-coatings on graphite. They showed that the sol–gel coating could overcome the pitfalls of including uncoated graphite’s in castables and should be explored for

commercial utilization (Fig. 20).

Salman Ghasemi-Kahrizangi *et al.* [96] evaluated the influence of Al₂O₃ nanoparticles addition on the microstructure and properties of bauxite self-flowing low-cement castables. Results showed that the use of Al₂O₃ nanoparticles let to formation of the platy and needle crystalline phases such as Hibonite (CaO·6Al₂O₃), CaO·2Al₂O₃, and mullite (3Al₂O₃·2SiO₂) inside the grain boundaries of the bauxite particles (Fig. 21). Refractories based on nano-structured materials are emergent technological products in several applications in

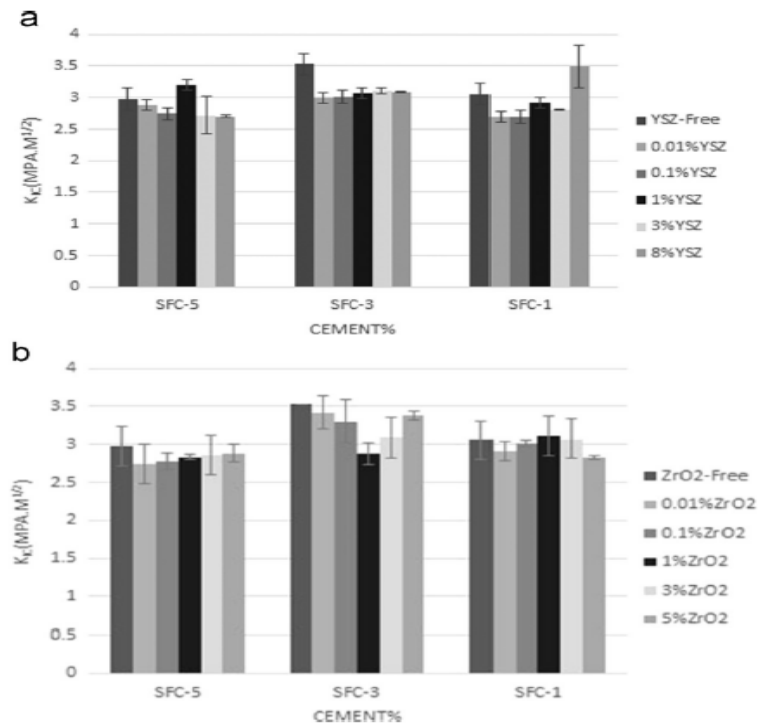


Fig. 19. experimental K_{Ic} value for a) various additions of YSZ and b) ZrO_2 additions SFCs as a function of cement content fired at 1573 k for 3h.

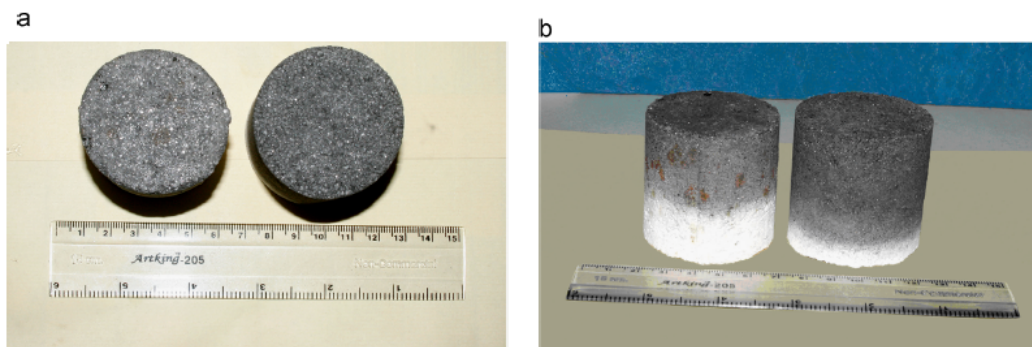


Fig. 20. (a and b). photographs of C+ (right) and C- (left) castables after oxidation resistance test [93]

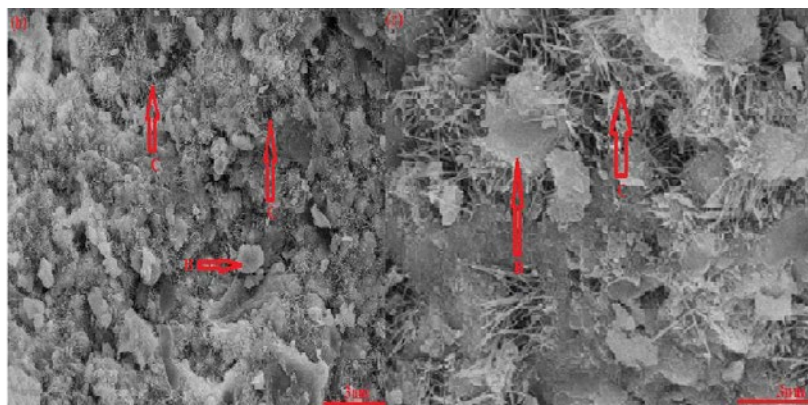


Fig. 21. Formation of the platy and needle crystalline phases inside the grain boundaries of the bauxite particles [96]

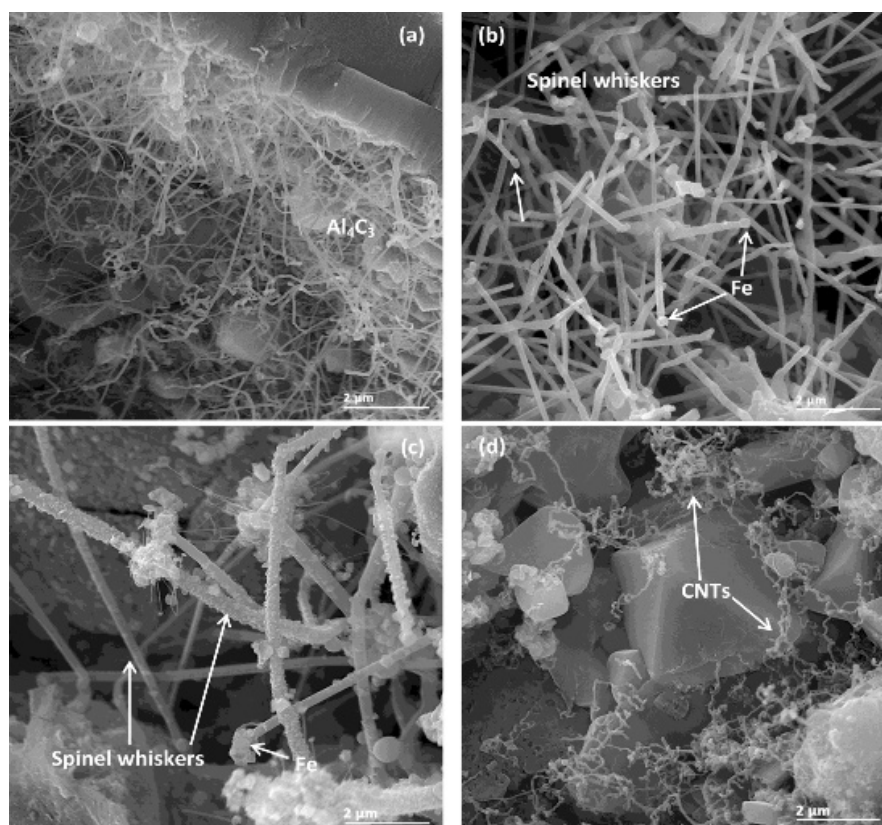


Fig. 22. Formation of nano-spinel whiskers using nano-additives [97]

the steel and cement industries. Important studies in recent years are related to the in-situ formation of nano phase/s during a controlled process. For example, Rastegar *et al.* [97] recently reported the effects of nano additive on the formation of nano spinel in the form of nano particles as well as nano whiskers. They showed that adding Iron nitride as an additive and formation of nano Iron particles, the formation of nano spinel phases (in different forms) were enhanced (Fig. 22)

CONCLUSION

In this paper we tried to present the prospects for using nanomaterials as well as nanotechnology in various refractory, especially in monolithic refractories. We tried to mention the other group's ideas for future directions of using nanomaterials and nanotechnology for improving the properties and performance of refractories. Many research groups have been working on this field by adding of different types of additives in refractories bodies, and have focused their investigations on the use of nano-additives, because of the advantageous of adding nano-particles to the ceramic bodies. The

in-situ control of nano-phase is another topic that is gaining attention in this field. We presented the summary of other researchers' results, in an effort to enhance the performance of monolithic refractories. It was concluded that the application of nano-additives and application of nanotechnology could improve the overall properties of refractories. The main challenge in the future is to reduce the overall cost of using nano materials and nanotechnology.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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