

Microstructural development and mechanical performance of mullite-alumina and hibonite-alumina ceramics with controlled addition of a glass phase

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**Abstract**

Robust mechanical properties of refractory ceramics are critical to their performance in industrial applications. To investigate the effects of glass on the sinterability and mechanical properties of refractory ceramics, a controlled amount of glassy phase (10 wt. %) was added to mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ )-alumina ( $\text{Al}_2\text{O}_3$ ) and hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ )-alumina composites. Two liquid compositions within the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{CaO}$  system were chosen to produce a glass at 1600 °C that exists in equilibrium with a mullite-alumina composite and a hibonite-alumina composite. We performed a comparative study of the mechanical properties (hardness, flexural strength, and creep resistance) of mullite-alumina and hibonite-alumina composites with and without glassy phases. The observed microstructures clearly affected the mechanical properties. The strong interface created

between the three phases in each subsystem and the reduced amount of residual porosity in the composites with an added glassy phase may explain the increase in strength, hardness, and creep resistance of the composites. However, better mechanical properties and finer grain sizes of mullite make the mullite-alumina (-glass) system a better candidate for refractory applications that require improved mechanical properties.

## **Keywords**

Mullite, Hibonite, Alumina, glass-ceramic, ceramic composite.

### **1. Introduction**

Alumina-based ceramics are the most widely used oxide materials for industrial applications. Alumina ( $\text{Al}_2\text{O}_3$ ) and alumina composites are often used for advanced structural ceramics, and alumina-based ceramics have exceptional combined properties like corrosion and oxidation resistance, hardness, and chemical stability. However, some structural applications also demand superior fracture toughness, thermal shock resistance, and creep requirements that alumina ceramics cannot fulfil. Alumina composites with oxide secondary phases consisting of mullite ( $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ ) or hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ ) are often fabricated to improve these properties [1-5]. Both phases have an important effect on the final mechanical properties of the composites compared to pure alumina ceramics, but these secondary phases affect the final properties differently. Mullite increases the thermal shock and creep resistance and hibonite raises fracture toughness values.

Composite material design and microstructural development after sintering are key for tailoring the final physical properties. For alumina composites with added mullite or

hibonite, the formation of a glassy phase during high temperature sintering is observed, which aids densification. Glass is a soft phase that can be thought to diminish mechanical properties, but, in fact, is important for increasing the final density. High ballistic performance and wear resistance in alumina–mullite composites [6] is typical for composites with a low glassy phase content. The stress extrusion effect and the morphology of the sintered crystals for glass-containing mullite-alumina composites has been proposed [7] to explain physical property improvements, but these mechanisms have not yet been considered for explaining property improvements in hibonite-alumina composites.

Still, many studies have revealed the improvement of fracture toughness values by the addition of secondary phases that act to deflect cracks and induce grain-bridging mechanisms. When secondary phases are introduced in the form of platelets, whiskers and needles, low density ceramics may result, requiring unconventional sintering techniques to achieve high density composites [8, 9]. This mechanism of self-reinforcement has been proven to increase both density and fracture toughness values in alumina-hibonite composites [10]. Hibonite, or calcium hexaluminate ( $\text{CaAl}_2\text{O}_9$ ;  $\text{CA}_6$  in short), grows in the form of platelets or elongated crystals within the alumina matrix [11]. This mechanism, of self-reinforcement achieved with unconventional sintering techniques, is also observed in alumina-mullite ceramics [12].

The main scope of this study is to assess microstructural development and mechanical properties after the introduction of a controlled amount of a glassy phase in both mullite-alumina and hibonite-alumina composites under identical sintering conditions. In the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  system, the composition of the selected glass phases are in thermodynamic equilibrium at 1600 °C with the mineral phases at the sintering

temperature [13, 14]. The temperature of 1600 °C was chosen as a conventional sintering temperature for the composites of both subsystems (mullite-alumina-glass and hibonite-alumina-glass), and two different glasses were prepared for each subsystem. Ten wt. % of each glass was added to the mullite-alumina and hibonite-alumina mixtures. Density values and microstructures of the sintered composites were systematically examined for the same amount of second phase addition in each subsystem. The evaluation of the glass phase presence in both subsystems can help predict the physical properties for these composites, which are frequently used as refractory materials in industrial applications.

## 2. Material and methods

### 2.1. Glasses in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system

The phase diagram for the system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> published in [13] has been used as the basis for choosing the appropriate glass composition. Compositions *Lm* (in equilibrium with mullite and alumina) and *Lh* (in equilibrium with hibonite and alumina), as shown in Figure 1, were selected in order to exist in thermodynamic equilibrium at 1600 °C in the subsystems mullite-corundum-glass and hibonite-corundum-glass, respectively. Figure 1 shows the ternary phase equilibria diagram, and the lines of the tie triangles connecting the phases in equilibrium at 1600 °C are highlighted therein. As evident in the diagram, *Lh* is poorer in SiO<sub>2</sub> compared to *Lm*, and richer in CaO and Al<sub>2</sub>O<sub>3</sub>.

The reagents used to manufacture the glasses were Al<sub>2</sub>O<sub>3</sub> Nanoteck, SiO<sub>2</sub> Strem Chemical and CaCO<sub>3</sub> Asturcal and the melting procedures for obtaining both glass frits are presented in Figure 2.

To ensure the suitability of these glass frit formulations for forming a glassy phase at 1600 °C, side-view hot-stage microscopy (HSM) EM 201 equipped with an image analysis system and electrical furnace (1750/15 Leica) was performed on both *Lm* and *Lh* frits. The melting temperature in both cases is below 1600 °C, as shown in Figure 3.

## **2.2. Mullite and hibonite used in the final mixtures for sintering**

Commercially available Sasol SPA Al<sub>2</sub>O<sub>3</sub> and Cermatco Mullite were used together with hibonite synthesized in the laboratory following the method described elsewhere [15]. The initial mullite D<sub>50</sub> was 4.8 μm, while the corresponding D<sub>50</sub> of hibonite was 1 μm. The commercial mullite powder was then heat treated and milled to obtain similar particle sizes for both phases in order to obtain comparable results after sintering. The as-received commercial mullite was calcined at 1000 °C, and exhibited up to 1.30 wt. % loss-on-ignition in XRF analyses, and then was attrition milled for 4 hours. The mullite powder was free of volatile components and displayed a D<sub>50</sub> grain size of 1 μm after the treatment.

## **2.3. Sample fabrication and evaluation**

Table 1 shows the sample description of the manufactured composites and the nomenclature used for this study. The compositions and percentages of each phase were deduced from the triangular relations in the subsystems mullite-*Lm*-alumina and hibonite-*Lh*-alumina, as shown in Figure 4. For each subsystem, six composites have been manufactured, three with glass and three others without glass, so there are a total of 12 composites for the assessment.

Mixing of the powders for composites in the subsystems mullite-alumina-*Lm* and hibonite-alumina-*Lh* was achieved by ball milling in ethanol. After ball milling, the

solvent was evaporated in an oven at 70 °C overnight, and the powders were sieved and pressed into pellets by cold isostatic pressing at 200 MPa. The composites were sintered in air at 1600 °C for 2 hours with a heating rate of 5 °C/min.

Density was measured using the Archimedes method and relative density values were obtained from the theoretical density values of each specimen measured by helium pycnometry.

Flexural strength at different temperatures was measured with a mechanical test machine (Instron Fast Track 8520, using Bluehill software) in a three-point bending apparatus with an inner span of 15 mm and a crosshead speed of 0.5 m/min. Specimens were cut into 3 x 4 x 18 mm parallelepipeds for three-point bending tests and creep experiments. The tensile faces of all specimens were polished with diamond paste down to 3 µm (Struers, RotoPol-31) and the edges were chamfered (~45°) in order to avoid the influence of microcracks on creep behaviour. Bars of the sintered specimens were prepared following the standard ASTM C1161-02c (2008) with a size of 3 x 4 x 40 mm for four-point bending test and flexural strength measurements. Hardness was measured by micro-indentation (Buehler Micromet 51 03) using a force of 2 N and an indentation time of 10 s for each composite. The fracture toughness ( $K_{IC}$ ) values of specimens were calculated from the crack lengths of the indentations on the polished samples [16]. For that purpose, a Leco AMH43 macroindenter with a 98 N load was used.

In order to study the effect that these strains have on the high-temperature deformation of the materials, creep behaviour was measured by means of three-point bending tests, using the same machine and apparatus as for the flexural strength measurements. The approximation proposed by Hollenberg et al. [17] was used to calculate the deformation

and creep rate. The elongation was measured with a precision of 1  $\mu\text{m}$  and the tests were performed at 1200 °C. To ensure the homogeneity of temperature in the chamber, a load (50 N) was applied after 1 h of soaking time at 1200 °C. The sintered microstructures were observed by scanning electron microscopy (SEM) (Quanta FEG-650-FEI) on polished and Au coated sections of samples.

### **3. Results**

#### **3.1. Microstructural analyses**

Figure 5 is an example of the diffractograms obtained in order to check mineral phase stability at the sintering temperature. The results indicate that at the sintering temperature of 1600 °C, the initial phases remain unreacted and the glass phase did not experienced devitrification, demonstrating thermal stability.

SEM images of the sintered samples in both subsystems can be observed in Figures 6 and 7. General aspects of the microstructures and comparison between both subsystems are shown in Figure 6. For the sake of brevity, the microstructures for the 70 %  $\text{Al}_2\text{O}_3$  content composites are not shown. It should be mentioned that some polishing difficulties were encountered for composites with high  $\text{Al}_2\text{O}_3$  contents and the softer second phases, i.e. hibonite, mullite, and the glass itself. Figure 7a depicts a more detailed micrograph (higher magnification) of a sample in the mullite subsystem where each of the phases has been labelled. Alumina is identified in polished sections as the brightest grey phase compared to mullite and glass. Because alumina and hibonite have a very small Z-contrast in back scattered electron images, their identification has been based on crystal morphology and size. Glass phases in hibonite composites were identified with a contrasting grey colour in the images (Figure 7b).

The grain size of the MA and MLA composites (nomenclature following Table 1 above) appears to be around 1  $\mu\text{m}$  in the composites without an added glass phase and 3  $\mu\text{m}$  in the composites with a glass phase. Idiomorphic and well recrystallized mullite crystals [1] can be observed in MLA50 (light grey crystals in the image). Porosity is reduced in the samples with added glass, in good agreement with the density values obtained (Table 2). The formation of a transitional glass phase can be deduced from this fact, although it cannot be clearly observed in the SEM photomicrographs.

The improvement in the relative density values was not as clear for the composites in the hibonite-alumina-glass subsystem. In this subsystem, the hibonite crystals underwent extensive grain growth, both with increasing alumina and glass content in the composites. Typical plate-like hibonite crystals [2] were observed in the samples CLA30 and CLA50, but also in CA50 (without added glass). Crystal grain size in the CA composites increased from 6  $\mu\text{m}$  (in CA30) to up to 40  $\mu\text{m}$  in (CA70). Notice that the image magnification is 5000 $\times$  for the mullite composites and only 2000 $\times$  for the hibonite composites. Hibonite crystals grew more readily than mullite crystals at 1600  $^{\circ}\text{C}$ . This, as will be discussed below in section 4, can be due to differences in the composition of each subsystem.

### **3.2. Physical properties**

Table 2 shows the results for the physical properties characterized in the sintered composites, including density, flexural strength, and toughness. As described in section 2.3, flexural strength values were estimated by three- and four-point bending test experiments. Table 2 shows that for similar relative density values (close to 99%) the composites with added glassy phases in both subsystems had superior hardness, flexural strengths, and toughness values. As expected, the density and mechanical property

values also increased with increasing alumina content in each subsystem, since alumina has better properties than the minor components.

Comparing the hardness values for both subsystems with added glass, the mullite subsystem had higher hardness values when alumina contents were low, but the hardness values for the mullite subsystems were lower than those for the hibonite subsystems when alumina contents were high. This is not the case for the flexural strength and toughness values, which were always higher for the mullite subsystem, regardless of the alumina content in each composite.

The results obtained for the creep resistance characterization are outstanding for the mullite subsystem. Representative sintered samples of each subsystem were chosen for these tests. Three different specimens of each composition were evaluated, and the mean values are plotted in Figure 8. Figure 8a shows the deformation registered at 1200 °C and 40 MPa over 120 hours. Samples with and without glass did not deform, regardless of the alumina contents. Significant creep resistance was also obtained in the hibonite subsystem for the samples with added glass, as shown in Figure 8b. At 50 % alumina content, samples without added glass in this subsystem break without deformation, and samples with 70% alumina only last 1 hour before breaking. After 120 hours, samples with a glassy phase are deformed only 0.4 % for CLA70 and 0.6% for CLA50.

#### **4. Discussion**

Liquid glass aids the wettability of the phases present in the mullite-alumina-glass and hibonite-alumina-glass composites [18]. The wettability depends on the intermolecular forces of the materials in contact with the glass: the adhesive force between the liquid

and the solid spreads the liquid over the surface. This leads to a decrease in porosity, thereby increasing the values of relative density. The mechanism by which pores and gaps are captured by the liquid phase, leading to a reduction of open porosity, is known as the Stress Extrusion Model, proposed by Kong et al. [7]. In this model, interstices are filled by a glassy phase until a saturation point is reached. When the glass avoids the defects acting on the matrix, the strength of the ceramic is improved. An excess of glass phase would reduce the connection among crystals, thereby diminishing the strength of the samples.

The presence of a glass phase also increases ionic diffusivity, promoting crystal growth. This was clear for the mullite subsystem where mullite grain size increased when glass was added to the composites, compared with composites without glass (Figure 6). In the case of the hibonite subsystem, ionic diffusivity also increased due to the presence of  $\text{Ca}^{2+}$  compared to the mullite system [2], as demonstrated by the clear grain growth in these composites with and without added glass.  $\text{CA}_6$  crystals reached 40  $\mu\text{m}$  in length, whereas mullite grains in the mullite subsystems only grew up to 10  $\mu\text{m}$ . These  $\text{CA}_6$  crystals grew fast and displayed intragranular porosity. This fact along with the poorer mechanical properties of hibonite suggests that mullite composites are a better choice when flexural strength and hardness are required (Table 2).

Toughness values also increased when glass was added to composites of both subsystems, and mullite had a slightly higher value than the hibonite composite subsystem. MLA70 exhibited 6.3  $\text{MPa}\sqrt{\text{m}}$ , which is remarkable compared to the previous published values between 2 – 3.5  $\text{MPa}\sqrt{\text{m}}$  for composites without glass [19, 20]. In the hibonite subsystems, values between 4 and 5  $\text{MPa}\sqrt{\text{m}}$  were also significant in relation to the published values of hibonite-alumina composites [21] for higher alumina

contents than in present study. Both crack bridging and crack deflection mechanisms may be responsible for toughness improvement in the glass-containing composites, since high aspect ratio grains and a weak interface between these grains and the grain boundary phase are typical of these mechanisms. Also, the formation of residual stress fields due to the thermal coefficient mismatch [22] between the crystals and the glass may play a role in improving toughness in the glass containing composites. These points will be studied in future work.

Creep resistance of the mullite composites is outstanding. Deformations higher than 0.25% are expected in mullite composites with less than 10 % mullite [19, 23-25]. It is clear that a higher mullite content influences the creep behaviour. In the present case, both mullite and the added glass phase increase the elasticity of the material, improving its creep resistance. The creep resistance results in the hibonite subsystem confirm an improvement in the elasticity of the material due to the addition of glass. Samples are deformed after 120 hours at 1200 °C, but the values were as low as 0.4-0.6%, well below the 10-20% obtained in other studies at 1400 and 1650 °C [26].

Although the addition of a glassy phase (liquid at the working temperature) lowers the creep resistance values, this glassy phase is an amorphous solid (not liquid) in the working temperature range in the present creep tests, which helps to increase the elasticity of the materials. In the mullite composites, this glassy phase is mainly located at triple points (Figure 7 a) joining crystal grains, which enhances the adhesion between crystals. This adhesion increases density without inhibiting mullite-mullite grain boundary diffusion associated with the low surface energy [001] of the crystals [25]. The distribution of the glass phase in the hibonite composites is more random, and although it can be found at triple points, it usually formed a thin layer on crystal

surfaces (Figure 7 b). Due to the lower theoretical density values of the added glasses (2.70 and 2.49 g/cm<sup>3</sup>) compared to those of alumina, mullite, and hibonite (3.99, 3.16, and 3.84 g/cm<sup>3</sup> respectively), the theoretical density of the composites with added glass slightly decreases compared to that of composites without glass, which would make them more interesting for some structural applications [27].

Results on the assessment of the controlled glass phase addition to mullite-alumina and hibonite-alumina composites clearly indicate that the mullite-alumina system is superior to the hibonite-alumina system for the properties observed in this study. For both systems, the measured properties are better in those composites with an added glass phase. The differences in the microstructural development for both systems with added glass and slight density differences can explain the differences in mechanical behaviour.

## **5. Conclusions**

The results of this assessment of mullite- and hibonite-alumina composites with and without added glass showed that adding a controlled small amount of glass phase to each system improved the physical and mechanical properties. The addition of the glass phase increased the relative density of the composites and decreased the theoretical density. Higher values for relative densities consequently improved the hardness and flexural strength of the composites, compared to those of identical materials without an added glass phase. This improvement in the mechanical properties is greater in the case of the mullite-alumina composites. Adding glass to mullite resulted in an increased grain size, but grain growth was more pronounced in the case of hibonite composites due to Ca ion diffusivity. CaAl<sub>12</sub>O<sub>19</sub> or CA<sub>6</sub> crystal growth was very fast and formed intragranular porosity, which diminished the mechanical properties in comparison to the mullite composites.

The most outstanding results were obtained for the creep resistance values. All the tested material compositions were in the steady-state creep stage, or secondary stage. As none of the samples reached the tertiary stage, the materials remain in the security zone because they did not undergo any microstructural changes. Hence, the addition of a controlled glass phase amount in both hibonite- and mullite-alumina composites makes them suitable for applications requiring strong creep resistance.

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**Figure captions.**

**Figure 1.** System  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ . E.F. Osborn and A. Muan. Redrawn with the Lm-mullite-alumina and Lh-hibonite-alumina tie triangles.

**Figure 2.** Melting procedures for obtaining both glass frits.

**Figure 3.** Side-view hot-stage microscopy results for the manufactured glasses, a) Lm; b) Lh.

**Figure 4.** Triangular projections of the subsystems Lm-mullite-alumina and Lh-hibonite-alumina with the locations of the tested compositions.

**Figure 5.** Interpreted diffractograms for the subsystems Lm-mullite-alumina and Lh-hibonite-alumina with and without added glass, for 50% alumina

**Figure 6.** SEM images (Back-scattered scanning electron microscopy) of the composites with and without 10% added glass phase within the Lm-mullite-alumina and Lh-hibonite-alumina tie triangles. Phases: G: Glass;  $\text{A}_3\text{S}_2$ : Mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ); A: Alumina ( $\text{Al}_2\text{O}_3$ );  $\text{CA}_6$ : Hibonite  $\text{CaAl}_{12}\text{O}_{19}$ .

**Figure 7.** Detailed SEM-BSE images of MLA50 (a) and CLA50 (b). Each phase is identified with the following labels: G: Glass;  $\text{A}_3\text{S}_2$ : Mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ); A: Alumina ( $\text{Al}_2\text{O}_3$ );  $\text{CA}_6$ : Hibonite  $\text{CaAl}_{12}\text{O}_{19}$ .

**Figure 8.** High temperature creep experimental results.