Influence of Corn Flour as Pore Forming Agent on Porous Ceramic Material Based Mullite: Morphology and Mechanical Properties

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Abstract:
Porous material was processed by the mixing, molding and pressing the ceramic material, afterward burnout and sintering; through the forming porous, using corn flour at different concentration (10, 15 and 20 wt.%) as a pore forming agent; in order to determine the influence of porous on the mechanical, morphological and structural properties. The effect of the volume fraction of corn flour in the mullite matrix, at various sintering temperature from 1100, 1200, 1300 and 1500 °C were tested by Diffraction X ray, showing changes in crystalline phases of mullite (3Al₂O₃-2SiO₂), as result of sintered temperatures. Presence of talcum powder in formula, also cause the formation of the cordierite and cristobalite crystalline phases, giving stability and adhesion to the structure of ceramic material. When sintering at temperatures between 1300 to 1500 °C, and it was used the concentration of corn flour 15-20 wt.% as forming agent porous, it was found the better mechanical properties. The scanning electron microscopy analysis shows the presence of open porosity and anisotropy.

Keywords. Corn flour, Porous forming-agent, Mullite, Porosity, Crystalline phases, Mechanical properties.

1. Introduction

Porous ceramics have a wide range of applications, ranging from filtrations membranes and catalyst supports to biomaterials, thermally or acoustically insulating bulk
materials or coating layers [1-2]. Well-controlled microstructures of porous size and pore distribution permit various applications [3]. These porous ceramics can be categorized in terms of their porous microstructures as: 3D-type with three-dimensionally connected and distributed open pores, 2D-type with slit-shaped open pores and 1D-type with unidirectionally oriented pores. Porous ceramics with 3D structures are useful as catalysts, catalysts supports, filters, scaffolds or adsorbents, because of the high accessibility of their pores. One interesting porous ceramic, with a well ordered 3D porous structure is an inverse opal structure mimicking the microstructure of opal, which consists of ordered packing of fine uniform submicron amorphous SiO$_2$ particles. Also, in case of 2-D porous ceramic structures, typically are observed in activated carbons and pillared clays, this last ones have the highest specific surface areas of all the porous materials (3000-4000 m$^2$/g). Pillared clays show high adsorption properties and solid acidity with moderate acid strength. One important application of porous ceramics is as filters and membranes for use in severe environments at high temperatures and in reactive and corrosive solutions. The ideal porous microstructure for high permeability and separation are well-ordered and unidirectionally oriented cylindrical through-holes (1D-structure) [2, 4-5].

Mullite has largely been known as one of the most common constituents of traditional ceramics, it composition ranges vary from 3Al$_2$O$_3$-2SiO$_2$ to 3Al$_2$O$_3$-SiO$_2$. It is considered the only stable compound of the silica-alumina system, under normal conditions of pressure and temperature [6]. The remarkable combination of low thermal-expansion coefficient, good thermal-shock resistance, as well as excellent mechanical and chemical stability at elevated temperatures, has received interest in recent years in the development of porous mullite ceramics, because of desirable properties for using as thermal insulators. Besides, recently mullite’s functionality has been extended to other fields like energy, environment and health [7-9]. Cordierite also has been studied due to their good mechanical properties, chemical and abrasion resistance and thermal stability. Cordierite phase is one of the important phases of the MgO-SiO$_2$-Al$_2$O$_3$ systems and is known to have a low coefficient of thermal expansion and low cost. In addition, it presents excellent thermal shock resistance due to their low thermal expansion coefficient; low dielectric constant, high refractoriness and high mechanical strength [10], as well as it could be used as the bonding phase to fabricated porous ceramics [11].

Preparation of porous ceramics with controlled microstructure has been a subject of constant interest by researchers. A porous structure can be achieved through a conventional powder-processing route with the incorporation of some pore forming agents such as sawdust, starch, graphite or organic particulates [7]. Each application requires a unique set of pore structures that could be quite complex. The amount of open and closed porosity, pore size and shape, pore uniformity and degree of pore interconnectivity; all play crucial roles in determining the degree of success of a porous component in its intended applications. Specific pore requirements are met through the selection and control of an appropriate ceramic processing method [12]. Among preparation techniques in porous ceramic materials, can be consider sol-gel, polymeric foam templates, biomimetic processing, ceramic hollow spheres and sacrificial pore-forming agents [1,13]. Several materials used to form porosity have been studied by researchers and can be cited graphite [7,11], phenolic resins [14], starch [10,15-17], starch corn [18], flour [19], clay and sawdust [20], ice [12], poppy seeds [1], oxides [21-22].

Biopolymers have been used in ceramic technology since the ancient times, but in the last decade, such biopolymers also are used as pore-forming agents in advanced fine ceramics, to attain certain structural and/or functional properties as result of controlled porosity, pore size and pore shape [19]. Starch is one of the biopolymers, which is frequently used as pore-forming agent in ceramic technology. Due to its chemical composition (polysaccharides consisting essentially of C, H and O), is easily burnt out during firing, without residues in the final ceramic body and it can be used in the sacrificial (pyrolizable)
technique, because of easy handling and processing [1,17]. Due to natural origin, it is clear that all product characteristics of native starch, including size and shape, exhibit a relatively broad variance, depending on genetic type of the plants, breeding, growth conditions and extraction procedure; which contribute in the native unmodified starch granules (unswollen state) to the porosity in ceramic materials. The most used starch in porous ceramics comes from tuber or roots (potato, tapioca) and cereals (wheat, corn and rice) [18].

In the present study, the mullite ceramics with high porosity were prepared from corn flour at different concentrations (10, 15 and 20% of total mixture), and the effect of sintering temperatures on morphology, XDR, bulk density, apparent porosity, open porous volume, flexural strength and young’ moduli properties were investigated.

2. Experimental procedure

2.1 Raw materials

Commercially available mullite was used as the starting material in this study (Kyanite Mining Corp., USA); 3Al$_2$O$_3$-2SiO$_2$ with a purity of 56.9% and 39.9% respectively and a mullite particle size range from 530 μm to 760 μm. The pore forming-agent was a commercial trend of corn flour, Maseca (Gimsa, S.A.B de C.V., México). The particle size analysis reveals that the range size of this raw material is from 20 to 65 μm (Fig. 1b). To reduce sintering temperature of mullite, but also as high temperature binder it was used 8 wt.% of powder talc (Mg$_3$Si$_4$O$_{10}$(OH)$_2$) in the total mixture; it was acquired from Feldspar Corp., USA. Caolin (12% wt./wt.) and the additive (Sodium silicate, 2 wt.%, also were acquired from Feldspar Corp., USA, to promote the dispersion of particles in blend and formation of green bodies.

2.1 Experiments process

Firstly raw materials were mixed in a container at room temperature at different concentrations, according to Tab. I. Then the mixture was put into a wood mold and covered with a cap. After it was applied a constant pressure to form the green body, which was preheated at 100°C for 1 hour. Ones this temperature was riches, dried samples were heated again, now at 700 °C for 1 hour more. After this thermic treatment, samples were sintered in a high temperature furnace at 1100, 1200, 1300 and 1500°C for 4 hours more to promote sintering of raw materials. Afterwards, internal temperature from furnace, diminish slowly to avoid fracture of material.

![Differential volumen](image)

**Fig. 1.** Particle size of corn flour.
Tab. I Chemical composition of the mullite green bodies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mullite (%)</th>
<th>Corn flour (%)</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1100</td>
<td>68</td>
<td>10</td>
<td>1100</td>
</tr>
<tr>
<td>10-1200</td>
<td>68</td>
<td>10</td>
<td>1200</td>
</tr>
<tr>
<td>10-1300</td>
<td>68</td>
<td>10</td>
<td>1300</td>
</tr>
<tr>
<td>10-1500</td>
<td>68</td>
<td>10</td>
<td>1500</td>
</tr>
<tr>
<td>15-1100</td>
<td>63</td>
<td>15</td>
<td>1100</td>
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<td>15-1200</td>
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<td>1200</td>
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<tr>
<td>15-1500</td>
<td>63</td>
<td>15</td>
<td>1500</td>
</tr>
<tr>
<td>20-1100</td>
<td>58</td>
<td>20</td>
<td>1100</td>
</tr>
<tr>
<td>20-1200</td>
<td>58</td>
<td>20</td>
<td>1200</td>
</tr>
<tr>
<td>20-1300</td>
<td>58</td>
<td>20</td>
<td>1300</td>
</tr>
<tr>
<td>20-1500</td>
<td>58</td>
<td>20</td>
<td>1500</td>
</tr>
</tbody>
</table>

2.2. Test and characterization

The microstructure of green bodies was observed by Scanning Electron Microscopy, Jeol JSM-6060LV, working at 20 kV; previously samples were covered with four gold caps, due to porosity of material. Size particle was conducted in a Beckman Counter LS32 (Particle Characterization). X- Ray (XRD) patterns of raw material and samples were tested by X-ray diffractometer Rigaku MiniFlex with Cu Kα radiation (wavenumber 1.54 Å). Bulk density and porosity were determined by the ASTM C20 method (Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water). The flexion test was carried out through two support points (80 mm of distance between points) in a universal testing machine Zwick Roell; with a loading speed rate of 5 m/min.

3. Results and discussion

3.1. Raw materials

Fig. 2. shows the XRD patterns of mullite raw material at room temperature. Peak shows that main crystalline phases correspond to mullite and quartz. This reveals, that material present a high purity of composition, which is desirable for the purpose of this investigation. In addition, Fig. 2. displays the average grain size of corn flour as pore forming agent. Particle size presents a bimodal pattern, been the maximum volume bulk (5%) of 20 and 70 µm size; the minimum range size correspond to 0.4-0.6 µm (less than 1% of volume bulk). This measure is important, considering that corn flour will serve as pore forming-agent.
3.1. Microstructure of green bodies

Fig. 3 shows the microstructure of samples sintered at 1200°C at 10, 15 and 20% of corn flour as porous agent. Clearly exists the presence of internal porosity and interconnected tunnels through pores (open porosity). Meanwhile, percentage of corn flour in mixture plays an important role in porosity, which can be observed in Fig. 3(a-b). Porous tend to be bigger with increasing the quantity of corn flour from 10 to 20% (pore forming-agent), in addition microstructure is more open. In Fig. 3c, appears interconnected structures, related to the proper sintering of mullite (3Al₂O₃-2SiO₂), powder talc [Mg₃Si₄O₁₀(OH)]₂ and corn flour, and the amalgamate of raw materials; with the correspond enhance of mechanical properties and crystal phases (X-ray pattern), as we will soon see. The appearance of interconnectivity of porous was seen throughout the samples and was not controlled in this experiment. In the structure also appears closed porous, Fig. 3(d-f). This last kind of porous seems to be part of cavities formed during the burning out of corn flour; where porous size is in the range to the grain size of corn flour (Fig. 2); furthermore it could be retained gas, formed during sintering.

Fig. 2. X-ray diffraction patterns mullite of raw material at 25 °C: M, Mullite; Q, Quartz.

Fig. 3. SEM micrographs of porous mullite ceramics sintered at 1200 °C; with a) 10%, b) 15% and c) 20% at 100 X, and d) 10%, e) 15% and f) 20% at 500 X, of corn flour as pore forming-agent.
However, there are not exist enough results to support or dismiss the phenomenon. Likewise, heterogeneity of sintered green body is result of preparation sample; size of raw materials, mixing, casting pressure and molding step. Diverse authors [3,19] had reported that milling time affects the microstructure homogeneity and reproducibility of the process. Besides J.H. Lee [23]; mention that solid loading, sintering temperature; but also compaction and molding pressure [24-25] are processing variables to determine the characteristics as microstructure, porosity and mechanical properties; of sintered porous ceramic materials.

3.2. X-ray

XDR patterns of mullite raw material powder and sintered materials at 1200, 1300 and 1500°C are shown in Fig. 4. From the diffractogram, it can be observed that most of the diffraction peaks correspond to the mullite phase, but also can be found the quartz and cristobalite peaks. The intensity of diffraction peaks of quartz became large between 1200 and 1300°C (2θ=26° and 43°), however the same peaks decreases at 1500°C, which indicate that the crystalline phase is stable in this temperature range, also this is in agreement with the phase diagram of the SiO₂. Over 1300°C starts the dissolution of β-quartz in the vitreous phase, especially when the heating rate is quickly. Cristobalite peak behavior tends to diminish (2θ=22°), when increase the sintering temperature around 1500°C, in spite of fact that the peak’s intensity at 2θ=35° remains whit out change, this behavior is related to the anisotropy of the ceramic structure. This shows that temperature of 1300°C is the transition zone of mainly crystalline phases of mullite (β-quartz, β-cristobalite-cubic). On the other hand, peaks intensity at 2θ=10 and 2θ=30 are related to the formation peak of cordierite, which only appears around 1300°C [25] and according to the ternary phase diagram of SiO₂-MgO-Al₂O₃ it develops at 1365°C.

![Fig. 4. XRD pattern of porous mullite ceramics processed with 10% of corn flour as pore forming-agent as function of sintering temperature: M, Mullite; Q, Quartz; C, Cristobalite and c*, Cordierite.](image)

3.3. Porosity and bulk density

Fig. 5. compares de porosity achieved at different concentrations of pore forming-agent, as function of sintering temperatures. As the sintering temperatures increases from 1100 to 1500°C, percentage of porosity decreases in just 8 units (≅ 63-55%), this decrement is
related to the quantity of pore forming-agent, the higher porosity was present in those samples where corn flour was added at 20% and the lower values when corn flour was 10%. These results clearly show that temperature and quantity of pore forming-agent are key factors to control porosity in mullite ceramic materials [3]. In spite of the fact, that change in the range of porosity is not considerable, this property affects in mechanical behavior as seen in Tab. II, better flexural strength and young’s modulus when green bodies sintering at 1500°C and 20% of corn flour; even though at this point porosity present one of the highest values (61.37% of porosity). On the opposite site bulk density behave in the inverse proportion, while increasing percentage of pore forming-agent the bulk density decreases; same performance was found by F. Yang [9]. This is due to burned out corn flour leave empty spaces, which initially are occupied by this material during sintering process. Sh. Li [26]; attributed this performance to the anisotropy grown of mullite. However bulk density is quit higher than 1 gr/cm³, it results in a dense material when the quantity of corn flour added is just 10%. Temperature also affects the densified raise.

![Fig. 5. Porous mullite ceramics processing with 10, 15 and 20% of corn flour as pore forming-agent, a) Apparent porosity and b) Bulk density.](image)

3.4 Flexural strength and Young’s modulus

Fig. 6 and 7 shows mechanical properties of mullite porous ceramics, as function of sintering temperature. With corn flour loading and sintering temperature increasing, flexural strength increase significantly after 1300°C (Fig. 6 and Tab. II).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Young’s modulus (MPa)</th>
<th>Flexural strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10%</td>
<td>15%</td>
</tr>
<tr>
<td>1100</td>
<td>268</td>
<td>91</td>
</tr>
<tr>
<td>1200</td>
<td>319</td>
<td>197</td>
</tr>
<tr>
<td>1300</td>
<td>486</td>
<td>217</td>
</tr>
<tr>
<td>1500</td>
<td>909</td>
<td>681</td>
</tr>
</tbody>
</table>

Note: 10%, 15% and 20% are quantities of corn flour added as pore forming-agent to green bodies.

This trend is related to the appearance of crystalline phases of mullite as seen before in DRX analysis, mainly cristobalite and cordierite. Cordierite phase is related to high mechanical strength [10]. As sintering temperature goes from 1300 to 1500 °C, flexural
strength improve from 1.28 MPa to 6.83 MPa at 20% of corn flour added. Phase diagram of the system SiO$_2$-MgO-Al$_2$O$_3$, indicates that cordierite can also appears around 1500 °C with a stoichiometry relation of 2MgO-2Al$_2$O$_3$-5SiO$_2$ and cristobalite SiO$_2$. In spite of the fact that the cordierite peak in DRX does not appear at this temperature, the stability and bonding in the network structure of the ceramic remains, resulting in better flexural strength [27]. This trend also can be seen in young’s modulus pattern (Fig. 7), where the highest value was present at the same conditions of temperature and corn flour added (1500 °C and 20% ) with a value of 1132 MPa, been the initial value of 67 MPa at 10% of pore forming-agent and 1100°C of sintering temperature. Presence of crystalline phase enhances mechanical properties, even though at 20% of corn flour added in ceramic porous mullite green compacts, causes the 62% porosity (open porous network) in the material.

![Fig. 6. Flexural strength of porous mullite ceramic processed with corn flour as pore forming agent as a function of sintering temperature.](image)

Researchers also focus on the analysis of flexural strength versus porosity, according to Rice and Knudsen equation [4], strength varies exponentially with porosity as follows; 

$$\sigma = \sigma_o \exp(-bP)$$

Where $\sigma_o$ is the strength of the porous structure, $b$ is an empirical constant that is depending on the pore characteristics and $P$ is the porosity. Fig. 8 shows the graphics of

![Fig. 7. Young’s modulus of porous mullite ceramic processed with corn flour as pore forming agent as a function of sintering temperature.](image)
flexural strength as a function of porosity of samples at different quantities of pore forming-agent. The performance that fits with the equation is 15% of corn flour, corroborating this with values in Tab. III, where $R^2 = 0.998$, the other two graphics at concentration of 10 and 20% of corn flour are too far away to fit with the exponential equation mentioned above. As it can be seen in Fig. 9 at a porosity of 62% the experimental flexural strength is lower than the fitting curve, the rest of the experimental data follow the exponential pattern of the equation. It can be explained by the bonding of the cristobalite and cordierite phases, being this threshold concentration of corn flour, where the stoichiometry relation improve mechanical properties of mullite porous ceramic material. Also, b values indicate that microstructure reflect an anisotropy behavior when corn flour is added at quantities of 10 and 20%, as pore forming-agent [22].

**Fig. 8.** Flexural strength of mullite porous ceramics as function of porosity.

**Fig. 9.** Fitting curve of mullite porous ceramic with 15% of corn flour as pore forming-agent.

4. Conclusion

In this paper highly porous mullite were fabricated by addition corn flour as pore forming-agent and talc as bonding phase, mainly at high sintering temperature. From results it
has been shown that exist an open porosity microstructure, with a tendency to the anisotropy performance. The DRX analysis reveals that the presence of MgO (talc composition), bring about the formation of cristobalite and cordierite crystalline phases, which improve mechanical properties, at a boundary concentrations of 15 and 20% of corn flour in the range of 1300 and 1500°C, flexural strength riches values of 5.18 MPa and 6.83 MPa respectively.

5. References

својства. Утицај запреминског удела брашна у матрици мулита на различитим температурама синтеровања од 1100, 1200, 1300 и 1500 °C испитиван је рендгенском дифракцијом, указујући на промене у кристалној фази мулита (3Al₂O₃-2SiO₂), као резултат температуре синтеровања. Присуство талка у формули, такође је условило формирање кордијерита и кристобалита, дајући стабилност и адхезију структури керамичког материјала. Боља механичка својства су пронађена код узораца синтерованих између 1300 и 1500 °C, при концентрацији брашна од 15-20 wt.%. СЕМ указује на присуство отворене порозности и анизотропије.

Кључне речи: кукурузно брашно, агенти за формирање пора, мулит, порозност, кристалне фазе, механичка својства.