

# Novel Engineered Routes for Advanced $\text{Al}_2\text{O}_3$ -MgO Refractory Castables

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The use of ultra fine particles of alumina and magnesia in  $\text{Al}_2\text{O}_3$ -MgO refractory castables could lead to a well distributed in-situ spinel ( $\text{MgAl}_2\text{O}_4$ ) formation and, then, a better corrosion resistance, a higher volumetric stability and a faster spinel generation. Consequently, adding  $\text{Al}_2\text{O}_3$ , MgO or  $\text{Al}_2\text{O}_3$ -MgO nano-scaled powders is a suitable alternative to attain the above mentioned effects. Nevertheless, although the trend in castables is the increasing use of nano-particles, drawbacks related to their high costs, agglomeration trend and the possibility of particles growth during sintering should not be disregarded. A further and cheaper alternative to speed up the spinel formation is the use of mineralizers, such as  $\text{B}_2\text{O}_3$ . However, the studies published up to now are mainly directed to the spinel powder synthesis instead of spinel-forming castables design, which is also a promising technological route for attaining high-performance  $\text{Al}_2\text{O}_3$ -MgO castables, as long as the refractoriness drawbacks could be kept under control. As the reaction rates are commonly increased through liquid phase formation, thermo-mechanical properties could deteriorate. Therefore, this work addressed the evaluation of which one of these novel routes (nano x mineralizers) would be the most promising to be applied in the  $\text{Al}_2\text{O}_3$ -MgO castable design. A slight advantage was attained adding mineralizers, as they are cheaper, could speed up the aimed reactions, their expansion level can be designed and displayed outstanding hot properties, indicating a greater likelihood for a better general performance during the application in steel ladles.

## 1 Introduction

The addition of fine particles of alumina and magnesia to alumina-magnesia castables could lead to a well distributed in-situ spinel ( $\text{MgAl}_2\text{O}_4$ ) formation throughout the whole

matrix and, as a consequence, a better corrosion resistance. Furthermore, according to Nakagawa et al. [1] and Kiyota [2] the magnesia and alumina grain sizes are of major importance to the overall in-situ spinel

( $\text{MgAl}_2\text{O}_4$ ) expansion. Considering the one-way diffusion from MgO to  $\text{Al}_2\text{O}_3$  during the spinel generation, the reduction of the magnesia grain size leads to lower expansion, due to the formation of smaller pores. This result was previously evaluated by Ide and co-workers [3]. Besides this, the reduction of the alumina grain size could also result in lower expansion, as a consequence of shrinkage during sintering [4, 5].

Taking these aspects into account, Zargar and co-authors [6] analyzed the effect of nano-boehmite addition to the  $\text{MgAl}_2\text{O}_4$  formation, suggesting that the homogeneous microstructure obtained would enhance the expansion control ability. Nevertheless, the successful incorporation of nano-particles into refractory castables is not a straightforward task, due to their high agglomeration. Therefore, attention to dispersion and sintering must be drawn when adding nano-scaled powders [7, 8]. Additionally, despite

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the several efforts carried out in the literature to produce  $MgAl_2O_4$  nano-powders [9 – 11], information regarding to their effect during application to refractory castables is scarce. Consequently, a novel alternative to improve the performance of in-situ spinel-forming castables would be the addition of nano-scaled  $Al_2O_3$ ,  $MgO$  or  $Al_2O_3$ - $MgO$  particles.

Although the addition of nano-materials to these castables could lead to benefits such as a better corrosion resistance, a higher volumetric stability and a faster spinel generation, their costs are considerably high. As a consequence, further alternatives should be explored in order to attain high performance of in-situ spinel castables. In this context, the use of mineralizer compounds (low-melting point temperature substances) could also be a route to speed up the spinel formation. Moreover, as this sort of castables is commonly bonded with calcium aluminate cement, the calcium hexaluminate ( $CA_6$ ) formation takes place [12], leading to further expansion and also better thermal shock and corrosion resistance. Therefore, this reaction could also be speeded up and, as these castables are commonly fired at high temperatures during their use in steel ladles, higher homogeneity would be attained and, thus, their properties would be more suitable

to withstand the harsh application environment.

One of the main possibilities to manage the spinel and  $CA_6$  formation is the use of boron-containing compounds. *Bhattacharya* and co-authors [13] indicated the greatest  $B_2O_3$  ability to mineralize spinel formation, most likely due to a dissolution-precipitation mechanism by the generation of a magnesia-modified boroaluminate glass. Additionally, these authors pointed out that the use of inorganic salts, such as magnesium fluoride, could also speed up the spinel formation. Nevertheless, the expansion behavior associated with the  $MgAl_2O_4$  formation [14] inhibits its densification [15]. Therefore, additives such as titanium oxide [15, 16] have been already evaluated and presented great performance on the densification of spinels. Despite the benefits that could arise from the addition of these compounds, properties such as hot modulus of rupture and creep resistance could be deteriorated as the mineralizers commonly increase the reaction rate through liquid phase generation. Considering that these castables are commonly applied in the steel ladle bottom (for instance, impact pads or well blocks), care must be taken when selecting these additives, as impact and creep resistance are two of the main requirements as well as the cor-

rosion one. As a consequence, as both routes (nano and mineralizers) present advantages and drawbacks, an overall analysis of them is essential in order to attain technological advances in the design and production of in-situ spinel forming refractory castables.

## 2 Experimental procedure

Tab. 1 summarizes the different compositions produced for this study. Initially, different alumina and magnesia grain sizes were evaluated and nano-scaled powders were prepared by a centrifugal-type high-energy ball milling (MHNANO, Brazil). Fine alumina ( $D_{50} = 4 \mu m$ ) and magnesia ( $D_{50} = 20 \mu m$ ) powders were used as initial materials, resulting in the production of nano-scaled  $Al_2O_3$  (NA) or  $MgO$  (NM) powders with crystallite sizes in the range of 20 – 90 nm, as indicated by TEM. A reference composition (REF) was prepared with the initial  $Al_2O_3$  and  $MgO$  grain sizes. Finer alumina (A1,  $D_{50} = 1 \mu m$ ) and magnesia ( $< 13 \mu m$  – M13) grains were also evaluated, as well as a coarser  $MgO$  source ( $< 100 \mu m$  – M100). Furthermore, colloidal alumina (CA, 40 mass-% solids,  $D_{crystallite} = 13 nm$ , *Evonik*, Germany) was added to the composition. An additional composition comprised a nano-scaled  $Al_2O_3$ - $MgO$  powder (AM), taking into account an alumina-magnesia ratio [in

**Tab. 1** Compositions of the evaluated castables

Compositions	MgO grain sizes				Al <sub>2</sub> O <sub>3</sub> grain sizes			Nano-AM	BCM or TiO <sub>2</sub>
	REF	M100	M13	NM	A1	NA	CA		
Raw materials [mass-%]									
Tabular alumina (D < 6 mm)	80				80			77,3	80
Dead-burnt MgO	6 (< 45 μm)	6 (< 100 μm)	6 (< 13 μm)	6 (nano)	6 (< 45 μm)			4 (< 45 μm)	6 (< 45 μm)
Reactive alumina (D <sub>50</sub> = 4 μm)	7				4			4,7	7
Reactive alumina (D <sub>50</sub> = 1 μm)	–				3	–	–	–	–
Alumina nano-powder	–				–	3	–	–	–
Colloidal alumina	–				–	–	3	–	–
Nano-AM	–				–			7	–
Calcium aluminate cement	6				6			6	6
Microsilica	1				1			1	–
Mineralizing compound	–				–			–	1
Water content [mass-%]	4,1	4,1	4,1	4,1	4,5	4,7	6,0	4,3	4,3

mass-%] of 15 : 6 (1 : 1 molar) with the target of keeping the spinel stoichiometry.

In order to investigate the effect of the nano-scaled alumina or magnesia powders and colloidal alumina on the castables' expansion behavior and initial spinel expansion temperature, vibratable castables (80 % of flowability) were prepared according to an Alfred packing model ( $q = 0,26$ ). Their matrix comprised 6 mass-% of dead-burnt magnesia with different grain sizes (95 mass-% MgO,  $\text{CaO/SiO}_2 = 0,37$ , *Magnesita Refratários S.A*, Brazil), 7 mass-% of different reactive alumina sources (CL370 or A1000SG, *Almatis*, Germany, and nano-scaled particles), 6 mass-% of calcium aluminate cement (Secar71, *Kerneos*, France) and 1 mass-% of microsilica (971U, *Elkem*, Norway). To complement the composition, 80 mass-% of fine ( $D < 0,2 \text{ mm}$ ) and coarse ( $6 \text{ mm} < D < 0,2 \text{ m m}$ ) tabular aluminas were used (*Almatis*, Germany). The dispersion was carried out using 0,2 mass-% of an electrosteric dispersant (*BASF*, Germany).

Regarding the mineralizing compounds, a boron-containing one (BCM, *Magnesita Refratários S. A.*, Brazil) was selected and replaced microsilica in the standard composition (REF) in order to provide an alternative liquid phase. Additionally, titania ( $\text{TiO}_2$ , also supplied by *Magnesita Refratários S.A.*, Brazil) was tested (again replacing microsilica), due to its ability to promote spinel densification during sintering.

The expansion behavior of these castables was evaluated by the assisted sintering technique. In this test, cylindrical samples (height and external diameter = 50 mm and central inner diameter = 12,4 mm) were analyzed after the initial castable processing steps (24 h curing at 50 °C in a humid environment, 24 h drying at 110 °C and calcination at 600 °C for 5 h) and the linear expansion was obtained as a function of temperature (up to 1500 °C) and time (dwell of 5 h), using a refractoriness-under-load equipment (Model RUL 421E, *Netzsch*, Germany – compression load of 0,02 MPa and heating rate of 3 °C/min).

The microstructure evaluation was carried out using scanning electron microscope (JEOL JSM-5900 LV, Japan) for samples fired at 1300 °C for 5 h and the phase content was determined by X-ray diffraction quantitative analysis (Rietveld method, TOPAS 4.1,

*Bruker*, Germany) for samples fired at 1150 °C, 1300 °C or 1500 °C for 5 h. Additionally, corrosion cup tests were conducted at 1550 °C for 2 h under an oxidizing atmosphere for samples previously pre-fired at 1500 °C for 5 h, using a mixture of 10 mass % of iron oxide and 90 mass-% of a calcium aluminate slag.

The creep resistance was also evaluated using the refractoriness-under-load equipment. In this test, the cylindrical samples were firstly pre-fired at 1550 °C for 24 h and then evaluated at 1450 °C for 24 h, under a compression load of 0,2 MPa. This procedure was selected in order to avoid deformation due to sintering during the creep tests.

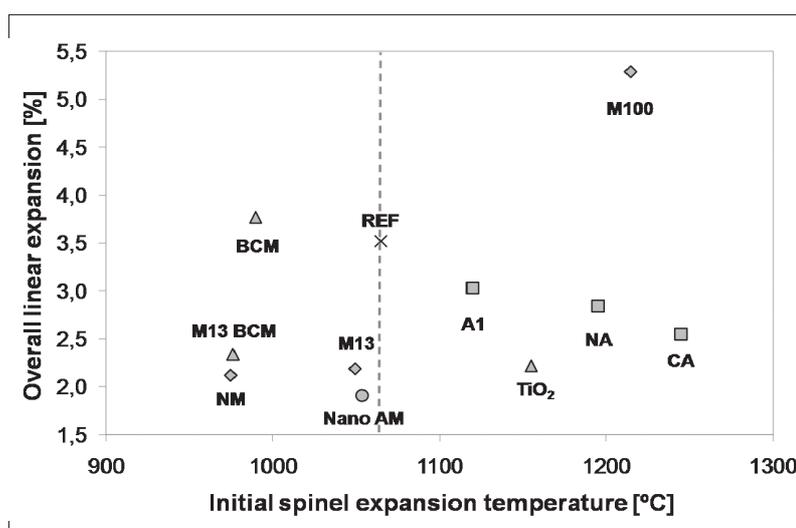
### 3 Results and discussion

According to the assisted sintering technique expansion curves, the initial spinel expansion temperature can be determined, as presented in Fig. 1, indicating the different roles of alumina and magnesia on the spinel formation, as well as the behavior of the boron containing mineralizer (BCM) and  $\text{TiO}_2$ . Considering the reference composition (REF), the reduction of the MgO grain size (M100 – REF – M13 – NM) led to lower expansion levels and a lower spinel starting temperature. Reducing the alumina grain size (REF – A1 – NA – CA) also resulted in lower expansion. Nevertheless, two main differences were detected when comparing the alumina and magnesia grain size effect:

- the expansion values were slightly higher for the different fine alumina grains and
- the starting spinel expansion temperature increased with the alumina reactivity, pointing out its counterbalancing effect on the spinel expansion and leading to higher sinterability.

Regarding the nano-AM powder, it resulted in the lowest overall expansion level, but did not attain the lowest initial expansion temperature, due to the competition between MgO, which speeds up the expansion starting temperature due to its faster diffusion, and  $\text{Al}_2\text{O}_3$ , that compensates the expansion with its sintering effect. For all the nano-scaled materials (NM, NA, CA or AM) greater volumetric stability was attained.

Conversely, the boron-containing mineralizer (BCM) presented a high expansion level (close to REF), but lower initial spinel expansion temperature ( $< 1000$  °C, close to nano-MgO), pointing out its reaction speeding up effect. In order to compensate the high expansion level, the use of titania ( $\text{TiO}_2$ ) is a suitable option, leading to an expansion value close to those detected for the nano-scaled particle compositions. As a further alternative to reduce the high overall expansion level displayed by BCM, the MgO  $< 45 \mu\text{m}$  source was replaced by a finest one (MgO  $< 13 \mu\text{m}$ ) – M13 BCM – leading to a suitable combination of low expansion level and faster spinel formation (both similar to NM) coupled with its lower



**Fig. 1** Initial spinel expansion temperature [°C] versus assisted sintering technique test (1500 °C – 5 h), for sizes and the compositions containing nano-scaled  $\text{Al}_2\text{O}_3$  (BCA) or titania ( $\text{TiO}_2$ ); REF is a reference composition containing size ( $< 45 \mu\text{m}$ ) and a traditional reactive alumina source

**Tab. 2** XRD quantitative analyses [mass-%] for samples fired at 1150, 1300 and 1500 °C for 5 h

Temperature	1150 °C		1300 °C		1500 °C	
	MgO	Spinel	Spinel	CA <sub>6</sub>	Spinel	CA <sub>6</sub>
REF	3	9	18	0	22	16
NM	traces	18	20	0	22	16
CA	3	11	17	0	23	17
Nano-AM	2	16	18	0	21	17
BCM	0	22	22	16	24	22
TiO <sub>2</sub>	4	8	13	12	18	22

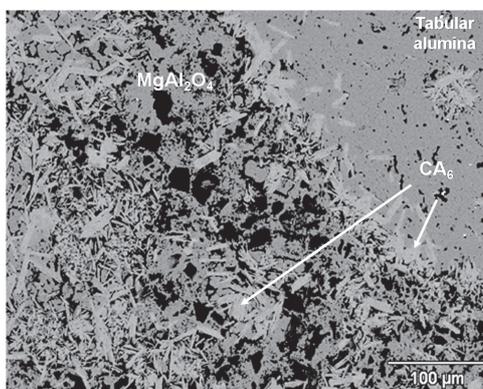
costs when compared to the nano-scaled particles.

The microstructure evaluation of these compositions pointed out additional benefits of the mineralizer route. Tab. 2 shows the XRD quantitative analyses results, which indicated three main features:

- the faster spinel generation for the boron-containing mineralizer composition (BCM) at a low temperature (after firing at 1150 °C for 5 h 22 mass-% of spinel was formed against only 9 mass-% for the reference – REF)
- the CA<sub>6</sub> formation speeding up effect for the mineralizer and densifier (BCM and TiO<sub>2</sub>). This phase is commonly detected at temperatures above 1400 – 1450 °C, and, therefore was not detected after firing at 1300 °C for 5 h for all the compositions containing nano-scaled particles (NM, nano-AM or CA), but conversely for the castables containing these compounds
- the spinel and CA<sub>6</sub> contents (22 and 16 mass-%) of the BCM-containing composition after firing at 1300 °C were the

same as those detected for the reference (REF) but at a higher firing temperature (1500 °C).

The SEM analyses of the BCM-castable fired at 1300 °C for 5 h (Fig. 2) concurred with this third aspect, highlighting well developed CA<sub>6</sub> and spinel grains, which is a common microstructure observed for this system, but at temperatures above 1450 °C [12, 14]. Therefore, higher homogeneity would be achieved by the boron-containing mineralizer castable and, because the aimed phases would be developed at lower temperatures, better thermomechanical and chemical properties would be attained, as both spinel and CA<sub>6</sub> are known to increase the castables' corrosion and thermal-shock resistances, which most likely would increase the lining working life during the application in steel ladles.



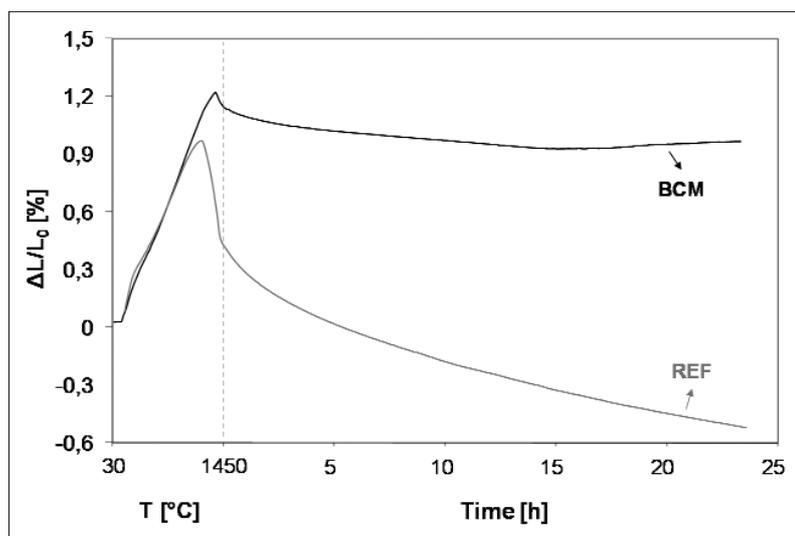
**Fig. 2** Microstructure of the boron-containing mineralizer (BCM) composition, after firing at 1300 °C for 5 h

Such mineralizer (BCM) speeding up effect was due to the liquid phase generation at lower temperatures than the usual ones observed in the system Al<sub>2</sub>O<sub>3</sub> – MgO – CaO – SiO<sub>2</sub>. Considering this aspect, the evaluation of this additive in terms of castable's hot properties becomes essential.

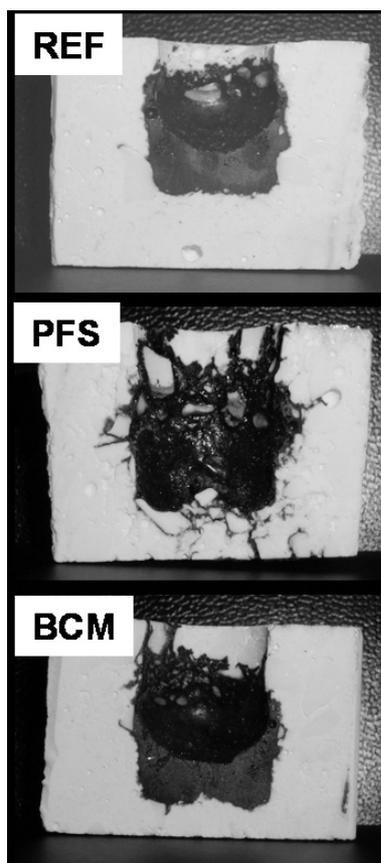
Fig. 3 indicates the creep behavior for castables containing MgO < 45 μm and 1 mass % of microsilica (REF) or 1 mass-% of the boron-containing mineralizer (BCM). The lower creep deformation attained for the boron-containing mineralizer pointed out a suitable transient liquid at high temperature, formed at lower temperatures (speeding up the spinel and CA<sub>6</sub> formation), but, at higher temperature, either led to another crystalline phase formation or to boron volatilization. The main benefit was that the castables' hot properties were not spoiled as those detected for the microsilica-containing composition (considerable creep deformation due to a permanent liquid phase).

Furthermore, taking into account a systemic approach in order to attain novel alumina-magnesia castables suitable to display high performance during the application in steel ladles, slag resistance should be evaluated. Initial tests were performed using an iron-oxide-rich steel ladle slag (calcium aluminate source) and the boron-containing mineralizer composition which presented low slag infiltration and high corrosion resistance.

Fig. 4 points out the samples' slag corrosion profile, for the reference castable (REF) and



**Fig. 3** Creep resistance of alumina-magnesia castables containing 1 mass-% of microsilica (REF) or boron-containing mineralizer (BCM). Testing conditions: 1450 °C x 24 h, under a compression load of 0,2 MPa



**Fig. 4** Slag corrosion profile (1550 °C/2 h) of the reference castable (REF), of the boron-containing mineralizer (BCM) composition and of a castable that did not display a suitable behavior (PFS)

for the boron-containing mineralizer (BCM) compositions. Both of them presented lower infiltration when compared to other compositions (for instance, containing pre-formed spinel – PFS – instead of in-situ spinel) that displayed cracks and thus considerable infiltration.

#### 4 Conclusions

According to the attained results, both routes presented promising features for the development of advanced in-situ spinel castables. The nano-scaled particles led to greater volumetric stability and faster in-situ spinel generation. Neverthe-

less, these materials could only affect the spinel formation and not the  $CA_6$  one, besides their higher costs. Conversely, the mineralizer route presented outstanding features and could be a much more feasible option for the production of high-performance alumina-magnesia refractory castables.

Although the boron-containing mineralizer (BMC) led to high overall linear expansion level, such aspect could be designed either by the use of densifier compounds (such as titania) or by addition of a finer MgO grain size source ( $< 13 \mu\text{m}$ ). Thus, a cheaper option was engineered leading to the same volumetric stability benefit as the one displayed for nano-powders.

In addition, this route presents a further advantage related to the faster  $CA_6$  formation, ensuring higher castable's homogeneity during firing at high temperatures in the steel ladles. Lastly, higher creep resistance and suitable slag infiltration resistance were attained. Therefore, the mineralizer route and their proper selection seems to be the most suitable alternative to produce industrial alumina-magnesia refractory castables and a better performance in use.

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