Update on the Use of Spherical Particles in NCC

B. Myhre, H. Peng

Dedicated to the 10th Anniversary of refractories WORLDFORUM

No-cement castables have the last few years become increasingly popular, particularly since the introduction of SioxX®-Zero (microsilica-gel bond) and DAReS (Dry Advanced Refractory System) binder technologies. In parallel with the development of these binder systems, development of highly specialised raw materials has progressed, and the current paper focuses on the use of spherical alumina for no-cement applications in general, and silica-free corundum-spinel systems in particular.

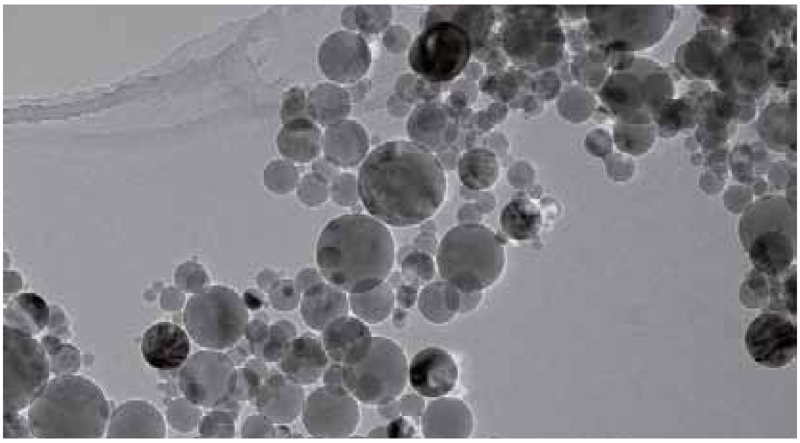

Fig. 1 Microalumina TEM micrograph

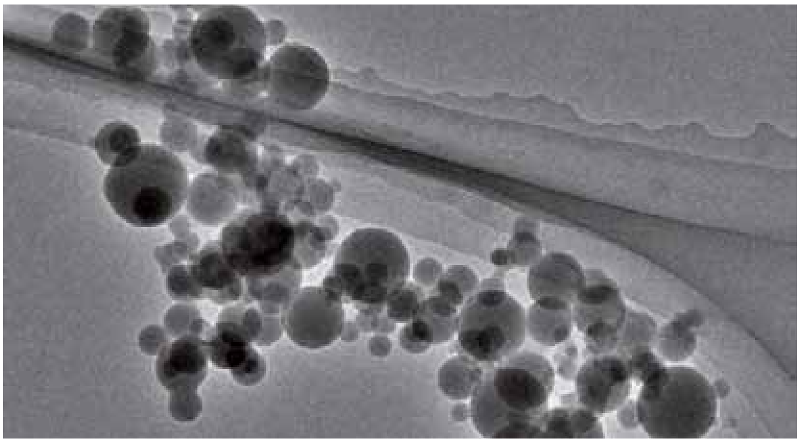

Fig. 2 Elkem Microsilica 971, TEM micrograph

1 Introduction and background

"The rheology of a castable has been demonstrated to be influenced by the particle size distribution of the mix, so that in practice, self-flowing or vibratables can readily be designed based on their total PSD [1]. Self-flow is facilitated if the particle size distribution contains an increased amount of fine particles."

This is quoted from the "Introduction and Background" of a presentation at the ALAFAR meeting in 2012 [2] that introduced the use of spherical, submicron alumina particles for the first time. The focus was on the dilatancy that is experienced with silica-free alumina castables. It was demonstrated that dilatancy could be avoided if spherical submicron particles were used as superfines.

The shape of the ultrafine particles was found to have a decisive influence on the tendency to dilatancy. A spherical shape as represented by microsilica and spherical microalumina (from here on denominated as microalumina) almost eliminated dilatancy, whereas plate-like elementary particles as seen in reactive alumina seemed to promote dilatancy. This effect was particularly obvious with narrow PSD of the reactive alumina.

The paper from ALAFAR 2012 focused on submicron alumina in castable mixes containing among others calcined alumina.

Later, a coarser grade of spherical alumina has become commercially available. This alumina has roughly the same size as calcined alumina and is available from Elkem as AloxX-Spheres (from here on called spherical alumina). At UNITECR in 2015 [3] its flow enhancing properties was demonstrated, producing castables that could easily be placed with water levels down to 2,7 %.

Bjørn Myhre, Hong Peng
Elkem Silicon Materials
Kristiansand
Norway

Corresponding author: *B. Myhre*
E-mail: Bjorn.Myhre@elkem.no

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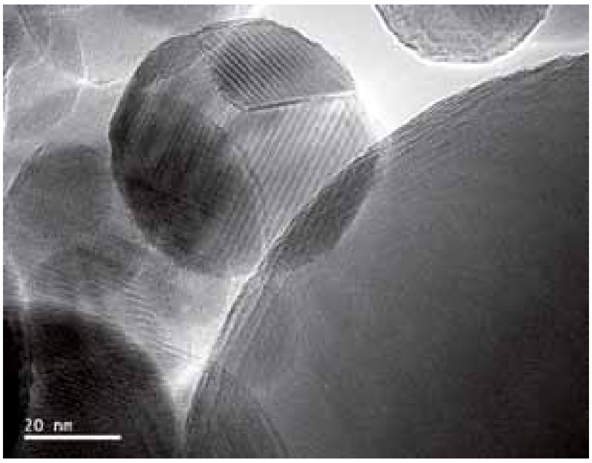

Fig. 3 **Microalumina close-up: most of the crystals are twinned, showing mirror planes as interfaces between the twin domains; faceted small crystal**

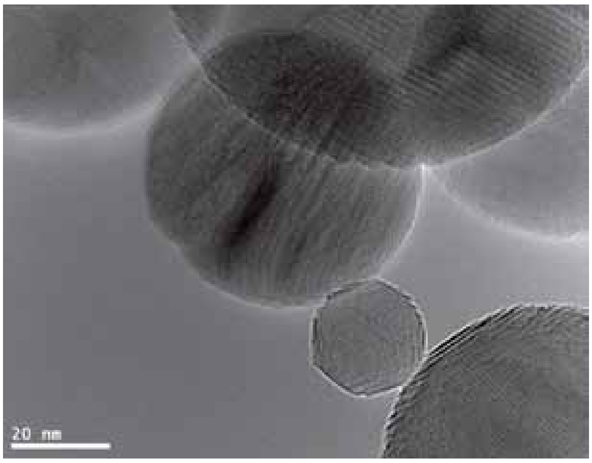

Fig. 4 **Microalumina close-up: at a closer view some of the "spherical" crystals show the beginning of faceting; the curved surfaces show small steps**

Both microalumina and spherical alumina is today available; microalumina is essentially submicron, extending from normally 0,01–1 µm. Coarser sizes, roughly 100-times larger, from 1–100 µm, are covered by the Spherical alumina. The submicron sizes will reduce or remove dilatancy that can be a problem in microsilica-free alumina castables, the coarser ones have several beneficial properties, improved flow is perhaps the most obvious. Positive effects as binder systems have also been reported [4], even though the exact mechanism behind is not fully understood.

2 Characterisation

2.1 Microalumina

Fig. 1–2 show TEM micrographs of microalumina and for comparison also of Elkem Microsilica 971 at the approximate same magnification. The similarity is striking and based on these TEM micrographs alone, it is difficult to differentiate between the two microfine powders.

However, at higher magnification (HR-TEM), it is seen that the microalumina has a stepped surface while the microsilica has not. This is a clear indication that the microalumina is crystalline while the microsilica is amorphous.

To the authors fascination, they found that most microalumina crystallites (Fig. 3–4) are twinned, and many are monocrystals: spherical monocrystals! Some of them show tendencies to faceting and the curved surfaces are created by steps in the crystal lattice.

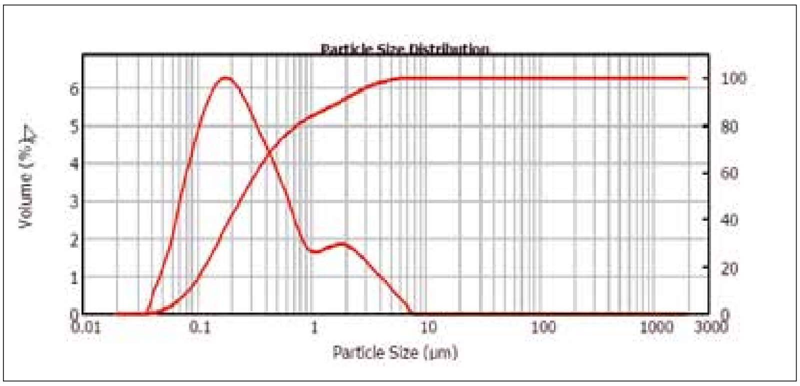

Fig. 5 **Typical PSD of microalumina**

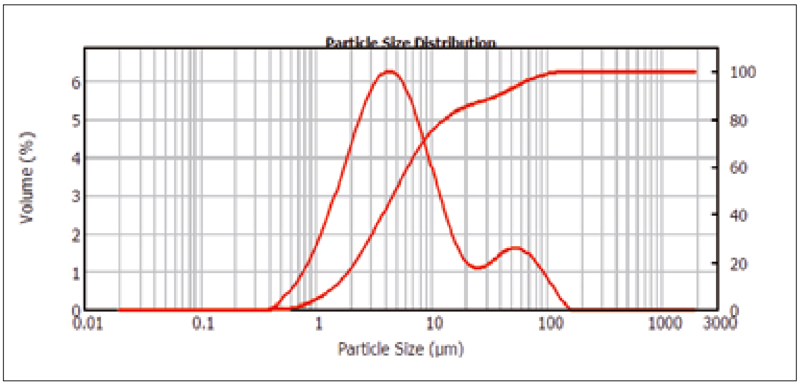

Fig. 6 **Typical PSD of spherical alumina**

2.2 XRD of microalumina

The exact structure is so far unknown, but the specific gravity has been found (He-pycnometer) to be approximately 3,59 g/cm³.

Somewhat surprisingly, neither alpha-alumina (the thermodynamically stable polymorph) nor the most common metastable gamma-alumina match the XRD powder patterns.

Alpha-alumina cannot be identified and only some of the reflections are in agreement with the gamma-phase.

Common for all the matches are lattice parameters of approx. 800 pm and an orthogonal crystal system.

From high-resolution TEM nearly tetragonal projections with distances of approx 800 pm are found.

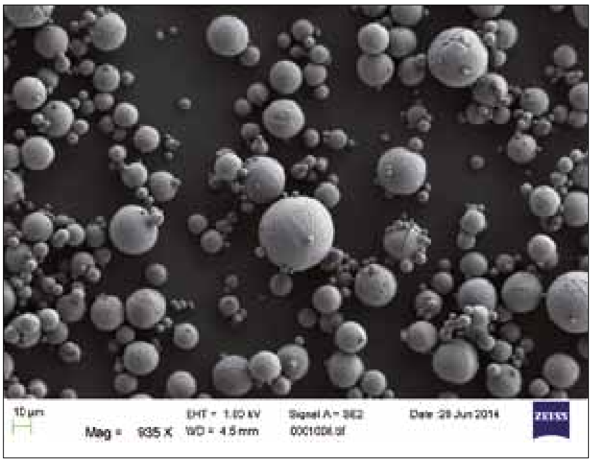

Fig. 7 Spherical alumina: this alumina quality contains both small and larger spheres

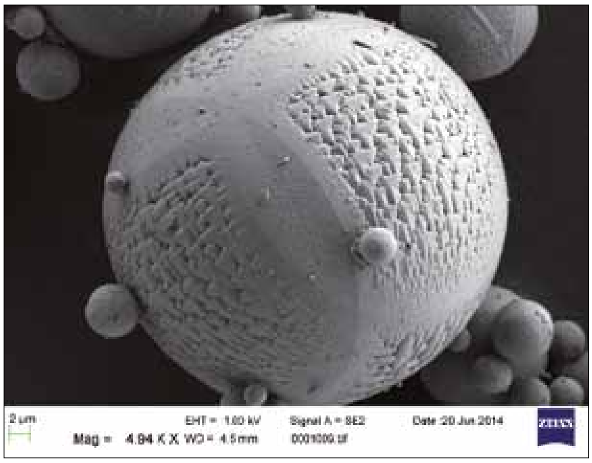

Fig. 8 Spherical alumina close-up of the textured surface often found on the coarser spheres

2.3 Spherical alumina

Spherical alumina is produced in several size classes, but mostly in sizes similar to calcined alumina. This means that the size of a typical Spherical alumina sphere is 10–100 times bigger than the particles of microalumina. Fig. 5–6 are PSD of micro-alumina and spherical alumina respectively. SEM pictures of spherical alumina are found in Fig. 7–8. The spheres are compact and the crystallographic make-up is alpha-alumina, or corundum, with a SG of approximately 3,9 g/cm^3.

3 Use of novel spherical aluminas

3.1 Effect on placement properties

3.1.1 Dilatancy

The particle shape has a strong impact on placement properties of castables, particularly if the castable has "shear-thickening tendencies", also known as dilatancy. An early investigation was presented at ALAFAR in Cancún (2012) [2] that showed how silica-free castables could be transformed

Tab. 1 Alumina based castables: numbers are parts (weight) or grams, and do not have to sum up to 100

	Alumina	Microsilica	Microalumina
CA-cement (70 %)	0,5	0,5	0,5
FA 3–5 mm	10	10	10
FA 0,5–3 mm	31	31	31
FA 0– ,0,5 mm	15	15	15
FA <74 µm	19	19	19
Calcined alumina	12,5	12,5	12,5
Reactive alumina	12		
Elkem Microsilica 971U		6,8	
Microalumina			10,9
PCE-dispersant 1	0,1		0,1
PCE-dispersant 2		0,05	
Water	4,25	4,25	4,25
Flow (ASTM-cone) Self-flow [%]	108	136	132
Vibra-flow [%]	128	>160	152
Wet-out time [s]	110	60	20

Fig. 9 Hammer hitting the alumina castable: approx. 0,03 s after impact

Fig. 10 Alumina castable: approx. 0,1 s after impact

Fig. 11 Alumina castable: approx. 0,25 s after impact; hammer bouncing back; due to dilatancy just a shallow indentation from the hammer blow is observed, no penetration

Fig. 12 Microsilica castable: hammer penetrating the castable, approx. 0,03 s after impact, no signs of dilatancy

Fig. 13 Microalumina castable: approx. 0,03 s after impact, hammer deeply sunken into the castable, dilatancy is almost non-existent; the castable surface is curved due to high surface tension

from dilatant to "easy to handle" by substituting the plate-like reactive alumina with a spherical microalumina. In that paper, all the submicron particles were substituted and this had a very convincing effect, yielding a silica-free castable with placement properties very similar to its microsilica-containing equivalent.

The rheological differences were demonstrated using the Hammer Test, a test in which the castable was subjected to a heavy blow with a hammer while a film was recorded. Still pictures were then taken from the film at 0,03 s and 0,1 s after impact, and also after 0,25 and 0,3 s for the castable without spherical alumina nor microsilica. This castable served as reference and contained an equivalent volume of the more plate-like reactive alumina. Tab. 1 shows the castable compositions.

The following pictures show the effect of hammering into the alumina castables, i.e. the castable using reactive alumina as finest component (Fig. 9–11), microsilica castable (Fig. 12) and "microalumina" castable (Fig. 13).

At UNITECR 2015 in Vienna [3] it was demonstrated that by using Spherical alumina castables with ultra-low water additions could be made. Tab. 2 shows the compositions from the paper.

Tab. 2 Castable compositions for ultra-low water addition

Component [Parts]	1	2	3	4	5
Elkem Microsilica 971	8	8	8	8	8
CAC 70 %	0,5	0,5	0,5	0,5	0,5
Hydr. alumina	0,5	0,5	0,5	0,5	0,5
Tabular alumina:					
8–15 mm					20
2–5 mm	24	24	24	24	24
1-2 mm	10	10	10	10	10
0,5–1 mm	8,5	8,5	8,5	8,5	8,5
0,2–0,6 mm	14	14	14	14	14
0–0,2 mm	25	25	25	25	25
Calc. alumina	9,5	19,5			
Spherical alumina			9,5	19,5	19,5
Dispersant	0,05	0,05	0,05	0,05	0.05
Total [parts]	100,05	110,05	100,05	110,05	130,05
Water [parts]	3,55	3,55	3,55	3,55	3,55
Water [%]	3,55	3,23	3,55	3,23	2,73

The resultant flow and porosity are given in Fig. 14–15, and show that it is possible to make castables with less than 10 % porosity after drying and still have a good self-flow. The porosity was measured after drying at 110 °C. The compositions are of the NCC-type (microsilica-gel bond), and experience have shown that for this type of (laboratory) samples porosity after drying at 110 °C is close to the porosity measured after firing at higher temperatures.

At UNITECR 2017, the effect of both microalumina and spherical alumina were reported for cement-free Al_2O_3–MgO compositions. The MgO content was 3 % and was added as deadburned MgO fines. Compos-

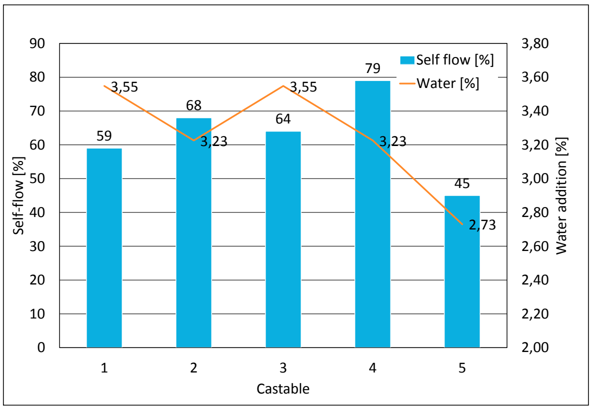

Fig. 14 Flow, porosity and water addition for the castables in Tab. 2

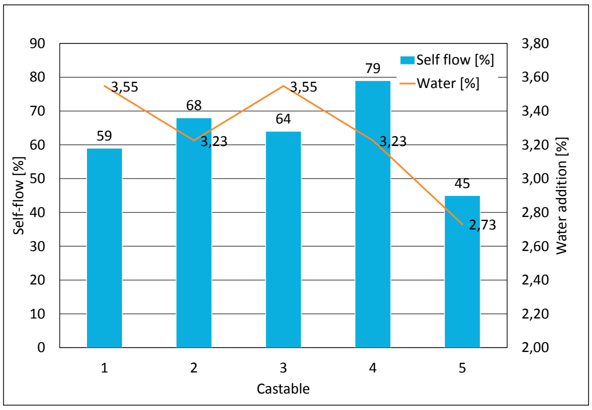

Fig. 15 Porosity and water addition for the castables in Tab. 2 after drying

Tab. 3 **Castable composition for making NCC corundum-spinel castables**

Component	Corundum-Spinel Castable
MgO (–325 mesh)	3
Additives	1
Tabular alumina:	79
Reactive alumina (submicron)	8–0
Calcined alumina	10–0
Microalumina	0–8
Spherical alumina	0–10
Water	4,09

ition is given in Tab. 3. The work was later presented in more detail at the Annual Symposium on Refractories in St. Louis in 2018. Here the effect of the spherical powders was thoroughly investigated with respect to both placing properties and hot strength, as well as RUL.

It was quickly discovered that unless microalumina was added in the recipe, dilatancy was to be expected. In Fig. 16–17, these dilatant castable mixes are indicated by red triangles. It was found (Fig. 16) that microalumina addition reduced the wet-out time significantly. Not unexpectedly, also flow was positively influenced (Fig. 17–18). All castables were cured at >95 % RH and 22 °C ± 2 for 24 h before demoulding and green-strength measurement. In Fig. 17, the self-flow, green strength (MOR), and Hot-MOR at 1200 °C are shown, also here red triangles indicate dilatancy.

The green-strength is unfortunately on the low side but can be improved if spherical alumina is added at a level above 5 %.

At 1200 °C, the improved reactivity of the microalumina as compared to reactive alumina is shown as an increase in Hot-MOR, an effect probably attributable to the metastable crystal structure of the microalumina. Another possible use of microalumina could be in bricks. The increased reactivity as compared to reactive alumina has been found to reduce firing temperature in alumina brick by 50–100 °C (1–2 % microalumina, proprietary information, details lacking).

With spherical alumina a slightly lower Hot-MOR is often measured. This is believed to be connected to microcrack generation that is considered to give improved thermal behaviour. This has been seen for compositions used in steel-making applications

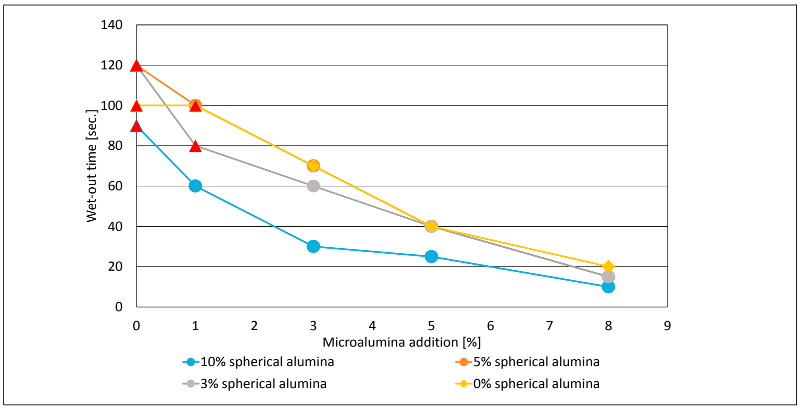

Fig. 16 **Wet-out time for the corundum-spinel castables as a function of content of spherical particles: there is a profound effect on wet-out by replacing reactive alumina with microalumina. Also, dilatancy is influenced heavily. Red triangles are indicative of casting difficulties, like dilatancy; hence, the castables without microalumina additions (those indicated with red triangles) can in practise not be made at the current water addition level**

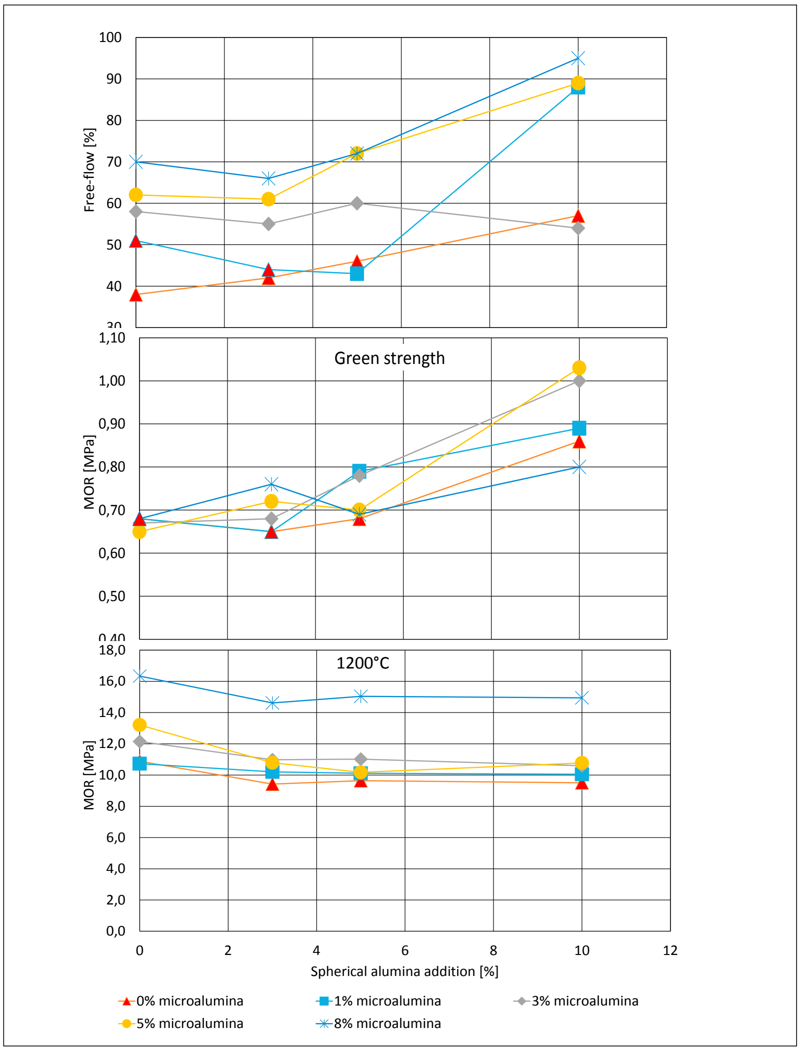

Fig. 17 **Flow, green-strength (MOR), and Hot-MOR after 24 h firing at 1200 °C of the CC corundum-spinel castables, showing the effect of spherical particles on self-flow and the improvement of the green strength by the replacement of calcined alumina by spherical alumina**

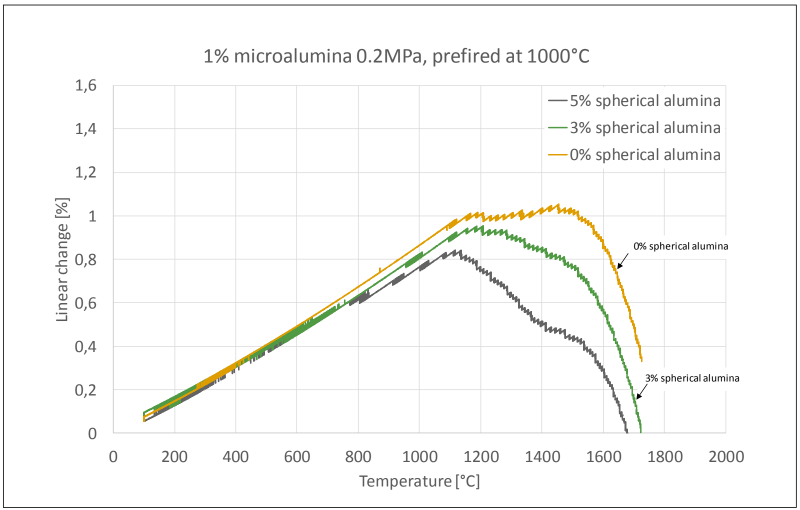

Fig. 18 RUL of alumina–MgO samples with 1 % microalumina pre-fired at 1000 °C prior to testing; samples with 0, 3 or 5 % spherical alumina respectively

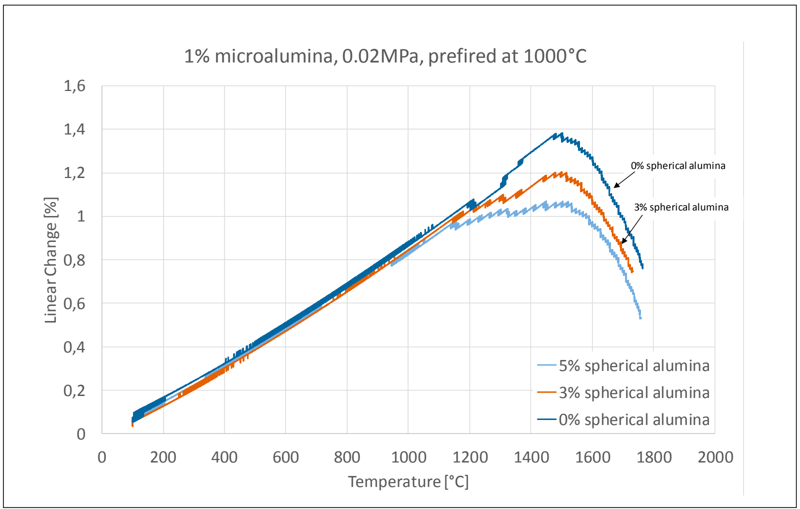

Fig. 19 Assisted sintering of alumina–MgO samples pre-fired at 1000 °C prior to testing; samples with 0,3 or 5 % spherical alumina respectively, and 1 % microalumina

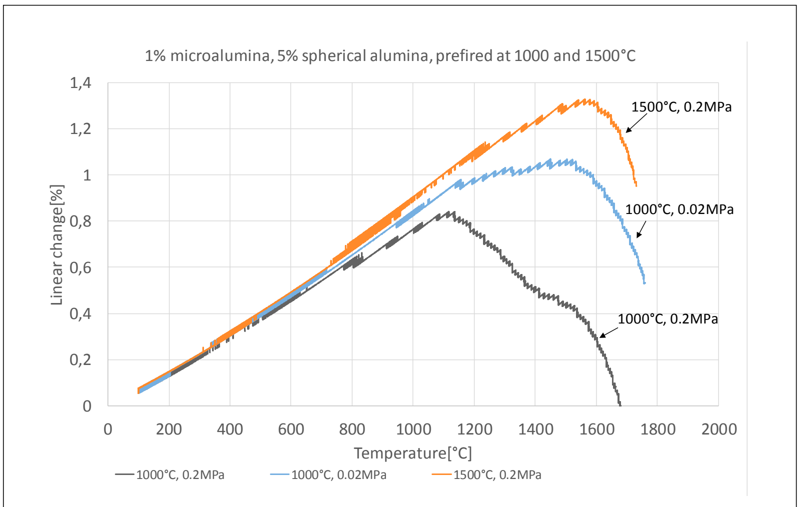

Fig. 20 RUL of alumina-MgO samples with 1 % microalumina pre-fired at 1000 °C, and 1500 °C prior to testing; load 0,2 MPa and 0,02 MPa; samples with 5 % spherical alumina

(proprietary), but is neither well understood nor documented.

3.1.2 Refractoriness Under Load and assisted sintering

Selected compositions with 1 % microalumina were subjected to Refractoriness Under Load (RUL) testing to assess the high temperature reactions further. First, samples were pre-fired 1000 °C before being placed in the RUL machine at a load of 0,2 MPa. The heating followed a rate of 300 °C/h while recording the height of the samples. Fig. 18 shows the resulting curves for the samples with 0,3 and 5 % spherical alumina respectively. It is seen that increased amount of spherical alumina gives a larger subsidence at lower temperature. One could easily attribute this to liquid formation due to impurities, but in this case the spherical alumina was purer than the calcined alumina it replaced, so liquid formation is very unlikely.

This accelerated subsidence can be caused by liquid formation (due to other reasons than impurities), increased reactivity (sintering) or some other, unknown effect. In an attempt to clarify this, the load was decreased to a level "barely touching", 0,02 MPa. This setup is sometimes called "assisted sintering technique". The RUL measurements were repeated with new samples, but this time with a load of 0,02 MPa (Fig. 19).

Also at this very low load, the effect of the spherical alumina addition is obvious. Increased amounts increase the magnitude of the subsidence at temperatures up to approximately 1600 °C, and lowers the temperature for the onset of the subsidence. This can be attributed to some (unknown) metastable liquid formation, or to increased reactivity. The phenomenon could possibly be linked to the spinel-formation, so to check, similar cement and silica free castables were made without MgO. These almost pure alumina compositions were then subjected to similar tests in the RUL machine.

Also for the MgO-free castables it seems that addition of spherical alumina has some effect on reactivity. Not as pronounced as in the case with MgO and spinel formation, but nevertheless, additions of spherical alumina seems to lower the temperature of the onset of the subsidence. Apparently, the positive effect of the spherical alumina

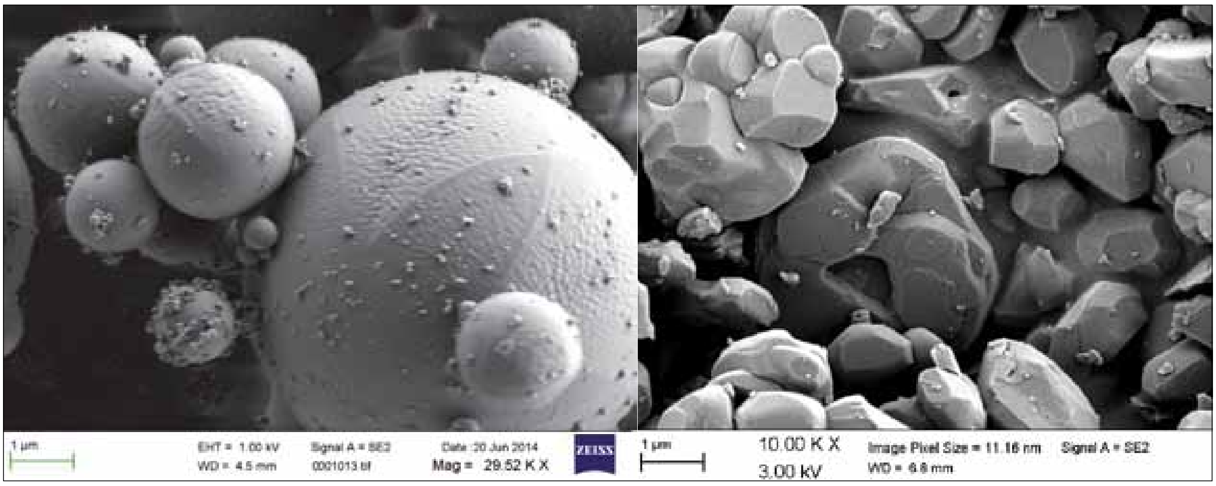

Fig. 21 Comparison of spherical alumina and calcined alumina at approximately same magnification (bar = 1 µm)

is most pronounced for low and moderately low amounts.

The standard conditions for RUL testing involves samples that have been pre-fired to 1500 °C prior to testing. This gives curves without the early subsidence associated with drying, decomposition, mineral formations, etc. that occur during heating of refractory castables. To visualise the differences, Fig. 20 shows three measurements of a sample with MgO and 5 % spherical alumina for three sets of parameters. One was pre-fired at 1500 °C, and two at 1000 °C. The 1500 °C and one of the 1000 °C samples were loaded with the standard 0,2 MPa loading, the other 1000 °C sample had a reduced load of 0,02 MPa.

Based on Fig. 20, it is tempting to propose that the reaction between MgO and Al_2O_3 to give spinel could be responsible for the apparent softening that is observed for castables pre-fired at 1000 °C. This softening is not unexpected as the spinel formation involves transport of matter, particularly MgO from the MgO grains to the Al_2O_3 surfaces where spinel forms. Once spinel is formed, this transport ceases and the apparent refractoriness improves. The early softening by the improved reactivity for spherical alumina containing mixes also disappears upon firing at 1500 °C (Fig. 20). So, what is the reason for this improved reactivity of the spherical alumina? If one compares the spherical alumina with the calcined alumina in a SEM, there are some features that are different. Firstly, the shape, round versus blocky and plate-like. Then it appears that spherical alumina has some dust-like spherical particles attached to the surfaces. These are probably just sticking to the surfaces but may add to the reactivity. Also, the surface differs from calcined alumina. Spherical alumina has a rougher surface than calcined alumina as seen in Fig. 20. Whether this contributes to the reactivity is still an open question.

4 Conclusions

Microalumina and spherical alumina are two novel spherical aluminas that have particle size distributions matching microsilica and calcined alumina. The particles are spherical and are easy to disperse. Rheological behaviour of silica-free castable can be improved, not only by reducing dilatancy, but also by shortening the wet-out time of the castables.

Due to the meta-stable crystallography of the microalumina, increased reactivity is also expected, and found. At 1200 °C the hot-MOR increases with microalumina content, which can be attributed to increased reactivity (sinterability) as compared to reactive alumina (submicron).

Spherical alumina has a demonstrated good flow enhancing effect, increasing self-flow significantly in some cases. Also, the green-strength was considerably improved by increased additions of spherical alumina, an effect that may be connected to the improved flow and possibly the surface roughness of the spherical alumina. There are also strong indications that spherical alumina improves the sinterability of alumina castables by lowering the onset temperature for sintering.

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Interall Srl, Via G. Marinuzzi 38, 41122 Modena, +39059282390
info@interall.it – aluminium2000@interall.it – www.aluminium2000.com