

## BEHAVIOUR OF ALUMINA-SPINEL SELF-FLOWING CASTABLES WITH NANO-ALUMINA PARTICLES ADDITION

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*The purpose of this study is to determine the influence of nano-alumina particles on the self-flow characteristics of alumina-spinel self-flowing castables. For this reason, the self-flow characteristics such as; self-flow value and working time of the alumina-spinel castables with different amount of nano-alumina particles have been studied. Also, the mechanical properties and microstructure of these castables have been studied. For the study of nano-alumina ( $d_{50} = 4.3 \text{ nm}$ ) addition on self-flow characteristics and other properties of these castables, reactive alumina is substituted by nano-alumina powder in 0-4 wt.% range. The results show that the nano-alumina particles have great effect on the self-flow characteristics and mechanical strength. With increase of nano-alumina particles in castable composition, the self-flow value and working time tends to decrease and cold crushing strength is enhanced at all temperatures. By use of 1.5 wt.% nano-alumina contents in the castable composition, the alumina-spinel self-flowing castable with adequate working time and very high mechanical strength can be obtained.*

### INTRODUCTION

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 can be improved if one can favorably tailor the interaction of nano-phases with the other particles [1, 2]. The self-flow castables are one of the interesting fields for use of nano-particles in the refractory castables. Self-flow castables are characterized by their consistency after mixing, which allows them to flow and de-air without the application of external energy (i.e., vibration). It is easily recognized that the particle size distribution (PSD) of the castables is an important factor in improving the flow ability of the mix. The fine and ultra-fine particles will increase the distance between aggregate particles and improve flow ability. The main advantages of self-flowing castables in comparison with vibration castables are flowing and densifying without any external force, installation easier and less dependant on the skill and the carefulness of the workers, fill complicated or narrow space, noise-free, saving man-power, time and vibration facilities and good service performance.

Applications such as monolithic ladle lining, where pump ability of the refractory material is critical for quick and easy installation, have strongly influenced the use of self-flowing castables. Hence, alumina-spinel self-flowing castables have been used as steel ladle lining below the slag line because of increasing labor costs and the severe secondary steel-making environment in the ladle [3-5].

The present work describes the effect of nano-alumina particles, which are the extremely fine particles, on the self-flow value, working time, cold crushing strength and microstructure of alumina-spinel self-flowing castables.

### EXPERIMENTAL

#### Raw materials and composition

The castable composition used for alumina-spinel self-flowing castable is listed in Table 1. Also; the chemical composition of raw materials used for this study is shown in Table 2. The used nano-alumina powder (as reactive type) in this study is 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 self-flow characteristics and other properties of these

castables, reactive alumina is substituted by nano-alumina powder in 0-4 wt.% range. The TEM micrograph of nano-alumina consumed is shown in Figure 1.

The Particle size distribution was calculated from the Andraesen's equation (1) as follow:

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

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 should be in the range 0.21-0.26. The *q* = 0.24 was considered for the present study, with respect to our previous investigations [5]. The particle size distribution of the castable with this value of *q* and without nano-alumina particles is represented in Figure 2.

Self-flow measurement

Self-flow value 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 Equation (2):

$$\text{Self-flow (\%)} = (D_2 - D_1) \times 100 / D_1 \quad (2)$$

where *D*<sub>2</sub> is the final average diameter after removal of mould and *D*<sub>1</sub> 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 [12].

Table 1. Raw materials and composition of the studied alumina-spinel 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 μm		
Spinel .....	White Circle, Spinwhite 78	23
..... 0-0.5 mm		
Reactive.... d50 = 1.90 μm	Alcoa Chemicals, CTC-20	11
Alumina		
Cement .....	Lafarge, Secar-71	6
d50= 3.03 μm		
Deflocculant .....	S.K.W., Castament FS 10	0.1

Table 2. Chemical composition of used raw materials.

Oxide (wt.%)	Tabular Alumina	Spinel	Reactive Alumina	Cement
Al <sub>2</sub> O <sub>3</sub>	99.4	76-77	99.8	72.7
Na <sub>2</sub> O	0.36	0.15	0.06	0.19
CaO	0.05	0.3	0.02	26.5
MgO	0.1	22-23	0.02	0.09
SiO <sub>2</sub>	0.02	0.06	0.03	0.2
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.1	0.03	0.01

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

Al <sub>2</sub> O <sub>3</sub> (%)	Specific surface area (m <sup>2</sup> /g)	Crystal phase	Loose density (g/cm <sup>3</sup> )	Average grain size (nm)
99.99	35	α	0.33	43

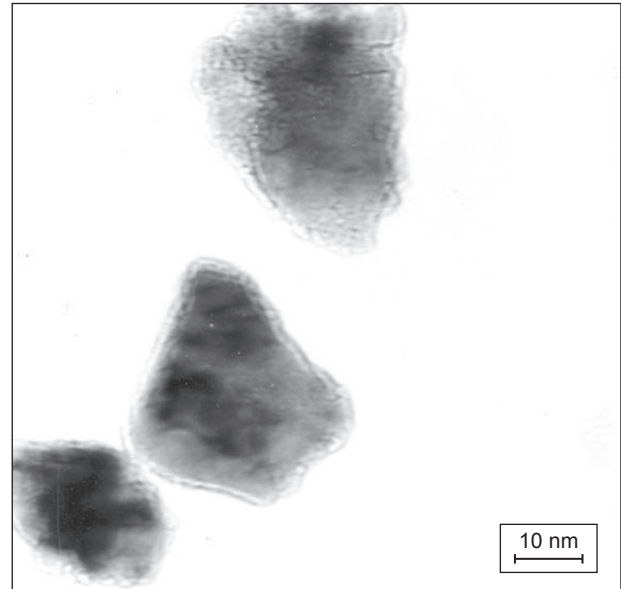


Figure 1. TEM image of nano-alumina particles.

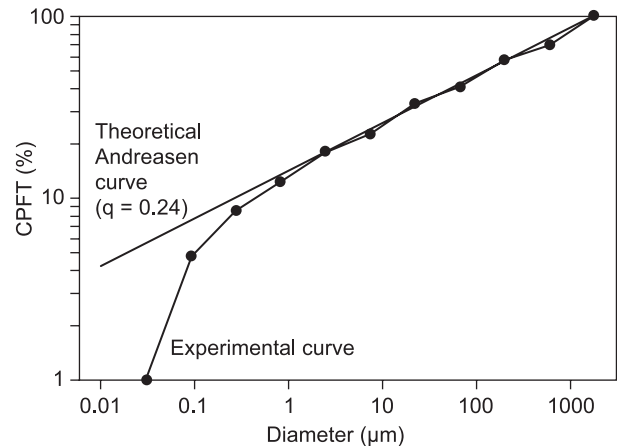


Figure 2. Theoretical and experimental particle size distribution of self-flowing castable without nano-alumina particles.

### Castable preparation

In order to make the nano powder distribute evenly throughout the mixture, firstly, nano-alumina 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 and water and cast in molds ( $7 \text{ cm}^3$ ), wrapped in plastic and cured at room temperature for 24 h. 5.1 wt.% water amount is added constantly for mixing of castables for all compositions. After curing, the specimens were taken out of the mold, dried for 24 h at  $110^\circ\text{C}$  and fired at  $1000$  and  $1500^\circ\text{C}$  for 3 h. The cold crushing strength (C.C.S) of the specimens was measured after drying and firing at each temperature. Cold crushing strength was performed in accordance with ASTM C 133-97. Mechanical strength data presented in this article correspond to an average of five specimens for each composition and at each firing temperature.

### Microstructural evaluations

The cross sections of samples after drying and firing at  $1500^\circ\text{C}$  were evaluated by scanning electron microscope (SEM). Microstructural evaluations were performed using Cambridge S-360 SEM at 10-20 kV.

## RESULTS AND DISCUSSION

### The influence of nano-alumina on the self-flow characteristics

Figure 3 shows the effect of nano-alumina particles content on self-flow value of the alumina-spinel castable as a function of time. The results indicate that with increase of nano-alumina particles in castable composition, self-flowing value tends to decrease.

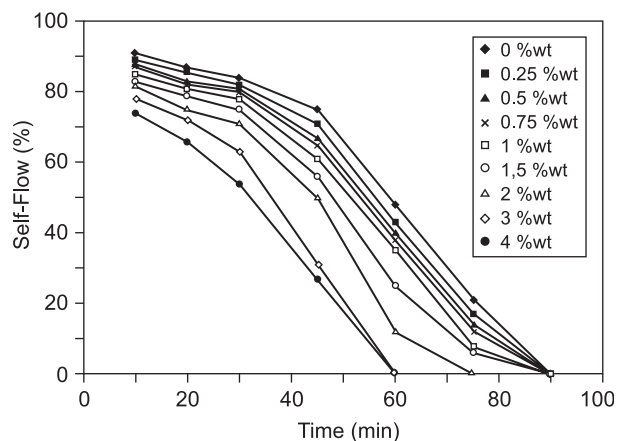


Figure 3. The influence of nano-alumina particles on self-flow value of alumina-spinel castable as a function of time.

The nano-alumina particles have high surface area that leads to attraction forces between particles. These attractions between nano-alumina 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. From Figure 3, one can see that the addition of nano-alumina 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. The proper working time long enough for appropriate placement of castables is actually between 30 to 100 min. Therefore, castables containing up to 1.5 wt.% nano-alumina particles will have adequate working time and can be installed properly.

### The influence of nano-alumina on mechanical properties and microstructure

The effect of nano-alumina particles on cold crushing strength of the castable as a function of sintering temperature is shown in Figure 4. It can be seen from Figure 4 that cold crushing strength is enhanced considerably with the increase of nano-alumina particles content (especially higher than 0.5 wt.%) after drying and firing at all temperatures. A very important characteristic is the strength development of a castable. In practice the higher cold crushing strength leads to the higher erosion resistance of castable and then more life time. Hence, the alumina-spinel castables must have cold crushing strength values above 60, 60 and 150 MPa at  $110$ ,  $1000$  and  $1500^\circ\text{C}$  respectively. With respect to results, if the nano-alumina particles content in castable composition be used higher than 0.5 wt.%, the high-strength alumina-spinel castable will be obtained. By using of

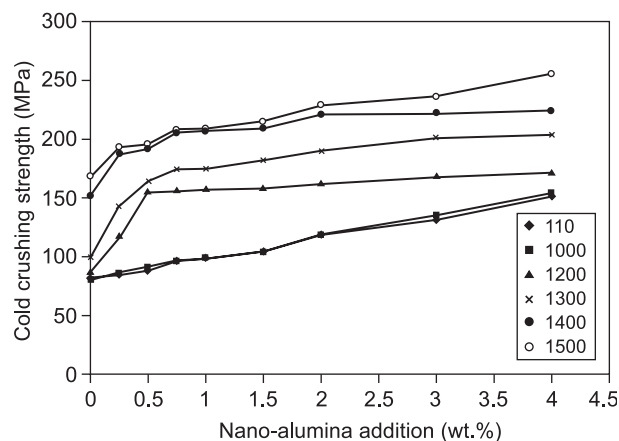


Figure 4. The influence of nano-alumina particles on the C.C.S of samples as a function of firing temperature.

nano-alumina particles instead of reactive alumina in the castable composition, the packing density can be increased hence, the mechanical strength.

On the other hand, this Figure shows that nano-alumina particles content over than 0.5 wt.% has great effect on the strength increasing at 1200°C and higher. This means that sintering of the refractory castable occurred in the lower temperature when nano-sized particles in the composition are increased (higher than 0.5 wt.%). Adding nano-alumina in high alumina refractory castables, the solid phase sintering of the nano-sized particles occurred in the lower temperature because of the difference of surface area and special surface area energy between the matrix particles and the nano-alumina particles.

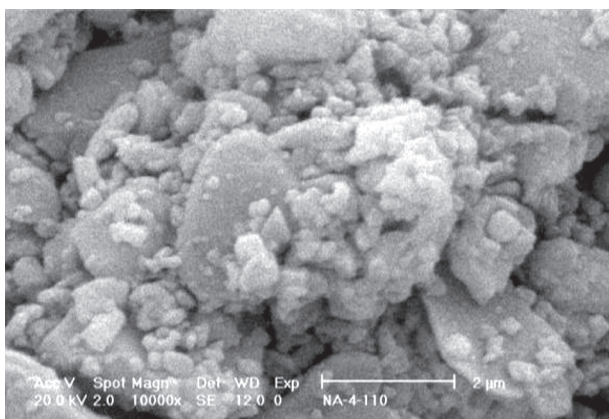


Figure 5. SEM photomicrograph of alumina-spinel castable containing 4 wt.% nano-alumina particles after drying.

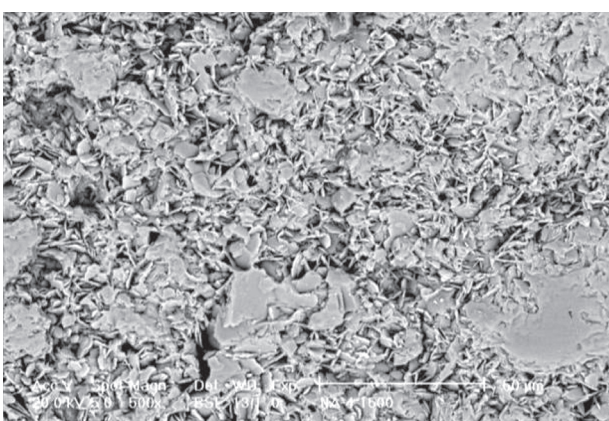


Figure 6. SEM photomicrograph of alumina-spinel castable containing 4 wt.% nano-alumina particles after firing at 1500°C.

Figures 5 and 6 demonstrate the microstructure of alumina-spinel castable containing 4 wt.% nano-alumina particles after drying and after firing at 1500°C. Figure 5 shows high packing microstructure, in which the finer particles occupy the voids between the coarser particles, enabling a decrease in the porosity and increase of the density and mechanical strength. It can be seen from Figure 6 that fine particles in the matrix has grown as flake shape and interlocked. This led to increasing of strength at high temperatures. When the nano-alumina particles come into contact with the matrix in the process of sintering, the transference will happen from nano-sized and fine particles to big particles because of the difference of curvature radius. In this process, the particles coarsening occurred, which made the surface energy decreased.

## CONCLUSIONS

This study confirmed the strong influence that extremely fine alumina particles exert on the properties of self-flowing alumina-spinel castables. An attraction between nano-alumina particles and other fine particles in the castable matrix appears to promote lower flow ability in this system. Also, the addition of nano-alumina particles in the castable composition decrease working time. The results also indicate that the nano-alumina particles have a great effect on the green and firing strength of these castables. Adding nano-alumina in alumina-spinel castable, the solid phase sintering of the nano-sized particles occurred in the lower temperature because of the difference of surface area energy between the matrix and the nano-alumina particles. The best results are obtained with 1.5 wt.% nano-alumina addition which defines the self-flowing castable with sufficient working time and high mechanical strength.

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