

# Evaluation of a Microsilica-Based Additives in Al<sub>2</sub>O<sub>3</sub>–MgO Refractory Castables

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The first heating cycle of MgO-containing refractory castables is usually considered a challenge by the producers of such products due to the significant mass loss, associated with magnesium hydroxide decomposition between 350–450 °C, that might result in their spalling or even explosion. In order to allow faster and safer drying of this sort of refractory system, a microsilica-based additive (SioxX-Mag) has been developed. Thus, this work focused on investigating the action of this commercial additive in high-alumina castables bonded with 6 mass-% of MgO and prepared with the addition of formic acid. Flowability, hot Young's modulus, thermogravimetric analyses, cold and hot mechanical measurements were carried out to infer the properties of the compositions with and without the selected SiO<sub>2</sub>-based product. According to the collected results, the addition of 1 mass-% of the microsilica-containing additive to the designed castables resulted in higher flow and reduced MgO hydration. Consequently, even when subjecting these samples to a very high heating rate (20 °C · min<sup>-1</sup>), no explosion was detected. When increasing the firing temperature, the interaction among Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub> induced the increase of the castables' mechanical strength up to 900 °C, but liquid phase formation was identified in the tested compositions above 1000 °C, causing the drop of their mechanical properties. Nevertheless, thermodynamic calculations and experimental tests indicated that the formed liquid should progressively react with the castables' components, giving rise to refractory phases such as mullite and forsterite. Hence, the evaluated microsilica-based additive can be a potential solution to adjust the drying behavior and prevent the explosion of MgO-containing castables.

## 1 Introduction

Besides its high melting point (2800 °C), good compatibility with basic slags and great likelihood of reacting with alumina at high temperatures for spinel (MgAl<sub>2</sub>O<sub>4</sub>) generation, magnesium oxide (MgO) is pointed out as a potential binder compound, which can replace the traditional calcium aluminate cement, in refractory castable systems comprising low CaO content [1–4]. This binder action is related to MgO hydration reaction with water and further brucite [Mg(OH)<sub>2</sub>] formation, as indicated in eq. 1. Consequently, the brucite crystals tend to fill in pores and voids found in the consolidated structure, increasing the cohesion among the refractory constituents and the overall mechanical strength level of the samples during their curing and drying stages.



Although eq. 1 is a simple reaction, the control of brucite formation in the matrix fraction of MgO-containing castable compositions during mixing, curing and/or drying stages is a difficult task, as various parameters (i.e., temperature, water amount and magnesia granulometry, surface area and volume) might affect the growing of this hydrated phase [5–10]. Consequently, it is of utmost importance to optimize the nucleation and growing rate of Mg(OH)<sub>2</sub> during the processing of such refractories, in order to inhibit cracking and flaws formation in their structure. Many studies reported the use of different additives that allow the adjustment of MgO-water reaction, which can induce an effective incorporation of MgO as binder in monolithic products [4, 11–15]. Some authors also stated that, when this hydration reaction is speed up during the early magnesia-water contact, Mg(OH)<sub>2</sub> crystals may be better accommodated in the resulting structure

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as the castables will not be fully hardened yet [3, 16].

Among the MgO hydrating agents, formic and acetic acids proved to be good options to control brucite formation in high-alumina compositions, leading to the development of refractories with high green mechanical strength [3, 4, 15–17]. However, in general, the high hydration level of such magnesia-bonded products results in a significant spalling/explosion trend for the prepared samples, when they are subjected to their first heating cycle. As observed in previous research [15], the detected explosions of MgO-bonded castables took place mainly in the 350–450 °C temperature range, due to the steam pressure derived from brucite decomposition and carboxylates' desorption. Thus, in order to minimize or prevent the formation of cracks or even the explosion of MgO-containing castables, likely solutions consist of inducing the in situ formation of hydrotalcite-like phases [18], or incorporating polymeric fibers [3, 19, 20] or amorphous silica sources [21] into the designed compositions. Such alternatives will play a role by changing the resulting microstructure and favoring easier steam withdrawal. Silica fume and additives derived from this raw material are pointed out as efficient options to control MgO hydration in refractory systems [14, 22–24]. According to the literature [14, 23, 25], microsilica can be partially dissolved in basic pH aqueous medium, giving rise to silicic acid ( $\text{HSiO}_3^- \cdot \text{OH}_3^+$ ). This compound might also react with brucite phase formed on MgO surface in a further moment, which generates amorphous hydrated magnesium

silicates (M-S-H gels) with distinct stoichiometry, depending on the MgO and  $\text{SiO}_2$  molar ratio (M/S). For instance, Kalousek et al. [26] reported that a gel phase with chrysotile stoichiometry,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ , can be obtained when M/S is equal to 1,5. On the other hand, when M/S is around 0,75, talc phase [ $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ] might be formed. These amorphous compounds limit the hydration of MgO grains, as they coat the surface of this oxide inhibiting its interaction with water. Consequently, cracking and flaws formation in the consolidated castables can be minimized with the reduction of brucite content formed in the matrix fraction of the microstructure, and the likelihood of further spalling/explosion event during the first thermal cycle of these materials is significantly decreased. Moreover, some studies [14, 25] highlight that it is more appropriate to induce the generation of chrysotile-like gels (M/S ~1,5) in refractory mixtures because the decomposition of these compounds above 800 °C can give rise to forsterite ( $\text{Mg}_2\text{SiO}_4$ ). The latter phase helps to improve the castables' thermomechanical properties due to its high refractoriness (melting point ~ 1840 °C).

Refractory users and producers have been constantly interested in finding alternatives to promote fast and save drying of ceramic linings. In this sense, new additives have been developed to enhance the permeability of castables, without affecting in a greater extent their green mechanical strength [21, 27–30]. This is the case of a silica-based drying agent (SioxX-Mag), which was designed for magnesia monolithics presenting microsilica in their matrix

fraction. According to the supplier of this product [31–33], the addition of 2 mass-% of SioxX-Mag to MgO castables containing 6 mass-% of  $\text{SiO}_2$  resulted in improved flowability, mechanical strength and large pieces were molded without showing cracking associated with magnesia hydration. Additionally, the tested compositions presented higher explosion resistance.

Although SioxX-Mag have been designed for magnesia-based castables, most likely this additive can act minimizing the explosion trend of high-alumina compositions containing MgO in their matrix fraction. It is also expected that this product may favor a better control of magnesia hydration and improve the castables' flow and green mechanical strength levels. Thus, this work investigated the effect of adding SioxX-Mag to high-alumina vibratable castables containing 6 mass-% of fine MgO and processed with formic acid (hydrating agent).

## 2 Materials and methods

Vibratable castables were designed based on Alfred's particle packing model and using distribution modulus  $q = 0,26$  [34]. Tab. 1 shows more information about the raw materials and water contents used during the preparation of such compositions. The main constituents of the formulations were tabular alumina ( $d \leq 6$  mm, Almatís/DE), calcined and reactive aluminas (CT3000SG and CL370, Almatís/DE) and dead-burnt MgO with  $d_{50} = 15$   $\mu\text{m}$  (M30 < 212  $\mu\text{m}$ , RHI Magnesita/BR). The castables processed with formic acid contained 0,34 mass-% of this additive. A total of 1 mass-% of SioxX-Mag (35 mass-%  $\text{SiO}_2$ , 50 mass-%  $\text{Al}_2\text{O}_3$ , 15 mass-% others, Elkem/NO) was incorporated into the mixtures prepared with and without formic acid and, as the microsilica-based product already contained a dispersing agent in its composition, no Castament® FS60 (BASF/DE) addition was required processing castables C and D. The reference compositions (A and B, without SioxX-Mag) were mixed with 4 mass-% of distilled water, whereas the ones containing this microsilica-based additive (C and D) contained 4,5 mass-% of liquid.

The compositions were mixed in a rheometer specially developed for refractory castables. Two processing routes were adopted during the preparation of the mixtures with

**Tab. 1** General information of the castable compositions evaluated in this work

	A	B	C	D
Remarks	Only MgO	MgO and Formic Acid	MgO and SioxX-Mag	MgO, Formic Acid and SioxX-Mag
Components	[mass-%]			
Tabular alumina	87	87	87	87
Fine aluminas (CL 370 C e CT 3000 SG)	7	7	7	7
M30 < 212 $\mu\text{m}$	6	6	6	6
Formic acid	0	0,34	0	0,34
Castament® FS60	0,2	0,2	0	0
SioxX-Mag	0	0	1,0	1,0
Water	4	4	4,5	4,5

and without formic acid. Distilled water was directly added to the powdered components (alumina, MgO, dispersant) of the acid-free compositions, whereas a suspension comprised by distilled water, formic acid and MgO was firstly prepared for the processing of castables containing this hydrating agent. After that, this aqueous suspension was mixed to the remaining solid fraction of the refractory. Castable samples were molded under vibration, cured at 50 °C for 24 h and dried at 110 °C for 24 h. Vibratable flow measurements (ASTM C1445) as a function of time (up to 90 min) were carried out after the castables' mixing step. A conical mold for casting the flow specimen (diameter of the bottom and top opening was ~100 mm and 70 mm, respectively, and height was 50 mm) was filled with the fresh castable mixtures. The mold was carefully lifted away from the compositions and the samples were vibrated for 1 min. The castables' spreading were measured with a caliper and the final flow was calculated as follow:

$$\text{Vibra flow (\%)} = 100 \times \frac{D - D_0}{D_0} \quad (\text{eq. 2})$$

where,  $D$  corresponds to the final diameter of the sample after 1 min of vibration and  $D_0$  is the bottom diameter of the conical mold (100 mm). The flow measurements were carried out each 15 min after the end of the mixing step and up to a total of 90 min.

Cylindrical specimens (40 mm diameter and 40 mm height) were prepared for the thermogravimetric tests. These experiments were carried out in a device developed for analyzing the drying behavior of refractory compositions [35] and two heating rates, 5 °C·min<sup>-1</sup> and 20 °C·min<sup>-1</sup>, were employed during the evaluation of the designed MgO-containing castables. The mass loss (TG) and drying rate (DTG) collected for the dried (110 °C·24 h<sup>-1</sup>) samples in the 50 °C–600 °C temperature range were calculated according to eq. 3 and eq. 4.

$$\text{Mass loss (\%)} = 100 \times \frac{M_0 - M}{M_0 - M_f} \quad (\text{eq. 3})$$

$$\text{Drying rate (\%·min}^{-1}\text{)} = \frac{d(\text{mass loss})}{dt} \quad (\text{eq. 4})$$

where  $M_0$  is the initial mass,  $M$  is the measured mass at time  $t$  and  $M_f$  is the final mass of the evaluated sample.

**Tab. 2 Chemical composition of the castable's matrix fraction**

Composition	B	D
Components	[mass-%]	
Al <sub>2</sub> O <sub>3</sub>	83,72	83,06
SiO <sub>2</sub>	0,13	1,21
MgO	16,15	15,73
Total	100	100

The phase transformations in the castables microstructure were monitored via in situ Young's modulus ( $E$ ) measurements during drying at 110 °C or along various thermal cycles up to 1400 °C. The bar resonance technique (ASTM E1875) was used for analyzing the stiffening evolution of bar samples (150 mm x 25 mm x 25 mm) and further details of the applied method can be found elsewhere [36, 37].

Cold mechanical strength and apparent porosity of the designed compositions were evaluated after curing at 50 °C·24 h<sup>-1</sup>, drying at 110 °C·24 h<sup>-1</sup> and firing at 600 °C, 900 °C or 1450 °C for 5 h. The Modulus of Rupture (MOR, 3-point bending test) of a total of 5 bar samples for each tested condition was determined according to ASTM C133 [38], using a mechanical testing machine (MTS 810, MTS/US) and based on eq. 5. On the other hand, the apparent porosity level of the prepared specimens was analyzed as suggested by ASTM C830 [39], by using kerosene as immersion liquid and calculating the results as indicated in eq. 6.

$$\text{MOR (MPa)} = \frac{3PL}{2bd^2} \quad (\text{eq. 5})$$

$$\text{Apparent porosity (\%)} = 100 \times \frac{P_w - P_s}{P_w - P_d} \quad (\text{eq. 6})$$

where,  $P$  is the maximum load applied at rupture,  $L$  is the span between supports (127 mm), and  $b$  and  $d$  are the width and depth of the specimen, respectively.  $P_w$ ,  $P_s$  and  $P_d$  correspond to wet, suspended and dry mass of the samples. For both tests a total of 5 specimens for each evaluated condition were analyzed, and the reported values represent the average results with their standard deviation.

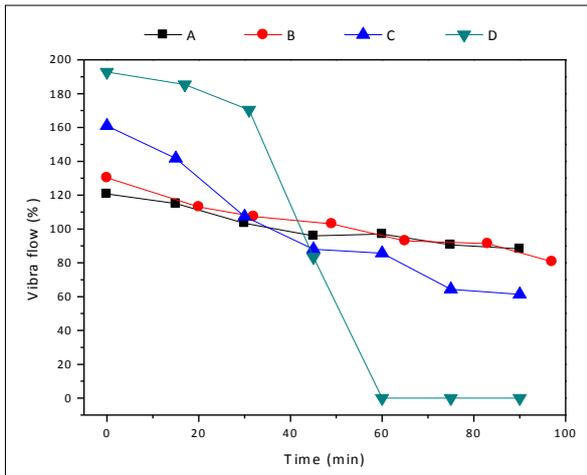
Hot Modulus of Rupture (HMOR) of bar samples (similar to the ones used for the MOR measurements) pre-fired at the same testing temperature for 5 h were determined according to ASTM C583 [40] and using HBST 422 equipment (Netzsch/DE).

Moreover, the thermal shock resistance of the castables were analyzed when they were exposed to  $\Delta T \sim 1000$  °C. Bar samples (150 mm x 25 mm x 25 mm) were previously fired at 1450 °C for 5 h and, after that, they were subjected to 10 heating-cooling cycles. The damage induced by the thermal fluctuations was investigated by the evolution of the Young's modulus of the prepared compositions. The  $E$  analyses were carried out according to the bar resonance technique and using the ScanElastic 02 device (ATCP Engenharia Física/BR). Four samples of each refractory were used in these tests and the obtained results are presented as the average percentual of the retained Young's modulus.

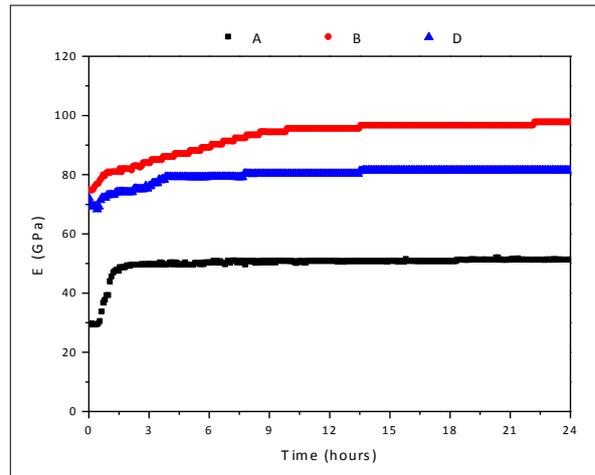
Thermodynamic simulations were also performed in order to predict the likely phases that could be formed in the matrix fraction of the castables in the 600–1500 °C temperature range and in an equilibrium condition. These calculations were carried out using FactSage™ software (Thermfact/CRTC/CA and GTT-Technologies/DE), version 6.4, and Fact53 and FTOxid databases. The chemical composition of the matrix fraction of the designed castables are shown in Tab. 2.

### 3 Results and discussion

Initially, SiOX-Mag influence on the rheology of the designed compositions was evaluated via vibratable flow measurements as a function of time (Fig. 1). As observed, higher flow values could be detected for the SiO<sub>2</sub>-containing castables (C and D) when compared to the mixtures dispersed with Castament® FS 60 (A and B). Nevertheless, the latter presented few changes of the flow level with time, whereas C and D showed a major decrease of this property in the analyzed conditions. When formic acid and SiOX-Mag were used (castable D), a faster flow decay was observed after 40 min of the end of the mixing step, which suggests



**Fig. 1** Vibra flow values of the prepared compositions as a function of time



**Fig. 2** In situ Young's modulus (E) evolution during the drying process at 110 °C·24 h<sup>-1</sup> of the samples containing formic acid previously cured at 50 °C·24 h<sup>-1</sup>

that a likely interaction between these two additives might have been responsible for such behavior.

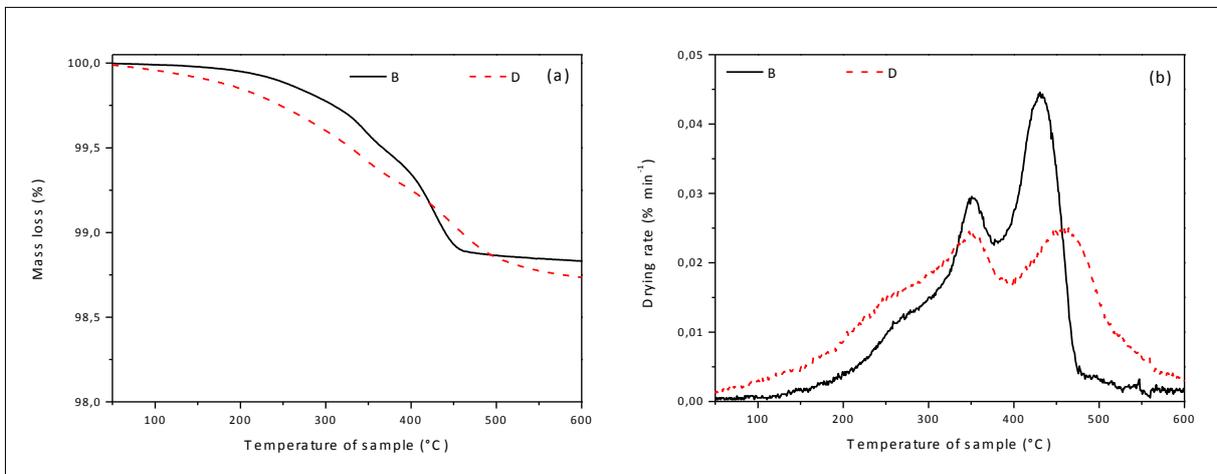
Besides having the highest initial vibra flow, castable D was selected for further characterizations due to the presence of formic acid in its composition, which may result in better brucite formation control and inhibit crack generation in the prepared samples [15]. As castable C did not contain formic acid, this composition was not further characterized.

The effect of formic acid in the development of the green mechanical strength of the refractories during drying at 110 °C is presented in Fig. 2. According to the Young's modulus evolution of the cured samples, composition B (containing 0,34 mass-% of formic acid) showed final E result (after 24 h) of ~100 GPa, which is twice when

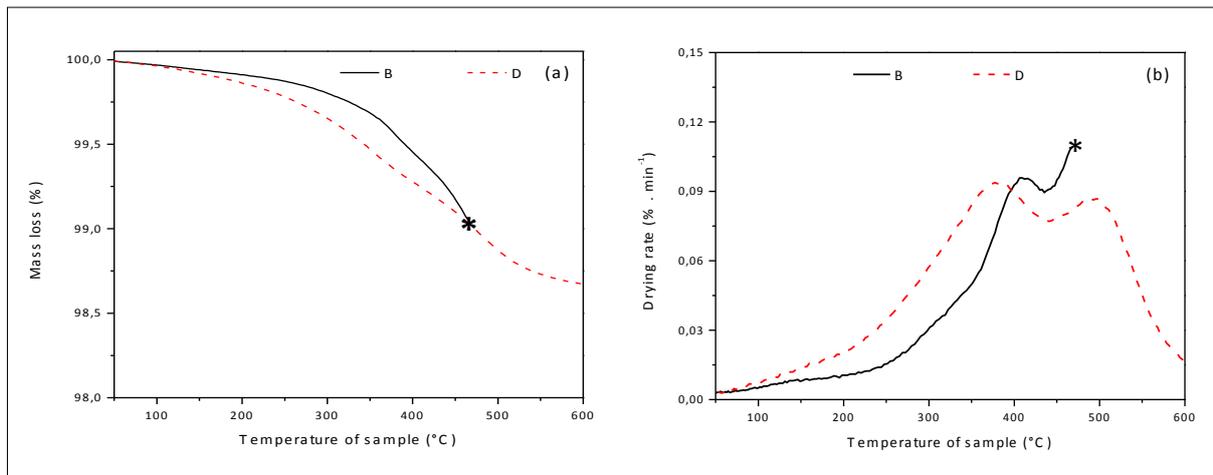
compared to A material (50 GPa). Such data indicate that the selected hydrating agent acted enhancing the cohesion of the resulting microstructure and, most likely, a more controlled brucite crystals' growth took place in the evaluated conditions. On the other hand, when SioxX-Mag was combined with formic acid addition in castable D, the final Young's modulus value measured after 24 h was lower than the one of B samples, which can be related to the limited MgO hydration in this system due to the presence of the silica-containing additive.

The thermogravimetric results, obtained when using 5 °C · min<sup>-1</sup> as heating rate, indicated that the microsilica-based additive contained in sample D partially inhibit Mg(OH)<sub>2</sub> formation during the previous curing and drying steps (Fig. 3). The drying

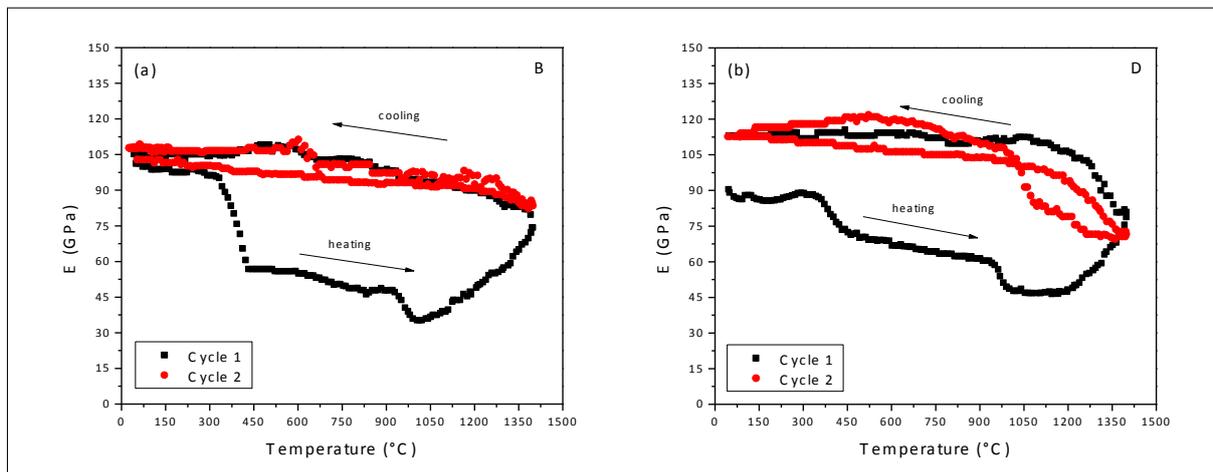
rate profiles shown in Fig. 3b point out that samples' mass loss took place mainly in two different temperature ranges. The first one around 350 °C is associated with magnesium hydroxide decomposition, giving rise to water vapor as reaction product. Whereas, the second one (between 420–450 °C) is related to the carboxylates' desorption, that should be responsible for releasing some gas phases to the furnace environment [41–43]. Both transformations were more intense for castable B, as this material presented higher brucite content due to the interaction of formic acid with MgO. Hence, SioxX-Mag may play two important roles in alumina-based MgO-containing compositions, as it can inhibit magnesia hydration and limit the interaction of this oxide with the hydrating agent (formic acid).



**Fig. 3 a–b** Mass loss (a) and drying rate (b) of castables B and D obtained for thermal treatments carried out with heating rate equal to 5 °C·min<sup>-1</sup>. The analysed samples were previously cured at 50 °C·24 h<sup>-1</sup> and dried at 110 °C·24 h<sup>-1</sup>



**Fig. 4 a–b** Mass loss (a) and drying rate (b) of compositions B and D obtained for thermal treatments carried out with heating rate equal to 20 °C·min<sup>-1</sup>. The analysed samples were previously cured at 50 °C·24 h<sup>-1</sup> and dried at 110 °C·24 h<sup>-1</sup>. The asterisk (\*) indicates sample B explosion



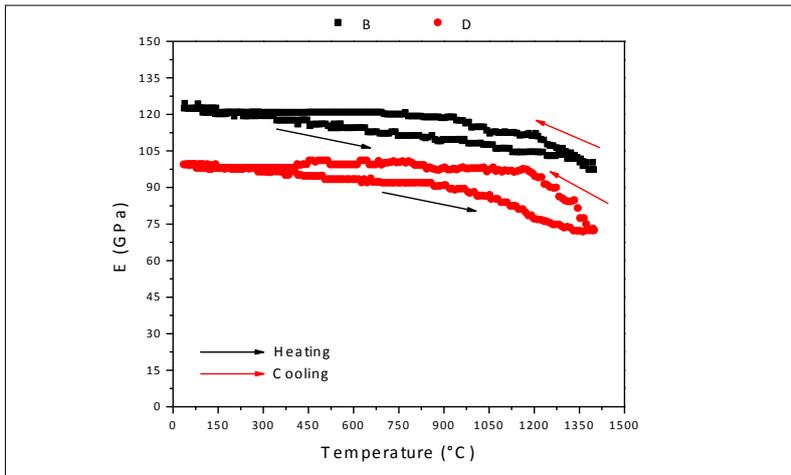
**Fig. 5 a–b** Young's modulus (E) evolution as a function of temperature for the dried samples (110°C·24 h<sup>-1</sup>) of composition B (a) and D (b)

The microsilica-based additive also induced the samples' mass loss in a wider temperature range (Fig. 3a). Considering that the earlier decomposition of hydrated phases (at lower temperatures than brucite decomposition and carboxylate desorption) may change the refractory microstructure and even induce easier steam withdrawal at higher temperatures, the spalling likelihood of castable D should be decreased due to the combined action of SiOX-Mag and formic acid. In order to investigate the explosion resistance of samples B and D, additional thermogravimetric measurements were carried out using higher heating rate (20 °C·min<sup>-1</sup>).

According to Fig. 4, castable B exploded approximately at 450 °C, as water vapor and other gases derived from carboxylate des-

orption led to high steam pore pressure that exceeded the green mechanical strength of the evaluated sample. On the other hand, the higher explosion resistance of composition D can be associated with the lower brucite content, limited carboxylic acid adsorption on MgO particles and more pronounced mass loss at lower temperatures. The anti-hydrating effect of SiOX-Mag could also be identified in the E profiles obtained during the thermal treatments of the dried samples up to 1400 °C (Fig. 5). The first heating cycle of the castables presented E drop between 300 °C and 450 °C due to Mg(OH)<sub>2</sub> decomposition. As observed, D samples showed lower stiffness decrease as a consequence of the reduced amount of brucite in its composition (Fig. 5b). Besides that, a new E decrease could be detected

at 900 °C for both evaluated materials, which is related to the recuperation of MgO crystalline structure that takes place at this temperature range and leads to pore formation in the resulting microstructure [44–46]. After that, a continuous Young's modulus increase was observed for B refractory above 1000 °C due to its sintering process and the further spinel formation in the matrix region, whereas the same transformations could only be verified for D samples at temperatures higher than 1200 °C and during the beginning of the cooling step down to 1000 °C. The delayed stiffening of the latter castables might be derived from liquid phase generation in the sintered microstructure at high temperatures. Moreover, the presence of this liquid phase might help to relieve the thermomechanical stress



**Fig. 6** Young's modulus evolution as a function of temperature of the pre-fired (1450 °C·5 h<sup>-1</sup>) castable samples

associated with spinel formation (expansive reaction) [22, 23], leading to a slower stiffening effect of the specimens during heating.

The second thermal cycle of sample B did not lead to significant E changes (Fig. 5a), which highlights that the main phase transformations took place during the first firing cycle and a stable microstructure was obtained. Composition D still showed the Young's modulus decrease close to 1000 °C during the second heating cycle (Fig. 5b), suggesting that a permanent liquid phase was contained in this refractory as a result of the Si<sub>3</sub>N<sub>4</sub>-Mag addition to this system. Additionally, castables samples pre-fired at 1450 °C for 5 h were also analyzed via hot Young's modulus measurements to confirm whether the liquid phase would still be

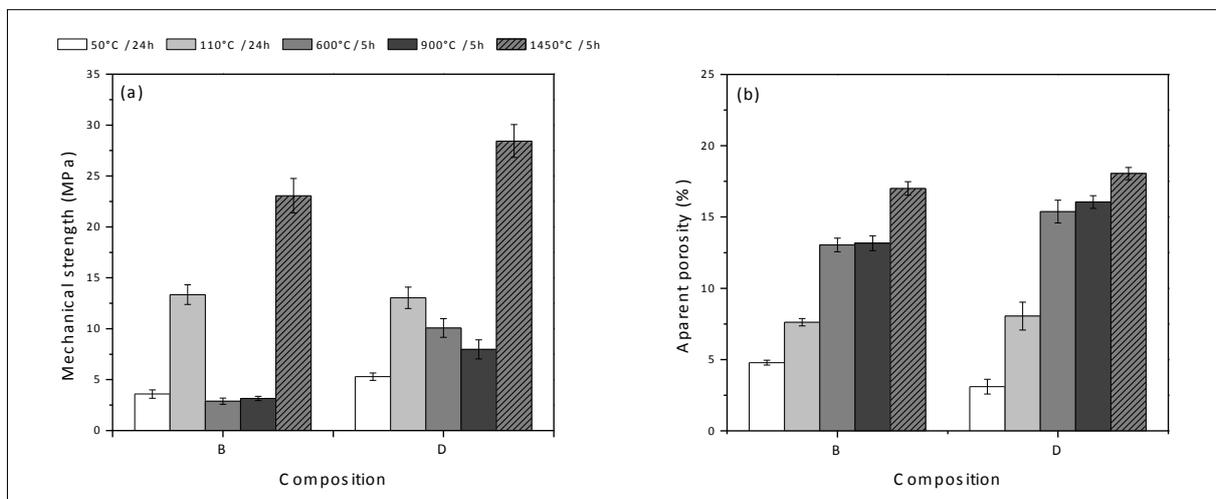
formed in composition D after previously keeping this material for a longer time at high temperatures. According to the obtained results (Fig. 6), almost no E change could be detected for sample B, whereas a small softening of refractory D (lower E drop when compared to Fig. 5b) was observed, indicating that a fraction of the liquid could react with the other constituents of this material and, consequently, give rise to new crystalline compounds.

Fig. 7 shows the flexural strength (3-point bending test) and apparent porosity of samples B and D. Both compositions presented significant mechanical strength (Fig. 7a) increase between curing (50 °C·24 h<sup>-1</sup>) and drying (110 °C·24 h<sup>-1</sup>) steps, which was followed by free-water withdrawal and, consequently, an important increment of

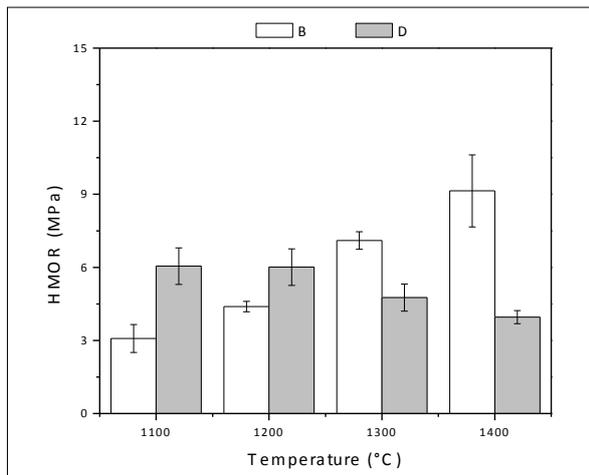
the overall pore content of such materials (Fig. 7b). After brucite decomposition and carboxylates desorption during heating up to 600 °C, B samples presented an expressive flexural strength decay from 13 MPa down to 3 MPa. As indicated in Fig. 5b, composition D showed lower E decay up to 600 °C, which is in tune with the less intense mechanical strength decrease observed in Fig. 7a. Besides that, both castables fired at 600 °C·5 h<sup>-1</sup> presented an increase in their apparent porosity levels (Fig. 7b) mainly due to the magnesium hydroxide decomposition.

An additional modulus of rupture decrease could also be identified after firing castable D at 900 °C·5 h<sup>-1</sup> (Fig. 7a), which is a result of MgO crystalline structure recuperation and most likely the generation of forsterite phase, as this transformation is followed by volumetric shrinkage, increasing the overall pores content of the castable [21, 47]. On the other hand, samples B did not present significant changes in their mechanical strength and apparent porosity results after firing at 900 °C (Fig. 7). The formation of spinel phase (MgAl<sub>2</sub>O<sub>4</sub>) and strong ceramic bonds (due to sintering process) in both refractory materials fired at 1450 °C·5 h<sup>-1</sup> led to improved cold mechanical strength values (Fig. 7a).

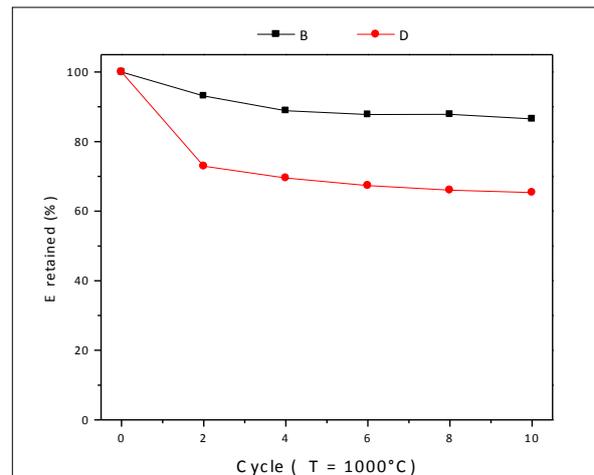
Aiming to identify the influence of the liquid phase formation on the mechanical strength of the designed refractories at high temperatures, hot modulus of rupture (HMOR) measurements were carried out using specimens pre-fired at the same test-



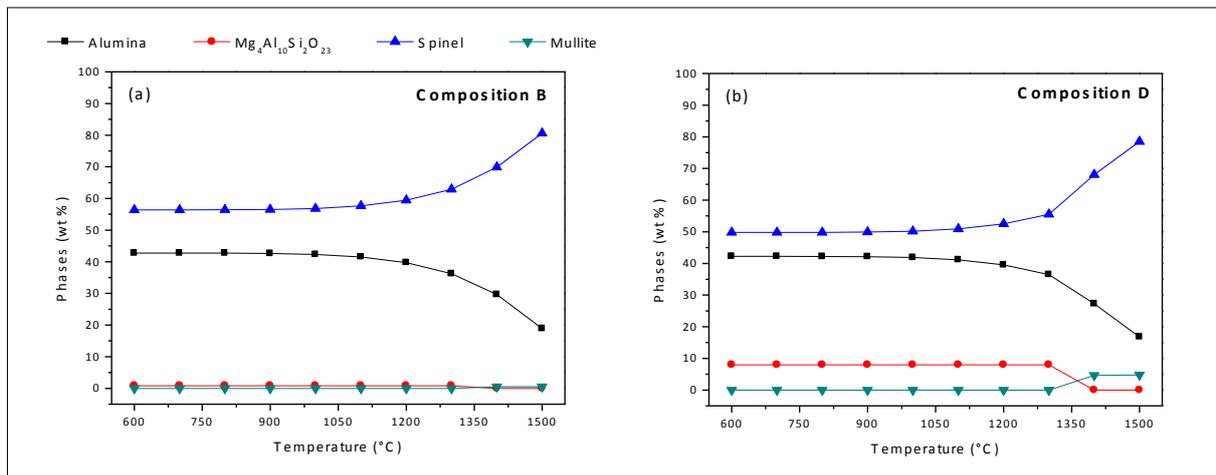
**Fig. 7 a-b** Flexural strength (a) and apparent porosity (b) of compositions B and D after curing at 50 °C·24 h<sup>-1</sup>, drying at 110 °C·24 h<sup>-1</sup> or firing at 600 °C, 900 °C or 1450 °C for 5 h



**Fig. 8** Hot Modulus of Rupture (HMOR) of compositions B and D; the samples were previously fired at the same testing temperature for 5 h



**Fig. 9** Young's modulus (E) of pre-fired samples (1450 °C·5 h<sup>-1</sup>) of castables B and C retained after thermal shock cycles with ΔT = 1000 °C



**Fig. 10 a–b** Predicted phases to be formed in the matrix fraction of castables (a) B and (b) D according to thermodynamic simulations and for an equilibrium condition between the temperature range of 600–1500 °C

ing temperature for 5 h. Fig. 8 shows that castable B presented a continuous increase of HMOR results between 1100–1400 °C, whereas the softening of the microsilica-containing composition (D) resulted in lower mechanical strength values above 1200 °C, due to the liquid phase presence in this microstructure.

Although the in situ Young's modulus tests pointed out that the liquid phase contained in samples D could be partially consumed during their thermal treatment at 1450 °C·5 h<sup>-1</sup> (Fig. 6), the remaining vitreous compound in this composition influenced not only the hot mechanical strength but also the thermal shock resistance of this refractory. Fig. 9 indicates that a decrease of the samples' stiffness could be observed for composition D after two thermal cycles

(ΔT ~ 1000 °C) and a continuous reduction of this property was detected up to 10 cycles. The E retained for the SiOX-Mag containing castable at the end of the thermal shock tests was around 70 %, whereas the SiO<sub>2</sub>-free composition (B) presented better performance, keeping approximately 90 % of its initial Young's modulus.

The experimental results of this work indicated that the liquid phase generated in composition D might be progressively consumed with time, especially when the samples were kept at temperatures higher than 1000 °C.

Hence, in order to understand the phase transformations that can induce liquid formation or consumption in the evaluated materials, thermodynamic simulations were carried out in order to predict the likely

phases that could be found in the matrix fraction of refractories B and D at high temperatures. Fig. 10 highlights the phases that may coexist in the matrix region of castables B and D between 600–1500 °C under thermodynamic equilibrium condition.

The predicted phases were alumina (Al<sub>2</sub>O<sub>3</sub>), mullite (3Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>), spinel (MgAl<sub>2</sub>O<sub>4</sub>) and a silicate with stoichiometry equal to Mg<sub>4</sub>Al<sub>10</sub>Si<sub>2</sub>O<sub>23</sub>. Due to the presence of SiOX-Mag in composition D, a greater amount of silicate can be formed in this material and, as the temperature increases, Mg<sub>4</sub>Al<sub>10</sub>Si<sub>2</sub>O<sub>23</sub> should be decomposed around 1275 °C, favoring further generation of mullite and MgO in the resulting microstructure. After that, the latter oxide may react with alumina to induce spinel formation. According to the equilibrium condition, both evaluated

systems should present liquid phase formation only above 1575 °C.

Considering that the evaluated refractories are heterogeneous materials and contain components with a wide range of particle sizes, the thermodynamic equilibrium for such systems should be only reached after keeping them at high temperatures for a very long time. Consequently, Al<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub> castables containing microsilica tend to give rise to metastable microstructures [22], comprised by micro-regions presenting distinct chemical composition from the overall refractory product. Some studies presented in the literature pointed out forsterite (2MgO · SiO<sub>2</sub>) formation already at 815 °C in mixtures containing MgO:SiO<sub>2</sub> molar ratio higher than 1,25 [14, 25, 26]. The cold mechanical strength and apparent porosity results of composition D, obtained after firing at 600 °C and 900 °C, suggest that forsterite might also have been formed in this refractory. The generation of this phase is desired due to its high melting point (1840 °C), which is higher than the decomposition temperature of the other silicate compound predicted via thermodynamic simulations.

#### 4 Conclusions

This work evaluated the influence of adding a microsilica-based additive (SioxX-Mag) to Al<sub>2</sub>O<sub>3</sub>-MgO castables prepared with and without formic acid (hydrating agent) in order to minimize their spalling/explosion trend during heating. According to the obtained results, this SiO<sub>2</sub>-containing additive (which already presented a dispersant compound in its composition) led to the development of compositions with better flowability along the 30 min after the end of their mixing process. The interaction of SiO<sub>2</sub> and MgO during the mixing, curing and drying steps of such castables led to lower amounts of brucite formation. Consequently, no explosion was detected even when subjecting those samples to high heating rate (20 °C·min<sup>-1</sup>) and the most significant mass loss of the SioxX-Mag containing samples took place mainly at temperatures lower than 350 °C. On the other hand, the reference materials (SiO<sub>2</sub>-free castables), prepared with the addition of a polymeric dispersant, exploded during heating and under the same testing conditions.

Another benefit of SiO<sub>2</sub> presence in the analyzed refractories is the fact that samples with higher mechanical strength levels could be obtained at intermediate temperatures (600 °C and 900 °C). Nevertheless, liquid phase formation affected the stiffness and hot modulus of rupture results for these castables above 1000 °C. According to the experimental tests and thermodynamic simulations, this liquid can be progressively consumed when the SioxX-Mag-containing refractories are kept at high temperatures and for long periods of time. Thus, the softening of the samples might be minimized with the decrease of the liquid phase content in the resulting microstructure.

Besides favoring an improvement of the flowability, mechanical strength and drying behavior of the Al<sub>2</sub>O<sub>3</sub>-MgO castables, the selected microsilica-based compound can also induce the generation of phases with high refractoriness, such as forsterite and mullite. In this sense, a suitable temperature and time must be selected during the firing step of the castables. Therefore, SioxX-Mag product might also be a promising additive to high-alumina compositions containing MgO in their matrix-fraction.

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