BIO INSPIRED REFRACTORIES BASED ON NACRE STRUCTURE

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ABSTRACT

Structural ceramic materials are usually strong or tough, although both properties are required for high temperature applications. During the past decades, intensive research has been carried out to engineer the ceramics' microstructure, which allowed the development of advanced materials with improved toughness (due to the action of different toughening mechanism) while maintaining their strength. Other approach consisted on mimicking the structure of natural materials, as these components can be strong and tough (despite the fact that they are comprised by brittle constituents). One example is the mother of pearl shell (*Abalone Nacre*) with approximately 95 % of calcium carbonate platelets imbedded in 5 % of protein layers. This material presents strength and toughness 20 times higher than its constituents and do not follow the rule mixture of properties. This behavior is only possible due to the nacre structure which presents high level of organization from nano to micro scale. Considering these aspects, this work addresses the design of alumina refractories with nacre-like structure, based on the use of the Magnetically Assisted Slip Casting (MASC) technique and Transient Liquid phase sintering (TL) procedure. Cold and hot mechanical tests were carried out to evaluate the prepared samples. The nacre-like refractories (NLR) had a structure comprised by alumina platelets with aluminum borate as a second phase. The latter played two important roles: (i) stabilized the structure, and (ii) enhanced the mechanical properties by increasing the bond strength between platelets. The NLR showed average flexural strength of 672 MPa, fracture toughness of 11 MPa.m$^{1/2}$ at room temperature and stable crack propagation. The samples evaluated at 1200°C presented high mechanical strength (280 MPa) and fracture toughness of 6 MPa.m$^{1/2}$. When compared to Ceramic Matrix Composites (CMCs), the prepared NLR presented twice the specific strength of these ceramics in the temperature range of 750-1200°C. Therefore, due to their enhanced performance, nacre-like refractories can be considered as novel structural materials for specific high temperature applications.

Keywords: refractory, toughness, high temperature, bio inspired, nacre

1 INTRODUCTION

Materials for high temperature applications need to be stiff, strong and tough at the considered working temperature. Furthermore, they might face extreme conditions when submitted to aggressive environment [1]. The chemical and mechanical features of ceramics fit these requirements, although they are usually brittle due to the absence of intrinsic toughening mechanisms which limits their usage where catastrophic failure is not an option [2].

Improvements on the toughness of ceramics have been made by introducing extrinsic mechanisms [2] for instance, with the addition of micro particles with high aspect ratio to their matrix [3-5]. The difference in the mechanical properties of the particulate reinforcement and the original material greatly improve the overall toughness but it does not prevent catastrophic failure of such composites [3-5].

Other option consists in introducing oriented long fiber reinforcements into the ceramic composition [6]. In this approach, the resulting material which is named ceramic matrix composite (CMCs), present's outstanding mechanical properties through a broad range of temperature, which depend directly on the fibers orientation [6]. Their processing route are quite complex and expensive requiring several steps to achieve higher densities. Consequently, the CMCs oriented in more than one direction always present high porosity (between 15 to 50 %) which spoils its strength, although stable crack propagation can be achieved [6]. Moreover, these composites are sensitive to delamination due to the mechanical properties differences between matrix and fibers [6].

Recently, various researches based on the development of the ceramics with structures mimicking the architecture of nacreous part of the abalone shell (nacre), have pointed out the likehood of developing strong and tough materials [7,8]. Nacre microstructure is highly organized from nano to micro scale and comprises calcium carbonate platelets placed in a brick wall fashion with proteins as mortar [9]. This hierarchical structure results in a material with high strength and toughness, despite the brittle feature of its main constituent (95 wt % CaCO3) [9]. Different processing routes have been developed in recent years aiming the manufacture this bio inspired material. Magnetically Assisted Slip Casting (MASC) is one of them resulting in ceramics with highly organized hierarchical structures reproducing the one of the abalone shell. Nevertheless, care must be taken when choosing the composition and ceramic phases, as they will play a role and affect the mechanical properties at high temperature [7].

An alternative to optimize the refractoriness of these complex composites is by introducing additives that may induce transient liquid sintering of the microstructure at intermediate temperatures. This process has been widely used in different materials, such as metals, ceramics and refractory castables [10]. In the latter case, the sintering process may take place at temperatures as low as 850 °C, resulting in ceramics with good thermo-mechanical properties [10]. The selection of the most suitable additive to generate the transient liquid phase must be carried out aiming to favor its reaction with the matrix components and forming other crystalline phases. For example, the use of boron-based additives may induce in situ formation of $9Al_2O_3.2B_2O_3$ which is a strong crystalline phase with high melting point (1945 °C) and can present mechanical properties close to mullite [10].

The present work combines the MASC [7] processing route with the transient liquid phase sintering [10] in order to produce a bio inspired refractory of $Al_2O_3/9Al_2O_3.2B_2O_3$ to keep the properties at high temperature (>1000 °C). The use of alumina platelets, nanoparticle and boron based additive into the designed refractory aims to induce faster and more effective sintering of the specimens (via transient liquid phase sintering) and increase the bond-strength between platelets with the *in situ* generation of $9Al_2O_3.2B_2O_3$. As the MASC process is a wet processing route, H_3BO_3 was used as a boron source due to its partial solubility in water (0.0472 g/ml at 20 °C) and its suitable adsorption onto the alumina particles surfaces [11].

2 MATERIALS AND METHODS

The Magnetically Assisted Slip casting (MASC) processing route consists in the merge of two different techniques: the slip casting and magnetic alignment of particles with high aspect ratio. The slurries raw materials used in its preparation are: magnetically responsive alumina platelets, alumina nanoparticles (TmDar – Taimei – mean diameter 180 nm), boric acid (H_3BO_3-Sigma Aldrich – analytic purity 99.0 %), Dolapix (Zschimmer & Schwartz) and polyvinylpyrrolidone (PVP – Sigma Aldrich).

The functionalized platelets were obtained from the adsorption of the super paramagnetic iron nano particles (Fe_3O_4) onto the alumina platelets surfaces (Ronaflair Whitesapphir-Merck). The procedure is carried out by adding the ferrofluid suspension (EMG 705 - Ferrotech) into an alumina platelets suspension with deionized water and under constant agitation. The procedure takes close to 24h to be completed. Afterwards, the functionalized platelets are filtered and dryed at 110 °C for 2h00.

The slurries were prepared with a solid volume fraction close to 25 v. %. Firstly, 3.152 g of deionized water and 0.042 g of dispersant are mixed together prior to the addition of 0.082 g of boric acid, resulting in a clear solution. Later the 0.120 g of alumina nano particles are added into the solution and sonicated in water bath for 30 min. Then, 4. g of functionalized platelets are added in the previous suspension which is subsequently sonicated for 10 min at 60 % of its maximum power. Afterwards, 0.158 g of PVP was added in the suspension which was maintained under stirring for 4 h. Additionally 0.1 mL of ethanol was added into the suspension in order to completely remove the bubbles generated from the mixing steps.

The slurries were cast on the porous gypsum mold under a rotating magnetic field (RMF). The RMF was generated by a 400 mT permanent magnet. The rotating magnetic field allows the alignment of the magnetized alumina platelets while the solvent is withdrawn from the slurry through the porous mold. After the casting is completed, the sample was dried for 4 h at 60 °C. A schematic illustration of the processing route is shown in Figure 1.

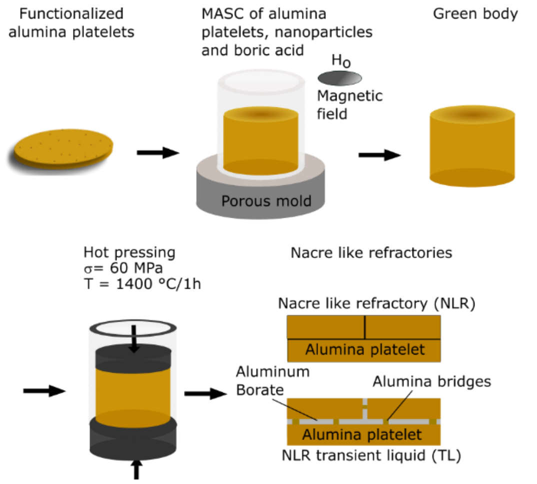

Figure 1: Schematic illustration of the processing route steps.

All samples were heat treated at 500 °C/4h in air to burn out of the organic compounds contained in the green body and induce the boric acid decomposition. Then, the green samples were placed in a graphite die (20 mm, 30 mm and 50 mm diameter) coated with boron nitride for the hot press sintering. The samples were sintered under a uniaxial pressure of 60 MPa applied with a loading rate of 4KN.min^{-1} using a hot press (HP – FCT Systeme GmbH). The heating rate for all procedures was 20 °C/min and a dwell time of 1h at 1400 °C was used.

Reference samples (containing only alumina platelets and nanoparticles) were produced by the same process described above. The two compositions are named Nacre Like Refractory (NLR) for the boron-free (reference) and Nacre Like Refractory – Transient Liquid phase sintering (NLR-TL) for the materials containing aluminum borate as secondary phase.

2.1 Characterization

The nacre like refractories were characterized through different techniques in order to evaluate its structural and mechanical properties with different temperature. The crystalline phases identification was carried out via X-ray diffraction analysis using ground samples and a Bruker equipment (D8 Focus, CuKα radiation [α = 1.5418 Å] with nickel filter, scanning step = 0.02). The microstructure features and composition map were assessed by SEM/EDX analysis by SEM, LEO 1530, Zeiss, Germany.

Nano mechanical properties of the different phases contained in the nacre like refractories were accessed through nano indentation tests. A grid of 225 nano indents distributed in a regular square grid of 25 x 25 points spaced by 500 nm were performed on the polished surfaces of samples of each evaluated composition. The tests were carried out with CSM Ultra Nanoindenter (Anton Paar TriTec, Peseux, Switzerland).

The cold and hot mechanical measurements was based on ASTM C1421-15. Disc shaped sintered specimens with 20-mm diameter were cut into beams around 14 x 2 x 2 mm^3. Such materials were mirror polished and chamfered to avoid any crack initiation from the sides. Single-edge beam test specimens were firstly notched with a wire saw of 300 µm thickness. The bottom of each dent was then sharpened by repeatedly passing a razor blade coated with diamond past (1/4 µm). At least 4 specimens for each composition were tested in a Shimadtzu testing machine in 3-point bending. The fracture toughness of the nacre like refractories was determined by monotonically loading them to failure at constant displacement rate of 1 µm s^{-1}. The high temperature mechanical tests were performed using a universal testing machine (Instron) coupled with a in house built high vacuum (10^{-5} torr) furnace. Larger beams (20 x 3 x 4 mm^3) were obtained from disc shaped sintered samples with 30-mm diameter. The un-notched beams for three-point bending tests were mirror polished and chamfered to avoid any crack initiation from the sides.

3 RESULTS AND DISCUSSION

The selected processing route allowed the synthesis of the bio-inspired refractories with organized structure at different scales. Figure 2 shows the comparison between the obtained microstructures and the abalone shell nacre at different scales. The resemblance and organization of the synthetic and natural structures are really close. This was possible as the sintering process of the bio-inspired composites took place under uniaxial pressure which kept the organization of the micro platelets in the green body during the densification process.

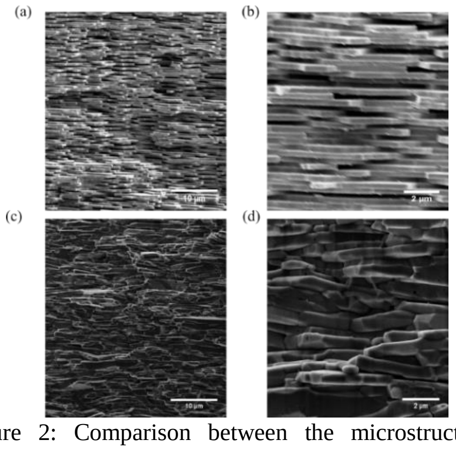

Figure 2: Comparison between the microstructures of the nacreous part of the abalone nacre shell [(a) and (b)] and the nacre like refractory [(c) and (d)] obtained by scanning electron microscopy.

In order to assess the location and composition of different phases present in the bio inspired refractories structure, various characterization techniques were used. Figure 3 (a) shows the XRD profiles of both compositions indicating that the NLR-TL contained corundum and $9Al_2O_3.2B_2O_3$ as main phases. The aluminum borate formation was expected to take place based on the Al_2O_3-B_2O_3 phase diagram [12]. High-alumina boron-containing compositions usually present $9Al_2O_3.2B_2O_3$, which is a crystalline component with higher melting point (1950°C) than the selected sintering temperature (1400°C) [10]. As the XRD analysis only shows the content of the major crystalline phases contained in the refractories, SEM/EDX composition mapping analysis were performed to evaluate other minor phases, amorphous and crystalline, that could be present. Figure 3 (b) shows the SEM/EDX mapping of broad ion beam polished cross section of the NLR-TL. The obtained map highlights the presence of iron microparticles. As the microparticles containing iron did not show any trace of oxygen, it indicates that this mettalic particles formation might be associated with the reducing environment derived from the graphitte dies.

The presence, properties and location of the different phases in the nacre structure has strong influence on its macroscopic failure behavior [13]. In order to measure the mechanical properties of the different phases contained in the bio-inspired refractory, nano indentation tests were carried out [14]. Figure 3 (c) shows the frequency plot of the measured Young modulus values obtained for the composition with boron (NLR-TL) indicating the presence of two peaks. One of them can be associated to the alumina phase (309 GPa) whereas the other to the aluminum borate phase (265 GPa). These measured values are similar to the ones previously reported in the literature indicating that the nano indentations procedure had enough resolution to probe the single crystalline phases [15,16]. The average Young's modulus were 360 ± 50 GPa for NLR and 305 ± 20 GPa for NLR-TL samples. The higher standard deviation of NLR Young modulus is related to greater presence of defects in its structure, showing that the transient liquid sintering also favored the structure homogeneization. On the other hand, the lower E values of NLR-TL shows that even probing solely one phase in the nano structure, the presence of the others affect the measurements, even when the nano indentations penetrated only 50 nm.

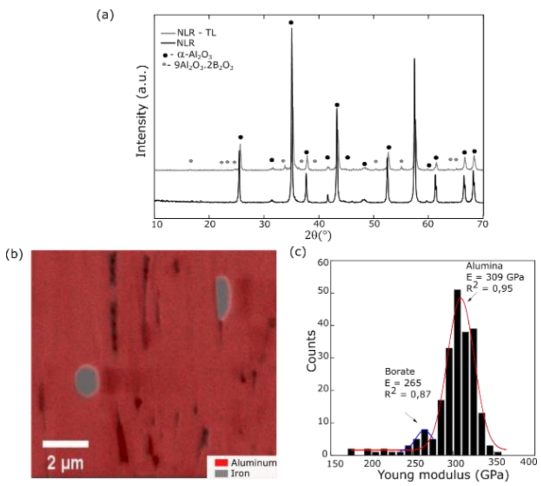

Figure 3: Structural characterization of the bio-inspired refractories: XRD pattern with crystalline phase identification, (b) SEM/EDX composition map of the cross section of the NLR-TL and (c) frequency plot of Young modulus obtained from the nano indentation tests.

To evaluate the macro mechanical properties of the bio inspired refractories, 3-point bending tests on regular and single edge notch beams were carried at room and high temperature (750, 900 and 1200 °C).

The effect of the borate phase in the mechanical properties of the bio inspired refractories is presented in Figure 4 (a), which shows the load versus displacement curves of the 3 point bending tests performed on single edge notched samples with a constant displacement of 1 µm.s^{-1}. In Figure 4 (a) curves, 3 different regions can be identified: linear elastic (until point 1), stable crack propagation (between point 1 and 2 and after 3) and unstable crack propagation (between 2 and 3). Between points 1 and 2, the gradual change in the curve slope shows that the bio inspired refractories present stable crack propagation before reaching the peak load. At the peak load (point 2) the fracture toughness of both compositions can be calculated using the data from Figure 4 (a) according to the standard ASTM C1421-15 [17]. Figure 4 (c) shows the fracture toughness values obtained for the bio inspired refractories highlighting a 57 % improvement in the fracture toughness (K_{Ipb}) of the refractory containing the borate phase.

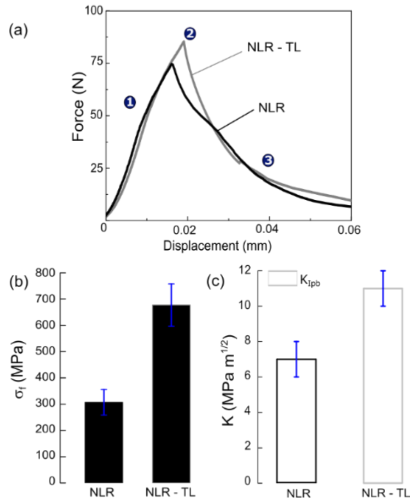

Figure 4: Mechanical characterization of the nacre like refractories at room temperature: (a) load versus displacement curves, (b) strength versus composition histogram and (c) fracture toughness versus composition histogram.

The same beneficial trend seen on the fracture toughness data in Figure 4 (c), when the borate phase is added to the system of the bio-inspired refractories, was detected for the strength (σ_f) values measured for the boron containing material (Figure 4 b). The joint improvement of K_{Ipb} and the σ_f can be explained by two main factors: the increase of the bonding strength between platelets due to the presence of the interphase (aluminum borate) and the reduction in the number of flaws contained in the microstructure. The stronger bond between the interphase and alumina platelets are most likely related to the coefficients of thermal expansion (CTE) mismatch between phases [4]. Similar behavior has been observed on zirconia advanced ceramics with enhanced toughness.

The outstanding mechanical behavior of the bio-inspired refractories at room temperature is also observed at high temperature. Figure 5 (a) presents the flexural strength of the bio inspired refractories and other selected ceramics as a function of temperature [3, 5, 16, 18]. NLR-TL is the strongest material for the evaluated temperature range. When increasing the testing temperature, the strength of all materials decreased except for the 2D reinforced CMC 2D Nextel 720 composite [18]. The fracture toughness (K_{Ipb}) as shown in Figure 5 (b) present a similar trend to the one attained for the flexural strength (Figure 5 (a)). The presented results show that the NLR-TL attained higher strength than 2D composites when tested in the 750-1200°C range. Furthermore, it is also the toughest material.

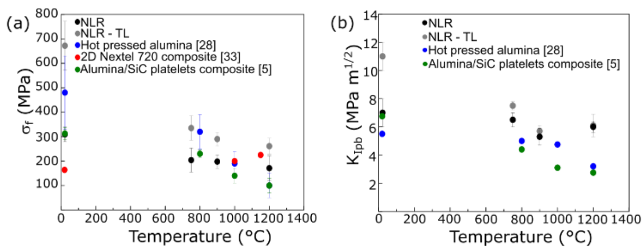

Figure 5: High temperature mechanical properties of the nacre like refractories obtained from 3-point bending tests: (a) strength and (b) fracture toughness.

The properties shown in Figure 5 places the bio inspired refractories as a new material with potential application at high temperature refractory application. Furthermore, it presented better properties when compared to the CMCs at high temperature.

4 CONCLUSION

The chosen experimental route allowed an easier and effective fabrication of bio-inspired refractories. The use of the transient liquid sintering with boron based additives was suitable in order to generate the aluminum borate in between the alumina platelets, as might be seen at the XRD patterns, SEM/EDX and nano indentation experiments where the presence of both phases was identified. The interlayer phase promoted a strong bond between the phases present in the microstructure. The resulting bio-inspired composite is strong, stiff and tough with high strength and fracture toughness at room (672 MPa and 7.4 $MPa.m^{1/2}$) and high temperature (270 MPa and 6.2 $MPa.m^{1/2}$ at 1200 °C). Furthermore, the failure behavior pointed out stable crack propagation for the bio-inspired composites. The same failure profile is achieved by the ceramic matrix composites. Additionally, the nacre like refractory proposed outperforms all the other ceramic composite compared, from room to high temperature.

The new strategy adopted for the development of refractories was successful providing materials with nacre like structure (Figure 2) with enhanced antagonistic properties, such as high mechanical strength and crack growth resistance (Figures 4 and 5).

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