Thermomechanical evaluation of self-flowing refractory castables with and without the addition of aluminate cement

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Abstract

Much has been discussed about the advantages regarding the thermomechanical performance of self-flow refractory castables (SFRC), with very little or no addition of calcium aluminate cement (CAC) when compared to conventional composites with cement. Previous works demonstrated that a 100% alumina SFRC with optimized particle size distribution simultaneously results in high-flowability fresh paste and high mechanical strength.

In this work, the thermomechanical behaviour of zero-cement ceramic matrix is compared to that of the equivalent composite with 1% CAC content.

The results show that the differences in performance can be related to differences in hydration mechanisms, namely the formation sequence of calcium aluminate hydrates, which results in increased open porosity. With lower dried strength, the all-alumina castable presents lower porosity, higher mechanical strength and uncompromised thermal shock resistance, being a valuable option when fast drying or rough green handling can be avoided.

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1. Introduction

Refractory castables are supplied as dry powdered materials to which water, or other specified liquid, is added for in situ mixing and casting into monolithic linings. After mixing with water, they contain a mixture of aggregate coarse particles bound by a matrix of fine particles that must flow and harden in place to yield a dense refractory lining. Refractory castables provide a unique example of the antagonism in the particle requirements for consolidated powders and those for loose powder systems. Set and sintered castables require low porosity and high mechanical strength for adequate service; this condition demands the use of a broad particle size distribution for dense particle packing, with large aggregates for mechanical strength and smaller particles to fill in the interstices between aggregates. However, fresh castables require workability and easy flow for application; this condition precludes

the use of small particles and is usually met with water addition, which promotes coarse particle segregation and, upon drying, leaves behind porosity. Workability of fresh castables can be improved by external vibration but when external vibration is not possible or not advisable, self-flow refractory castables (SFRC) are used. Added water promotes the flowability of the particulated system but water has to be kept to a minimum (typically between 3 and 8 wt.% in conventional castables), to avoid coarse particle segregation and the increase in the final porosity [1–5].

Earlier studies [6–9] based on particle packing strategies, using statistical design of experiments and calculation of mathematical models to describe the various properties (response surfaces) [10,11], enabled the optimization of the size composition of a model castable (100 wt.% alumina) aimed at minimizing added water and porosity, and maximizing fresh paste flowability (self-flow castable) and sintered body mechanical strength.

The construction of monolithic refractory linings relies on a bond system frequently based on calcium aluminate cement (CAC) that sets via hydration reactions at ambient temperature

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and refractory castables are usually divided into classes [1] depending on their CAC content: low (4–8 wt.%), ultra-low (1–4 wt.%) and zero cement (<1 wt.% CAC). Once installed and set, these refractories are dried and fired to develop ceramic bonds. However, microsilica has become a common ingredient in refractory castables and the presence of CAC (or lime) in the refractory matrix leads to liquid phase formation at temperatures above ∼1200 °C, causing the castable to soften and loose strength (poor high-temperature properties) [12]. Consequently, CAC contents have been steadily decreased and alternative lime or cement-free systems have been developed, often based on transitional aluminas such as γ- or ρ-Al_2O_3.

The obvious advantage of lowering the cement content of refractory castables is avoidance of the detrimental effects of a liquid phase, with the consequent improvement of mechanical strength at high temperature (15–20% higher) and of abrasion, corrosion and creep resistance, accompanied by a decrease in porosity and permeability [4,5].

Lower cement content also means better workability and longer working time for in situ application. However, the use of cement seems to be needed to guarantee that the castable sets with the adequate dried mechanical strength for the first service.

The present work was aimed at throwing some light into the generally accepted need to include a minute amount of calcium aluminate cement (CAC) in the composition of self-flow refractory castables (SFRC), to fulfil the often opposing requirements of easy application and high sintered mechanical strength. To this purpose, the model castable (100 wt.% alumina) with optimized particle size composition [6–9], with self-flow character and no cement, is compared to the equivalent castable containing 1 wt.% aluminate cement, in terms of performance of consolidated and sintered bodies (particle packing, density, porosity and water absorption, mechanical strength and thermal shock resistance).

2. Experimental

Tabular (T60) and reactive (CT3000SG) commercial aluminas (Almatis) were used as raw materials. The aggregate was prepared by combining three coarse size classes (0.2–0.6 mm, 0.5–1 mm, 1–3 mm). The matrix was prepared by combining the CT3000SG alumina with two other fine size classes (<63 μm and <25 μm) obtained from the commercial <0.2 mm size class [9].

The optimization of the matrix particle size distribution [6] followed a design of experiments (software Statistica, StatSoft, Inc.) [10,11], and the ideal matrix composition was found to be 60 wt.% CT3000SG and 20 wt.% of each of the other size classes (<25 μm and <63 μm), which was kept constant throughout this work.
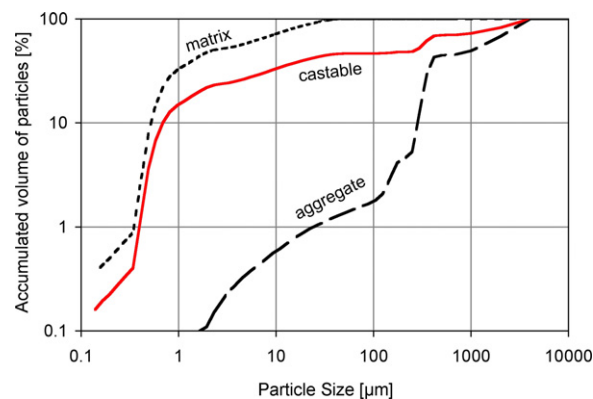

Fig. 1. Optimized particle size distributions of matrix, aggregate and final SFRC.

Earlier work [8,9] showed that the required minimum matrix content for castable self-flow was 47.5 wt.%. The ideal aggregate composition was found to be 10 wt.% [0.5–1 mm] and 45 wt.% of each of the other size classes ([0.2–0.6 mm] and [1–3 mm]), which was also kept constant throughout this work. Fig. 1 shows the optimized particle size distributions of matrix, aggregate and final SFRC.

For the ceramic castable with ultra low cement content, the aluminate cement CA25 (Almatis) was used. Given the similarity of particle sizes, the added cement content (1 wt.%) was compensated by the corresponding reduction in the amount of CT3000SG alumina (Table 1).

Powders in the selected proportions were mixed with water (28 mg/m^2 surface area, constant) in a mortar-blender (Tecnotest, 5 litres) using citric acid (0.36 mg/m^2 surface area) as deflocculant, as described in the Portuguese Patent 103432 (2008) [13].

Fresh pastes were cast into metal moulds (25 mm × 25 mm × 150 mm) and left to harden in the open for 24 h. The hardened bars were then demoulded, oven-dried at 110 °C for further 24 h, and sintered at 1600 °C for 90 min, following the specifications of the ASTM C865 Standard.

Dried samples were characterized by X-ray diffraction against JCPDS-ICDD files (XRD, Rigaku Geigerflex D/max-C Series, Cu Kα radiation, 10–80° 2θ, 3° 2θ/min), thermal analysis (TG and DTA, Netzsch 402 EP, 10 °C/min up to 1000 °C, Pt-Pt10Rh thermocouple) and dilatometry (Bähr GmbH 2000, Dil 801L, 10 °C/min up to 1450 °C, Pt6Rh-Pt30Rh thermocouple).

The ceramic castables expansion behaviour was also evaluated in assisted sintering tests, carried out on cylindrical samples (DIN 51053) pre-sintered at 600 °C for 5 h. The tests were carried out using a refractoriness under load equipment (Netzsch RUL 421E) with a compressive load of 0.02 MPa, and

Table 1
Size composition (weight %) of SFRC mixtures.

	CA25	CT3000SG	<25 μm	<63 μm	0.2–0.6 mm	0.5–1 mm	1–3 mm
MA	0	28.5	9.5	9.5	23.63	5.25	23.63
MAC1	1.0	27.5	9.5	9.5	23.63	5.25	23.63

consisted in recording the changes in sample's height during heating up to 1500 °C (3 °C/min) and a dwell time of 5 h at this temperature.

Apparent and bulk densities, apparent (open) porosity and water absorption of sintered test bars were determined after 72 h immersion in water (ASTM C20).

Cold mechanical strength was evaluated as three-point bending strength (MoR, ASTM C133), both for dried and sintered (1600 °C, 90 min) test bars. Mechanical behaviour at high-temperature (up to 1500 °C) was characterized also in three-point bending tests (HMoR, ASTM C583) carried out on sintered test bars, using a specially developed prototype testing machine equipped with a high temperature furnace and a hydraulic load application device, using a heating rate of 3 °C/min, 3 h dwell at the selected temperature and 780 N/min loading rate.

Resistance to thermal shock was evaluated (ASTM C1171) as retained MoR after 5 and 15 thermal shock cycles from 800, 1000 and 1200 °C.

3. Results and discussion

As described in previous works [6–9], the optimized all-alumina composite without cement (MA) was found to present a fresh paste flowability index (FI) above 130% with minimum added water (28 mg/m^2 surface area) and sintered modulus of rupture above 50 MPa.

The introduction of calcium aluminate cement (CAC) in the MA composition significantly shortens the setting time, with obvious effects on the workability and casting behaviour, which might entail significant structural changes in the dried and sintered microstructures. However, no significant differences were observed between the corresponding X-ray diffraction patterns, or between them and those of the original aluminas. In all cases, along with the expected corundum peaks, aluminium

Fig. 3. Thermal analysis curves (DTA and TG) of dried MA (no cement) and MAC1 (1 wt.% CAC).

oxide hydrate peaks could clearly be observed. Given that the CAC content in MAC1 is very low, any cement hydrates that might have been formed might be below diffraction detection level. Fig. 2 illustrates this, for the MA and MAC1 dried ceramic castables.

The presence of the hydrates was confirmed by thermal analysis, as shown in Fig. 3. In both cases, after the initial endothermal moisture release (~100 °C), there is an exothermal event near 400 °C accompanied by a smooth weight loss, which can be attributed to the decomposition/crystallization of the aluminium oxide hydrate observed in the X-ray patterns. In the MAC1 composition, containing 1 wt.% CAC, a second exothermal event can be observed near 700 °C, also accompanied by a smooth weight loss, which should be attributed to the decomposition/crystallization of the calcium aluminate hydrates that might have been formed.

Nevertheless, hydrates decomposition does not upset the expansion behaviour of the dried ceramic composites, as shown by the dilatometric curves of dried MA and MAC1 (Fig. 4). It can be seen that the presence of 1 wt.% CAC does not change the ceramics linear thermal expansion coefficient, which was found to be 7.73×10^{-6}/K (200–800 °C) for MA and
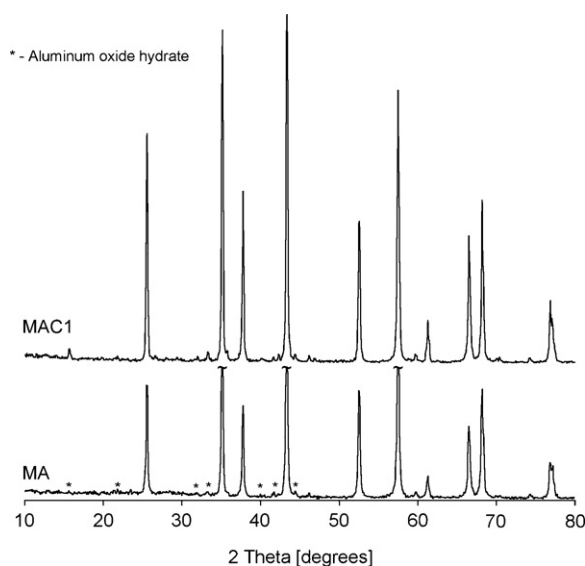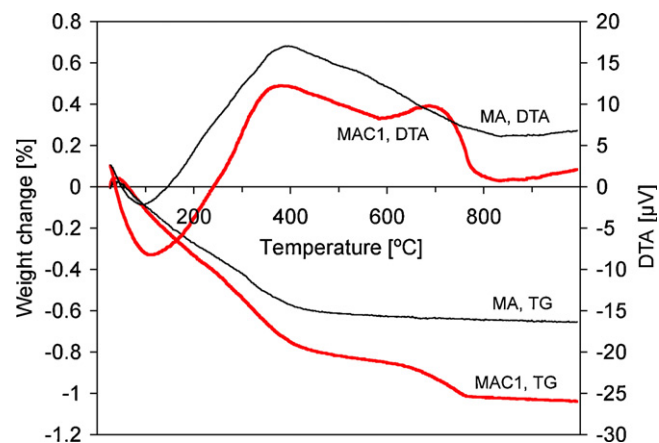

Fig. 2. X-ray diffraction patterns of dried MA (no cement) and MAC1 (1 wt.% CAC), showing the characteristic peaks of corundum and aluminium oxide hydrate (marked with *).
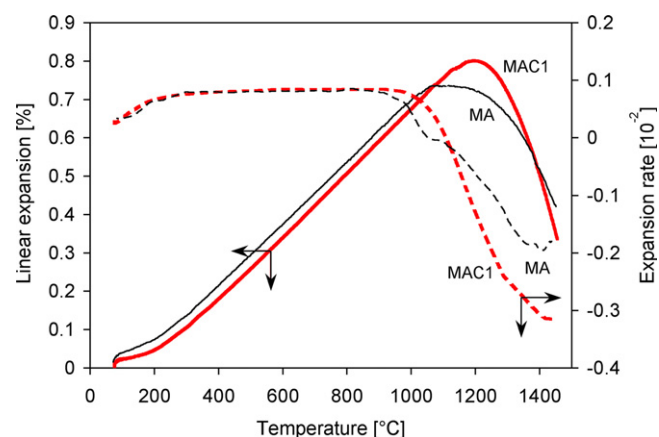

Fig. 4. Expansion behaviour (dilatometry) of dried MA (no cement) and MAC1 (1 wt.% CAC). Expansion rate curves (derivative, dashed lines) are also shown.
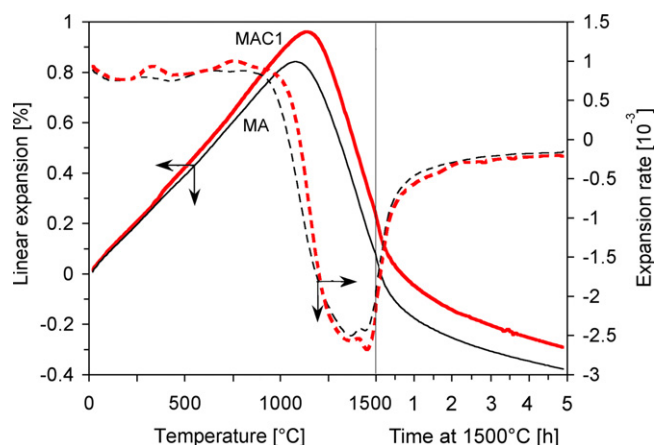
Fig. 5. Expansion behaviour (assisted sintering) of MA (no cement) and MAC1 (1 wt.% CAC). Expansion rate curves (derivative, dashed lines) are also shown.
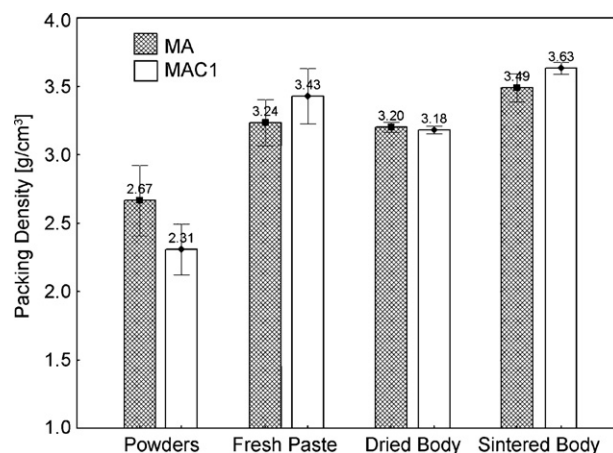

Fig. 6. Changes in particle packing density in compositions MA (no cement) and MAC1 (1 wt.% CAC): dry loose powders, fluid fresh paste, dried hardened body and sintered body (mean value ±0.95 confidence interval).

8.01×10^{-6}/K (400–800 °C) for MAC1. Also, first signs of shrinkage occur at ∼1000 °C in both cases, as shown by the derivatives of the dilatometric curves, and maximum shrinkage (sintering well) occurs near 1400 °C for both. However, the expansion rate of MA suggests that an expansive event occurs near 1100 °C.

To further differentiate the ceramics expansion behaviour, expansion curves were recorded in assisted sintering tests under a compressive load of 0.02 MPa, as a function of temperature during constant heating up to 1500 °C, and then as a function of the time spent at this maximum temperature (isothermal dwell), as shown in Fig. 5.

Under the small applied load, MAC1 presents a slightly higher expansion coefficient but, other than that, the expansion behaviour is rather similar to that already observed in Fig. 4. Again, first signs of shrinkage occur at ∼1000 °C in both cases, as shown by the expansion rate curves, and maximum shrinkage (sintering well) occurs near 1400 °C for both. As before, sintering shrinkage takes over thermal expansion earlier for MA (MAC1 reaches a higher maximum expansion, although still below 1%) but the expansive event detected by pressureless dilatometry was not observed here. During the isothermal dwell, the shrinkage rate decreases and is gradually counter-balanced by normal thermal expansion. The irregularities observed in both expansion rate curves near 1500 °C are likely artifices due to the construction of the derivative curves, rather than the result of the expansive formation of the very small amount of crystalline calcium hexa-aluminate (CA_6) at ∼1500 °C [14] expected to occur only in MAC1. Both expansion curves show no further events and, after 5 h at 1500 °C, the estimated permanent linear change is low (∼0.3%) and comparable for the two ceramics.

Fig. 6 compares the changes in packing density of compositions MA (no cement) and MAC1 (1 wt.% CAC), determined at four fundamental processing steps, namely, dry powders, fresh paste, dried hardened body and sintered body.

While loose powders pack better without cement (near 15% denser), fresh pastes with cement appear to be denser. Nevertheless, the dried bodies reach similar densities and,

upon sintering, the composition with cement is slightly better (∼4%). Thus, the differences between the two compositions, at all four processing stages, can be regarded as meaningless.

The same can be said about apparent and bulk density of sintered bodies (determined after 72 h water immersion), which are compared in Fig. 7. However, Fig. 7 shows that important differences exist between water absorption and apparent (open) porosity, for which the composition with 1 wt.% CAC presents higher values (∼22% higher). Similar results can be found in other works, which report porosity values usually above 20% [15]. The present results are likely related to the differences in hydration mechanisms, namely to the formation sequence of the various calcium aluminate hydrates: the transformation of metastable hydrates CAH_{10} and C_2AH_8 into the stable cubic hydrate C_3AH_6 results in a volume reduction (53% from CAH_{10} to C_3AH_6, and 16% from C_2AH_8 to C_3AH_6) and an increase in porosity [16]. Thus, although the ceramics reach comparable bulk densities, the type of porosity might play a determinant role in the performance of the sintered refractory. Having a smaller proportion of open pores, refractory castables prepared
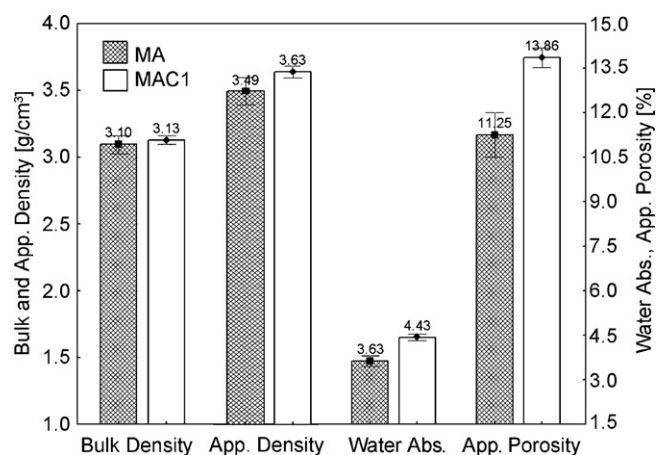

Fig. 7. Properties of sintered MA and MAC1 (72 h water immersion): bulk and apparent densities, water absorption and apparent porosity (mean value ±0.95 confidence interval).
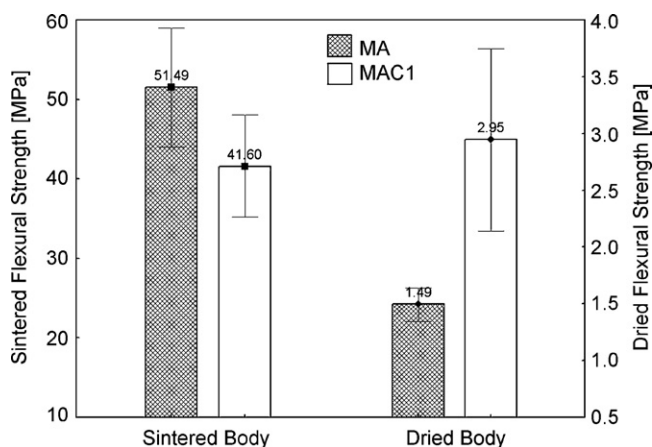
Fig. 8. Flexural strength (MoR) of dried and sintered MA and MAC1 (mean value ±0.95 confidence interval).

without cement might show better abrasion and corrosion resistance than those containing CAC, and superior high temperature mechanical strength.

Fig. 8 compares the flexural strength of dried and sintered compositions and, again, significant differences can be observed. The dried mechanical strength is much better (twice the value) for the composition MAC1 with 1 wt.% CAC, which, coupled with longer setting and drying times, might result in some difficulties while demoulding and handling hardened MA bodies. These results suggest that the aluminium oxide hydrates provide a weaker bonding system as compared to calcium aluminate hydrates. However, upon sintering, the composition without cement (and less open pores) shows a flexural strength 23% higher than that with CAC.

Fig. 9 shows the effect of high temperature on the mechanical strength of MA (no cement) and MAC1 (1 wt.% CAC). It can be observed that the mixture without cement (MA) has a quasi linear strength degradation with increasing temperature up to 1200 °C, reaching ~34% of the original MoR at this temperature, followed by a more abrupt resistance reduction at 1500 °C (~60%). On the contrary, mixture MAC1, with 1 wt.% AC, shows a nearly constant small strength reduction up to 1200 °C (less than 15% of the corresponding original value), but at 1500 °C a significant reduction in
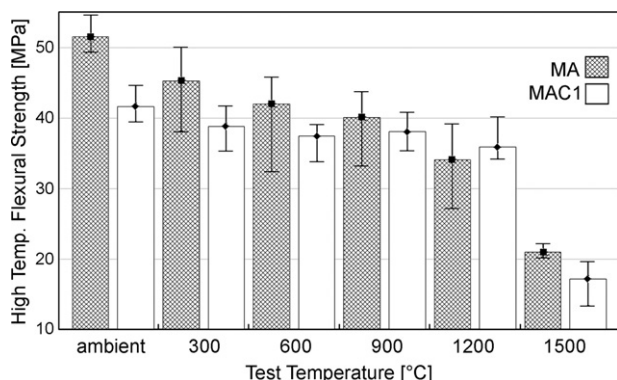

Fig. 9. High temperature flexural strength (HMoR) of MA and MAC1. Room temperature MoR of sintered compositions is also shown for comparison.
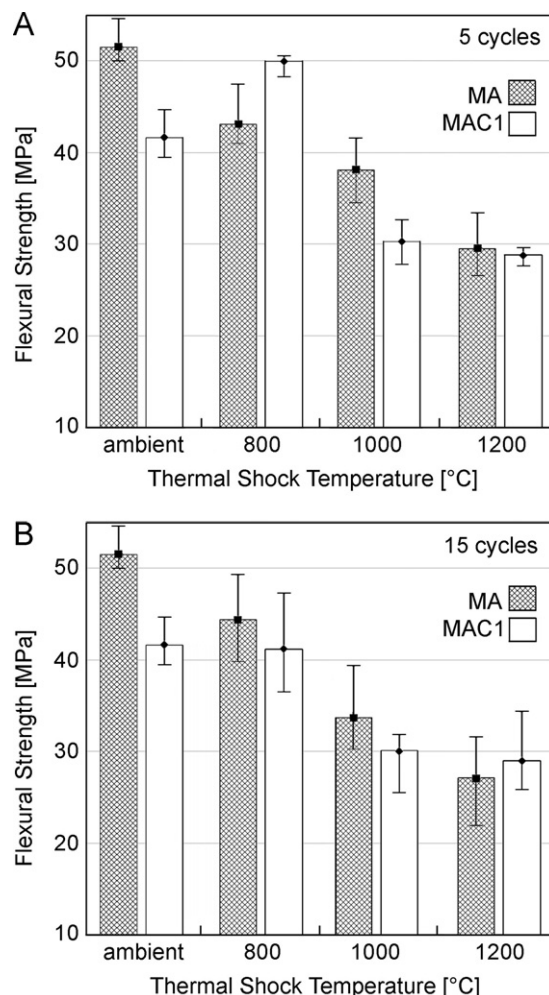

Fig. 10. Room temperature flexural strength (MoR) of compositions MA and MAC1, after thermal shock cycling. Original MoR of sintered compositions is also shown for comparison.

mechanical strength (~60%) can also be observed. It must be reminded that there is no expected liquid phase formation in either system in this temperature range, although liquid phases that form near 1600 °C in the alumina–lime system might be felt in a transient way (non-equilibrium) in MAC1. Therefore, the observed softening in both compositions is likely related to microstructural rearrangement. Despite the scatter in experimental results, mixture MA without cement clearly shows a tendency for a superior mechanical performance at high temperature, particularly above 1500 °C, when the corresponding HMoR value is approximately 20% higher than that of mixture MAC1. This reflects, once again, the deleterious effect of CAC additions and constitutes an advantage for no cement castables.

Fig. 10 shows the degradation of mechanical strength of composition MA (no cement) and MAC1 (1 wt.% CAC) after 5 and 15 thermal shock cycles. The first point to note is that, in both cases and as expected, the retained strength decreases as the number of cycles and their severity increases. After 15 thermal shock cycles from 1200 °C, the flexural strength is reduced to nearly half of the original value. However, the

mechanical strength degradation of MA is progressive, whereas that of MAC1 only becomes obvious for thermal shocks from above 1000 °C. If this trend holds, mixture MAC1 might show a superior 15 cycles thermal shock performance from temperatures close to 1500 °C.

Nevertheless, as a second observation, the thermal shock resistance of MA (retained mechanical strength) is generally higher than that of MAC1.

4. Conclusions

As expected, the presence of cement improves the mechanical strength of the dried refractory castables and consequently promotes faster demoulding and easier handling. However, the high temperature behaviour of the optimized no cement ceramic surpasses that of the competing refractory castable. The observed differences in performance are no doubt related to the differences in hydration mechanisms, namely to the formation sequence of the various calcium aluminate hydrates, which results in increased open porosity. Although the ceramics reach comparable bulk densities, the type of porosity seems to play a determinant role. As a consequence, MA reaches high temperature bending strength values higher than those for MAC1, even if the latter is capable of holding its lower high temperature strength longer, while a gradual reduction with increasing temperature is observed for MA. A softening of the structure is observed near 1500 °C in both cases, which likely derives from the severing of the matrix-aggregate interface and subsequent grain sliding and crack propagation. Also, the thermal shock resistance is generally higher for MA than for MAC1.Having a better understanding of the effects of the CAC, this work demonstrates that all – alumina SFRC (without cement) can be a valuable option when fast drying or rough green handling can be avoided, resulting in a sintered lining with high mechanical strength at high temperature and uncompromised thermal shock resistance.

Acknowledgements

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