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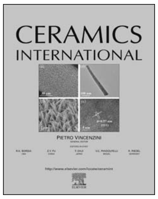

B_4C mineralizing role for mullite generation in Al_2O_3-SiO_2 refractory castables

A.P. Luz[a,*], J.H. Gagliarde[a], C.G. Aneziris[b], V.C. Pandolfelli[a]

[a] Federal University of São Carlos, Materials Engineering Department, Rod. Washington Luiz, Km 235, São Carlos, SP 13565-905, Brazil
[b] Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Agricolastrasse 17, 09599 Freiberg, Germany

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ABSTRACT

Based on refractory end-users' requirements, continuous efforts have been made to design engineered products able to withstand high temperatures (800–1500 °C) and severe thermal gradients. One alternative to enhance the mechanical properties of alumina-based compositions consists of inducing in situ generation of phases with platelet or acicular shape within their matrix fraction, which may improve crack deflection and grain bridging mechanisms. Mullite and $Al_{18}B_4O_{33}$ are some compounds that present such interesting features. Thus, this work addresses the evaluation of alumina refractory castables bonded with SioxX-Zero and/or microsilica, containing 0 or 1 wt% of B_4C (sintering additive), aiming to: *(i)* induce transient liquid sintering, *(ii)* point out which silica source could favor a more effective mullite formation at high temperatures, and *(iii)* analyze the influence of B_4C in the phase transformation and thermo-mechanical properties of the designed compositions. Comparing SioxX-Zero and microsilica-bonded refractories, the latter showed more likelihood to give rise to the mullite phase during the samples' thermal treatments. Moreover, adding B_4C to the castables containing 3 wt% of SiO_2 induced the generation of a boron-rich liquid phase with transient features during the samples' firing step, favoring earlier sintering and faster mullite and $Al_{18}B_4O_{33}$ formation. These transformations resulted in refractories with enhanced creep, thermal shock resistance and HMOR behavior in a broader temperature range (600–1550 °C), which may enable them to be used in various industrial applications (petrochemical, steel-making, etc.).

1. Introduction

The driving force to continuously improve refractory materials performance derives from the requirements and needs of many industrial sectors. Great efforts have been carried out in recent years in order to design engineered products able to withstand high temperatures (800–1500 °C) and harsh thermal gradients due to temperature changes faced during operational conditions of cracking units, ladle and electric-arc furnaces, torpedo-cars, and others.

Despite the interesting features of alumina (i.e., high hardness, corrosion and oxidation resistance and chemical stability), the application of this oxide as a structural material is limited due to its relatively low fracture energy and thermal shock resistance. In order to enhance the mechanical properties of alumina-based compositions, whiskers, fibers or platelets may be dispersed within the matrix fraction due to their role in improving crack deflection and grain bridging mechanisms [1–4]. However, incorporation of high aspect ratio particles results in the buildup of transient stresses during sintering, leading to poor densification of the ceramics [5]. A more efficient alternative consists of designing toughened alumina composites based on in-situ generation of phases with platelet-like or acicular morphology (such as $CaAl_{12}O_{19}$ or CA_6, $Al_6Si_2O_{13}$, $Al_{18}B_4O_{33}$, etc.) via liquid-phase sintering [1,6–13]. The resulting liquid usually enhances densification at lower temperatures, allowing material to be transported to and from all regions of the microstructure. Furthermore, the interfacial bond strength between platelets and other grains may also be improved via transient-liquid sintering (with further precipitation of solid compounds and liquid consumption at high temperature) [10,14].

Mullite is an important structural ceramic material due to its low thermal expansion and conductivity, excellent creep resistance, high temperature stability and good chemical resistance [11,15–17], whose composition may be described as a solid solution series, $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$ ($0.18 \leq x \leq 0.88$) [18]. Aluminum borates represent another interesting class of materials, as they are structurally related to mullite and stable up to relatively high temperatures [11,15,19]. $Al_{18}B_4O_{33}$ or A_9B_2 (where A = Al_2O_3 and B = B_2O_3) has aroused specific interest in ceramics due to its low thermal expansion, high elastic modulus and tensile strength (depending on the microstructural design), etc.

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[*] Corresponding author.
E-mail address: anapaula.light@gmail.com (A.P. Luz).

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[19,20]. A_9B_2 whiskers are commercially available under the names of Alborex and Alborite (Shikoku Chemical Corporation, Japan). These products are usually added to aluminum alloys in order to obtain composite materials with higher mechanical strength [19].

The in situ generation of the two compounds, mullite and A_9B_2 (giving rise to a solid solution named “boron-mullite” [11,15,16,21]), in refractory castables has great potential for designing enhanced materials. Another important aspect is the faster reaction rate and earlier generation of mullite in boron-containing alumina-silica compositions [11,13–16]. Lührs et al. [11] highlighted that long-term thermal stability at 800 °C was obtained for B-mullite$_{(ss)}$, whereas complete decomposition of this compound (into boron-free mullite and corundum) was observed at 1400 °C after 90 h of thermal treatment. Furthermore, the boron incorporation into the alumino-silicate crystal structure reduced its thermal expansion coefficient by 15%, when compared to the B-free phase [13].

Despite the great potential of boron-mullite$_{(ss)}$ to be used to develop advanced refractory compositions, its formation and effect on castables' performance at intermediate and high temperatures are still not well explored. Therefore, this work addresses the evaluation of alumina refractory castables bonded with SioxX-Zero and/or microsilica and containing 0 or 1 wt% of B_4C (sintering additive), aiming to: *(i)* induce transient liquid sintering, *(ii)* point out which silica source could favor a more effective mullite generation at high temperatures, and *(iii)* analyze the influence of B_4C in the phase transformation and thermo-mechanical properties of the designed compositions.

2. Experimental

Six vibratable castable formulations were prepared according to the Alfred's particle packing model (q = 0.26 [22], Table 1), containing tabular alumina (aggregates with $d < 6$ mm and fine fractions with $d < 0.045$ mm, supplied by Almatis, Germany), calcined (CL370, Almatis, Germany) and submicron Al_2O_3 (SMA, $d < 8$ µm, Elkem, Norway) as main raw materials. SioxX-Zero (SZ, which is an alumina-silica based binder) and microsilica (MS, 971U), both provided by the Elkem company (Norway), were the binders added to the compositions. Myhre et al. [23] reported that mullite formation could be identified in ultra-low cement (0.5 wt%) white fused-alumina-based refractories containing SiO_2 amounts higher than 2 wt%. Based on that, formulations comprising 3 (3S) or 6 wt% (6S) of different silica sources (SZ or MS) or the combination of 3 wt% of SiO_2 with 1 wt% of boron carbide (B_4C, $d < 45$ µm, China Refractories, China), were evaluated, as this latter additive may speed up mullite generation and induce the formation of aluminum borates in the designed compositions.

The incorporation of 0.5 wt% of calcium aluminate cement to the dry-mixes was carried out as the binding effect of silica-bonded systems is triggered by the presence of Ca^{2+}, which reduces the overall net repulsion of SiO_2 particles and gives rise to the link among the coarse and fine components of the castables [24,25]. Additionally, 0.2 wt% of the dispersant Castament FS20 (Basf, Germany) was used during the preparation of the microsilica-bonded materials (MS-3S, MS-3S-B and MS-6S, Table 1).

The compositions were dry-homogenized for 1 min and mixed for an additional 3 min in a rheometer [26]. The required water amount and attained vibratable flow (ASTM C860) are presented in Table 1. After that, prismatic samples (150 mm × 25 mm × 25 mm) were cast under vibration, cured at 50 °C for 24 h, dried at 110 °C for another 24 h and fired in the range of 600–1550 °C for 5 h.

Cold flexural strength (ASTM C133-97) and apparent porosity (ASTM C380-00, using kerosene as the immersion liquid), creep, refractoriness under load and hot modulus of rupture (HMOR) measurements were selected to evaluate the refractories' thermo-mechanical performance. The latter test was carried out at 600 °C, 815 °C, 1000 °C, 1200 °C and 1400 °C (using samples pre-fired for 5 h at the same testing temperature or at 1400 °C) in HBTS 422 equipment (3-point bending device, Netzsch, Germany). The materials were evaluated at 815 °C, which is the standard reference temperature to select refractories for the petrochemical industry (which is one of the likely applications by using the compositions analyzed in this work).

Creep was measured to find out the thermal stability of the samples at 1450 °C for 24 h. Cylindrical specimens (height and external diameter = 50 mm and central inner diameter = 12.5 mm) were prepared according to the 51053 DIN standard and pre-fired at 1550 °C for 24 h. For testing, the castables were heated up to 1450 °C (heating rate = 5 °C/min) under a compressive load of 0.2 MPa.

Aiming to understand the elastic modulus (E) changes with temperature, dried and pre-fired (1400 °C/5 h) samples of the designed refractories were also analyzed according to the ASTM C 1198-91 standard using the bar resonance technique (Scanelastic equipment, ATCP, Brazil), which is based on the sample excitation and detection of the correspondent vibration spectrum, using piezoelectric transducers. In such experiments, wide frequency scanning is carried out in order to excite and capture the natural resonance frequencies of the ceramic bars. Elastic modulus is calculated based on the resulted vibration spectrum applying Pickett equations, which correlates the *E* values, the natural vibration frequencies and the sample dimensions [27]. For the fundamental flexural frequency of a rectangular bar, the Young's modulus is given by:

$$E = 0.9465\frac{mf_f^2}{b} \times \frac{L^3}{t^3} \times T_1 \tag{1}$$

where, *E* is the Young's modulus (Pa), *m* the mass (g), *b* the width (mm), *L* the length (mm), *t* the thickness (mm), f_f the fundamental resonance frequency of the bar in flexural mode (Hz), and T_1 the correction factor to account for the finite thickness of the bar, Poisson's ratio and others. Tests were conducted in the 30–1400 °C temperature range in air (pO_2 = 0.21 atm) with heating and cooling rates of 2 °C/min. The same method was also used to follow (at room temperature)

Table 1
General information of the evaluated refractory castables.

Raw materials (wt%)		**SZ-3S**	**MS-3S**	**SZ-MS-6S**	**MS-6S**	**SZ-3S-B**	**MS-3S-B**
Tabular alumina	T60, d ≥ 6 mm	91.7	91.5	88.7	90.5	90.7	90.5
Calcined alumina	CL370C	–	2.0	–	–	–	2.0
Microsilica	MS	–	3.0	3.0	6.0	–	3.0
Submicron alumina	SMA	3.0	3.0	3.0	3.0	3.0	3.0
SioxX-Zero*	SZ	4.8	–	4.8	–	4.8	–
Calcium aluminate cement	Secar 71	0.5	0.5	0.5	0.5	0.5	0.5
Boron carbide	d ≤ 45 µm	–	–	–	–	1.0	1.0
Dispersant	Castament® FS20	–	0.2	–	0.2	–	0.2
Water content (wt%)		4.2	4.3	4.8	4.7	4.4	4.5
Vibratable flow (%)		137	139	129	137	135	142

* SioxX-Zero overall chemical composition (wt%): SiO_2 = 65.8, Al_2O_3 = 32.5, Na_2O = 1.2.