

# FABRICATION OF POROUS ALUMINA CERAMICS WITH CORN STARCH IN AN EASY AND LOW-COST WAY

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*Porous alumina ceramics with different porosity were fabricated by combining the starch consolidation process with the gel-casting process using corn starch as a pore-forming agent and a binder. The bulk density, porosity, and microstructure of the obtained alumina ceramics were studied. It was found that the total porosity range of sintered samples with contents varying from 0 to 50 vol. % is 14.8 - 55.3 % and the total porosity increased with the increase of starch content. Moreover, a relationship between the total porosity of alumina ceramics after sintering and corn starch content was obtained. This relationship indicates that the total porosity of alumina ceramics fabricated in this work was higher than that of the ceramics made by traditional slip-casting. The range of total porosity of ceramics in this work was broader than that of the ceramics produced by starch consolidation casting. The relation between the linear shrinkage of porous alumina ceramics and the starch content also was discussed. The compressive strength of the sintered samples varied within the range of 5 - 24 MPa, corresponding to starch content of 50 - 10 vol. %.*

## INTRODUCTION

Porous ceramics are frequently used for a variety of applications, including catalyst supports, filters, preforms for pressure filtration processes, membranes, hot gases media, and lightweight structural materials [1-5]. Many different preparation methods for porous ceramics have been studied over the past decade. Yao et al. prepared the reticulated porous silicon carbide ceramics using polymeric foam replication by a recoating technique [6-8]. Gregorová et al. presented that the porous alumina ceramics between 25 and 50 % porosity were produced by starch consolidation casting (SCC) and the limits of pore size and porosity were discussed [9-11]. Sepulveda et al. made open-cell hydroxyapatite (HA) foams with relative porosities from 72 to 90 % [12]. Each of these routes has its own disadvantages, e.g. the mechanical properties of the ceramics prepared by the polymeric foam replication are poor because of the drawbacks of the pyrolysis process and its pore sizes were limited to macro scale and millimeter scale. To fabricate porous ceramics without the drawbacks mentioned, some studies developed procedures combining these techniques to produce ceramics with improved properties that cannot be obtained by single technique. Ramay et al. reported that the macro porous hydroxyapatite scaffolds, which possessed an open, uniform, and interconnected porous structure with a pore size of 200 - 400 μm and a compressive yield strength of 5 MPa by combining the replication method with the gel-casting method [13].

Mao et al. developed a new technique to make ceramics with hierarchical pore structure using starch consolidation casting and foaming methods [14].

In this paper, porous alumina ceramics with different porosity were fabricated by combining the starch consolidation process with the gel-casting process using corn starch as the pore-forming agent. The bulk density, porosity, and microstructure of the obtained alumina ceramics were studied. Moreover, a relationship between the total porosity of alumina ceramics after sintering and corn starch content was obtained. Relation between the linear shrinkage of porous alumina ceramics and the starch content also was discussed. Finally, the compressive strength of the sintered samples was measured.

## EXPERIMENTAL

### Materials

As ceramics' raw materials, alumina powder (main size less than 0.5 μm, A16SG, Alcoa Inc., New York City, USA) was chosen as received in this study. Alumina nanopowder (40 - 80 nm, gamma-phase > 99 %, Alfa Aesar Co., Ward Hill, USA) was used as a sintering additive. 5 wt. % polyvinyl alcohol (PVA) solution was added as an adhesive agent. Commercially available corn starch (Hodgson Mill Inc., Effingham, USA) was selected as the pore-forming agent and binder. The corn starch in this study received no pre-processing.

## Preparation process

The micron scale alumina powder and alumina nanopowder were combined with the weight ratio of 95 %/5 %, and then mixed using a ball mill with beads (2 - 3 mm in diameter) for 8 h. Both jar and milling beads consisted of agate while milling medium is deionized water. 5 wt. % polyvinyl alcohol (PVA) solution was added to the alumina suspension. PVA has excellent adhesive property which could help sample molding during molding process and can undergo pyrolysis above 200 °C. Amounts of 0 - 50 % corn starch mixed with the stabilized alumina suspension were then measured by the volume fraction of raw ceramics powders. 0.5 wt. % commercial dispersant for Al<sub>2</sub>O<sub>3</sub> (Dolapix CE64, Zschimmer & Schwarz Inc., Milledgeville, USA) also added with the corn starch. The resulting mixtures were prepared to a slurry with 15 vol. % solid loading, including Al<sub>2</sub>O<sub>3</sub> powders, starch, PVA, and dispersant and then were agitated using an electromagnetic stirrer at room temperature for 24 h. After that the slurry was agitated and heated on the electromagnetic stirrer at 80 °C for 1 h. This process was based on the swelling and absorbing ability of starch in the aqueous ceramics suspensions after heating to around 80 °C [10]. The slurry was then dried in an oven at 60 °C for 2-3 days. The dried powders were compacted under 100 MPa into samples of 16 mm-diameter and 5 mm-thickness. The compacted samples were then sintered in an air environment at atmospheric pressure in an electric heating furnace. After sintering all samples were cut to a size of 12 mm-diameter and 4 mm-thickness. The compressive strength was tested with a cross head speed of 0.05 mm·min<sup>-1</sup> on an Instron 3369 Testing Machine. Eight samples were utilized to obtain average values and standard deviations.

In this study, the PVA and corn starch must be burnt out during the sintering process to develop the desired porosity. According to the thermogravimetric and differential thermal analysis of the compacted ceramics body [15], the crucial temperature range for burning starch out before ceramic sintering is from 300 to 600 °C.

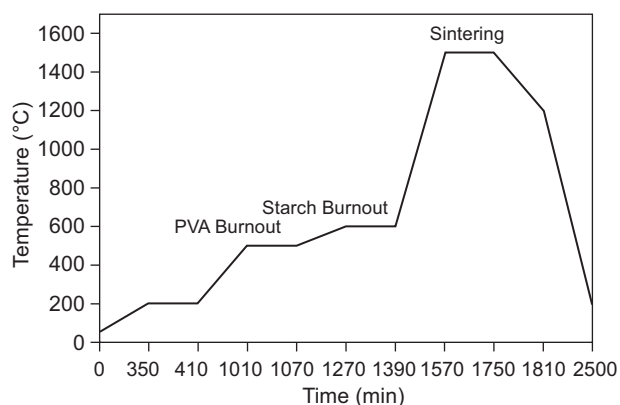


Figure 1. Heating schedule for the sintering process.

Therefore, the samples in this study were heated from room temperature up to 500°C at a heating rate of 0.5°C·min<sup>-1</sup>, as well as dwelled at 200°C for 1 h to remove the water content of samples in order to reduce cracks in samples during the heating process. The samples were held at 500°C for 1 h to eliminate PVA completely. Then the samples were heated from 500 °C to 600°C at a rate of 0.5°C min<sup>-1</sup>, and assisted by dwelling at 600°C for 2 h to burn out the corn starch. Thereafter, the heating rate was changed to 5°C min<sup>-1</sup> and then the sintering was accomplished at 1500°C for 3 h. The heating schedule is shown in Figure 1. Figure 2 shows the block diagram of the preparation process.

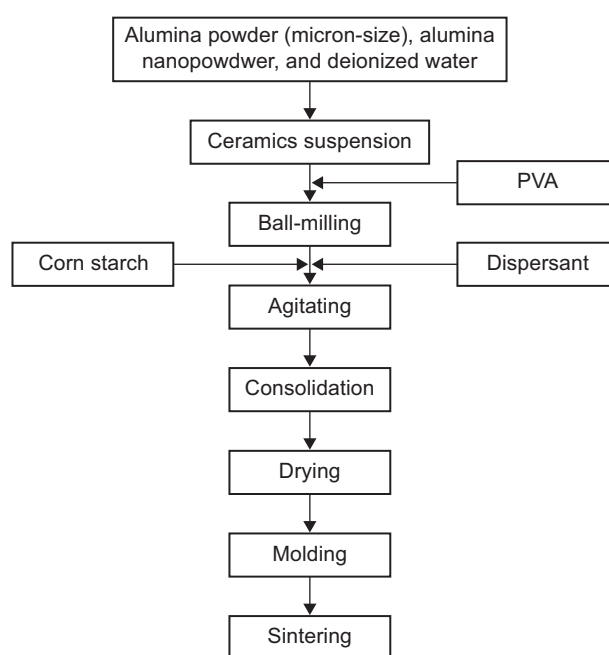


Figure 2. Flow chart of preparation process for porous alumina ceramics in this study.

## RESULTS AND DISCUSSION

The bulk densities of alumina ceramics with different amounts of added corn starch is shown in Figure 3. The densities were measured by the Archimedes Technique. This figure shows that the density decreased linearly with increasing starch content. The alumina ceramics with approximate 80 % theoretical density (theoretical density of alumina ceramics = 3.95 g·cm<sup>-3</sup>) was attained with 10 % starch content. The density reduced to the minimum value 1.33 g·cm<sup>-3</sup> at 50 vol. % starch content. This result indicates that the burnout of corn starch during the sintering process does not influence the sintering of ceramics and the forming of porous structure. Moreover, the densities of alumina ceramics obtained in this study were greater than that of ceramics prepared by the gel-casting technique [15].

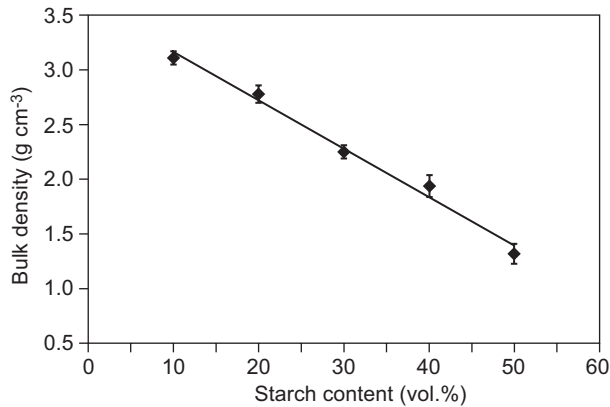


Figure 3. Bulk density of sintered samples vs. starch content.

Figure 4 illustrates the relationship between linear shrinkage of alumina ceramics and starch content. The relationship indicates that the linear shrinkage was not dependent on the amounts of corn starch. As presented in Figure 4, linear shrinkages after sintering were from 13.0 to 14.4 %. In general, the linear shrinkages presented an upward trend with increasing corn starch content. The shrinkages under 20 vol. % starch content had a similar value and from 30 to 50 vol. % had a similar value but greater than the ones under 20 vol. %. It was believed that the linear shrinkage was only dependent on the large pores formed in the burnout process of starch [9-11]. As mentioned above, PVA acted as an adhesive agent which might cause the agglomeration of corn starch in this study. If so, the linear shrinkage would change a lot when increasing corn starch content. However, the linear shrinkages were nearly the same in this study. Thus, the linear shrinkage result of this work presented that the PVA did not cause the agglomeration of corn starch and the burnout process of PVA had no impact on the linear shrinkage when sintering ceramics.

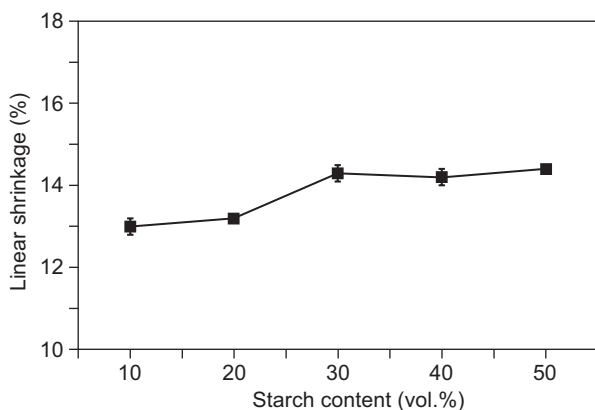


Figure 4. Linear shrinkage changes as a function of starch content.

The total porosity obtained in this study as a function of starch content is shown in Figure 5. As shown in Figure 5, the linearly increasing trend was observed

when the starch content increased from 10 vol. % to 50 vol. %. The total porosity of 14.8 % was obtained at 10 vol. % starch content while it increases to 55.3 % at 50 vol. % starch content. This suggests that the compressive molding after the starch consolidation step did not affect the total porosity.

Figure 5 also makes a comparison between the results achieved in this study and that of the traditional slip casting. In the process of traditional slip casting no starch swelling step occurs since starch is only used as a pore forming agent. Therefore, the amounts of starch content when preparing the raw materials of ceramics are equal to the total porosity of sintered ceramics (cf. the solid line in Figure 5). As another method to produce porous ceramics, the starch consolidation casting can produce the total porosity ranging from 25 % to 50 %. Total porosities less than 20 % are not easy to achieve [9]. For alumina ceramics fabricated in this study, however, the total porosities were typically greater than the amounts of starch added in the preparation process (cf. the dashed line in Figure 5). The limits of starch consolidation casting and traditional slip casting were reported in [16-20]. Thus, the relationship found in this study demonstrates that the total porosity of alumina ceramics fabricated using the method combining the starch consolidation and gel-casting process was higher than that of the ceramics made by traditional slip-casting. The range of total porosity of ceramics in this work was broader than that of the ceramics produced by starch consolidation casting.

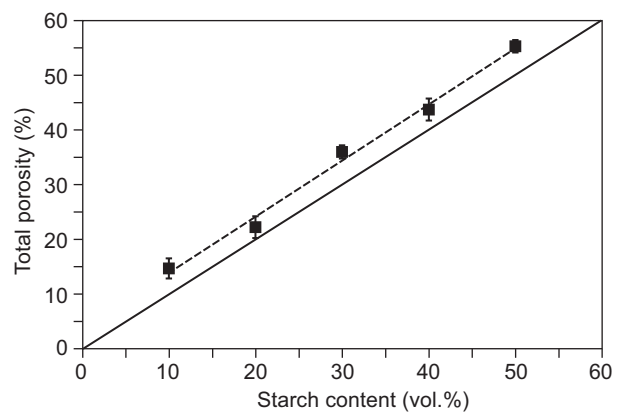


Figure 5. Total porosity of sintered alumina ceramics as a function the starch content.

Figure 6 shows SEM micrographs of typical fracture surfaces of the porous alumina ceramics with different starch contents (0 - 50 vol. %) after sintering at 1500°C for 3 h. The microstructure of the alumina ceramics without corn starch is shown in Figure 6a. As revealed, lower porosity and grain growth can be observed for the samples sintered at this temperature. According to references [10, 17, 20], the densification and the phase transition from gamma to alpha of alumina ceramics had completed typically under this temperature.

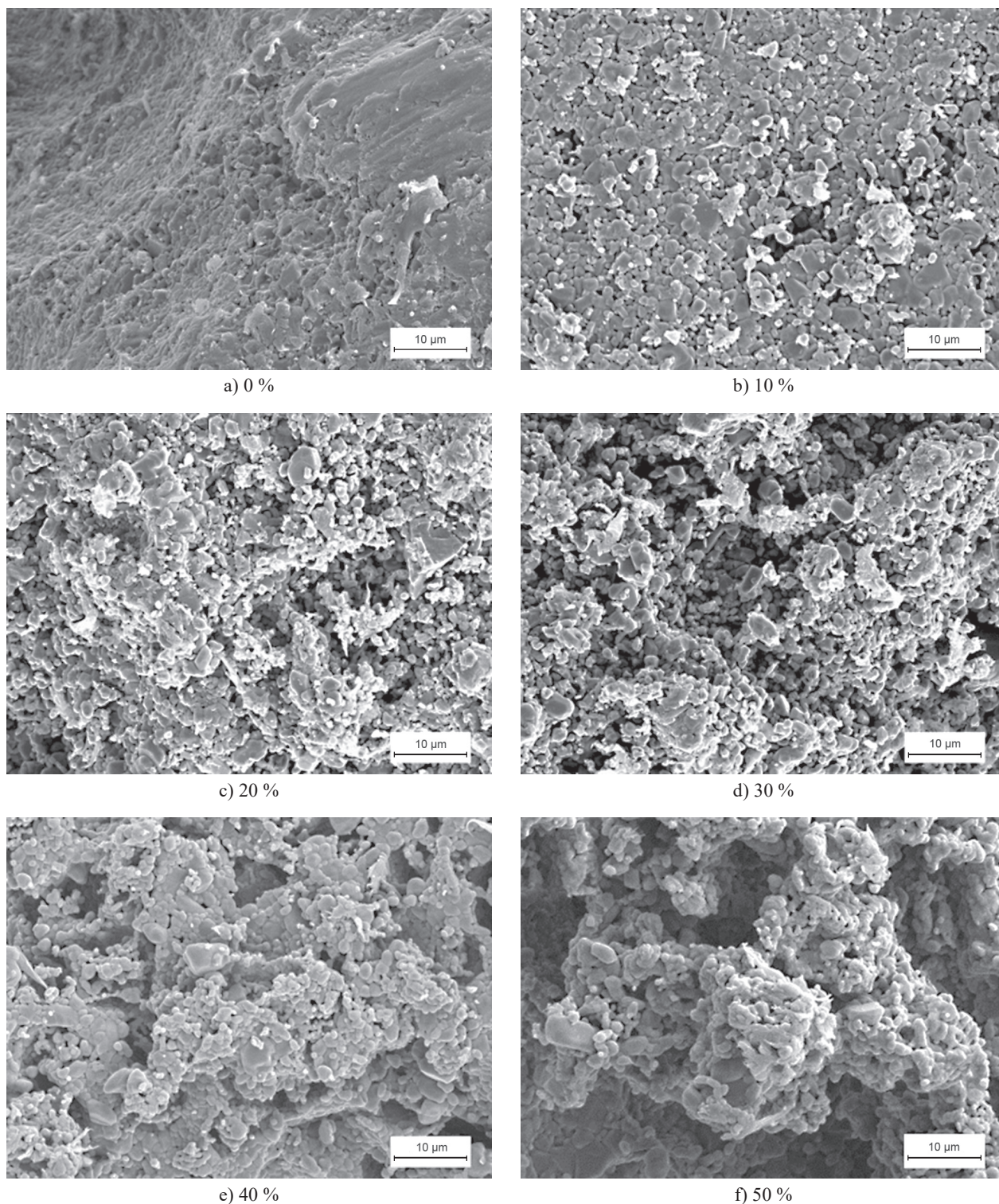


Figure 6. SEM micrographs of porous alumina ceramics with different amounts of corn starch a) 0 %, b) 10 %, c) 20 %, d) 30 %, e) 40 %, and f) 50 %.

As shown in Figure 6b-f, the amorphous materials completely burned and the skeleton was formed through the grains connecting. The porosity and porous structures of the alumina ceramics added starch increased when the amounts of corn starch increased from 10 to 50 vol. %. The reason is that more starch grains connected with each other when more corn starch was added into the

ceramics' raw materials, which led to the rise of porosity and porous structures. Moreover, the grains-connecting of corn starch resulted in the increase of channels among pores after sintering. Similar results were also attained by other work using other methods for fabrication of porous alumina ceramics [18, 21-23]. Comparing the micrographs in Figure 6, the alumina samples with

40 vol. % corn starch possessed a more uniform pore size.

The compressive strength of porous alumina ceramics as a function of starch contents is shown in Figure 7. The compressive strength decreased significantly when the corn starch contents increased from 10 to 50 vol. % corresponding with a compressive strength of 5 - 24 MPa. The decreasing trend of compressive strength with increasing starch content indicates that size changes of crucial loading area occurred in the samples when sintering with different starch contents. The increasing corn starch content resulted in the higher porosity and more porous structure that can lead to the weak skeletons among pores within the samples.

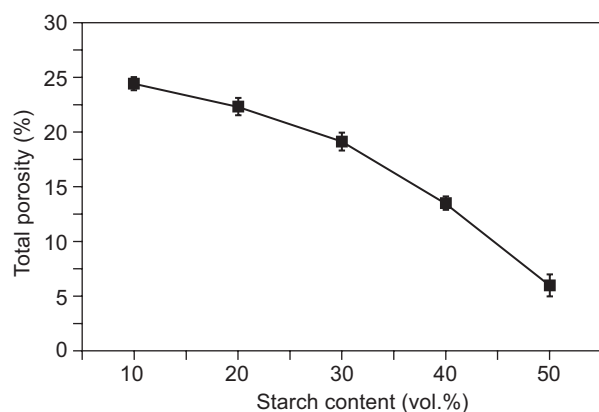


Figure 7. Compressive strength of sintered samples vs. starch content.

## CONCLUSIONS

Porous alumina ceramics with different porosity were fabricated by combining the starch consolidation process with the gel-casting process using corn starch as pore-forming agents and also as binders. The bulk density, porosity, and microstructure of the obtained alumina ceramics were studied. It was found that the total porosity range of sintered samples with different amount of starch contents from 0 to 50 vol. % is 14.8 - 55.3 % and the total porosity increased with the increase of starch content. A relationship between the total porosity of alumina ceramics after sintering and corn starch content was obtained. This relationship indicates that the total porosity of alumina ceramics fabricated in this work was higher than that of the ceramics made by traditional slip-casting. The range of total porosity of ceramics in this work was broader than that of the ceramics produced by starch consolidation casting. The relationship between the linear shrinkage of porous alumina ceramics and the starch content also was discussed. The compressive strength of the sintered samples varied within the range of 5 - 24 MPa, corresponding to starch content of 50 - 10 vol. %. The porous alumina ceramics fabricated in this work with high porosity would be used as preforms

for pressure filtration in authors' next research stage and may have potential for other applications such as hot gases media, catalyst support and lightweight structural materials.

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