Microstructural and mechanical investigation of high alumina refractory castables containing nano-titania

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ABSTRACT

In this study, mechanical and structural properties of two high alumina refractory castables, i.e. without nano-titania and with 0.4 wt% TiO2, are investigated. Bulk density, apparent porosity, cold compressive strength, cold modulus of rupture, permanent linear changes, hot modulus of rupture and shock resistance tests were performed on the samples. The microstructure and phase analyses were conducted by field emission scanning electron microscope equipped with EDX analyzer and X-ray diffraction, respectively. Results showed that hibonite phase formation in refractory is dependent on the temperature which could be decreased by addition of nano-titania, leading to the improvement of refractory strength. On the other hand, the decrease of hot modulus of rupture and shock resistance was observed for the refractory castable containing nano-titania. Also, Ca9Ti8Al12O37 phase was produced after firing at 1000 °C in the presence of nano-titania. Probable mechanisms are proposed for phase and microstructural changes in high alumina refractory castable containing nano-titania.

1. Introduction

Persistent developments in high-temperature industries stiffly rely on the quality of their refractory materials. High alumina refractories are produced as extremely consumed compositions due to outstanding features at high temperatures including stability in oxidizing and reducing atmospheres, considerable slag and metal corrosion resistance, remarkable abrasion resistance and excellent refractoriness [1–8]. Today, everybody is talking about nano-materials, even advertisements for consumer products use the prefix “nano” as a keyword for special features [9]. Nano-materials either refer to materials with nano-scale dimensions or bulk materials containing nano-sized particles. Nano-particles are defined as particles of less than 100 nm in diameter. These materials often demonstrate characteristics which are surprisingly different from the same materials with larger dimensions [10]. Recently, trend on development of alumina refractories is focused on using of nano-materials. Nano-materials improve several properties of refractory products. It was found that colloidal silica (a stable dispersion of nano-sized particles of amorphous SiO2) is suitable as a calcium-free binder for high alumina ultra-low cement refractory castables [11,12]. Yaghoubi et al. [12] reported that the refractory castables containing optimum amount of colloidal silica show a remarkable increase in both fluidity and mechanical strength in dried and sintered states. It was also found that nano-SiO2 particles increase the rate of needle-shaped mullite formation during sintering at 1400 °C. Mukhopadhyay et al. [13] incorporated 8.0 wt% nano-MgAl2O4 in a high alumina-based low cement castables. They showed the improvement of thermal shock and slag resistance behavior of the refractory in corrosive environments. An improvement of the mechanical strength both at room and high temperatures as well as an improvement of the thermal shock resistance of Al2O3–C refractory by using nano-scaled powders of MgAl2O4, alumina sheets and carbon nanotubes has been reported by Roungos and Aneziros [14]. Ultra-low cement castables based on tabular alumina were prepared with nano-ZrO2 [15]. It was found that addition of 3 wt% nano-ZrO2 particles can increase the modulus of rupture values of refractory castables by up to 50%. The influence of additions of nano-TiO2, nano-ZrO2, nano-SiO2 and nano-MgO into alumina based materials for refractory applications has also been investigated [16].

TiO2 nanoparticles are commercially available. This nano-material has been employed in various applications including selective synthesis of organic compounds for solar cells, splitting of water for green-energy hydrogen production, photocatalysts for removal of organic and inorganic pollutants, photo-killing of pathogenic organisms and air purification [17] as well as their very important applications as additive in refractories. It was observed that the addition of 0.5 wt% nano-TiO2...
into silica brick composition leads to highest amount of tridymite phase formation [18]. It was reported that the incorporation of nano-TiO₂ into typical aluminosilicate refractory bricks leads to the improved mechanical characteristics with respect to the typical aluminosilicates, presumably because of a better compaction during the raw materials’ mixing stage [19]. The mullite-bonded alumina-silicon carbide refractories in the presence of nano-TiO₂ up to 1 wt% showed higher mechanical strength because of increasing of mullite phase and higher growth of its needle-like grains [20]. Tontrup used nano-TiO₂ as sintering aid in 99% alumina refractory bricks [21]. By using only 0.4% TiO₂ nanoparticles, the firing temperature was reduced from 1730 °C to 1500 °C and the cold crushing strength (CCS) increased from 8.5 MPa to 13.8 MPa [21]. The self-flow type of high-alumina low-cement refractory castables containing 0–1 wt% nano-TiO₂ particles are also investigated [22]. The results indicated significant effect of nano-TiO₂ on the flowability characteristics, phase composition, physical and mechanical properties of alumina castables. With increase of nano-TiO₂ particles, the flowability and workability of refractory castable tend to decrease. With addition of 0.5 wt% nano-TiO₂ to the refractory castable composition, the mechanical strength of refractory in all firing temperatures tends to increase. Addition of 1 wt% nano-titania can decrease the mechanical strength of refractory castable after firing.

In this research, the effect of nano-titania on mechanical and structural characteristics of high alumina castables is comprehensively investigated. Apparent porosity, bulk density, cold crushing strength, cold and hot modulus of rupture, permanent linear change, thermal shock resistance as well as phase and morphological analyses are performed for high alumina castable without nano-titania (i.e. pure castable) and refractory castable containing 0.4 wt% nano-TiO₂ (i.e. 0.4TiO₂ castable).

2. Experimental

2.1. Raw materials

Source of supply, purity, density and content of raw materials used for the preparation of the refractory castables are listed in Table 1. Tabular alumina was used with four size distributions, i.e. 3–6 mm, 1–3 mm, 0–1 mm and less than 45 µm. The nano-TiO₂ powder with anatase crystal structure as additive has mean particle size and specific surface area of 21 nm and 50 m²/g, respectively. Fig. 1 shows a transmission electron microscopy (TEM) image of the nano-TiO₂ powder provided by the supplier. Dolapix FF 26, which is a poly-carbonic acid, and citric acid were used as dispersing agent and setting controller of refractory castables, respectively. 0.4 wt% nano-TiO₂ was selected, because higher amounts of nano-TiO₂ significantly diminishes the flowability of the refractory castables.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Source</th>
<th>Purity (wt%)</th>
<th>Density (g/cm³)</th>
<th>Content (wt%)</th>
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<tr>
<td>Tabular alumina</td>
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<td>Nano-titania cement</td>
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<td>&gt; 99.5</td>
<td>0 or 0.4</td>
<td></td>
</tr>
<tr>
<td>Dolapix FF 26</td>
<td>Zschimmer &amp; Schwarz, Germany</td>
<td>&gt; 99</td>
<td>0.13 or 0.2</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>C₆H₈O₇, Panreac, Spain</td>
<td>Pure</td>
<td>1.66</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1

Raw materials used for the preparation of high alumina castable.

2.2. Sample preparation

The particle size distribution of the refractory castables was adjusted to a theoretical continuous curve based on the Dinger and Funk model [23] with distribution modulus equal to 0.28, which was suitable for vibration castable [24].

Raw materials were weighed (each batch 4.5 kg) and dry mixed for 4 min in a Eirich mixer. Then water was added and the wet mixing continued for another 4 min to form the castable. The water content for all refractory castables was 5.3 wt% based on dry weight of raw materials. Samples were vibro-casted into steel molds using a vibrating table at frequency of 60 Hz for 1 min. Samples in the molds were wrapped in plastic sheets and cured for 24 h at room temperature (24–26 °C). The cured samples were demolded and kept at room temperature for another 24 h before drying at 110 °C. Cured samples were then fired in laboratory electrical furnace at 1000, 1350 and 1550 °C with soaking time of 6 h. Two high alumina castables are prepared in this investigation. The first one was without nano-TiO₂ (i.e. pure castable) while the second one contained 0.4 wt% nano-TiO₂ (hereafter called 0.4TiO₂ castable). The 0.13 wt% and 0.20 wt% dispersant was used for pure and 0.4TiO₂ castables, respectively. The amount of dispersant was adjusted relative to the amount of the nanomaterial used in the formulation. Higher amounts of dispersing agent are needed for dispersion of nanoparticles because of their high surface area.

2.3. Characterization methods

Apparent porosity (A.P) and bulk density (B.D) were measured by the Archimedes procedure according to ASTM C20-06(2015) [25].

Cold crushing strength (CCS) of the samples were measured according to the ASTM C133-97 [26] in a compressive tester. Eq. (1) was used to determine the CCS of the refractory castables with size of 70 mm × 70 mm × 70 mm.

\[
CCS = \frac{F_{\text{max}}}{A_0}
\]

where, \(F_{\text{max}}\) is the load at which fracture occurs (kg) and \(A_0\) is the area of the sample (cm²).

Modulus of rupture (MOR) of the refractory castables was measured at two cold and hot states according to DIN EN 993-7 [27]. MOR is the maximum stress that a rectangular test piece (160 mm × 40 mm × 40 mm) can withstand when it is bent in a three-point bending device. The test specimen was kept horizontally in a support having two edges and then load was applied on the sample uniformly. The failure load (\(F_{\text{max}}\)) of the specimen was used for the calculation of MOR according to the following formula:

\[
MOR\left(\frac{kg}{cm^2}\right) = \frac{3}{2} \times \frac{F_{\text{max}}L_s}{b \cdot h^2}
\]

where \(L_s\) is the distance between bearing edges (cm); \(b\) is the width of

![Fig. 1. TEM image of nano-TiO₂ powder provided by the supplier.](image-url)
specimen (cm); h is the thickness of the specimen (cm). Cold modulus of rupture (CMOR) of the specimens was measured using a universal testing machine (SANTAM, Iran) at ambient temperature. Hot modulus of rupture (HMOR) of the samples was evaluated after pre-firing at 1350 and 1550 °C. Final temperature for the measurement of the modulus of rupture was 1350 °C with a heating rate of 5 °C/min. HMOR tests were done in air atmosphere by Netzsch apparatus.

Permanent linear change (PLC) of refractory castables (70 mm × 70 mm × 70 mm) fired at various temperatures was measured according to ASTM C 179-14 standard [28].

The thermal shock resistance of refractory castables was determined using DIN 51068 standard quench tests [29] in which the material is heated and cooled subsequently and the number of heating and cooling cycles that a refractory can withstand prior to failure is taken as its thermal shock resistance. The quantification was done by the number of cycles (up to 30 cycles) to withstand such temperature. Cylindrical specimens (50 mm × 50 mm) were heated at 950 °C for 30 min and then suddenly cooled down to ambient condition by quenching in water for 10 min. In addition, the number of cycles before creation of any crack in the specimen was reported as the spalling resistance.

The phase transformation during firing of refractory castables was determined by X-ray diffraction (XRD). For XRD analysis, the refractory castables were crushed and ground to very fine powders using an agate mortar. The XRD patterns were recorded on a unit (Philips PW1800, Netherlands) using CuKα radiation at 40 kV and 30 mA. The obtained diffraction patterns in the 2 theta range of 10° to 90° were analyzed using X-pert Highscore software.

The microstructure analysis of samples coated with gold was performed using field emission scanning electron microscope (FE-SEM, MIRA3 TESCAN-XMU) equipped with an electron dispersive X-ray spectroscopy (EDX) detector.

3. Results and discussion

3.1. Phase analysis

Fig. 2 shows XRD pattern obtained for pure castable after drying and firing at different temperatures. As shown in Fig. 2a, the main peaks obtained for refractory castable after drying at 110 °C correspond to Al2O3 (JCPDS No. 01-075-1862). Also some peaks with lower intensity including Al(OH)3 (JCPDS No. 01-074-1775) and Ca3Al2O6·(H2O)6 (JCPDS No. 01-071-0735) are also observed which are formed by hydration of CA and CA2 in alumina cement [30]. Because of the low concentration of alumina cement (2 wt%) used in the refractory castable, the amount of hydrated phases are comparatively low, so their peak intensity is very lower than that of alumina.

The main XRD peaks (Fig. 2b) obtained for pure castable after firing at 1000 °C correspond to alumina (JCPDS No. 01-075-1862) together with low-intensity peaks corresponding to Ca3Al2O6 phase (JCPDS No. 00-038-1429). Wang et al. [31] similarly showed that Al(OH)3 and Ca3Al2O6·(H2O)6 phases are formed in alumina castable containing 10 wt% high alumina cement without any microsilica after drying at 110 °C. They also reported that after firing the refractory castable at 1000 °C, Ca3Al2O6·3H2O and CaAl2O4 phases are formed in the structure. They observed that Al(OH)3 and Ca3Al2O6·(H2O)6 phases are dehydrated to Al2O3(OH) and Ca12Al14O33 phases at temperatures between 230 and 300 °C according to reactions (3) and (4), respectively.

\[ \text{Al(OH)}_3 \rightarrow 2\text{Al(OH)}_2 + 2\text{H}_2\text{O} \]  

(3)

\[ 7\text{Ca}_3\text{Al}_2\text{O}_6 \text{.} 6\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{Al}_2\text{O}_6 \text{.} 3\text{H}_2\text{O} + 9\text{CaO} + 42\text{H}_2\text{O} \]  

(4)

At temperatures about 650 °C, Al2O3 forms by reaction (5)

\[ 2\text{Al(OH)} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \]  

(5)

And at temperatures about 1000 °C, CaAl2O4 phase is partially formed by reaction (6). Reaction (6) completes at 1030–1120 °C.
\[ \text{Ca}_2\text{Al}_4\text{O}_{13} + 5\text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_4. \]  

[6]

XRD results also confirm the presence of \( \text{Ca}_3\text{Al}_2\text{O}_6 \) in addition to the main alumina phase. It seems that gibbsite (\( \text{Al(OH)}_3 \)) is removed by reactions (3) and (5), however, removal of structural water from \( \text{Ca}_3\text{Al}_2\text{O}_6\cdot(\text{H}_2\text{O})_6 \) and formation of \( \text{Ca}_3\text{Al}_2\text{O}_6 \) directly take place by reaction (7) instead of reactions (4) and (6). Therefore, \( \text{Ca}_3\text{Al}_2\text{O}_6 \) phase formed instead of \( \text{CaAl}_2\text{O}_4 \) phase that was also reported by Wang et al. [31].

\[ \text{Ca}_3\text{Al}_2\text{O}_6\cdot(\text{H}_2\text{O})_6 \rightarrow \text{Ca}_3\text{Al}_2\text{O}_6 + 6\text{H}_2\text{O} \]  

(7)

XRD pattern for pure castable after firing at 1350 °C is shown in Fig. 2c. The main peak again corresponds to alumina (JCPDS No. 01-010-0173). Peaks with relatively lower intensities are also observed which are related to \( \text{CaAl}_2\text{O}_7 \) (JCPDS No. 01-76-0706) and \( \text{Ca}_5\text{Al}_6\text{O}_{14} \) (JCPDS No. 00-003-0149). These phases may be produced through the following reaction:

\[ 2\text{CaAl}_2\text{O}_7 + 3\text{Al}_2\text{O}_3 \rightarrow \text{Ca}_5\text{Al}_6\text{O}_{14} + \text{CaAl}_2\text{O}_7 \]  

(8)

Wang et al. [31] also demonstrated the formation of \( \text{CaAl}_4\text{O}_7 \) through reaction of calcium aluminate phases, formed at low temperatures, together with fine grain alumina at temperatures in the range of 1120–1340 °C according to the following reaction:

\[ \text{Ca}_3\text{Al}_2\text{O}_7 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_4\text{O}_7 \]  

(9)

As can be seen in Fig. 2d, by increasing the firing temperature to 1550 °C, peaks with relatively high intensity corresponding to hibonite phase (\( \text{CaAl}_{12}\text{O}_{19} \)) (JCPDS No. 00-033-0253) are appeared in addition to main alumina peaks (JCPDS No. 01-010-0173). The hibonite phase forms by the following reactions:

\[ \text{CaAl}_2\text{O}_7 + 4\text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_7 \]  

(10)

\[ 2\text{CaAl}_2\text{O}_7 + 27\text{Al}_2\text{O}_3 \rightarrow 5\text{CaAl}_2\text{O}_7 \]  

(11)

Formation of hibonite phase at temperatures above 1400 °C through reaction (10) was also reported by Wang et al. [31].

XRD pattern for 0.4TiO\(_2\) castable after drying at 110 °C is shown in Fig. 3a which confirms that the main phase in the refractory castable is alumina (JCPDS No. 01-075-1862) with relatively low-intensity peaks corresponding to \( \text{Al(OH)}_3 \) (JCPDS No. 01-085-0611) and \( \text{Ca}_3\text{Al}_2\text{O}_6\cdot(\text{H}_2\text{O})_6 \) (JCPDS No. 01-079-1286). So, from phase point of view, there is no difference between the XRD patterns of 0.4TiO\(_2\) and pure castables. It should be mentioned that TiO\(_2\) peaks are not identifiable in Fig. 3a because of their relatively low intensity.

Fig. 3b shows the XRD pattern obtained for 0.4TiO\(_2\) castable after firing at 1000 °C. It is obvious from the figure that increasing the firing temperature has significantly affected the phase composition of the refractory castable containing nano-titania. Peaks corresponding to \( \text{Ca}_3\text{Ti}_8\text{Al}_{12}\text{O}_{37} \) (JCPDS No. 00-037-1232) are also observed in addition to the main alumina phase (JCPDS No. 01-075-1862).

Gibbs free energies for the formation of ternary and quaternary compositions from binary compounds (CaO, TiO\(_2\) and Al\(_2\)O\(_3\)) are listed in Table 2. Using these thermodynamic data, Jacob and Rajitha [32] depicted ternary phase diagrams of CaO-TiO\(_2\)-Al\(_2\)O\(_3\) system. The isothermal section of the diagram at 927 °C is illustrated in Fig. 4. The diagram (Fig. 4a) is valid in the temperature range of 646–1110 °C. It can be seen from the Fig. 4a that \( \text{Ca}_3\text{Ti}_8\text{Al}_{12}\text{O}_{37} \) is a stable compound in CaO-TiO\(_2\)-Al\(_2\)O\(_3\) system. Table 3 shows reactions and chemical potentials of CaO calculated by Jacob and Rajitha [32]. According to the table, it is evident that the least chemical potential difference corresponds to the formation of \( \text{Ca}_3\text{Ti}_8\text{Al}_{12}\text{O}_{37} \) phase. Consequently, it is possible for reaction (12) to occur at about 1000 °C.

\[ \text{Ca}_2\text{Al}_4\text{O}_{13} + 8\text{TiO}_2 + 5\text{Al}_2\text{O}_3 \rightarrow \text{Ca}_3\text{Ti}_8\text{Al}_{12}\text{O}_{37} \]  

(12)

Fig. 3c shows the XRD pattern obtained for 0.4TiO\(_2\) castable after firing at 1350 °C. By increasing the firing temperature to 1350 °C,
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through which Ca$_3$Ti$_8$Al$_{12}$O$_{37}$ phase transforms to tialite (Al$_2$TiO$_5$) and occurs at 1350 °C in refractory castables containing nano-titania from reaction (12), transforms to Ca$_3$Al$_2$O$_6$ by reaction (14) and then –

hibonite phase (Ca$_3$Ti$_2$O$_{12}$) (JCPDS No. 00-038-0470) is detected besides main alumina phase, while peaks corresponding to Ca$_3$Ti$_6$Al$_2$O$_{37}$ phase are disappeared. The isothermal section of CaO$\text{−}$TiO$_2$-Al$_2$O$_3$ system at 927 °C is shown in Fig. 4b which is valid for temperatures in the range of 1223–1431 °C.

Fig. 4. Isothermal sections of CaO$\text{−}$TiO$_2$-Al$_2$O$_3$ system at 927 °C. The diagram (a) and (b) are valid in the temperature range of 646–1110 °C and 1223–1431 °C, respectively.

It has shown that tialite (Al$_2$TiO$_5$) decomposes to its constituents by reaction (16) during cooling, so its detection is not possible in XRD pattern [33,34].

Ca$_3$Ti$_2$O$_{12}$ $\rightarrow$ Al$_2$O$_3$ + TiO$_2$ (16)

Badiee and Otroj [22] reported the formation of CaTiO$_3$ phase in alumina castable containing 1 wt% nano-titania after firing at 1250 °C, while they couldn’t identify CaTiO$_3$ phase in the refractory castable containing 0.5 wt% nano-titania. They found that by increasing the amount of nano-titania in alumina castable fired at 1250 °C, CaTiO$_3$ phase increases and Ca$_3$Al$_2$O$_6$ phase diminishes. Their results are in agreement with the results presented in the current study. It seems that increasing the amount of nano-titania results in more Ca$_3$Ti$_8$Al$_{12}$O$_{37}$ phase at 1000 °C and consumption of Ca$_3$Al$_2$O$_6$ according to reaction (12). Consequently, consumption of Ca$_3$Al$_2$O$_6$ causes less production of hibonite phase, hence less hibonite phase produces via reactions (14) and (15). On the other hand, by increasing the amount of Ca$_3$Ti$_6$Al$_2$O$_{37}$, the potential of CaTiO$_3$ formation by reaction (13) also increases.

Fig. 3d shows the XRD pattern obtained for 0.4TiO$_2$ castable after firing at 1550 °C. It can be seen that by increasing the firing temperature to 1550 °C, the relative intensity of hibonite to alumina peaks also increases which confirms that the amount of hibonite phase has been increased [35]. A weak peak corresponding to CaTiO$_3$ (JCPDS No. 00-040-0043) is also observed at 2θ = 46.46. It is probable that tialite and hibonite phases are responsible for the formation of more CaTiO$_3$ phase. After firing the alumina castable at 1550 °C, Badiee and Otroj [22] observed that more CaTiO$_3$ and Ca$_3$Al$_2$O$_6$ phases are formed by increasing the amount of nano-titania. It appears from reaction (17) that by increasing the firing temperature, perovskite is produced by the reaction of hibonite with tialite.

Ca$_3$Al$_2$O$_6$ + Al$_2$O$_3$ $\rightarrow$ 3CaAl$_2$O$_6$ (14)

Ca$_3$Al$_2$O$_6$ + 4Al$_2$O$_3$ $\rightarrow$ Ca$_3$Al$_2$O$_9$ (15)

Ca$_3$Al$_2$O$_9$ + TiO$_2$ $\rightarrow$ 3Al$_2$O$_3$ + CaTiO$_3$ (17)

Fig. 2d shows that hibonite phase is produced in pure castable after firing at 1550 °C. However, as shown in Fig. 3c, nano-titania has a significant effect on the phase formation in refractory castables. It causes hibonite phase to be formed at lower temperatures (i.e. 1350 °C). In other words, nano-titania accelerates the formation of hibonite phase. These observations confirm that the formation of hibonite phase depends on the temperature, and nano-titania can decrease this temperature.

Our results are in good agreement with [22,36] which demonstrated that nano-titania acts as mineralizer and decreases the formation temperature of hibonite phase. Two mechanisms are supposed for the
the mineralizing effect of nano-titania. Badiee and Otroj [22] believed that nano-titania acts as preferred sites for hibonite nucleation. However, some researchers suggested that the mineralizing effect of nano-titania arises from the formation of liquid phase [36]. Braulio and Pandolfelli [36] used different additives including magnesium fluoride, titania, zirconia, magnesium borate and borosilicate in alumina-magnesium castables with cement bonding. They found that borosilicate and zirconia had no effect on reduction of hibonite formation temperature while titania showed the most temperature reduction. So, in Al2O3-CaO system, additives which formed liquid phase could reduce hibonite formation temperature. Borosilicate doesn’t lower this temperature, although it forms liquid phase. They showed that borosilicate forms unstable liquid phase, while other additives form stable liquid phase [36].

According to the above discussion, it seems that the theory proposed by Badiee and Otroj [22] may not be true; because zirconia couldn’t decrease the hibonite formation temperature. So, the second theory on the effect of nano-titania on the formation of liquid phase is more relevant.

The hibonite phase formed in the presence of liquid phase should have planar morphology [37–39]. FESEM images presented in Section 3.4 show that the hibonite phase formed in 0.4TiO2 castable at 1350 °C has planar morphology while the hibonite phase formed at 1550 °C in pure castable has both planar and equiaxed morphologies. So, it can be concluded that the presence of trace impurities in pure castable is responsible for the formation of liquid phase at 1550 °C. This liquid tends to selectively wet low energy grain boundaries and forms planar hibonite phase. On the other hand, equiaxed hibonite phase form through nucleation and growth mechanism in grain boundaries which are not completely wetted by the liquid phase.

In refractory castable containing nano-titania, Ca3Ti8Al12O37 phase forms at 1000 °C. It seems that the formation and transformation of Ca3Ti8Al12O37 is the main mechanism for the formation of planar hibonite. Most likely, Ca3Ti8Al12O37 wets the grains. Badiee and Otroj [22] suggested that hibonite forms at 1250 °C in alumina castables containing 0.5 wt% nano-titania which is in accordance with the mechanisms proposed in the present study.

3.2. Apparent porosity and bulk density

The effect of nano-titania on the bulk density and apparent porosity of the refractory castables as a function of firing temperature is shown in Fig. 5a and b, respectively. It can be seen from the figure that the addition of nano-titania increases the porosity, so decreasing the density of the crude castable (before firing). As compounds containing nano-titania have low flowability, bubbles trapped within the structure increase the porosity, so decreasing the density.

It can be seen that, at 1000 °C, the porosity of both pure and 0.4TiO2 castables are increased after firing. The increase of porosity is slightly higher for pure castable in comparison with 0.4TiO2. The density of pure castable is also decreased, while that of 0.4TiO2 has not changed significantly. This can be due to the high-temperature decomposition of hydrated phases which have been formed during the setting of alumina cement. According to the phase analysis, formation of a quaternary compound with the composition of Ca3Ti8Al12O37 (density of 3.88 g/cm3) instead of Ca3Al2O6 (density of 3.03 g/cm3) may be the reason for the slight decrease in density in 0.4TiO2 castable despite the relative increase of the porosity.

Results show that rising of the firing temperature to 1350 °C enhances the densification process, resulting in lower apparent porosity and so, higher bulk density of pure castable. At 1550 °C, the porosity of 0.4TiO2 castable decreases which may be due to the formation of new phase(s) in the sample. The expansion of these phases can compensate for the contraction arises from the densification process. The phase transformations are discussed in detail in Section 3.1. In 0.4TiO2 castable, formation of hibonite with the chemical composition of CaAl12O19 is responsible for the structural expansion [22] which decreases the density. Porosity decreases by continuing the densification process at higher temperatures (i.e. 1550 °C) resulting in higher density for both refractory castables. Here again, the amount of the porosity reduction is higher in 0.4TiO2 castable.

3.3. Permanent linear changes (PLC)

Fig. 6 shows the permanent linear changes (PLC) of pure and 0.4TiO2 castables at three different firing temperatures, i.e. 1000, 1350
and 1550 °C. Both samples show expansion due to the formation of new phases at 1000 °C. It can be seen that the expansion of 0.4TiO₂ sample is less than that of pure castable which is attributed to the nature and type of these new phases. The difference is also noticeable at 1350 °C at which new phases are formed in 0.4TiO₂ castable, causing more expansion than pure castable (see XRD results in Section 3.3). Besides, 0.4TiO₂ castable shows about 0.6% contraction at 1550 °C due to the progress of densification process. On the other hand, pure castable shows positive volume stability despite the decrease of contraction. The result of competition between the contraction (due to densification process) and the expansion (due to the formation of new phases) in pure castable will be positive volume stability.

3.4. Structural examinations

Figs. 7, 8 shows the microstructure of the pure and 0.4TiO₂ castables fired at 1350 °C, respectively. The microstructure of pure castable (Fig. 7a) is relatively uniform; however, two distinct regions can be distinguished in 0.4TiO₂ castable (Fig. 8a). Higher magnification images of region 1 are shown in Fig. 8b while those of region 2 are illustrated in Fig. 8c. As can be seen, region 1 is composed of interconnected grains without grain boundary porosity which implies sintering of grains in 0.4TiO₂ castable, while region 2 mainly consists of interlocked planar particles. The XRD pattern shown in Fig. 3c and the EDX analysis (not shown) demonstrated that these particles are hibonite phase and result in a porous matrix as shown in Fig. 8c.

Fig. 7b shows the higher magnification FESEM image of pure castable microstructure shown in Fig. 7a. In this microstructure, partially connected particles with high intraparticle porosity are observed, implying initial stages of sintering process [40–42]. Comparing Fig. 7b with Fig. 8b reveal that nano-titania not only accelerates the densification process, but also increases the grain growth rate. The grain growth of alumina grains in the presence of TiO₂ usually occurs at final stages of sintering [41,43,44]. So, one can claim according to the porosity distribution that the microstructure shown in Fig. 8b implies the final stage of the sintering process. Titania (TiO₂) is an aliovalent additive and its cationic capacity is different from that of the host. So densification of alumina at lower sintering temperatures in the presence of TiO₂ results from the change of diffusion mechanism as well as the limited dissolution of Ti⁺⁴⁺ cations as a substitute for Al⁺³ cations in alumina lattice. This substitution results in the formation of atomic vacancies in alumina hexagonal structure, providing more paths for bulk diffusion [45]. The structure shown in Fig. 8b demonstrates the acceleration of densification process in the presence of nano-titania.

The microstructure of pure castable fired at 1550 °C is shown in Fig. 9a and b which is composed of weak connected particles with interconnected porosity. Contrary to refractory castables containing nano-titania, there is no evidence of grain growth, implying intermediate stages of sintering process [41]. It is also observed that nucleation of equiaxed hibonite grains has occurred around alumina grains, although some hibonite grains are in the form of planar crystals. Despite the lack of a detectable liquid phase in the structure of the designed compositions at high temperatures, the generation of the elongated hibonite grains might be favored by the effective contact between CaO (formed due to the cement hydrates and presented in raw materials) and fine alumina [46]. It seems that the sintering temperature or time has not been sufficient for densification and removal of porosities. In addition, according to [47], the planar hibonite phase, which is produced in Al₂O₃-CaO system, makes Al₂O₃ matrix porous and inhibits densification.

Consequently, it is possible to increase alumina density by low-temperature sintering in the presence of nano-titania. This phenomenon has also been reported in previous works [45,48–50], however, based on the results obtained in the current study, the enhancement of densification at lower temperatures in the presence of nano-titania is more intense than what had been reported previously. In other words, the structure of 0.4TiO₂ castable fired at 1350 °C (Fig. 8b) is in the final stage of sintering, whereas increasing of firing temperature from 1350 to 1550 °C has not been sufficient for complete sintering of pure castable (Fig. 9a). So, a different sintering mechanism should be involved in refractory castables containing nano-titania.

Three possible driving forces which decrease the free energy of the system are particle surface curvature, external applied pressure and chemical reaction. If the chemical reaction can be used to increase the densification, it can provide the required driving force for sintering [41,51].

Gibbs free energy for the formation of hibonite (CaAl₁₂O₁₉) and calcium di-aluminate (CaAl₆O₁₄) phases can be obtained from Eqs. (18), (19) [52]. Eq. (20) is consistent with reaction (15) and its Gibbs free energy is derived from the difference of Gibbs free energies of reactions (18) and (19):

\[
\text{CaO} + 6\text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_{12}\text{O}_{19} \quad \Delta G^0 = -17430 - 37.2T \quad \text{(18)}
\]

\[
\text{CaO} + 2\text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_6\text{O}_{14} \quad \Delta G^0 = -16400 - 26.8T \quad \text{(19)}
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]
The required free energy for the formation of hibonite at 1350 °C according to reaction (20) is \(15,070 \text{ KJ mol}^{-1}\) which is much higher than the driving force of an applied stress. Formation of \(\text{CaAl}_4\text{O}_7\) and \(\text{CaAl}_{12}\text{O}_{19}\) phases in 0.4TiO_2 castable at 1350 °C involves 13.6 and 3.01 vol% expansion, respectively [53,54]. This expansion exerts pressure on the adjacent regions serve as nucleation sites for the formation of hibonite phase. This pressure acts as an external pressure which is applied in processes such as hot pressing. So, it seems that the pressure developed by the expansion together with the energy developed by reaction (20) provide extra driving force for sintering of alumina particles.

Fig. 9c and d shows FESEM images of two distinct structures in 0.4TiO_2 castable fired at 1550 °C. A complete-sintered structure with some intraparticle porosity is shown in Fig. 9c which can be considered as full sintering of the structures [41] corresponding to Fig. 8b. However, the alumina and hibonite grains (Fig. 9d and e) have become rounded by increasing the sintering temperature from 1350 to 1550 °C. This results in less interlocking of the grains, which finally decreases mechanical strength of the refractory castable. So, the increase of strength due to the decrease of porosity in 0.4TiO_2 castable at 1550 °C is balanced by the decrease of strength due to less interlocking of the grains. Additionally, as shown in Fig. 9f, CaTiO_3 phase deposited in some grain boundaries acts as a sintering aid and causes an integrated structure [55,56].

3.5. Strength of refractory castables

It is well known that strength varies exponentially with porosity and increases with decreasing the porosity [57]. Fig. 10 shows CCS, CMOR and HMOR variations of pure and 0.4TiO_2 castables as a function of firing temperature. The CCS (Fig. 10a) increase in 0.4TiO_2 castable, despite its higher porosity (Fig. 5b), may be attributed to the dispersion of fine nano-titania particles in the matrix of the castable, resulting in higher strength of 0.4TiO_2 sample. Results show that after firing at 1000 °C, the CCS of both refractory castables has been improved despite their higher porosity than their raw counterparts. In pure castable, this can be related to the formation of new phases on sub-micron particles after dehydration of hydrated phases in high-alumina cement, while in 0.4TiO_2 castable, this improvement can be related to the formation of \(\text{Ca}_3\text{Ti}_8\text{Al}_{12}\text{O}_{37}\) phase which bonds to the matrix, hence increases the CCS. The higher strength of 0.4TiO_2 castable in comparison with that of pure castable at this temperature may be associated with its relatively lower porosity. According to the results, nano-titania results in enhancement of CCS in all firing temperatures. Even at 1350 °C, the CCS of 0.4TiO_2 castable increases despite increasing of its apparent porosity. It seems that the strength of the matrix enhances due to the formation of hibonite phase, resulting in improvement of the CCS.

\[
\text{CaAl}_2\text{O}_7 + 4\text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_7 + \Delta G^\circ = -1030 - 10.4T
\]

(20)
Hibonite has a significant effect on mechanical properties of the refractory castable. Although planar particles develop porosity in the structure, their locking to the matrix results in the enhancement of the strength at 1350 °C. It is reported that the formation of elongated grains or secondary phases in the microstructure improves mechanical properties due to the mechanisms known as deviation or bridging of cracks [58]. It is reported that interlocked planar grains act as barriers for crack propagation [38,39,59].

Although the porosity increases, the higher strength of the matrix compensates for the stress concentration caused by this increment.

Fig. 9. FESEM images obtained for refractory castables fired at 1550 °C in different magnifications. (a-b) pure and (c-f) 0.4TiO2 castables.
Significant enhancement of mechanical properties was noticed at 1550 °C which may be arises from the formation and reinforcement of ceramic bonds as well as considerable decrease of porosity after sintering.

Variation of cold modulus of rupture (CMOR) for pure and 0.4TiO₂ castables as a function of firing temperature is illustrated in Fig. 10b. The variation of CMOR is similar to that of CCS except for the sample fired at 1550 °C. So, the same reasons can be considered for variation of CMOR.

In contrast to CCS, the CMOR of 0.4TiO₂ castable after firing at 1550 °C has been decreased in comparison with pure castable. This can be attributed to structural changes. Failure in compressive test stems from the growth and coalescence of defects following by the dissociation and breakdown of the sample. So, contrary to bending strength, compressive strength depends mainly on total defects, but not on the largest and sharpest crack [60]. As a result, pure castable has lower compressive strength than 0.4TiO₂ castable because of its relatively higher porosity. On the other hand, it seems that the microstructure of 0.4TiO₂ castable is more sensitive to the loading condition in bending tests. Further investigations are needed to find out the reasons of such sensitivity.

The HMOR results obtained for pure and 0.4TiO₂ castables fired at 1350 °C and 1550 °C are shown in Fig. 10c. It can be seen that the presence of nano-titania at both firing temperatures leads to improvement of HMOR. However, the HMOR of both refractory castables decreases by increasing the firing temperature.

Hot bending strength of refractory castables at temperatures above 1250 °C has been modeled by Adam-Gibbs theory [61] in which hot bending strength (σ) is proportional to viscosity at high temperatures (Eq. (21)):

\[
\ln \sigma = A + \frac{B}{T \ln(T/\gamma)}
\]

where T is thermomechanical temperature, and A, B and C are constants.

The presence of impurities, particularly in high-alumina refractory castables, leads to the formation of more glassy phase and reduction of viscosity at high temperatures [62]. On the other hand, formation of glassy phase has significant effect on hot bending strength of high-alumina refractory castables [61]. In particular, at temperatures above 1250 °C, hot bending strength obviously decreases due to the viscous flow of liquid phase. So it seems that at high temperatures, liquid phase forms in both refractory castables and remains in the structure as a glassy phase which results in decreasing of measured high-temperature strength of refractory castables. XRD and microstructural observations indicated the presence of CaTiO₃ phase in grain boundaries of 0.4TiO₂ castable which becomes mushy at 1350 °C and can be responsible for the strength reduction [63].

Fine grain microsilica in alumina castables causes formation of low melting phases (such as CAS₂ and C₂AS) and considerable reduction of high-temperature strength [64]. In pure castable, however, the high-temperature strength reduces although no additive (particularly microsilica) is used in raw materials. There is also no evidence of low melting phases in this sample. So, it seems that little amounts of impurities in raw materials lead to the formation of liquid phase at 1550 °C which finally transforms to glassy phase. There is always little amount of silica as impurity in alumina raw material which, along with other impurities, can produce liquid phases at high temperatures [63]. It has been observed that the liquid tends to selectively wet low energy boundaries, while leaving other boundaries unwetted [63].

### 3.6. Thermal shock resistance

Results obtained for thermal shock resistance of pure and 0.4TiO₂ castables fired at 1350 °C and 1550 °C are listed in Table 4. It can be seen from the table that both refractory castables fired at 1350 °C are not failed after 30 cycles. Pure castable fired at 1550 °C also withstands 30 cycles while 0.4TiO₂ castable fired at 1550 °C has broken after 24 cycles. In addition, both 0.4TiO₂ castables (fired at 1350 and 1550 °C) have cracked after 5 cycles, while the cracking in both pure castables occurs after 9 cycles. By increasing the firing temperature of 0.4TiO₂ castables from 1350 to 1550 °C, the thermal shock resistance of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Firing temperature (°C)</th>
<th>1350</th>
<th>1550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>30 24</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>0.4TiO₂</td>
<td>5 9</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>

| Thermal shock resistance | 30 24 | 30 30 |
| Spalling resistance     | 5     | 9     |

a Number of cycles prior to failure.
b Number of cycles before any cracking.
samples has decreased which may be due to the presence of CaTiO₃ phase in some grain boundaries which results in the failure of the samples after 24 cycles.

4. Conclusions

This work aimed at studying the effect of nano-titania addition to high alumina castables on the microstructural characteristics and mechanical properties. The obtained results can be summarized as follows:

1) Nano-titania addition decreased the fluidity of the crude castable and consequently, decreased the density due to enhanced porosity.

2) Hibonite phase was formed at lower temperatures due to the mineralizing effect of nano-titania. The formation and transformation of Ca₃Ti₈Al₁₂O₃₇ after firing at 1500 °C is the main mechanism for the development of planar hibonite in the nano-titania containing refractory castable.

3) Hibonite formation at lower temperatures exerts extra pressure on alumina during sintering which finally enhances the mechanical strength of refractory castable containing nano-titania.

4) The cold compressive strength of the refractory castable containing nano-titania fired at 1550 °C was increased while its cold bending strength was decreased.

5) The hot bending strength and thermal shock resistance of the refractory castable containing nano-titania were decreased due to the formation of CaTiO₃ phase deposited in alumina grain boundaries.

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