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Review article

Nanotechnology in castable refractory

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ABSTRACT

In recent times nanotechnology has drawn significant attention in the field of refractory research. Different nanopowders and colloidal suspensions have been utilized to improve the properties of refractory castables. Various studies have been carried out worldwide with nano scaled binders; such as, hydratable alumina (HA), colloidal alumina (CA), colloidal silica (CS), micro silica, etc.; to improve the thermo mechanical properties of refractory materials. Nano scaled additives are also being applied to reduce the energy consumption and to improve the densification process at lower temperatures. In this paper, the contributions of nanotechnology in selection of raw materials, the binders and choice of additives to improve the quality of refractory materials, and the future of nanotechnology in refractory research are reviewed.

1. Introduction

Refractories can be defined as the ‘non-metallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 538 °C’ [1]. Inorganic materials such as silicon nitride, zirconium oxide, zirconium carbide, aluminum nitride, silicon carbide, silicon dioxide, aluminum oxide, magnesium oxide, dolomite, etc. are widely used in making of refractories because these materials have the ability to withstand high temperatures without undergoing minimal physical or chemical changes in contact with molten slag, metals and gases. The basic functions of refractories include (1) to act as protective barrier for preventing the vessels from thermal erosion and chemical corrosion by the hot medium like flue gases, liquid metals, liquid slag, and molten salts; and (2) to retain heat (insulate) within the vessel. Refractory materials are commonly used in furnaces and kilns, burner blocks, boiler works, etc.

Refractories are shaped or unshaped in structure. Those having a definite shape are termed as bricks whereas unshaped refractories are called monolithics, which can be converted into a desired shape. Depending upon their applications, unshaped or monolithic refractories are classified as castables, gunning mass, plastic mass, refractory

mortars, etc. Castable refractories consist of precisely graded coarse and fine refractory grains. These grains are gelled by means of suitable binders and additives which facilitate the formation of strong bonds between the particles during heat treatment. The raw materials are gelled by means of suitable binders which facilitate the formation of strong bonds between particles during the heat treatment. Castable are installed either by pouring or pumping after mixing with water. Due to the quality performance and cost-effectiveness, refractory castables have increased in popularity [2–4]. Compared to bricks and shaped refractories, these materials can be used in a variety of demanding and harsh industrial applications mostly due to performance and easier installation [5]. A number of parameters such as calcium oxide (CaO) content, chemical composition, the binder source, bulk density, etc., govern the quality of a refractory castable. Based on these parameters, the classifications of refractory castables are available in the literatures [6,7].

In recent years, nanotechnology has gathered significant importance in the field of castable refractories. This is due to the fact that both physical and mechanical properties can be improved significantly when its microstructure is reduced to the nanometer range. Two factors responsible for such improvements are: (1) an exponential increase in the relative proportion of atoms at the grain boundary surfaces and, (2) the

Abbreviations: CA, Colloidal alumina; CA₂, Calcium dialuminate; CA₆, Calcium hexaaluminate; CAC, Calcium aluminate cement; CASH, CaO-Al₂O₃-SiO₂-H₂O; CVD, Chemical vapor deposition; CS, Colloidal silica; FCC, Fluid catalytic converter; HA, Hydratable alumina; HMOR, Hot modulus of rupture; LCC, Low cement castable; MAP, Mono aluminum phosphate; MCC, Middle cement castable; NAP, Nano alumina powder; NCC, No cement castable; NP, Nanoparticle; PEG-ME, Poly (ethylene glycol) monomethyl ether; SA, Sintering additives; SFV, Self flow value; ULCC, Ultra low cement castable; UNITCER, Unified international technical conference on refractories

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generation of dislocation, quantum confinement, etc in the microstructure [8]. The objective for the application of nanotechnology in refractories is to improve the compressive strength, tensile strength, ductility, resistance to thermal shock, abrasion and chemical corrosion, aggregate-paste bond strength, ability to control of cracks and self healing, etc [9–11]. Some of the initial research on the use of nanotechnology in refractories was presented and published in UNITER 2003, which has gathered significant interest among researchers [12,13]. The demand for castable refractory products has been increasing continuously in order to meet some of the essential requirements; including environmental issues and optimization of various industrial production processes [14–16]. To fulfill these demands, it is essential to modify or develop the designs for novel refractory compositions that enhance the properties over existing ones. In recent years experiments have been carried out using nano-powders and colloidal suspensions to improve the nature of bonding in castable refractory and to carry out densification at lower sintering temperatures. It has also been observed that by using nano sized additives, the oxidation resistance and compressive strength of the refractory materials can be improved significantly [17–21]. This paper is a comprehensive review of published literature on the application of nanotechnology to refractory castables and the impact on their properties.

2. Nano scaled precursor

For the production of refractories, both oxide and non-oxide materials are used. Oxide refractories usually contain silica, alumina, magnesia, zirconia, etc.; whereas silicon carbide, nitrides, borides, graphite, etc., produce non-oxide refractories. Refractories can also be manufactured by the combination of oxide and non-oxide materials; such as MgO-C brick, Al₂O₃-C brick, Al₂O₃-SiC-C brick, etc. Depending upon the chemical nature of these constituents, i.e., their reaction with the slag, refractories can be further classified into following categories–

- (a) Acidic refractories-silica, zirconia and alumino-silicate refractories.
- (b) Basic refractories-magnesite, dolomite and magnesia-chrome refractories.
- (c) Neutral refractories-carbon (graphite), chromite and alumina refractories.

In recent years, much research has focused on improving the performance of the refractory castables in severe service environments, particularly in the steel and cement industries. Oxide nanoparticles such as TiO₂ [21], Al₂O₃ [22], SiO₂ [23], ZrO₂ [24], etc., are used in the matrix of refractory castable formulations. In refractory castables, nano particles fill the voids and generate rapid diffusion paths for the removal of water molecules. This leads to an increase in the surface energy and improves particle packing of the system. As a result properties such as oxidation, corrosion, hydration, thermal shock resistance, etc., of the brick and castable refractories are improved significantly.

Silicon carbide (SiC) is popular among researcher as a refractory material because SiC can be stable above 2700 °C and it has high strength (~ 800–1000 MPa) and fracture toughness (6–10 MPa m^{1/2}). It can also be used in aggressive environments due to the formation of a protective coating of SiO₂ on its surface at high temperature. SiC refractories are available as both non-oxide and composite refractories. In the first type, SiC grains are interlinked with each other (i.e. self bonded); whereas in composite form, grains of SiC are interlinked with one or more of these compounds: alumina, silica, silicon nitride, graphite, mullite, titanium, etc [25]. Al₂O₃-SiC-C (ASC) based castable refractories have been widely used in blast furnaces. The services of these refractories can be improved by enhancing their slag resistance, anti-oxidation and mechanical properties [26–31]. It has been observed that the addition of nano sized Ni in the refractory matrix results in the formation of carbon fibers, which cause in situ formation of a three-dimensional structure [Fig. 1]. In the presence of nano-sized Ni, in-situ

formation of carbon fibers in Al₂O₃-SiC-C castable composites is also promoted, leading to an increase in the strength and elastic modulus of the castable [32]. But the disadvantage of using SiC and C is in their tendency to oxidize at high temperatures [33,34]. The addition of microsilicon in a Al₂O₃-SiC-SiO₂-C castable can be a solution to improve the anti-oxidation performance as it can form a protective layer on the surface of refractories by oxidizing and swelling to seal the pores [35].

In the iron and steel industry, carbon containing or carbon based refractories are extensively used. Detailed informations on carbon containing basic refractories, carbon containing non-basic refractories and refractories based on carbon bricks or blocks are available in the literature [36]. In conventional carbon containing refractories, graphite or carbon content varies between 5 and 20 wt%. Efforts have been made to manufacture low carbon (< 5 wt%) containing refractories by using nanosized carbon powders [37,38], nanofibres [39], graphite oxide nanosheet [40–42], carbon nanotubes [43–45], etc. The addition of nano sized carbon (1–2 wt%) has been found to be effective in improving properties like slag resistance and thermal shock resistance of the refractories [46]. In recent years, efforts were made to manufacture carbon containing refractory castables. But commercialization of these efforts is hindered because of poor water-wettability of graphite. To overcome these problems, three major techniques have been employed: (1) addition of surfactants/dispersants (2) addition of refractory oxide/carbon flake pellets and (3) flake graphite surface modifications. By using appropriate surfactants, demand for water can be reduced. But castables with high porosity and low mechanical strength are produced due to foaming tendencies of surfactants. In the second method, pellets are formed by binding the oxide grains and graphite flakes using binders such as resins. These pellets were then added to the castables. But this technique has some drawbacks, such as an increase in porosity, loss of homogeneity in the castable matrix, unstable microstructure of the castable due to a change in castable flow behavior, etc. To overcome these disadvantages, efforts have been made to modify the surface of graphite by employing coating techniques before using it as raw material in refractory castables manufacturing. Experiments have been conducted to coat a graphite surface with oxides or carbides to improve its wettability. A SiC coating on the surface of graphite by CVD can improve water wettability of the surface, but doesn't produce a uniform surface coating as materials get physically adsorbed onto the surface. This technique is expensive and hence commercially not viable [47]. Liu et al. employed a molten salt synthesis (MSS) technique to coat the graphite surface with titanium carbide (TiC). The raw materials used were natural flakes of graphite (100–300 μm), Ti powders (~ 45 μm) and alkali chloride salts (KCl, LiCl and NaCl). Different proportions of Ti powder and graphite were mixed and then heated with alkali chloride to a temperature between 650 °C and 950 °C for 4–8 h. Experimental studies indicated that heat treatment of a Ti and graphite mixture in KCl or KCl-LiCl at 850–950 °C resulted in the formation of a continuous and crack free graphite surface composed of nanosized TiC particles [48]. To improve water wettability, the surface of graphite coated with oxides such as Al₂O₃, TiO₂, etc. Al₂O₃ sol was prepared by employing sol-gel processing of aluminum diisopropoxide ethyl acetoacetate, aluminum tri-sec-butoxide, aluminum hydroxide lactate, etc. as the source of alumina. To coat with Al₂O₃, graphite was mixed with an alumina solution in a spinning mixture, then dried and heated at 500 °C [49,50]. Yu et al. used natural graphite flakes (grain size 50 μm) and tetra-*n*-butoxy titanium (TiO₂ content: 23.5 mass %) to coat graphite powders with TiO₂. Varying amounts of titania salt were dissolved in ethanol and used for coating over the surface of graphite in a Henschel mixer (1975 r.p.m for 3 min). The coated graphite powder was then dried at 120 °C for 12 h in air [51]. In most of the cases, however, it has been observed that the bond between the coating material and graphite substrate was weak and discontinuous. As a result surface coating becomes dislodged during mixing of materials [52]. Mukhopadhyay et al. described a technique in which a thin film of magnesium aluminate spinel (MgAl₂O₄) was coated over a graphite surface. A thin film

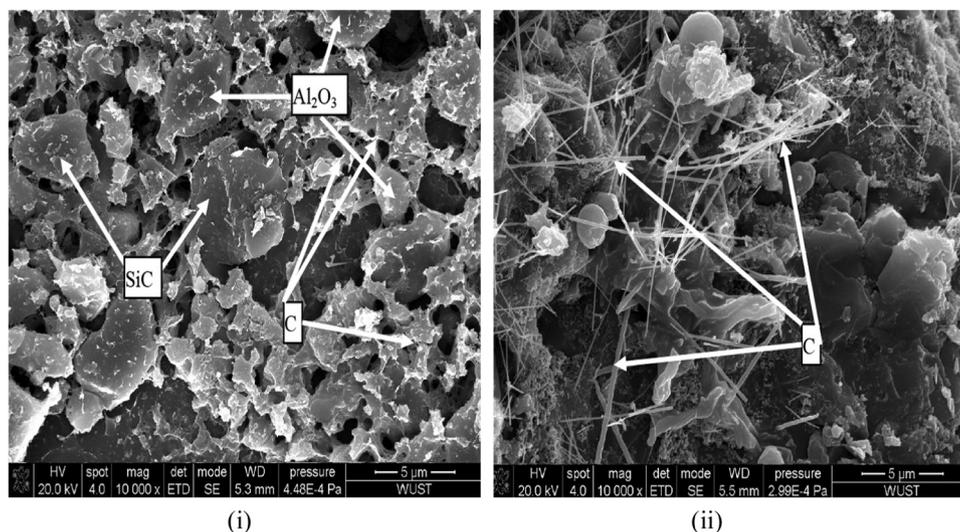


Fig. 1. SEM of ASC based castable refractory specimens (i) without and (ii) with Ni fired at 1500 °C for 3 h [32].

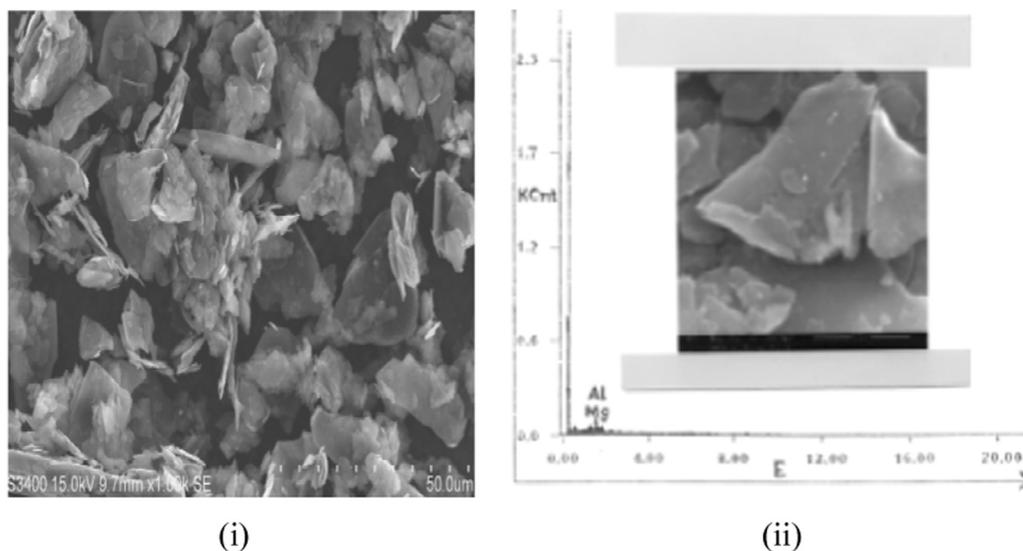


Fig. 2. SEM micrograph of (i) graphite before coating and (ii) spinel coated graphite with EDS at a specific region [53].

containing 1.5 wt% of spinel was prepared by employing sol-gel processing. Evaluation of the coated graphite surface using the SEM confirmed the formation of a distinct, crack-free, uniform and continuous surface over graphite flakes (Fig. 2). The coated layer acted a bridge between the graphite and oxide particles, and improved wettability by water. The coated graphite was then dried, calcined at 550 °C and sieved to below 75 μm and used in castables. The oxidation losses of coated graphite were reduced by almost 21% at 1200 °C. The castables obtained were found to have improved bulk density and apparent porosity compared to those of castables having uncoated graphite in the composition. In the castable, casting water was found to be reduced by almost 2.5% [53]. Although experiments have been performed with micro level materials, research work using nano scale raw materials to manufacture carbon based or carbon containing castables has not yet been studied.

Spinel containing refractories have gathered significant attention as these refractory materials possess superior thermal shock resistance, a high melting point and chemical stability. The general formula of spinel is AB_2O_4 , where 'A' is a divalent ions (such as Mg^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+} , etc) and B is a trivalent ions (such as Al^{3+} , Fe^{3+} , etc.). Spinel are categorized into normal and inverted spinels. In the normal form, the oxide ions form a close-packed cubic lattice with four octahedral

holes and eight tetrahedral holes per AB_2O_4 unit. Examples of such spinels include $MgAl_2O_4$, Mn_3O_4 , Co_3O_4 , etc. In inverse spinels, A (II) ions and one half of the B (III) ions exchange their positions i.e. A (II) ions occupy octahedral holes with one half of the B (III) ions and the remaining B (III) ions are present in the tetrahedral holes. $NiFe_2O_4$ and Fe_3O_4 are the example of inverted spinels. General structures of normal and inverted spinels are presented in Fig. 3. Spinel have the tendency to form substitutional solid solution in contact with slag. For example, $MgAl_2O_4$ reacts with slag containing Fe (II) and Mn (II) compounds, forming a complex structure that has a formula XOZ_2O_3 , where X stands for Mn (II) and Z stands for Fe (II). Calcium compounds present in slag reacts with excess Al_2O_3 of spinel forming hibonite crystals ($CaO_6Al_2O_3$), accelerating the densification of the structure [54,55]. Removal of MnO, FeO and CaO from slag increases the amount of SiO_2 in its composition, making it more viscous. This process reduces the slag penetration and slag corrosion [56].

In the steel industry, both Al_2O_3 -spinel and Al_2O_3 -MgO castables are widely used as steel ladle linings because of their higher refractoriness and better corrosion resistance versus alumina castable [57]. In the first instance, spinels are added to the mixture of Al_2O_3 -spinel castable as grains; whereas in Al_2O_3 -MgO castables, in situ spinel is formed during the reaction of MgO with Al_2O_3 . Although Al_2O_3 -MgO castables have

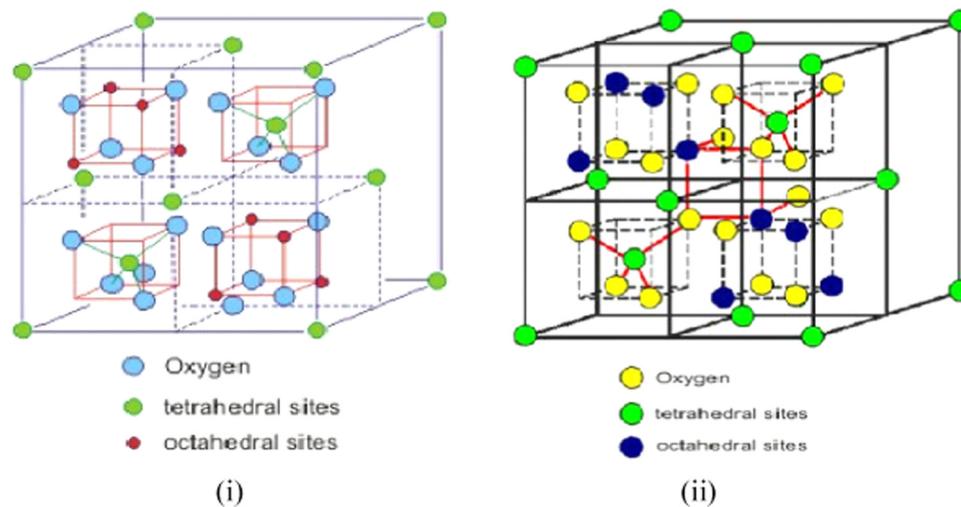


Fig. 3. General structure of (i) normal and (ii) inverted spinel.

lower cost and superior slag resistance, Al_2O_3 -spinel castables are most commonly used in the steel industry as alumina rich spinels because they offer advantages in refractory castables [58–62]. The reason is that Al_2O_3 crystals have hexagonal close packed (hcp) structures whereas MgO crystals are cubic in structure. Al_2O_3 crystals enhance the bonding forces and increase the flexural strength and thermal shock resistance of the castable. Raw materials which are extensively used to manufacture Al_2O_3 -spinel castable refractory include calcined and reactive alumina and MgAl_2O_4 spinels. MgAl_2O_4 spinel is used because of its high thermal shock resistance, wear and penetration resistance against slag, excellent hot strength, low thermal expansion values at elevated temperature, etc [63,64]. MgAl_2O_4 is the only stable compound in the binary systems of MgO and Al_2O_3 . Stoichiometric amounts of MgAl_2O_4 spinel have a molar ratio of (1:1) with weight percentage of 71.67 and 28.33 of Al_2O_3 and MgO respectively. The amount of spinel in a refractory should be in the range between 20 and 25 wt% to avoid a high rate of corrosion and slag penetration. A number of techniques are used to produce a spinel containing refractory synthetically, with a comprehensive study on important aspects of these techniques available in the review work done by Braulio et al. [65].

In recent years research has started adding nano sized materials in the compositions of spinel containing castable refractories. Nano particles have high surface area, high surface energy and the ability to diffuse rapidly. These properties make the nano particles highly reactive in the aggressive environment existing in steel production. Otraj and Daglighi [66] reported that the addition of nano alumina (43 nm, 2–4 wt%) enhanced the growth of self flowing alumina-spinel refractory castable. The raw materials used were tabular alumina (60 wt%), spinel (23 wt%), reactive alumina (11 wt%), CAC (6 wt%) and dispersant (0.1 wt%). In the composition, nano alumina powder substituted for the reactive alumina. It was observed that with the increase in nano-alumina content, apparent porosity of the samples decreased. Nano powders fill the voids between castable aggregates and enhanced bonding between particles. During the course of sintering, nano particles come in contact with the matrix and, due to difference of curvature radius, nano and micron sized particles or small nano-sized and big nano sized particles interchange positions. Due to the coursing of particles, surface energy was reduced and interface energy was increased. As a result, the sintering temperature of the castables reduced from 1500 °C (composition having conventional particle size) to 1300 °C. In the presence of nano sized alumina, hibonite phases ($\text{CaO} \cdot 6\text{Al}_2\text{O}_3$) started to form at a lower temperature (1300 °C). These phases have the ability to interlock the grains and develop excellent bond linkages between particles. Hibonite phases also have a high chemical resistance in an alkaline atmosphere, high stability in a CO atmosphere, and low wetting ability in

both ferrous and non-ferrous atmospheres [67,68]. The formation of these phases were found to accelerate at 1500 °C with higher nano alumina content (4 wt%). SEM images of a castable containing different amounts (0–4 wt%) of nano alumina particles after firing at 1500 °C are presented in Fig. 4. The micrographs showed the formation of clusters of flat crystals on the surface of tabular alumina and spinel aggregates. Grains were found to be more interlocked in the composition having a higher quantity of nano alumina (4 wt%). Further analysis revealed that these flat crystals were in hibonite.

3. Nano-scaled binder

Binding agents used in refractory system play a significant role in determining the processing route, service performance, etc. During the early history of refractory manufacturing, hydraulic bonding was employed, with high amount (15 wt% or more) of calcium aluminate cement (CAC) used. Although hydraulic bonding techniques are still used in some materials, the mode of binding has shifted first to polymerization, then to coagulation. In polymerization processes, refractory aggregates and the binder combine together to form a polymeric structure in which ceramic bonding processes start after sintering at high temperature (above 900 °C). Examples of binders used in polymeric processes of refractory manufacturing include MAP, phosphoric acids, sodium or potassium silicates, etc. Sometimes a setting agent is added to get desired setting properties. With phosphoric acids or MAP, commonly used setting agents are powdered MgO , CAC, etc. Coagulation, or colloidal processing, is employed in refractory processing to obtain a strong and homogeneous microstructure. This technique involves the coagulation of particles depending upon reaction conditions like pH, temperature, etc. The detail about the progress in binding systems for refractory castables is available in the literature [3,69].

The use of CAC has some disadvantages in systems containing microsilica and/or magnesia. At higher temperature, calcium oxide in CAC combined with other oxides form low melting temperature phases [70–72]. Again for cement based castables, curing and dewatering steps need to be conducted carefully to eliminate explosive spalling [73–76]. To overcome these difficulties, measures have been taken to manufacture low cement containing refractories such as NCC, LCC, MCC and ULCC [77–81]. The cement content of these castables is listed in Table 1. A number of calcium free binding systems have been developed, which include HA, CA, CS, micro silica, etc [5,17,18,70,82–87].

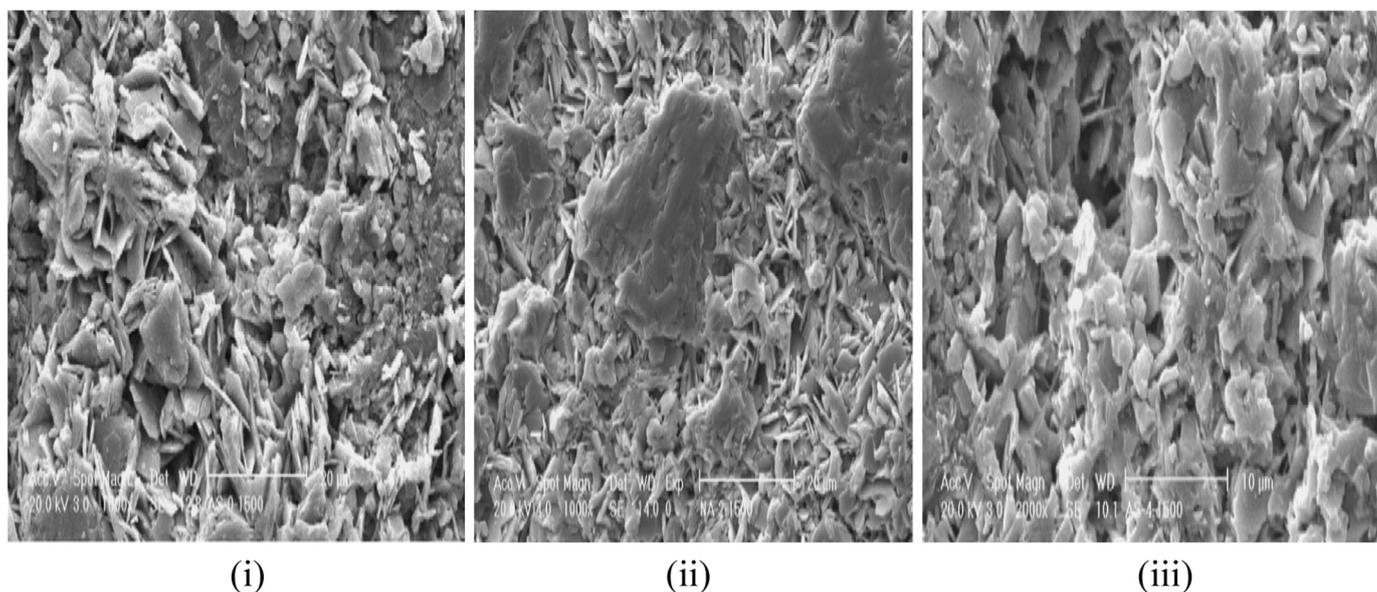


Fig. 4. SEM picture of alumina-spinel castables containing (i) 0 wt%, (ii) 2 wt% and (iii) 4 wt% nano alumina fired at 1500 °C [66].

Table 1
Cement content (wt%) of different types of castables.

Castable	Range of Cement Content (wt%)
Ultra Low Cement Castable	0.5–4
Low Cement Castable	4–8
Middle Cement Castable	8–15

3.1. Hydratable alumina (HA)

Flash calcination of gibbsite [Al (OH)₃] results in the formation of HA, which in contact with water rehydrates to form pseudo-boehmite and bayerite. The green mechanical strength of the structure is caused by the formation of these rehydrated products [88,89]. The mechanical strength is further improved when mullite is formed by the combination of micro silica in refractory castable and HA [90]. Note that terms like micro or colloidal are often used interchangeable with the term ‘nano particle’ by refractory users. HA is a nano material and has a high specific surface area. Hence the castable require a higher water content and longer mixing time compared with a CAC-based castable [91]. During the water dry-out, HA-containing castables can cause steam explosions as they lead to the formation of less permeable structures compared to CAC-based ones [75].

3.2. Colloidal suspension (alumina and silica)

Sol-gel based nanotechnology without CAC is being used by the researcher to produce refractory castables. In these cases, colloidal binders such as alumina (1–4 wt%) or silica (15–50 wt%) are mixed with a precursor powder such as fused alumina, calcined alumina, etc. The setting agents used for these processes are oxide, hydroxide, chloride and sulfate compounds of magnesium and calcium [2,17,18,92–95]. Due to the formation of stable hydrates by CAC and HA (hydraulic binders) based castables at an initial curing temperature (~ 110 °C); mechanical strength of these castable at this temperature is found to be higher than those of castables having colloidal binder. However as the firing temperature increases, hydraulic binders (CAC and HA) undergo faster decomposition, and consequently, the mechanical strength of these binder containing refractories is lower. Conversely the mechanical strength of colloidal binder containing castables increases due to higher sinterability of colloidal binders as the

temperature increases. To study the effect of colloidal binders (alumina or silica) on the tensile strength of refractory castables, Braulio et al. measured the splitting tensile strength of these castables at different firing temperatures [18]. Measurement of splitting tensile strength (or flexural strength) is one of the traditional methods used to determine the tensile strength and is a test that can be conducted by following procedure IS 5816:1999 [96]. The plot of splitting tensile strength with firing temperature (Fig. 5) indicated that as the firing temperature increased from 600 to 1000 °C, the strength of colloidal silica containing castables increases by almost 5 MPa due to the formation of mullite below 1000 °C. But the mechanical strength of CAC and colloidal alumina containing castables is almost the same within this temperature range. Above 1100 °C, CAC present in castables as a binder formed CA₂ and CA₆. This leads to volume expansions of 13.6% and 3.01% in CA₂ and CA₆ formation respectively, causing cracking during use of the castable [97,98]. But due to the absence of CA₂ or CA₆ phases, volume expansion is not possible in castables using a colloidal binder. The high specific surface areas of colloidal binders also enhance the sinterability of castables [69,95]. Jiquan et al. reported that nano sized silica can fill the packing gaps between particles by becoming adsorbed on the surface of α-alumina in alumina rich systems. During densification, silica and alumina form mullite. The process of mullitization improves the microstructure [99].

The addition of colloidal binders in castables has a positive impact on strength, but there are some disadvantages as well. Due to its high specific surface area, nano particles are highly reactive and undergo

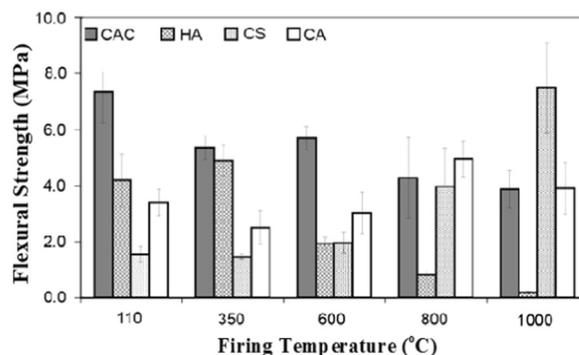


Fig. 5. Flexural strength as a function of firing temperature for CAC, HA, CS and CA [18].

agglomeration during mixing, leading to poor dispersion of the particles in the matrix. Again high nano content in cast materials causes segregation. In refractory castables, the average particles size of silica in silica sols should be higher than 14 nm as smaller size makes these particles highly reactive [100]. Silica contents in colloidal silica used as a binder ranges from 15 to 50 wt%. Higher silica content in the final castable can develop cracks because of induced shrinkage during drying, reducing its chances of being used in steel production [18,101]. In concentrated aqueous suspensions, nanoparticles are stabilized through adsorption and from layer formation. The thickness of the layer is important for the stabilization of suspensions. A thin layer of nano particles can lead to agglomeration, whereas the formation of thick layers results in volume expansion. Both situations reduce the concentration of nano particles in the suspension.

Experiments have been carried out to prepare aqueous solution with high concentrations of nano particles in the suspension. To increase the concentration of nanoparticles in fluid suspensions, dispersants can be used. Short chain dispersants can develop a thick adlayer around the particle causing its stabilization. It has been observed that for the preparation of fluid suspensions of alumina nano particles (up to 45 vol %, particle size ~ 65 nm), adlayer thickness should be in the range between 3 and 4 nm [102,103]. Studart et al. synthesized a dispersant using gallic acid and PEG-Me by employing an esterification reaction using the product to prevent agglomeration of nano particles. To obtain Gallol-PEG molecules, PEG-Me and gallic acid were mixed by maintaining a mass ratio of 10:1, with the esterification reaction conducted at 130 °C for 5 h. Oleum (fuming sulfuric acid) was added (4 wt% based on gallic acid) to gallic acid for its protonation and, consequently, to accelerate the etherification process. For water extraction during esterification, at first the reaction flask was flushed with nitrogen gas, then kept under vacuum (50 mbar). After completion of the reaction, a mixture of Gallol-PEG ester and PEG-Me (1:9 wt% ratio) was obtained. PEG-Me didn't show any dispersing effect on synthesized nanoparticles. Using this ester as dispersant, fluid suspensions (viscosity < 1 Pa s at 100 s⁻¹) with more than 40 vol% of alumina (particle size 65 nm) were obtained, compared with 30 vol% using a conventional dispersing agent [104].

During the use of colloidal silica or colloidal alumina as a binder, the problem is to find setting agents for those castables. Experiments have been performed using CAC as the setting agent for colloidal silica [105–107]. In the presence of CAC with colloidal silica, the overall net repulsion effect is reduced due to the release of Ca²⁺ and Al³⁺ ions during cement dissolution. Examples of other setting agents of colloidal silica include colloidal alumina [108,109], phosphates [110], etc. An increase in ionic strength proportional to the charge and concentration of the ions present in the solution can also be an alternative. Salts of Fe (III) or Al (III) can be added to increase the ionic strength of the solution.

Nouri-Khezrabad et al. used the combination of alumina, CS and CAC or HA as components in refractory castables [111]. The amount of colloidal silica (50 wt% of silica present in the sol) used in the composition as binder was 8 wt%. The amounts of HA and CAC were 2 wt% and 0.5 wt% respectively, when these gelling agents were used separately. A mixture of HA and CAC (1.5 wt% of HA and 0.5 wt% of CAC) was also used as a gelling agent. The water content of the batches was fixed at 4.5 wt%. To provide workability for the castable, citric acid was used as a setting retarder. By using a combination of CS, HA and CAC; the mechanical strength was improved by almost 5 MPa after curing at 50 °C.

3.3. Silica fume

Silica fume (micro silica) is found to be effective as an additive in the formation of nanostructures during cement hydration. During interactions between hydrating CAC and silica fume, a semi-amorphous submicro crystalline phase of CASH is developed through a sequence of

reactions. Fumed silica (5 wt%, average particle size was about 150 nm) are used to manufacture LCC, MCC and ULCC. These castables are found to have significantly higher thermal, physical and mechanical properties when compared with conventional refractory castables [112]. HMOR values of LCC and ULCC are found to be 12.4 and 13.3 MPa respectively at 1000 °C, whereas, HMOR value of NCC castables are less than 10 MPa at the same temperature, indicating almost a 30–40% increase in HMOR values as the amount of cement is reduced [14,81].

3.4. Other cement free binders

In addition to the above mentioned binders, there are examples of using other bonding agents. In order to study the effect of binder on physical and chemical properties, Mukhopadhyay et al. used mullite and spinel sols as bonding agents to manufacture high alumina based ULCC castables. Tabular and fused alumina was used as refractory aggregates. Alumina (boehmite) sol (72 wt%), silica fumes (5.5 wt%) and MgCl₂·6H₂O (13 wt%) were mixed to prepare mullite (M) and mag-al spinel (S) colloidal suspensions. The percentage of retained strength of M and S type samples was found to be 80 and 95 respectively. The porosity of the spinel containing castables was higher than that of mullite (M) containing castables. Spinel (S) containing castables were found to improve the spalling resistance by preventing the extension of cracks. The cold modulus of rupture values of M and S type samples were found to be 20 and 4 MPa. Hence mullite bonded castables can withstand greater breaking load than spinel bonded ones [113]. Singh et al. [114] used nano scaled mullite sol synthesized by sol-gel processing as a binder in a high alumina castable system. It was observed that the cement free binder (mullite) enhanced the strength, thermal shock resistance and corrosion resistance. Because of its refractoriness, hardness and corrosion resistance; alumina is also used in the refractory industry, including as coarse aggregates and fine matrix products. MgO powder has been found to be an effective setting agent, and citric acid has been effectively used as a dispersant in alumina suspensions and castables [115–119]. Salomao and Pandolfelli [120] reported that citric acid was used to prevent hydration of MgO. During mixing of water with MgO, MgOH⁺ species that formed on the MgO particles were absorbed by the citrate ions, forming a low solubility magnesium citrate protective coating which inhibits further magnesia hydration.

4. Nano scaled additives

To reduce energy consumption, improve the densification process at lower temperatures (600–1000 °C) and in the development of materials which can be applied to hot surface, additives have been used during manufacture of refractory castables [14–16,121–124]. The additives may act as a dispersant for fine particles, retarders/accelerators to control hydration of cement particles, wetting agents to improve wetting ability of some raw materials, foaming agents to introduce air bubbles into the castables, or as setting/coagulating agents to induce stiffening reactions, etc. Powdered materials as additives are not only easy to handle, but can also be directly incorporated into the dry mix of a castable. During reaction with the raw materials of a refractory castable, additives form a transient liquid, which favor faster diffusion and interaction with other materials present in the system. The transformation of the transient liquid phase to a rigid and strong solid structure depends on the particle size of the raw materials, how much of an additive is placed to a mix, the heating rate and the sintering temperature. A number of investigations were carried out to select the type and amount of additive required to enhance the thermo-mechanical properties of refractories at the desired working conditions [14–16,121,122]. To design advanced refractories for the petrochemical sector, the addition of boron based compounds to alumina castable compositions was found to be effective as boron based materials form a liquid phase at low temperatures. For example, the melting point of

B_2O_3 is 470 °C. If B_2O_3 is present in a refractory composition, its low melting temperature and the liquid phase formed will favor material transport by diffusion, facilitating interactions with other components of the system and strengthening the interfacial bond between platelet and other grains [125]. Boron based compounds such as sodium borosilicate; magnesium borate, etc. are also found to be potential sintering aids [16,121,123,126].

Otroj et al. used nano sized alumina (0–4 wt%) as an additive in alumina-spinel castables to study the effect of the material on the self flow value (SFV), working time, cold crushing strength and the microstructure of the castables. The SFV was found to decrease with an increase in concentration of nano-alumina particles in the castables. The high surface area of nano particles increased the attraction between the particles, leading to the formation of flocs in which free water molecules were trapped. As a result, both the flow and working time of the castables were found to decrease. Castables having up to 1.5 wt% of nano alumina particles in the composition were found to have good working time and installation properties. The cold crushing strength, erosion resistance and durability (life time) of the castables were found to increase with increasing concentration (> 0.5 wt%) of alumina nano particles [19]. With an increase in sintering temperature, nano particles started to occupy the voids between the coarser particles, leading to a decrease in surface energy and the formation of a close packed microstructure [19,66]. The SFV of castables was also found to decrease in the presence of nano scaled titania particles (anatase) [21]. The SFV of refractory castables is generally in the range of 80–110%. It has been observed that the SFV of castable can be reduced to 80% or less by the addition of nano titania particles (1 wt% or more). As a result, these castables can function as a ramming mix. Castables with 0.5 wt% nano titania particles in the composition can be installed, but the working time of the castables is reduced with increasing concentration of nano particles in the castables. X-ray diffraction patterns (Fig. 6) of the castables fired at 1250 °C showed the formation hibonite ($CaO\cdot 6Al_2O_3$), indicating that nano titania acts as a nucleating agent for hibonite and improves the mechanical strength of the castables. The addition of higher amounts of nano titania (> 0.5 wt%) can lead to the formation of a perovskite phase in the crystal. As a result, the bond between the particles becomes weaker, and therefore, the mechanical strength of castables is reduced [21].

5. Advantages of using nano-scaled materials

A comprehensive study on various parameters of applications of micro and nano scaled precursor, binder, sintering additive, etc., in the field of research on refractory castables has been conducted, with some

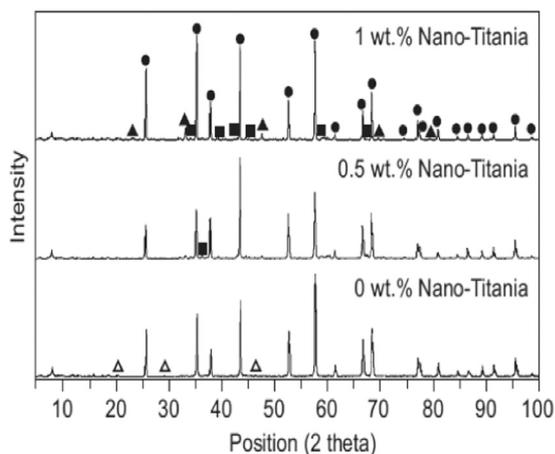


Fig. 6. XRD results of high alumina low cement refractory castable containing different amounts of nano-titania particles after firing at 1250 °C [21] (■-hibonite, ▲-Perovskite).

research carried out by using nano scaled materials listed in Table 2. It has been noted that the addition of nano particles in refractory compositions (both brick and castable) can improve their microstructure, green mechanical strength, high temperature properties, rheological performance, electrical conductivity, etc., if problems like agglomeration, segregation, etc., caused by nano particles can be avoided [60,127–129]. Ismael et al. studied the effect of CS on the mixing behavior of castable compositions compared with those containing CAC or HA as a binder [17]. At first, dry mixing of the powders was carried out to obtain a homogenous mixture, then 75 wt% of the total water was added over a short period of time (60 s). Within the next two minutes, the remaining water was added to the mixture. In the case of CS containing castable compositions, shorter mixing times were required during water additions. This is mainly due to the high viscosity of CS containing mixes (about 10 mPa.s) compared to those with only water additions. CS doesn't participate in any chemical change during water additions as observed in CAC or HA compositions. As CS impacts a higher viscosity, particles in CS based compositions remain apart and accelerate the mixing process. Badiie and Otroj studied the effect of nano silica content on different properties and the microstructure of high-alumina self-flowing non-cement castables [130]. Silica content in nano silica sol was ~ 40 wt%, with average grain size of 3 nm. Nano silica sol was added in the castable compositions in different volume to weight percentage (8–13 cc per 100 g batch), where it was observed that the working time of tabular alumina self-flow castable increased with an increase in the silica sol content due to the dispersing effect of silica. A gel-bonded high alumina castable with reasonable strength and well dispersed particles in the microstructure was obtained in samples having nano silica sol in the range of 10–11 wt% in the composition. Parr and Wohrmeyer compared the flow rate of CS bonded castable with hydraulic bonded HA and CAC (LCC and ULCC) based castables [101]. It has been observed that the largest decrease in flow rate took place in the case of reactive alumina containing LLC, whereas CS system has stable flow. It is thought that the differences in particle packing, water content, amount and particle size of the setting agent were the factors responsible for these differences. The determination of flow values involves complex measurements of viscosity and yield stress [131]. The oscillatory test was useful in evaluating the rheological behavior of colloidal suspensions [132,133]. It was observed that in the presence of both a colloidal binder and a sintering additive, the HMOR value remained high and independent of the testing temperature (800–1400 °C). The nano scale castables had high erosion resistance and were less susceptible to temperature changes. Hence these castable are widely used in FCC of the petrochemical industry and in alumina calciners [14].

In order to study the chemical and microstructural changes in castables during thermal treatment, the hot elastic modulus strength needs to be determined [57]. Braulio et al. [14] reported that when colloidal binders were used in castables, no reduction in elastic modulus values were observed up to 1000 °C due to the formation of a transient liquid phase. Again the final elastic modulus values of colloidal binders containing castable were very high (~170 GPa) compared with CAC based compositions (~140 GPa). In castable compositions having a colloidal binder but no additive, HMOR strength increases up to 1000 °C, but start to decrease thereafter. Castables having a colloidal binder and a sintering additive in the composition were found to have high HMOR strength irrespective of the test temperature. In the case of colloidal binders such as silica (15–50 wt%) and alumina (1–4 wt%), gel formed from the sol surrounds the refractory aggregates, which on sintering, develop strong bonding between the colloidal particles and refractory aggregates. As a result, the high temperature strength of refractory materials was higher than conventional binders (high alumina refractory cement), which produced low-melting phases and impurities.

Due to their high specific surface area, nano-scaled particles are highly reactive. To reduce the sintering temperature and self

Table 2
Examples of refractory castables compositions using nano-scaled materials.

Sl No	Castable Composition	Raw Materials	Binder	Additive	Gelling agent	Dispersant	Reference no
1	Calcined alumina + Fused alumina	CS (7.5 wt% of 40 wt% SiO ₂ solution)	CAC (6 wt%)	Citric acid	Sintered MgO (0.6 wt% of CS)	-	[17]
2	Tabular alumina (60 wt%) + Spinel (23 wt%) + Reactive alumina (11 wt%)	CAC (6 wt%)	CAC (6 wt%)	Nano alumina [particle size 43 nm, range 0–4 wt%]	-	Deflocculant (0.1 wt%)	[19,66]
3	Tabular alumina (80 wt%) + Reactive alumina (14 wt%)	CAC (6 wt%)	CAC (6 wt%)	nano titania [anatase form, particle size 21 nm, range 0–1 wt%]	-	Deflocculant (0.1 wt%)	[21]
4	Bauxite (77 wt%) + Reactive alumina (13 wt%) + micro silica (5 wt%)	CAC (5 wt%)	CAC (5 wt%)	nano alumina [particle size 20–50 nm, range 0–3 wt%]	-	Sodium hexa meta phosphate (0.2 wt%)	[22]
5	Black SiC grains (83 wt%) + Si powder (9 wt%) + SiO ₂ fumes (range 5.2–7.1 wt%)	Silica sol (3–9 wt%) [Nano sized silica (particle size 100 nm) in silica sol range 0.9–2.8 wt%]	CAC(3 wt%) + HA (1 wt%) + Calcined alumina(7 wt%) + microsilica (5 wt%) + NP (0.01, 0.1, 1, 3 and 5 wt% of ZrO ₂ & YSZ)	-	-	-	[23]
6	Tabular alumina (84 wt%)	Mixture of fumed silica & CAC (6 wt%) + α-Al ₂ O ₃ powder (5 wt %)	-	Nano sized Ni (0–0.8 wt%)	-	Sodium tripolyphosphate (TPP) (0.2 wt%)	[24]
7	Alumina aggregate (57 wt%) + alumina powder (10–10.8 wt%) + SiC (16 wt%) + Ball pitch (3 wt%)	Colloidal Silica (particle size 20–100 nm)	-	-	HA (2 wt%) or CAC (0.5 wt%) or HA + CAC (1.5 wt% + 0.5 wt%)	-	[32]
8	Reactive alumina + tabular alumina	Mullite precursor sol (particle size 10–100 nm) synthesized by using aluminum nitrate nonahydrate, silica sol and ammonia solution after maintaining pH	-	-	-	-	[111]
9	Tabular alumina + fused alumina + alumina fines	Colloidal Silica (7 wt%)	-	-	-	-	[114]
10	Tabular alumina (86 wt%) + Reactive alumina (9–12.1 wt%) + silica fume (1.9 wt%) + alumina powder (1.9 wt%)	Colloidal Silica (7 wt%)	B ₂ O ₃ (1.2 wt%)	-	MgO (0.01 wt%)	-	[123]
11	Tabular alumina (82 wt%) + reactive alumina (2 wt%)	Colloidal Silica (7.5–8 wt%, particle size 20–100 nm)	-	Citric acid (0.1 wt%) + gallic acid (0.1 wt%)	-	-	[128]
12	Tabular alumina (76.4 wt%) + reactive alumina (20 wt%) + micro silica (3.6 wt%)	nano silica sol (10–11 wt%, particle size 3 nm)	-	-	-	-	[130]

agglomeration problems during refractory making by using such raw materials, colloidal binders with high solid concentrations are used. Sample volume has been found to expand during in situ formation of the spinel (MgAl_2O_4) in low-cement alumina-magnesia castable [57,68]. It was observed that the addition of NAP, HA or CA with high specific areas resulted in low expansion. Colloidal alumina (~3 wt%) was found to be the most effective in lowering expansion, whereas, NAP was least effective due to the agglomeration of nano particles. Again colloidal alumina improved the slag corrosion resistance of alumina-spinel castable to a much greater extent compared to CAC or HA bonded castable [57]. This was due to the presence of a greater quantity of pores, followed by lower physical infiltration in colloidal alumina containing castable compared to CAC or HA ones.

6. Conclusions

The addition of nano scaled materials in castable compositions generally creates a positive impact in the process of making castable refractories. Nano powders occupy the voids between castable aggregates, promote coarsing of particles during sintering, and consequently, reduce the sintering temperature. Nano particles can improve oxidation, corrosion, hydration and thermal shock resistance of the castable refractories by enhancing the particle packing of the system.

Nano sized materials can be added to castable compositions as a raw material, binder, additive, etc. Examples of oxide nano particles used as raw materials to manufacture castable refractories include TiO_2 , Al_2O_3 , SiO_2 , ZrO_2 , etc. The addition of nano sized Ni or microsilicon in the refractory matrix can improve the anti-oxidation performance of Al_2O_3 -SiC-C and Al_2O_3 -SiC- SiO_2 -C castables. Poor water-wettability of graphite is considered to be a major problem for the commercialization of carbon containing refractory castables. To overcome it, efforts have been made to coat the graphite surface with nano sized carbides (SiC and TiC), oxides (Al_2O_3 and TiO_2), etc before using it in a castable. MgAl_2O_4 spinels are commonly used as raw materials to manufacture spinel containing castables, with the addition of nano sized alumina in the compositions enhancing the growth of these castables. Nano scaled binding agents used in castable refractory system include HA, CA, CS, micro silica, etc. HA based castables require higher water contents and longer mixing time when compared to CAC-based castables. The mechanical strength of colloidal binder containing castables (CA and CS) increases as the sintering temperature increases. Colloidal silica content needs to be maintained properly (15–50 wt%) in order to avoid cracking in the castables. When manufacturing LCC, MCC and ULCC, silica fumes have been used as binders. Nano scaled mullite sol as a binder has been found to be effective in enhancing the strength, thermal shock resistance and corrosion resistance of the castables.

Nano-scale additives can be used in castable compositions as dispersant, retarders/accelerators, wetting agents, foaming agents, setting or coagulating agents, etc, to reduce energy consumption, improve the densification process and in the development of materials which can be applied to the hot surface of the refractory castables. Examples of nano scaled additives used in castable composition include nano sized alumina, titania, etc. These additives act as a nucleating agent for hibonite, improving the mechanical strength of the castables.

7. Future challenges

The addition of nano scaled materials in refractory compositions has certain disadvantages. Nano particles may undergo agglomeration depending upon the types of materials being mixed. Again, the quantity of nano materials impacts final product properties. Segregation or shrinkage can also occur during casting. It has been observed that the addition of a colloidal suspension containing nano particles can reduce the rate of agglomeration and improve the rate of drying, sinterability, volumetric stability, mechanical strength at intermediate temperatures, thermo mechanical properties at high temperatures, etc. But there are

certain drawbacks; which include long setting times, lower values of as-cast green mechanical strength compared with CAC based castable, etc. Again in spinel-containing refractory castable, materials undergo expansion during the sintering.

In order to address above problems, the following suggestions should be considered as future area of research-

1. To reduce the tendency of agglomeration, properly designed dispersing agents can be added to the refractory formulation. In the fluid suspension, stability of nano particles can be enhanced by adding short chain dispersants. Such dispersants have the ability to develop a thick adlayer (~3–4 nm range) around the nano particle. Esterification reaction between gallic acid and PEG-Me can produce short chain dispersant which can be used to prevent agglomeration of nano particles.
2. To improve the setting time and green strength without negatively impacting the drying time in silica sol based castables, compounds having a low hydration resistance, such as dolomite, can be used as gelling agents.
3. To speed up the setting time, binders with silicate structure, such as alkali-activated aluminosilicate or geopolymer, can be used to reinforce in the gel.
4. The instances where both colloidal silica and colloidal alumina are used as binders, the problem is to determine setting agents for the castable. Investigations indicated that increases in the value of ionic strength can be an alternative. An increase in ionic strength can reduce particle-particle repulsions, promote particle packing at the interface, and lower the chances of formation of nanoparticle aggregates or flocs. Ionic strength is proportional with the charge and concentration of the ions. Salts of iron (III) and aluminum (III) can be used to increase the ionic strength and to prevent agglomeration of nano particles.

In order to overcome these drawbacks, additional research should be conducted by using novel additives so that the end result can provide an outstanding technological opportunity for designing nano engineered castables by considering the customer requirements and industrial conditions.

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