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Ceramics International 37 (2011) 1003–1009
CERAMICS INTERNATIONAL
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Microstructure and phase evolution of alumina–spinel self-flowing refractory castables containing nano-alumina particles

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Received 23 July 2010; received in revised form 29 September 2010; accepted 6 November 2010
Available online 2 December 2010

Abstract

The microstructure and phase composition of alumina–spinel self-flowing refractory castables added with nano-alumina particles at different temperatures are investigated. The physical and mechanical properties of these refractory castables are studied. The results show that the addition of nano-alumina has a great effect on the physical and mechanical properties of these refractory castables. With the increase of nano-alumina content in the castable composition, the mechanical strength is considerably increased at various temperatures. It is shown that nano-alumina particles can affect formed phases after firing. The platy crystals of CA_6 are detected inside the grain boundaries of tabular alumina and spinel grains in samples fired at 1500 °C. CA_6 phase can be formed at lower temperatures (1300 °C) with the addition of nano-alumina particles. As a result of using nanometer-sized alumina particles with high surface area, the solid phase sintering of the nano-sized particles and CA_6 formation can occur at lower temperatures.

Keywords: B. Microstructure; C. Mechanical properties; D. Al_2O_3; D. Spinel; E. Refractories

1. Introduction

The increasing application and demand for refractory castables as an alternative to conventional brick encourages researchers and producers to investigate their special characteristics. Physical, chemical and mechanical properties of refractory castables at high temperatures, as well as their processing, are the focus of such investigations [1].

In steel industry, there is a trend to increase the use of high-alumina refractory castables containing spinel $MgAl_2O_4$, because of their higher refractoriness and of their better corrosion resistance than Al_2O_3 castables [2]. Both Al_2O_3–spinel and Al_2O_3–MgO castables are widely used as steel ladle linings below the slag line because of increasing labor costs and the severe secondary steelmaking environment in the ladle. In Al_2O_3–spinel castables, spinel are added to the mixture as a grain phase, while in Al_2O_3–MgO castables MgO reacts with Al_2O_3 to form in situ spinel during service. Al_2O_3–MgO castables are replacing Al_2O_3–spinel castables because of their superior slag resistant properties and lower costs. However, Al_2O_3–spinel castables are still commonly used in the non-impact pad area of the steel ladle bottom [3–8]. The performance of Al_2O_3–MgO and Al_2O_3–spinel castables are investigated with profound interest in the past few years. The important criteria leading to improvements of these refractory castables are resistance towards high basic corrosive slags, molten metal and slag penetration, spalling and hot strength [1,8–13]. Generally, refractory castables can be considered as composites, with the bonding phase being the matrix and aggregates being reinforcement particles [2,14]. Successful performance of refractory castables containing fine (1–100 μm) and superfine (<1 μm) powders during the lining application and high-temperature services is attributed to the ability of these powders to fill the voids between castable aggregates (>100 μm) [15]. However, the most extensively used fine and superfine particles in Al_2O_3–spinel refractory castables are calcined and reactive alumina [8,16]. Refractory researchers recently started to engineer the quality of advanced castables by laying down nano-sized materials in the composition. Very high surface energy and rapid diffusion paths usually make the nano-particles far more reactive in the refractories, which frequently encounter the aggressive environment, particularly in the steel industries.

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doi:10.1016/j.ceramint.2010.11.013

As such, the strength, thermal shock and corrosion resistance of a refractory castable is improved if one can favorably tailor the interaction of nano-phases with the other particles [1,17,18]. Hence, in this work, the effect of addition of nano-alumina particles on the microstructure and phase composition of alumina–spinel self-flowing refractory castables is investigated. For this reason, reactive alumina is substituted by nano-alumina powder in 0–4 wt.% range in the castable composition. Then, castable compositions were fired at various temperatures and physical and mechanical properties of these refractory castables are investigated.

2. Materials and methods

2.1. Raw materials and composition

The composition used for alumina–spinel self-flowing refractory castable is listed in Table 1. The chemical composition of raw materials used for this study is shown in Table 2. The nano-alumina powder ($d_{50} = 43$ nm) is the product of Inframat Advanced Materials Co. (USA) which, its chemical composition and other physical parameters are shown in Table 3.

For the study of nano-alumina addition on the microstructure, phase composition and other properties of these refractory castables, reactive alumina is substituted by nano-alumina powder in 0–4 wt .% range. The particle size distribution was calculated from the Andreasen's equation as:

$$\mathrm{CPFT} = 100\left(\frac{d}{D}\right)^{q} \tag{1}$$

where CPFT, d, D, and q indicate the cumulative percentage finer than, particle size, the largest particle size (5000 μm) and the distribution modulus, respectively. In order to achieve self-flow, q values are in the range 0.21–0.26. For the present study, q is chosen to be 0.24 [8].

Table 1
Raw materials and composition of the alumina–spinel refractory castable.

Raw materials		Source (type)	wt.%
Tabular alumina	2–5 mm	Alcoa Chemicals, T-60	60
	1–2 mm		
	0.5–1 mm		
	0–0.5 mm		
	≤45 pin		
Spinel	0.5–1 mm	White Circle, Spinwhite78	23
	0–0.5 mm		
Reactive alumina	$d_{50} = 1.90$ μm	Alcoa Chemicals, CTC-20	11
Calcium aluminate cement	$d_{50} = 3.03$ μm	Lafarge, secar-71	6
Dispersant		BASF, castament FS 10	0.1

Table 2
Chemical composition of raw materials.

Oxide (wt.%)	Tabular alumina	Spinel	Reactive alumina	Cement
Al_2O_3	99.4	76	99.8	72.7
Na_2O	0.33	0.15	0.06	0.19
CaO	0.05	0.3	0.02	26.5
MgO	0.10	22	0.02	0.09
SiO_2	0.02	0.06	0.03	0.2
Fe_2O_3	0.10	0.10	0.03	0.11

Table 3
Chemical composition and physical parameters of nano-alumina particles.

Al_2O_3 (%)	Crystal phase	Specific surface area (m^2/g)
99.99	α	35

2.2. Castable preparation

In order to make the nano powder distribute evenly throughout the mixture, nano-alumina powder was mixed with the reactive alumina inside the mini type ball crusher in a definite proportion for 2 h. Then, the mix compounds were mixed with other raw materials for 4 min in a planetary mixer (Hobart). The amount of 5.1 wt.% water is added constantly for the mixing of castables for all compositions. After water was added, the whole composition was wet mixed for an additional 4 min. These refractory castables were cast into standard mold without vibration. After curing at 20 °C and 90% relative humidity for 24 h, the specimens were taken out of the mold, dried for 24 h at 110 °C and fired at 1000, 1300 and 1500 °C for 3 h, respectively.

2.3. Test methods

Dried and fired samples were tested for apparent porosity (A.P.) and cold crushing strength (C.C.S.). A.P. results were obtained through the Archimedes method using kerosene as the immersion liquid for dried samples and water for fired samples (in accordance with ASTM C 830-93). Also, C.C.S. was performed in accordance with ASTM C 133-97. An average of five samples was considered for all such tests. The cross sections of samples after drying and firing at different temperatures were evaluated by scanning electron microscope (SEM). Microstructural evaluations were performed using Cambridge S-360 SEM at 10–20 kV after gold coating. In order to characterize and detect different phases, X-ray diffraction (XRD) analyses (Cu K_α, Ni-filtered radiation, Philips model no. PW1050) were carried out on the fired samples.

3. Results and discussion

3.1. The influence of nano-alumina content on the physical and mechanical properties of refractory castable

The effect of nano-alumina content on the A.P. of the alumina–spinel refractory castable as a function of sintering temperature is shown in Fig. 1.

It can be seen that A.P. is decreased with the increase of nano-alumina content. This is attributed to the better ability of nano powders to fill the voids between castable aggregates in comparison with reactive alumina. Hence, a highly packed

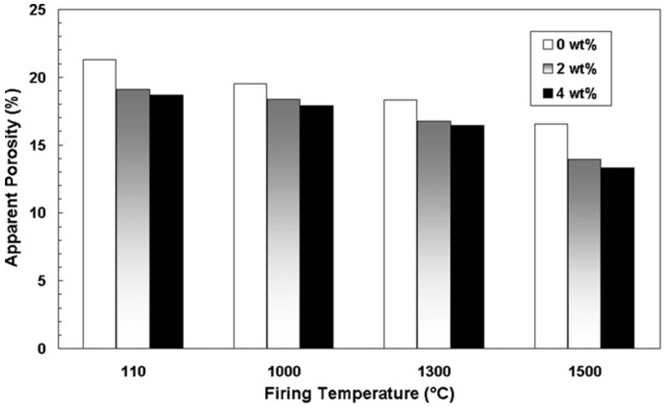


Fig. 1. The effect of nano-alumina content on the A.P. of refractory castable fired at various temperatures.

structure is obtained. On the other hand, the results indicate that when the firing temperature increased, A.P. of all compositions tends to decrease. The porosity of non-insulating industrial refractories typically falls in the broad range of 2–30%. Porosity provides the openings for the penetration and reaction of working face refractories that are directly exposed to service conditions such as molten metal and slag, cement clinker and molten glass. Therefore, nano-alumina addition that results in lower porosity will, in general, reduce or slow down the reactivity in service and extend the service life. After drying and firing at various temperatures, the C.C.S. results of refractory castable containing different amounts of nano-alumina particles are shown in Fig. 2.

It is found that C.C.S. is improved considerably with the increase of nano-alumina content. In addition, the results show that with the increase of firing temperature, the mechanical strength of compositions tends to increase. A very important characteristic is the green strength development of a refractory castable. It is created by the formation of hydrates of the clinker phases. In practice the higher C.C.S. leads to the higher erosion resistance of refractory castable and prolonged life time. Generally, several factors can affect the strength of refractory castables, including initial packing density, cement content and phases developed during sintering. The results indicate that the A.P. reduction is due to the highly packed structure of castable containing nano alumina. Therefore, the green strength of refractory castable is increased.

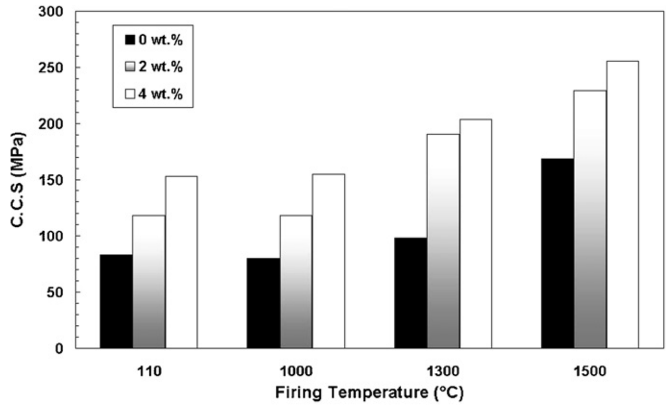


Fig. 2. The effect of nano-alumina content on the C.C.S. of refractory castable fired at various temperatures.

A sharp increase of the strength values at low firing temperatures (1300–1500 °C) is observed and it may be due to the enhanced ceramic bonding. This means that sintering of the refractory castable occurred at lower temperature than 1500 °C when nano-sized particles in the composition are increased. With the addition of nano-alumina, the solid phase sintering of the nano-sized particles occurred at lower temperatures because of the difference of surface area and special surface area energy between the matrix particles and the nano-alumina particles. Products sintered at 1500 °C show the highest strength values because of higher degree of sintering.

3.2. The influence of nano-alumina content on the phase composition

The XRD results of refractory castables containing different amounts of nano-alumina particles after firing at 1300 °C are shown in Fig. 3. With respect to these results, the $CaO\cdot 2Al_2O_3$ (CA_2) phase was found in addition to corundum and spinel phases at all compositions. Usually, in the 1000–1200 °C temperature range, mono-aluminate of calcium (CA) presented in calcium aluminate cement reacts with alumina to form CA_2 [19,2,20]. Also, the results show that with the addition of nano-alumina particles in the composition of alumina–spinel refractory castable, the $CaO\cdot 6Al_2O_3$ (CA_6) phase can be formed at 1300 °C. Thus, peaks intensities of this phase are raised with the increase of nano-alumina content.

Generally, the extra alumina reacts with calcium–aluminates from cement and CA_2 phase to form CA_6 (hibonite) crystals above 1450 °C [19,2,20]. Therefore, one can conclude that addition of nano-alumina particles in the composition of alumina–spinel refractory castable can decrease the formation

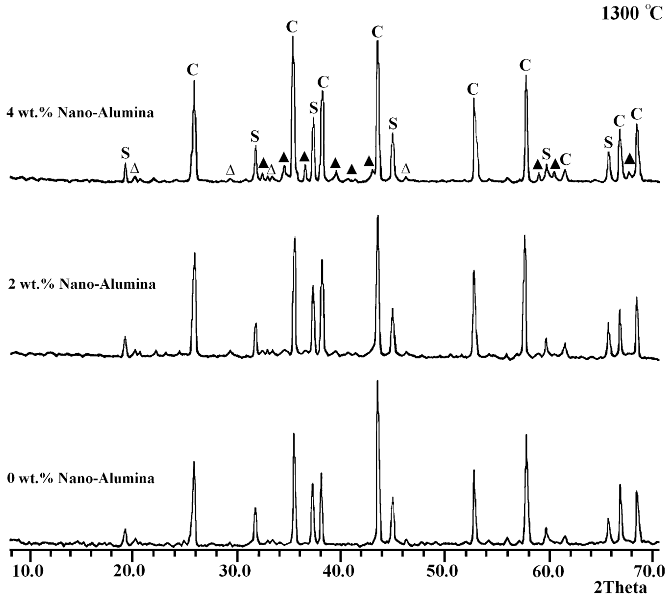


Fig. 3. XRD results of alumina–spinel refractory castables containing different amounts of nano-alumina particles after firing at 1300 °C. C: corundum, S: spinel, △: CA_2, ▲: CA_6.

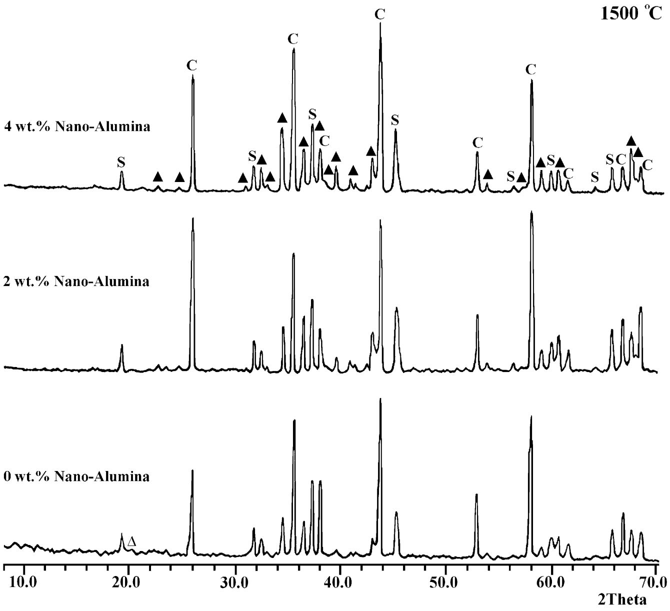


Fig. 4. XRD results of alumina–spinel refractory castable containing different amounts of nano-alumina particles after firing at 1500 °C. C: corundum, S: spinel, △: CA_2, ▲: CA_6.

temperature of hibonite phase. Because of using nanometer-sized alumina particles with high surface area in the composition, hibonite phase formation can occur at lower temperatures.

By comparing the XRD results with mechanical strength values (Fig. 2), it can be observed that formation of hibonite at 1300 °C leads to development of C.C.S. This phase has an important role on the improvement of the mechanical strength and other properties of refractory castables such as hot modulus of rupture and creep resistance. Therefore, addition of nano-alumina can improve the thermo-mechanical properties of alumina–spinel self flowing refractory castables at 1300 °C. Hence, the service temperature of these refractory castables can shift to lower temperature than 1500 °C.

The XRD results of alumina–spinel refractory castable containing different amounts of nano-alumina particles after firing at 1500 °C are shown in Fig. 4. The results show that all the compositions after firing at 1500 °C contain phases such as corundum, spinel, hibonite and CA_2. Comparison between XRD results of Figs. 3 and 4 reveals that the content of CA_2 phase is decreased with the increase of firing temperature and nano-alumina content. As stated above, CA_6 crystals above 1450 °C can form between the extra alumina with calcium–aluminates from cement and CA_2 phase. Therefore, CA_2 phase after reaction with alumina converts to CA_6 and its content is decreased.

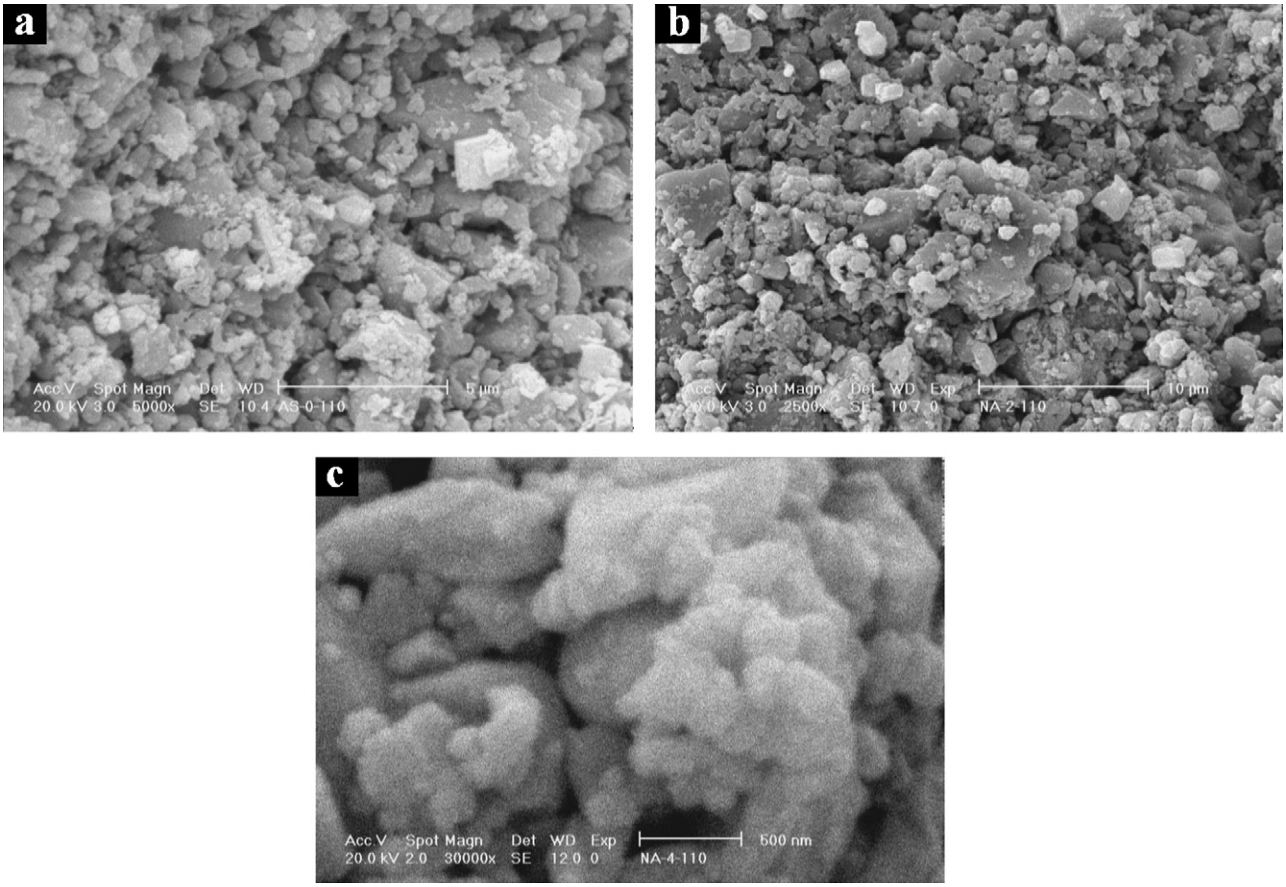


Fig. 5. SEM photomicrographs of alumina–spinel refractory castables containing different amounts of nano-alumina particles dried at 110 °C. (a) 0 wt.% (b) 2 wt.% and (c) 4 wt.%.

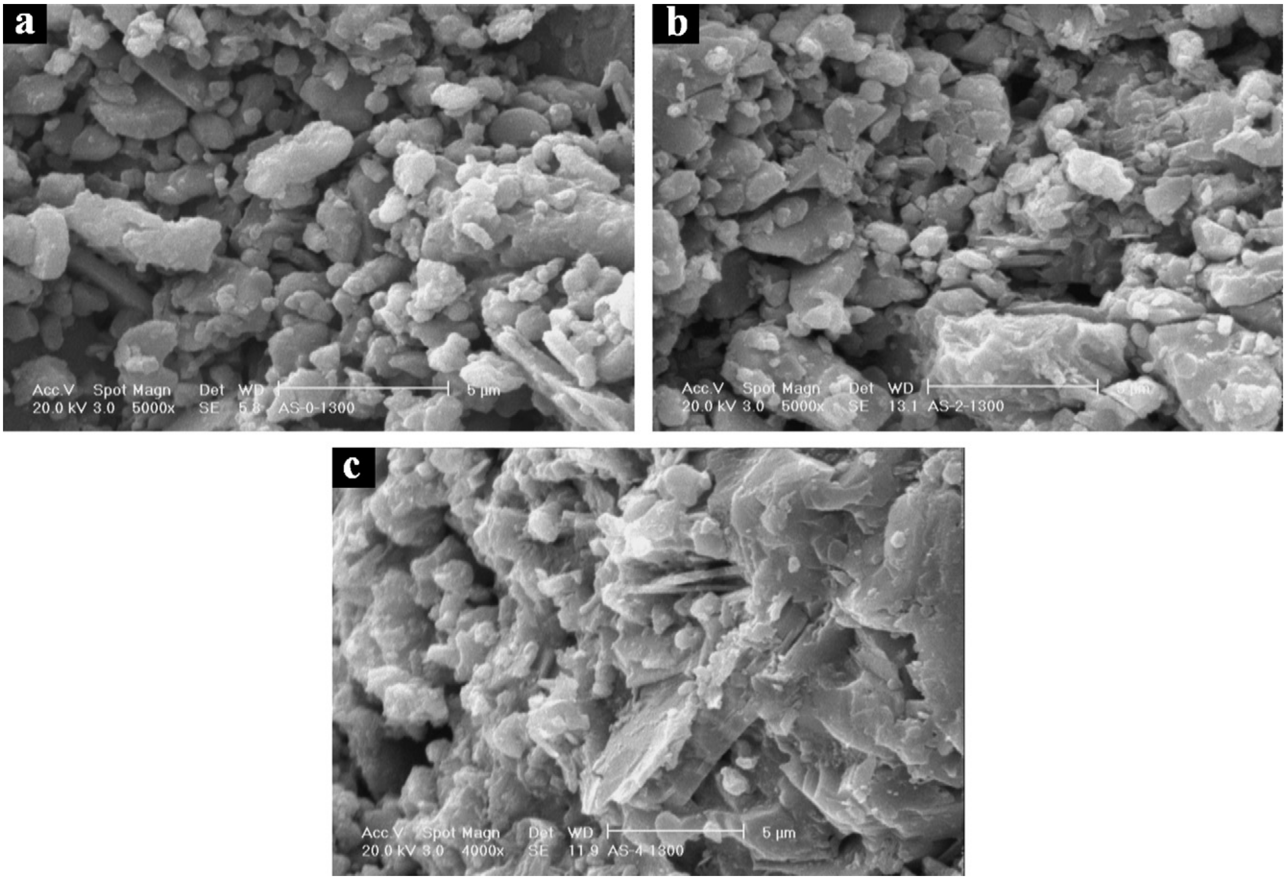


Fig. 6. SEM photomicrographs of alumina–spinel castables containing different amounts of nano-alumina particles fired at 1300 °C. (a) 0 wt.% (b) 2 wt.% and (c) 4 wt.%.

On the other hand, the results of Fig. 4 shows that the peak intensity of hibonite phase was increased with the addition of nano-alumina particles. Increasing of hibonite phase content at 1500 °C is related to the formation of this phase at lower temperatures (1300 °C). Comparison between XRD results of alumina–spinel refractory castables fired at 1300 °C and 1500 °C reveals that the nano-alumina addition can affect the amount of CA_6 phase in the 1300–1500 °C range.

3.3. The influence of nano-alumina content on the microstructure

Fig. 5 demonstrates the microstructure of alumina–spinel refractory castables containing different amounts of nano-alumina particles after drying.

As it can be seen, present phases in the alumina–spinel refractory castables contains alumina tabular and spinel aggregate that linked together by refractory castable matrix. The matrix of these refractory castables comprising of calcium aluminate cement hydrates with reactive alumina together with fine grains of spinel. Generally, particles with a small mean diameter (<100 μm) and a large specific surface area (>1 m^2/g) play a major role in bonding system of the refractory castable which, constitute the matrix of refractory castable. Fig. 5 reveals that with the addition of nano-alumina particles, the voids between the coarser particles can be filled further, enabling a decrease of porosity and an increase of the green strength. Also, by increasing the nano-alumina content, pores size of these refractory castables tends to decrease. Therefore, with the addition of nano-alumina particles, the packing of microstructure can increase considerably, which confirms the results of physical and mechanical properties.

The microstructures of alumina–spinel refractory castables containing different amounts of nano-alumina particles after firing at 1300 °C are presented in Fig. 6.

It can be seen that addition of nano-alumina particles can increase bonding system between fine particles, which produces lower porosity and smaller pore sizes resulting in higher strengths. Because of high surface area, on the other hand, addition of nano-particles can accelerate the improvement of the sintering densification impetus. When the nano-alumina particles come into contact with the matrix in the process of sintering, the transference will happen from small nano-sized particles to big nano-sized particles or big particles because of the difference of curvature radius. In this process, the particles coursing occurred, which made the surface energy decreased and interface energy increased. With microstructural evaluation of refractory castables containing 4 wt.% nano-alumina particles, one can see that a few flake shape crystals have grown and interlocked in the castable matrix. The inter-locking morphology of these crystals can lead to increasing of mechanical strength at 1300 °C. With respect to

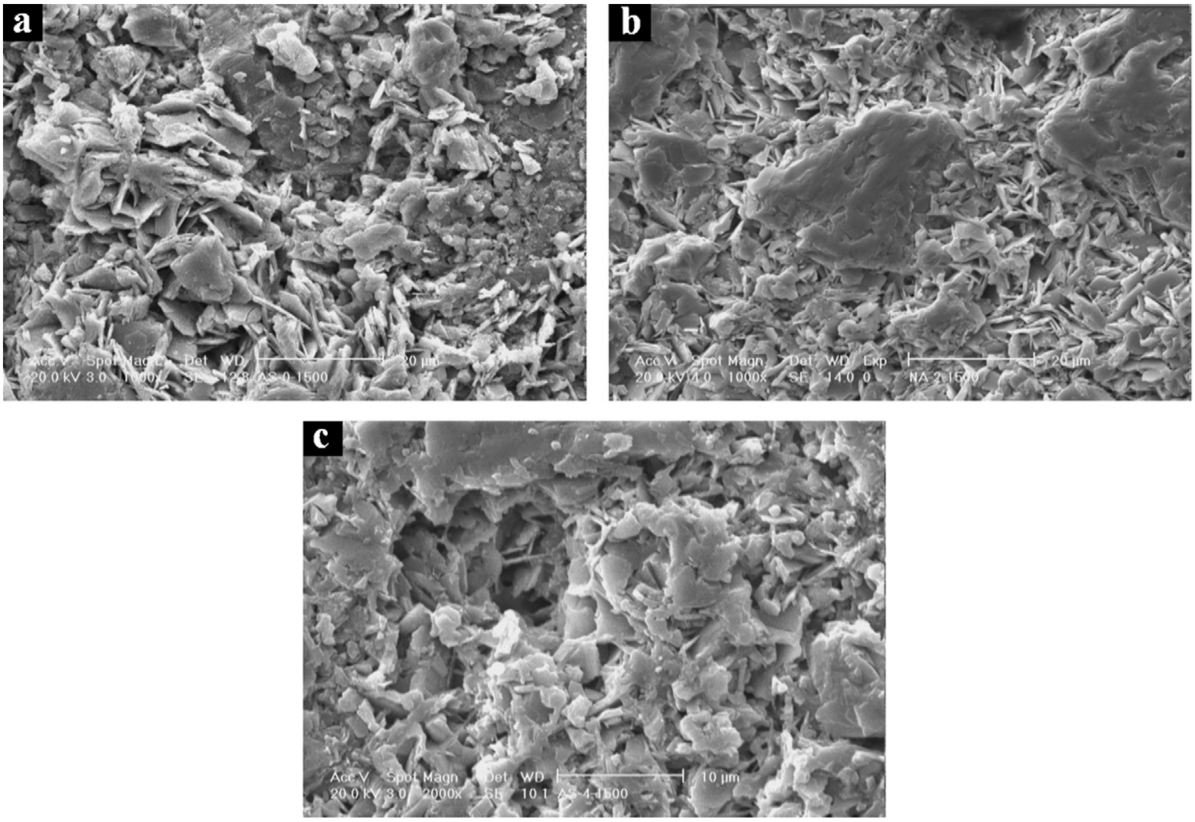
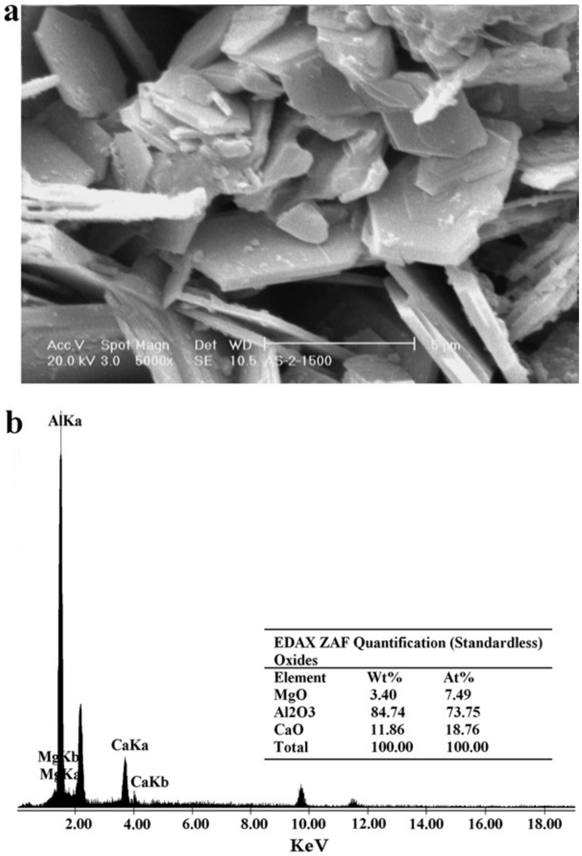


Fig. 7. SEM photomicrographs of alumina–spinel castable containing different amounts of nano-alumina particles fired at 1500 °C. (a) 0 wt.% (b) 2 wt.% and (c) 4 wt.%.



EDAX ZAF Quantification (Standardless) Oxides

Element	Wt%	At%
MgO	3.40	7.49
Al2O3	84.74	73.75
CaO	11.86	18.76
Total	100.00	100.00

Fig. 8. SEM photomicrograph and SEM/EDX analysis of platy crystals. (a) SEM photomicrograph and (b) EDX analysis.

XRD results of Fig. 3, these platy crystals are in hibonite phase. Fig. 7 demonstrates the microstructure of alumina–spinel refractory castable containing different amounts of nano-alumina particles after firing at 1500 °C.

As shown, the microstructure of alumina–spinel refractory castable after firing at 1500 °C comprises of alumina and spinel aggregates with some cluster of platy crystals on the surface of tabular alumina and spinel grains as matrix. The microstructure and SEM/EDX analysis of these platy crystals is depicted in Fig. 8. This analysis indicates that these platy shape crystals are in hibonite phase.

This calcium hexa aluminate provides an excellent bond linkage between grains in the matrix by an inter-locking morphology, which upgrades the properties at 1500 C. Hibonite phase have characteristics such as high stability in reducing atmospheres (e.g. CO), high chemical resistance in alkaline environment, and low wet ability by molten metals and slag (ferrous and non-ferrous) [21,22]. Therefore, the castables containing this phase can be used at different industrial furnaces e.g. in the aluminum melting furnace (low wet ability by molten aluminum), the cement kiln (high chemical resistance in alkaline environment), the steel furnaces (high refractoriness and low solubility in iron containing slag) and in the petrochemical industry (stability in reducing atmospheres).

The microstructures of alumina–spinel refractory castables containing different amounts of nano-alumina particles after firing at 1500 °C reveal that further hibonite phase is formed with the addition of nano-alumina particles.

4. Conclusion

This study confirmed the strong influence that nano-alumina particles exert on the microstructure and properties of self flowing alumina–spinel refractory castables. The results showed that green strength is improved considerably with the increase of nano-alumina content. It is attributed to the better ability of nano powders to fill the voids between castable aggregates in comparison with the reactive alumina. A sharp increase of strength value at low firing temperatures (1300 °C) is observed and is due to the formation of CA_6 phase and enhanced ceramic bonding. Because of using nanometer-sized alumina particles with high surface area and the difference of special surface area energy between these particles and matrix, solid phase sintering and hibonite phase formation are occurred at lower temperatures.

With respect to great effect of hibonite phase on the thermomechanical properties, addition of nano-alumina can improve the properties of alumina–spinel refractory castables at low temperatures. Therefore, the service temperature of these refractory castables can shift to lower temperatures than 1500 °C.

Acknowledgement

The author would like to thank Mr. R. Marzban, R&D manager of Niru (Gadhr) Refractory Company for providing samples.

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