THE EFFECT OF NANO-TITANIA ADDITION ON THE PROPERTIES OF HIGH-ALUMINA LOW-CEMENT SELF-FLOWING REFRACTORY CASTABLES

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The self-flow characteristics and properties of high-alumina low-cement refractory castables added with nano-titania particles are investigated. For this reason, the reactive alumina in the castable composition is substituted by nano-titania powder in 0-1 %wt. range. The microstructures, phase composition, physical and mechanical properties of these refractory castables at different temperatures are studied. The results show that the addition of nano-titania particles has great effect on the self-flow characteristics, phase composition, physical and mechanical properties of these refractory castables. With increase of nano-titania particles in castable composition, the self-flow value and working time tend to decrease. With addition of 0.5 wt.% nano-titania in the castable composition, the mechanical strength of castable in all firing temperatures tends to increase. It is attributed to the formation of CA_6 phase and enhanced ceramic bonding. Nano-titania particles can act as a nucleating agent for hibonite phase and decrease the formation temperature of hibonite. Because of perovskite phase formation, the addition of 1 wt.% nano-titania can decrease the mechanical strength of castable after firing.

INTRODUCTION

Over the last decades, use of unshaped monolithic refractories has been increasing greatly because of their significant advantages over other shaped refractories of the same class. Among the unshaped refractories, the refractory castables are one of the most important groups of these materials due to their superior technical and economical characteristics [1,2]. The increasing application and demand for refractory castables 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 [3-5]. Generally, refractory castables can be considered as composites, with the aggregates (>100 μm), fine (1-100 μm) and superfine (<1 μm) refractory grains together with bonding phase being the matrix [6]. The most common binder used in refractory castables is calcium aluminate cement (CAC). Refractory castables are mixed with water and then installed by either pouring or pumping [2, 5 and 7]. Successful performance of refractory castables during the lining application and high-temperature services is attributed to the ability of fine and superfine powders to fill the voids between castable aggregates [5, 8]. However, the most extensively used fine and superfine particles in high-alumina refractory castables are microsilica, calcined and reactive alumina and other fine particles [9, 10]. The presence of CaO resulting from calcium aluminate cement can be deleterious to the refractoriness of castables composition, such as those containing microsilica. The interaction among $CaO–Al_2O_3–SiO_2$ leads to the formation of low-melting temperature phases, such as gehlenite or anorthite [1]. 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. 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 [3, 5, 11 and 12]. Maitra, Das and Sen [13] studied the effect of titania micro-sized particles on the densification of low-cement Al_2O_3–MgO refractory castable. It has been observed that TiO_2 as an additive exhibited a positive influence on the densification, spinel formation and the reduction of the grain sizes of the formed spinels at elevated temperatures in this system, and modified the physical properties such as firing shrinkage, bulk density, apparent porosity and true density distinctly [13]. Also, microstructure of the fired bodies with TiO_2 additive became more uniform and contained less glassy phases. This observation is the basis for the present investigation, whether the addition of TiO_2 leads to the densification and phase formation [13, 14]. Hence, the effect of nano-titania particles on the self-flow characteristics and properties of high alumina self-flowing low-cement refractory castables is investigated in this work. Also, microstructure and phase composition of these refractory castables is studied.

EXPERIMENTAL

Raw materials and composition

The composition used for high-alumina self-flowing refractory castable is listed in Table 1. The chemical composition of raw materials used for this study is shown in Table 2. As viewpoint of refractoriness under load, microsilica was not used in the castable composition. The nano-titania powder is the product of AEROXIDE Co. (P25) which, its chemical composition and physical parameters are shown in Table 3.

For the study of nano-titania addition on the properties of these refractory castables, reactive alumina is substituted by nano-titania powder in 0-1 %wt. range. The Particle size distribution was calculated from the Andreasen's equation as:

$$CPFT = 100 \times (d/D)^q \qquad (1)$$

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 [9].

Self-flow measurement

Self-flow value (SFV) and working time measurement was performed according to ASTM C 1446-99. Based on this standard, after dry mixing of the batch for 30 s in a planetary mixer (Hobart), all the water (distilled) was added within 10 s while the mixer was running. The wet mixing was conducted for 5 min at a slow speed (Hobart, speed 1). After mixing, the prepared castable, was transferred to a sealed container and care was taken to keep the moisture constant. Ten minutes after addition of water, the mixed castable was poured into a standard cone with a base diameter of 100 mm according to ASTM standard number C-230. The cone was then elevated to allow the mix to flow, and after 60 s the patty diameter was measured. The percentage increase in spreading diameter after 60 s is taken as the self-flow value according to the following formula:

$$\text{SFV (\%)} = (D_2 - D_1) \times 100/D_1 \qquad (2)$$

where D_2 is the final average diameter after removal of mould and D_1 is the initial diameter (100 mm). The castable is considered as self-flow, when the above value lies within the range of 80-110% of the base diameter. During the self-flow evaluation, the ambient temperature was controlled to be in the range of 20-24°C [15].

Table 2. Chemical composition of raw materials

Oxide (wt.%)	Tabular Alumina	Reactive Alumina	Cement
Al_2O_3	99.4	99.8	72.7
Na_2O	0.33	0.06	0.19
CaO	0.05	0.02	26.5
MgO	0.10	0.02	0.09
SiO_2	0.02	0.03	0.20
Fe_2O_3	0.10	0.03	0.11

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

TiO_2 (wt.%)	Average grain size (nm)	Specific surface area (m^2/g)	Phase type
99.5	21	50	Anatase

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

Raw materials		Source (type)	wt.%
Tabular Alumina	2-5 mm	Alcoa Chemicals, T-60	80
	1-2 mm		
	0.5-1 mm		
	0-0.5 mm		
	45 µm		
Reactive Alumina	d_{50} = 1.90 µm	Alcoa Chemicals, CTC-20	14
Calcium Aluminate Cement	d_{50} = 3.03 µm	Lafarge, Secar-71	6
Dispersant		BASF, Castament FS-10	0.1

Castable preparation

In order to make the nano powder distribute evenly throughout the mixture, nano-titania powder was mixed with the reactive alumina inside the mini type ball crusher in a definite proportion for two hours. 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 hr, the specimens were taken out of the mold, dried for 24 hrs at 110°C and fired at 1250 and 1550°C for 3 hours, respectively.

Test methods

Dried and fired samples were tested for bulk density (B.D.), apparent porosity (A.P.), cold crushing strength (C.C.S.) and cold modulus of rupture (M.O.R.). A.P. results were obtained in accordance with ASTM C 830-93. Also, mechanical strengths were 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, D8ADVANCE, Bruker diffractometer) were carried out on the fired samples.

RESULTS AND DISCUSSION

The effect of nano-titania content on the self-flow characteristics

Figure 1 shows the effect of nano-titania content on SFV of the high-alumina low-cement refractory castable as a function of time. The results indicate that with increase of nano-titania particles in castable composition, SFV tends to decrease. The nano-titania particles have high surface area that leads to attraction forces between particles. These attractions between nano-titania particles and other fine particles in the castable matrix would lead to formation of flocculation structure in which free water is trapped and flow is decreased. Generally, the SFV of self-flow refractory castable lies within the range of 80-110 %. Therefore, the SFV of castable containing higher than 1 wt.% nano-titania content downs to under 80 % and castable can not flow under its weight. The result is a castable that, at best, can be a fairly vibratable or a ramming mix unless a significant amount of water is added. From Figure 1, one can see that the addition of nano-titania particles to the castable composition decrease working time. Generally, the first sequence in the setting of a castable is loss of flow, i.e. it becomes impossible to place. Control of the set time has always been one of the most wanted but also perhaps the most difficult aspect of refractory castable technology. In practice, 30 up to 100 min can provide working time long enough for appropriate placement of castables. Therefore, castables containing 0.5 wt.% nano-titania particles will have adequate working time and can be installed properly. On the other hand, the castables containing 1 wt.% nano-titania particles have short working time and only can be installed at early minutes.

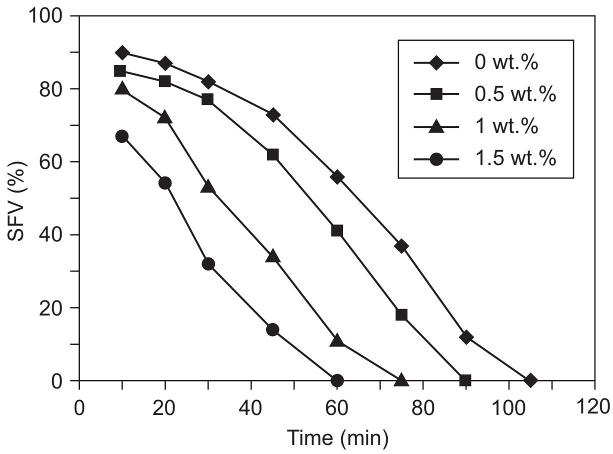

Figure 1. The effect of nano-titania content on SFV of refractory castable as a function of time.

The effect of nano-titania content on the physical and mechanical properties

The effect of nano-titania content on the B.D. and A.P. of the high-alumina refractory castable as a function of firing temperature are shown in Figures 2 and 3.

The results show that with increasing of firing temperature and enhanced sintering mechanism, A.P. is decreased and then, B.D. is increased in the compositions without nano-titania. On the other hand, the results indicate that A.P. is enhanced by increasing of nano-titania content after firing at 1250°C. Oppositely, with increasing of nano-titania content in the castable composition after firing at 1550°C, A.P. is decreased and then, B.D. is increased. The increasing of A.P. after firing at 1250°C with addition of nano-titania can be attributed to formation of expanding phases in the matrix. But, decreasing of A.P. after firing at 1550°C can be related to the enhanced sintering mechanism or phases developed during sintering. The C.C.S. and M.O.R. results of refractory castables containing different amounts of nano-titania particles after drying and firing at various temperatures are shown in Figures 4 and 5.

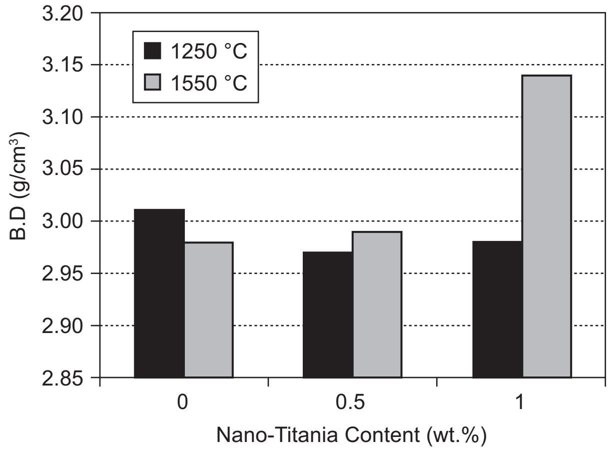

Figure 2. The effect of nano-titania content on the B.D. of refractory castable as a function of firing temperature.

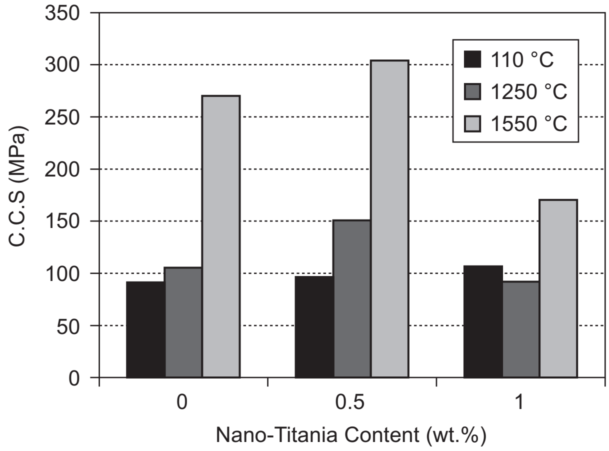

Figure 4. The effect of nano-titania content on the C.C.S. of refractory castable as a function of firing temperature.

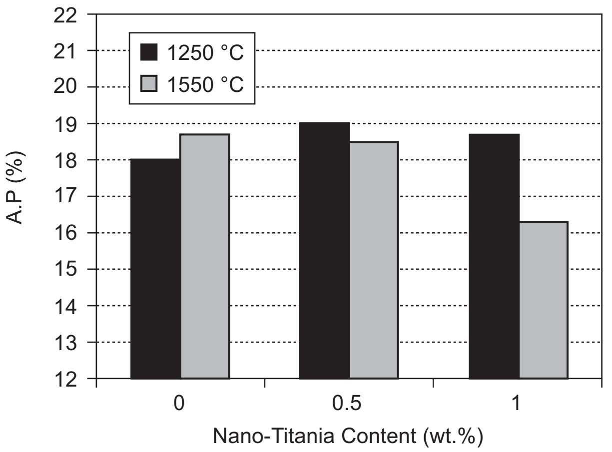

Figure 3. The effect of nano-titania content on the A.P. of refractory castable as a function of firing temperature.

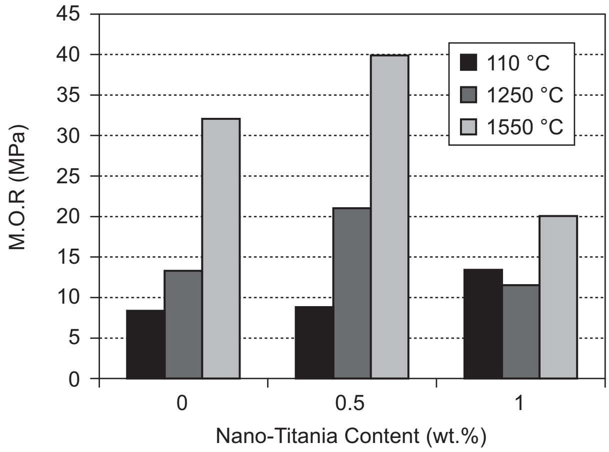

Figure 5. The effect of nano-titania content on the M.O.R. of refractory castable as a function of firing temperature.

It is found that C.C.S. after drying is improved with the increase of nano-titania 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 structure is obtained. The results indicate that with the increase of firing temperature, the mechanical strength of compositions tends to increase. A sharp increase of the strength values at high firing temperatures (1550°C) is observed and it may be due to the enhanced ceramic bonding. By comparison between results of A.P and mechanical strength, one can see that despite of A.P increasing after firing at 1250°C, the mechanical strengths tend to increase by addition of nano-titania particles. Generally, several factors can affect the strength of refractory castables, including initial packing density, cement content and phases developed during sintering. Therefore, increase of the strength values at low firing temperatures (1250°C) can be due to the formation of high bonding phases and enhanced ceramic bonding. The results show that the addition of 0.5 wt.% nano-titania in the castable composition, the mechanical strengths of castable in all temperatures tend to increase. This means that sintering of the refractory castable containing 0.5 wt.% nano-titania can occurred at lower temperature (such as 1550°C) when nano-titania in the composition are used. On the other hand, the addition of 1 wt.% nano-titania can decrease the mechanical strengths after firing at 1550°C. With respect to the results, one can conclude that the addition of nano-titania up to 0.5 wt.% improve the mechanical strength of high-alumina refractory castables after firing at all temperatures. Decrease in mechanical strengths after firing at 1550°C is associated with the decreasing of A.P. (see Figure 3) which can attribute to the formation of amorphous or undesirable phases.

The effect of nano-titania content on the phase composition

The XRD results of refractory castable containing different amounts of nano-titania particles after firing at 1250°C are shown in Figure 6.

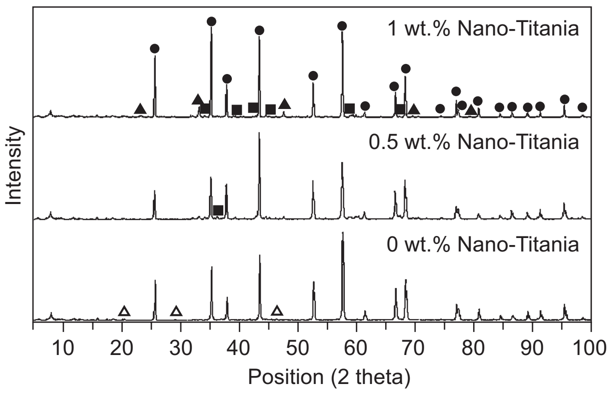

Figure 6. XRD results of refractory castable containing different amounts of nano-titania particles after firing at 1250°C (● - Corundum, Δ - CA_2, ▲ - Perovskite, ■ - CA_6).

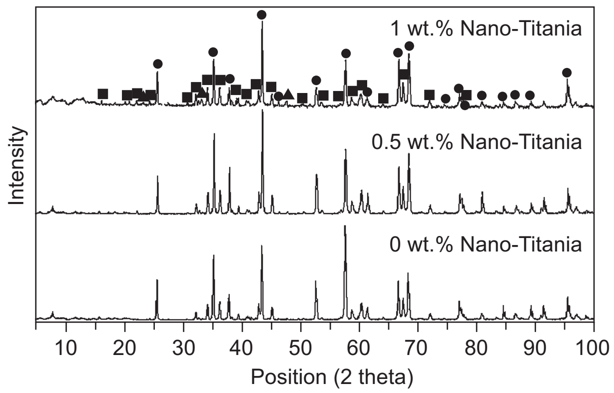

Figure 7. XRD results of refractory castables containing different amounts of nano-titania particles after firing at 1550°C (● - Corundum, ■ - CA6 , ▲ - Perovskite).

With respect to these results, the corundum and $CaO{\cdot}2Al_2O_3$ (CA_2) phases exist at all compositions after firing at 1250°C. Also, the results show that with the addition of nano-titania particles in the composition of high alumina refractory castable, the $CaO{\cdot}6Al_2O_3$ (CA_6) phase can be formed at 1250°C. 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. Then, the extra alumina reacts with calcium-aluminates from cement and CA_2 phase to form CA_6 (hibonite) crystals above 1450°C [16,17]. Therefore, one can conclude that addition of nano-titania particles in the composition of high alumina refractory castable can decrease the formation temperature of hibonite phase. It can form a solid solution with Al_2O_3, causing lattice defects with the formation of ionic vacancies, thereby promoting the formation of hibonite. Therefore, nano-titania particles can act as a nucleating agent for hibonite phase. By comparing the XRD results with mechanical strength values (Figure 2), it can be observed that formation of hibonite at 1250°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-titania can improve the thermo-mechanical properties of high alumina self-flowing refractory castables at 1250°C. Hence, the service temperature of these refractory castables can shift to lower temperature than 1450°C. Also, the results show that the compositions containing nano-titania particles after firing at 1250°C contain perovskite ($CaTiO_3$) besides of hibonite phase. Comparison between XRD results of Figure 6 reveals that the content of perovskite phase is enhanced and the content of hibonite phase was decreased with the increase of nano-titania content. Decreasing of hibonite phase content at 1250°C is related to the formation of perovskite phase with the increase of nano-titania content. These results show that 0.5 wt.% nano-titania can affect hibonite formation and higher contents of this oxide led to formation of perovskite. Therefore, up to 0.5% wt. nano-titania particles can act as a nucleating agent for hibonite phase. The XRD results of refractory castable containing different amounts of nano-titania particles after firing at 1550°C are shown in Figure.

The results of Figure 7 show that the corundum and hibonite phases exist at all compositions after firing at 1550°C. Also, the compositions containing nano-titania have perovskite phase. Comparison between XRD results of Figure 6 and Figure 7 reveals that the content of CA_2 phase is decreased with the increase of firing temperature. 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. On the other hand, the results of Figure 7 show that the peaks intensities of hibonite and perovskite phases were increased with the addition of nano-titania particles. Increasing of hibonite phase content at 1550°C is related to the formation of these phases at lower temperatures (1250°C).

The effect of nano-titania content on the microstructure

The microstructure of high-alumina refractory castables containing 0.5 wt.% nano-titania particles after firing at 1250°C is presented in Figure 8.

With microstructural evaluation of refractory castables containing 0.5 wt.% nano-titania 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 leads to increasing of mechanical strength at 1250°C. With respect to XRD results of Figure 6, these platy crystals are in hibonite phase. Also, growth of these flake shape crystals led to increasing of porosity. Figures 9, 10 and 11 demonstrate the microstructure of high alumina refractory castable containing different amounts of nano-titania particles after firing at 1550°C.

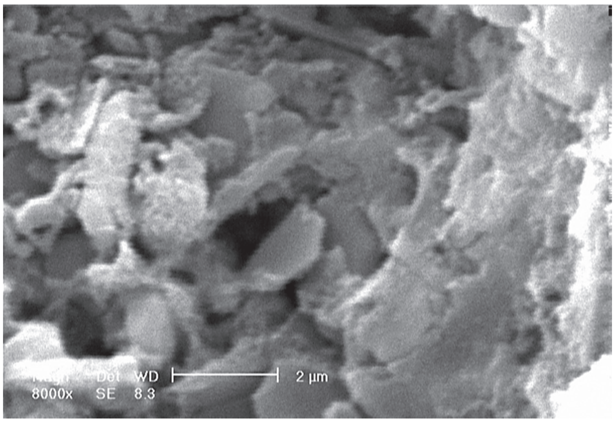

Figure 8. SEM photomicrograph of high-alumina refractory castable containing 0.5 wt. % nano-titania particles fired at 1250°C.

As shown, the microstructure of high-alumina refractory castable after firing at 1550°C comprises of alumina aggregates with some cluster of platy crystals on the surface of tabular alumina grains as matrix. The microstructures of high-alumina refractory castables after firing at 1550°C reveal that further hibonite phase is formed with the addition of nano-titania particles. Besides, with increasing of nano-titania content, the average size of CA_6 crystals tends to increase. On the other hand, the morphology of alumina tabular grains and CA_6 crystals are changed with addition of nano-titania so that the edges of alumina and CA_6 grains are rounded. Nano-titania can form a solid solution with Al_2O_3, causing lattice defects with the formation of ionic vacancies, thereby promoting the formation of hibonite and rounding of particles. With rounding of grains edges, the inter-locking effect of CA_6 crystals decreases. Therefore, with increasing of nano-titania content the mechanical strength of refractory castable at 1550°C tends to decrease. Corresponding to Figure 12, the perovskite cubic crystals are formed between CA_6 grains.

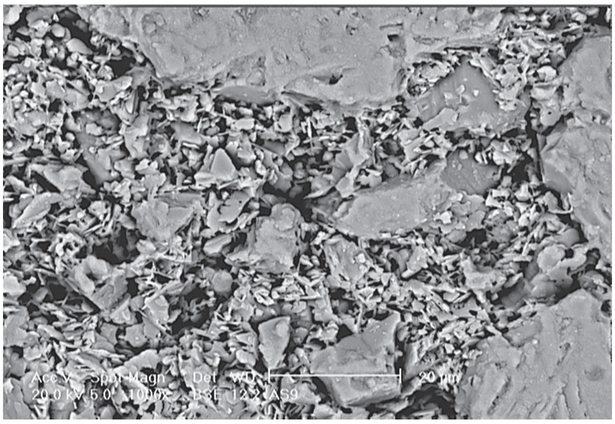

Figure 9. SEM photomicrograph of high-alumina refractory castable without nano-titania particles fired at 1550°C.

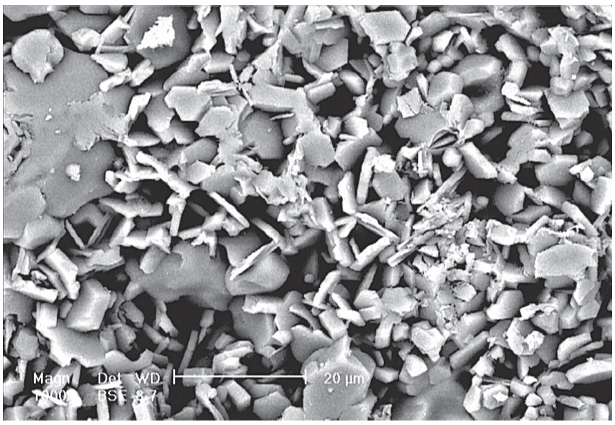

Figure 10. SEM photomicrograph of high-alumina refractory castable containing 0.5 wt.% nano-titania particles fired at 1550°C.

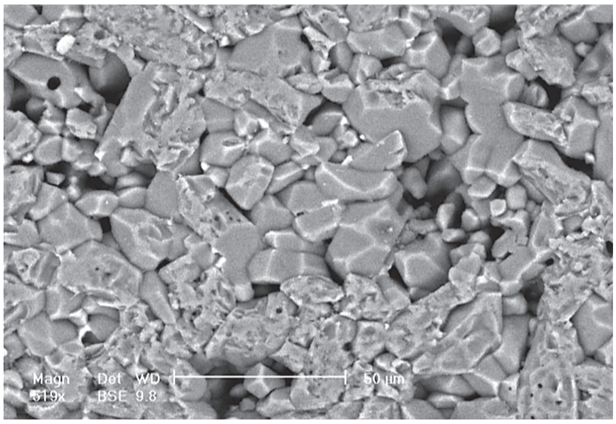

Figure 11. SEM photomicrograph of high-alumina refractory castable containing 1 wt.% nano-titania particles fired at 1550°C.

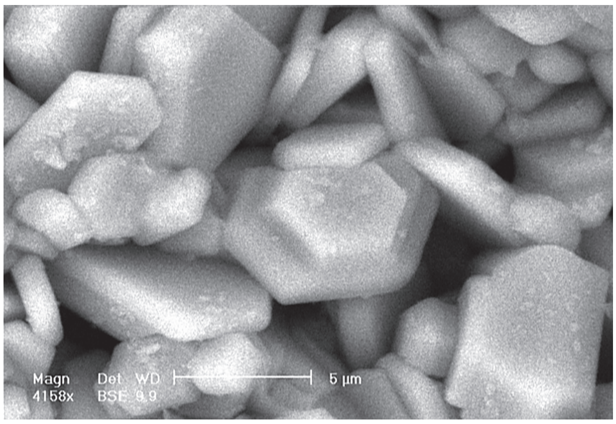

Figure 12. SEM photomicrograph of high-alumina refractory castablecontaining 1 wt.% nano-titania particles fired at 1550°C.

Formation of perovskite phase leads to the filling of porosity between particles and then, porosity of castable is decreased. These crystals have weak bond linkage with other particles. Therefore, despite decreasing of porosity the mechanical strength of refractory castable can not increased

CONCLUSIONS

This study confirmed the strong influence that nano-titania particles exert on the microstructure and properties of high-alumina low-cement self-flowing refractory castables. An attraction between nano-titania particles and other fine particles in the castable matrix appears to promote lower flow ability in this system. Besides, the addition of nano-titania particles in the castable composition decreases working time. The results also indicate that the nano-titania particles have a great effect on the green and firing strengths of these refractory castables. With addition of 0.5 wt.% nano-titania in the castable composition, the mechanical strengths of castable in all firing temperatures tend to increase. It is attributed to the formation of CA_6 phase and enhanced ceramic bonding. Nano-titania particles can act as a nucleating agent for hibonite phase and decrease the formation temperature of hibonite. The platy crystals of CA_6 are detected inside the grain boundaries of grains in samples fired at 1550°C. CA_6 phase can be formed at lower temperatures (1250°C) with the addition of nano-titania particles. Because of perovskite phase formation, the addition of 1 wt.% nano-titania can decrease the mechanical strength of castable after firing.

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