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The optimization of dispersant content in alumina castable containing nano-titania

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ABSTRACT

In this research, two series of ultra-low cement high alumina refractory castables containing 0 and 0.4 wt.% of nano-titania were prepared using different amounts of polycarbonic acid (DOLAPIX FF 26) as a dispersant. Several characteristics including microstructure, flowability, mechanical strength, bulk density and apparent porosity of the samples were analyzed. The results showed that the optimum amount of the dispersant was 0.13 wt.% and 0.20 wt.% for castable having no nano-titania and the one containing 0.4 wt.% nano-titania, respectively. The strength of castable containing 0.4 wt.% nano-titania dispersed by 0.20 wt.% of DOLAPIX FF 26 was 1.5 times higher than that of castable without nano-titania (dispersed by 0.13 wt.% of DOLAPIX FF 26). This can be explained by the fact that when the optimum amount of dispersant is used, the well-dispersed nano-titania particles act as a catalyst in the cement hydration reactions and will result in higher strength of the refractory castables.

1. INTRODUCTION

Refractory castables are progressively utilized in steelmaking, petrochemical, cement, glass, non-ferrous metallurgy industries and other high-temperature applications. With the growing demand to the refractory castables, researchers have tried to improve the mechanical and industrial properties of these materials. The low and ultra-low cement castables as well as cement free castables were most important developments of the refractory castable systems [1]. Alumina compositions are extremely used because of their excellent features [2-4]. Recently, researchers have started to improve the quality of the refractory castables using nano-sized materials in their formulation. Sako et al. have investigated the variations of the characteristics when the nano-scaled alumina and magnesia particles are added to the matrix of alumina-magnesia refractory castables [5]. These nano-scaled additives drastically reduce the residual expansion related to the in-situ spinel formation [5]. The effect of nano-titania particles on the self-flow characteristics, microstructure and phase composition of high alumina self-flowing low-cement refractory castables was investigated by Badiee and Otroj [6]. Their results showed that the addition of nano-titania particles had a great effect on the self-flow characteristics, phase composition, physical and mechanical properties of refractory castables [6]. Moreover, the influence of additions of nano-sized zirconia, titania, silica, and magnesia on the microstructure and mechanical properties of alumina-rich refractory was discussed by Dudczig et al. [7]. They reported that the generation of a micro-crack network due to the formation of phases with different thermal expansion coefficients and the formation and decomposition of aluminum titanate (Al_2TiO_5) lead to the higher strengths after thermal shock attack [7]. Furthermore, the microstructure and phase composition of alumina-spinel self-flowing refractory castables containing nano-alumina particles at different temperatures were inspected by Otroj and Daghighi [8]. They stated that by increasing the nano-alumina content in the castable composition, the mechanical strength was considerably enhanced at various temperatures [8]. It was shown that the nano-alumina particles can affect the formed phases after firing [8]. Sahoo and co-

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workers have used the nano-magnesia as an additive to manufacture the precast high alumina castable refractory [9]. It was observed that the addition of the nano-magnesia upsurges the thermo-mechanical, corrosion and erosion resistance of the precast high alumina products [9]. The effects of nano-calcium carbonate on the properties of corundum-based castables were investigated by Zhigang and colleagues [10]. Additionally, Braulio et al. have evaluated the addition of a nano-magnesia and its effects on in-situ spinel expansion of the high-alumina refractory castables [11, 12]. It is worthy to note that the magnesia grain size affects the kinetics of the in-situ spinel formation and expansion of the alumina-magnesia refractory castables [11, 12]. Mukhopadhyay and DasPoddar have evaluated and analyzed the slag corrosion and thermal shock resistance properties of the spinel-bonded castable by the nanocrystalline feature of the sol-gel spinel [13]. The effects of utilized nano-sized carbon black in the range of 0-10 *wt*.% on the physical and thermo-mechanical properties of Al_2O_3–SiC–SiO_2–graphite refractory castables were scrutinized by Amin and co-workers [14]. It was found that the addition of the nano-sized carbon black improves the relative heat and oxidation resistance of the composites [14]. Besides, Yaghoubi et al. have examined the influence of the nano-silica particles on the properties and microstructure of the high-alumina ultra-low cement refractory castables [15]. It was also found that the nano-silica particles increase the rate of needle-shaped mullite formation during sintering at 1400 °C [15]. In addition, Gogtas et al. have attempted to develop high strength and high toughness self-flowing castables through incorporating nano-zirconia and nano-yttria, which is stabilized zirconia additions, in ultra-low cement castables based on the tabular alumina [16]. It was clarified that the nanoparticles can be effectively de-agglomerated using the surfactants and ultrasonication process [16].

Particle dispersion is considered as an important issue for the refractory applications. Efficient dispersion is an indispensable requirement that inhibits the formation of agglomerates and hinders the optimum particle packing, so, it increases the flowability and pre-firing mechanical strength of the castable [17]. The most common approach to disperse the refractory castables is the addition of the specific charged molecules (dispersants) which can be absorbed on the surfaces of the particles [18]. The dispersants role is to decrease water demand and provide good flow for casting of the castable refractory into the mould [19]. The dispersants are most commonly used to modify the surface features of the particles through the electrostatic/electrosteric mechanism [18, 19].

In all aforementioned research works [5-16], a fixed quantity of the dispersant regardless of the nanomaterials amount, which is added to the refractory castable, was used. The microstructural and mechanical of the high alumina refractory castables containing nano-titania at high temperatures were extensively investigated in our previous research work [20]. The object of present report is to optimize the required dispersant content in the refractory castable containing nano-titania. For this purpose, the effect of the nano-titania particles and dispersant addition to the ultra-low cement high alumina refractory castable was simultaneously studied.

2. EXPERIMENTAL

2.1. Raw Materials

The used raw materials for the preparation of the ultra-low cement high alumina refractory castable are listed in Table 1. Tabular alumina with four particle size distributions from 3 to 5mm, 1 to 3mm, 0 to 1mm and 0 to 0.045mm was used as a raw material. The nano-titania powder as an additive was supplied by AEROXIDE Co. (P25) with a specific surface area and a mean particle size of 50 m^2/g and 21nm, respectively. DOLAPIX FF 26 is a polycarbonic acid (Zschimmer & Schwarz, Germany) which is utilized as a dispersing agent. The dispersant amount was selected in the range of 0.1-0.2 *wt.%*, while the nano-TiO_2 content was 0.4 wt%. It is necessary to mention that the additives were added into the total mixture of the raw materials. According to the previous research [21], the amount of 0.4 *wt.%* nano-titania was selected. Based on that research [21], with the aim of achieving the suitable flowability, nano-titania powder in the range of 0-1 wt.% were added into the total mixture of the castable. The results showed the castable containing up to 0.4 *wt.%* nano-titania can be a fairly vibrate, whereas the addition of a further amount of nano-titania is led to the poor flowability of the castable.

TABLE 1. Raw materials and characteristics of the high alumina castable

Raw materials	Source	Purity (*wt.%*)	Density (g/cm^3)
Tabular alumina	Nanjing HB refractory, China	>99	3.55
Reactive alumina	PFR 20, Alteo, France	>99.8	3.92
High alumina cement	Secar 71, Kerneos, China	(Al_2O_3)>70	2.93

2.2. Sample Preparation

The particle size distribution of the castables was adjusted to a theoretical continuous curve based on the Dinger and Funk model [22]. The cumulative percent finer than CPFT (cumulative percent finer than) is as follows:

$$CPFT = [\frac{(d^q - d_m^q)}{(D^q - d_m^q)}] \times 100 \quad (1)$$

Where d denotes the particle size of the considered fraction, d_m and D are the minimum and maximum particle size (0.1 µm and 6 mm) in the mixture. The exponent q is referred to the distribution modulus and made a condition to control the number of fines for a generated mixture in a certain range. For the present work, q was chosen to be 0.28 which was suitable for the vibration castable [19]. Table 2 shows the compositions of the investigated refractory castables.

TABLE 2. Experimental composition of the high alumina castable

Raw materials	Composition (*wt.%*)
Tabular alumina	
3-5 mm	20
1-3 mm	15
0-1 mm	33
0-0.045 mm	23
Reactive alumina	7
High alumina cement	2
nano-titania	0 or 0.4
Dispersant	0.1-0.2

Raw materials were firstly weighed (each batch was 4.5 kg), dried and mixed for 4 min in an EIRICH mixing system. Then water was added and wet-mixed for 4 min to form the castable. Based on the dry weight of the raw materials, the water content was 5.3 *wt.%* for all samples. It should be noted that the dispersant and nano-titania particles were dispersed in the water by an ultrasonic bath to ensure a uniform distribution of these additives in the castable matrix.

A sample was taken from the castable for the flowability measurements test and the remaining was vibro-casted into the steel moulds (160mm x 40mm x 40mm) using a vibrating table at a frequency of 60Hz for 1min. The last samples were wrapped in plastic sheets and cured for 24h at room temperature (24-26°C). The cured samples were removed from the mold and kept at room temperature for another 24h before drying at 110°C. All of them were tested for flowability and mechanical properties.

2.3. Characterization Methods

2.3.1. Flowability Measurement

Flowability is represented via the flow value (FV) which is measured by the flow cone (100 mm base φ, 100 mm top φ and 70 mm height) according to the ASTM C1445-99 method [23]. The results indicate the increase of the diameter of the sample, which is initially formed as a truncated cone, as follows:

$$FV(\%) = \frac{(D_f - D_i)}{D_i} \quad (2)$$

Where FV denotes the flow value, D_f is the final average diameter (after flow) and D_i is the initial diameter (100mm).

2.3.2. Mechanical Tests

Mechanical strengths including modulus of rupture (MOR) were determined established upon the ASTM C133-97 in a universal testing machine [24].

2.3.3. Apparent Porosity and Bulk Density Measurement

Bulk density and apparent porosity were measured by the Archimedes procedure based on the ASTM C20-97 [25] using formula (3) and (4):

$$B \cdot D = \frac{W_1}{(W_3 - W_2)} \quad (3)$$

$$A \cdot P = \frac{W_3 - W_1}{(W_3 - W_2)} \quad (4)$$

Where $B.D$ (in g/cm^3) is the bulk density, $A.P$ is the apparent porosity (in %) and W_1, W_2 and W_3 are the masses of the dry, immersed and soaked test specimen in that order.

2.3.4. Microstructure Analysis

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

4. RESULTS AND DISCUSSION

The flowability values of the alumina castable without nano-titania and the one containing 0.4 *wt.%* nano-titania are shown in Fig. 1. It can be seen that in the castable without nano-titania, the flowability increases with the addition of 0.13 *wt.%* dispersing agent and then it decreases. Such behavior in the presence of the dispersant has already been verified. It should be noted that the addition of the dispersing agent results in higher dispersion of fine particles in the castable mainly due to the initial increase of electrostatic/electrosteric repulsion forces [18, 26]. After reaching an optimum value, however, further addition of the dispersant will develop ionic strength which detrimentally affects the castable flowability [26]. The novel phenomenon observed in this research corresponds to the flowability behavior of the alumina castables containing 0.4 *wt.%* nano-titania.

As can be seen in Fig. 1, the castable containing nano-titania with low amounts of the dispersant (i.e. up to 0.13 *wt.%*) has yet insufficient flowability so that it is lower than that of the one having no nano-titania. By increasing the amount of the dispersant up to 0.20 *wt.%*, the flowability increases and reaches its maximum value. It seems that higher amounts of the dispersing agent are needed to disperse the nanoparticles because of their very high surface area. The increase of the castable flowability using higher amounts of the dispersant may be related to the electrostatic mechanism. In fact, nanoparticles need to more quantities of dispersant molecules surround them.

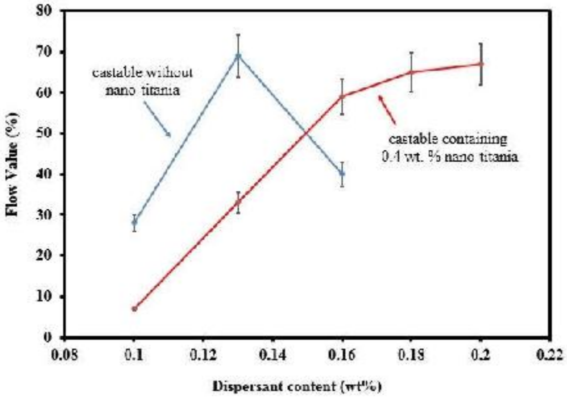

Figure 1. Flowability behavior of alumina castable without and with 0.4 *wt.%* nano-titania

Figure 2 shows the mechanical strength of the castables without and with 0.4 *wt.%* nano-titania. The highest strength for the castable having no nano-titania was obtained for the sample containing 0.13 *wt.%* dispersing agent. It can be concluded that the higher flowability of this sample (according to Fig. 1) results in less entrapment of the voids during sample preparation. Therefore, lower porosity and higher strength will be obtained after the preparation step. It should be mentioned that it was not possible to test the mechanic strength of the castable containing 0.1 *wt.%* dispersant because its flowability was too low to fill the mould. As can be seen in Fig. 1, the strength of the castable containing 0.4 *wt.%* nano-titania and optimum amount of the dispersant (i.e. 0.2 *wt.%*) increases up to 1.5 times more than the one without nano-titania.

The effect of nano-titania in the presence of an optimum amount of the dispersant on the bulk density (B.D.) and apparent porosity (A.P.) of the castable is illustrated in Fig. 3. According to the results, the porosity increases by adding nano-titania which in turn decreases the bulk density of the castable. On the other hand, the castable containing 0.4 *wt.%* nano-titania showed very higher strength in spite of their lower bulk density.

Strengthening of the refractory castable related to cement hydration behavior. With the addition of TiO_2 nanoparticles, no new hydrate was generated in the cement pastes. However, it has been recently shown that the diffraction peaks of the hydration product related to the cement pastes containing TiO_2 nanoparticles compared to the ordinary ones were more intense [27]. The specimen having TiO_2 nanoparticles showed a comparatively denser microstructure with the closely bonded gels. TiO_2 nanoparticles also had the ability to accelerate the cement hydration [27].

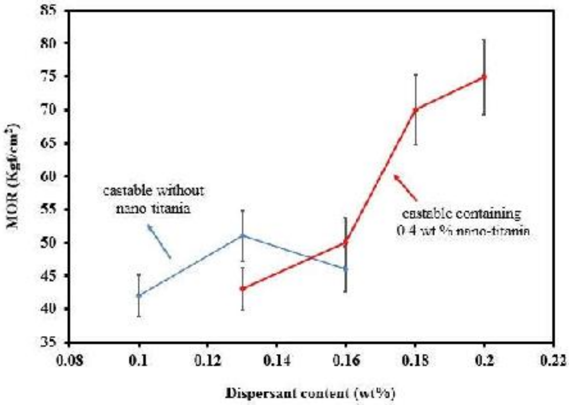

Figure 2. Mechanical strength of alumina castables without and with 0.4 *wt.%* nano-titania

Chen and coworker [28] have reported that the addition of the nano-TiO_2 powders significantly improves the hydration rate and degree of the cementitious materials at early ages. The acceleration of the hydration rate and change of the microstructure also affects the physical and mechanical properties of the cement-based materials. It was concluded that the nano-TiO_2 acts as a catalyst in the cement hydration reactions [28].

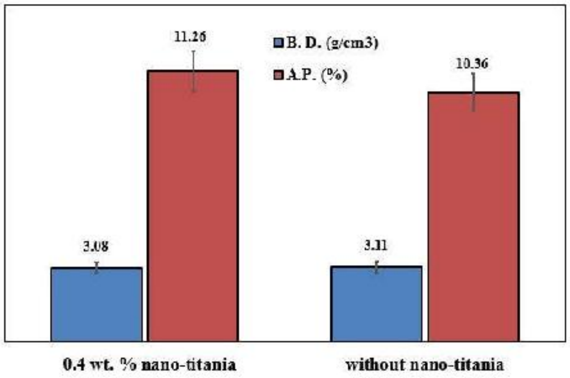

Figure 3. Bulk density and apparent porosity of alumina castables without and with 0.4 *wt.%* nano-titania

Figure 4a indicates the high magnification image of the castable containing nano-titania and 0.13 *wt.%* dispersant. Figure 4b presents the EDX analysis of the selected area of Fig 4a. Figure 4c shows the high

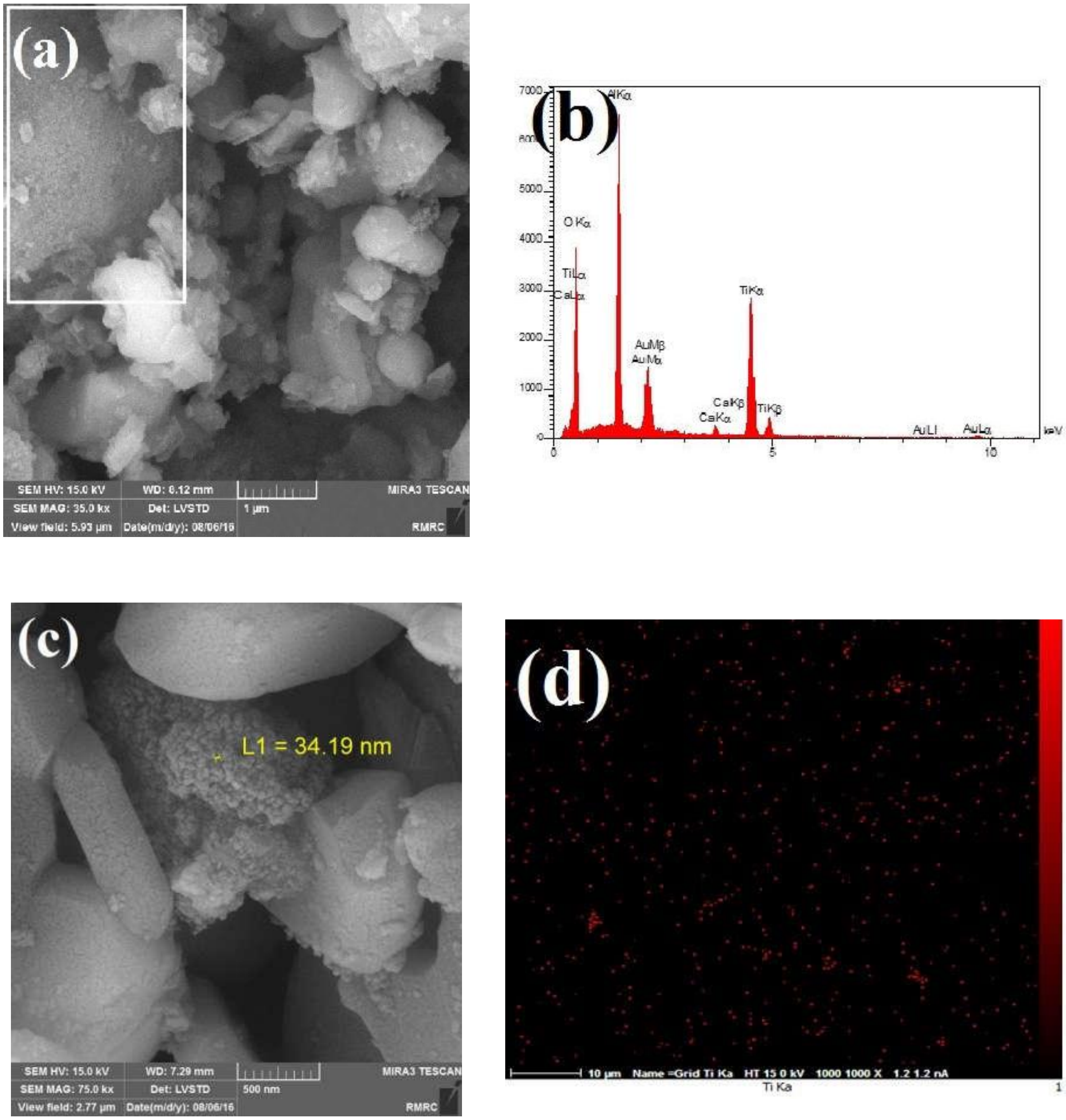

Figure 4. Microstructure images of castables containing nano-titania in the presence of 0.13 *wt.%* (a) and 0.20 *wt.%* dispersant (c), EDX analysis of the area shown by rectangular (b), and X-ray map of titanium obtained for the image shown in c (d)

magnification image of the castable containing nano-titania with 0.20 *wt.%* dispersant. The distribution of the Ti can be related to the presence of the titania nanoparticles in the sample (X-ray map in Fig. 4d). It can be observed that the nano-titania particles in the sample containing 0.13 *wt.%* dispersant are agglomerated and not distributed uniformly in the structure of the castable. While in the sample containing nano-titania, by increasing the amount of the dispersant up to 0.20 *wt.%,* the distribution of the nano-titania particles is improved and they are less agglomerated. The results are in accordance with [29]. According to Lee et al. [29], the size of the nanoparticles and dispersibility are critical factors in determining the hydration rate.As it was mentioned above, the alumina castable containing nano-titania had higher strength than the one without nano-titania. This can be explained by the fact that when the optimum amount of the dispersant is used, nano-titania particles exhibit an improved dispersion in the castable structure, so, they can more efficiently act as a catalyst in the cement hydration reactions and result in higher strength. Otherwise, nano-titania particles become agglomerated owing to their very high surface area, and they not only cannot be distributed uniformly but also decrease the flowability of the castable because of higher water uptake.

5. CONCLUSIONS

1) The amount of the dispersant should be adjusted relative to the amount of the nanomaterial used in the formulation.
2) High alumina castables containing 0.4 *wt.%* nano-titania need 0.2 *wt.%* dispersant while the optimum amount of the dispersant in castable without nano-titania is equal to 0.13 *wt.%.*
3) The main factor in increasing the strength of the castables containing nanoparticle is the proper distribution of them in the castable microstructure and voids.

6. ACKNOWLEDGMENTS

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