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Preparation and characterization of porous alumina ceramics through starch consolidation casting technique

R.M. Khattab, M.M.S. Wahsh *, N.M. Khalil

Refractories, Ceramics and Building Materials Dept., National Research Center, 12622, Dokki, Cairo, Egypt

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Abstract

This work aims at studying the influence of thermal treatment on the microstructure, resistivity and technological properties of porous alumina ceramics prepared via starch consolidation casting (SCC) technique. Colloidal suspensions were prepared with three different contents of alumina solid loading (55, 60 and 65 mass%) and corn starch (3, 8 and 13 mass%). The sintered samples at 1400, 1500, 1600 and 1700 °C, show open porosity between 46 and 64%, depending on the starch content in the precursor suspensions and sintering temperature. The pore structures were analyzed by SEM. The effect of corn starch content on the apparent porosity, pore size distribution, linear shrinkage and electrical resistivity as well as cold crushing strength of the sintered porous alumina ceramics was also measured. These porous alumina ceramics are promising porous ceramic materials for using in a wide range of thermal, electrical and bioceramics applications as well as filters/membranes and gas burners, due to their excellent combination properties.

Keywords: D. Al_2O_3; A. Suspensions; A. Sintering; B. Porosity; B. Electron microscopy

1. Introduction

Porous ceramics are widely used for a variety of applications, including burners, thermal barrier coatings, insulating layers, filters for gases and liquids, catalyst support and thermally or acoustically insulating bulk materials [1,2]. The use of pore-forming agents is one of the frequently used methods to produce porous ceramics with controlled microstructure (porosity and pore size) [3,4]. During heating up to the final firing temperature of the ceramics, these pore-forming agents are burnt out, leaving void pores in the ceramic. Among the various pore-forming agents, those of biological origin, in particular starch, have gained a prominent position. They are cheap, non-toxic, environmentally friendly and exhibit defect free burnout between approximately 300 and 600 °C [5,6]. A specific advantage for porous ceramics is the fact that the pore size can be controlled by choosing the appropriate starch type and that the pore size distribution is in most cases sufficiently narrow to make technological process control efficient [7]. The pore sizes achievable with commercial starch types ranging from ~5 μm in rice starch to ~50 μm in potato starch [6].

Starch grains are normally white, dense and water insoluble at room temperature. Most starches consist of mixtures of two polysaccharide types, a linear one, amylose, and a highly branched one, amylopectin. Amylose gives the starch its gelling property in aqueous suspensions. The glucose units that build up the polymeric chains in starch expose a large amount of hydroxyl groups and, therefore, give a strong hydrophilic character to starch granules (Fig. 1) [8]. These have some favorable characteristics such as good thickening, stabilizing, membrane-forming and gelling properties [8].

The water insolubility of starch granules below about 50 °C means that they can be handled and processed at room temperature without significant impact on the granule structure. However, when the starch suspension is heated to a temperature between 55 and 80 °C (depending on type and concentration), the intermolecular bonds holding the granules together are weakened. During this process the granules undergo a rapid and irreversible swelling by water

* Corresponding author. Tel.: +20 1007561987; fax: +20 233370931.
E-mail address: mmswahsh@yahoo.com (M.M.S. Wahsh).

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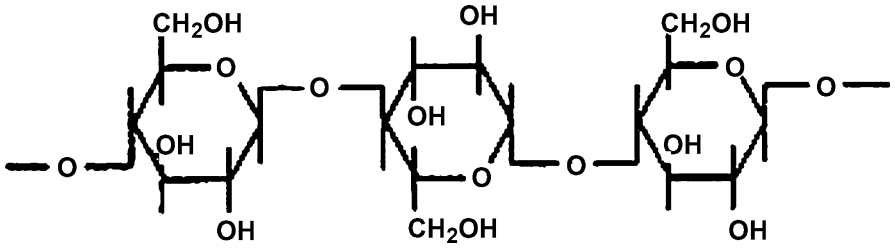

Fig. 1. Starch as a polymer consisting of condensed glucose units.

uptake which results in an increased granule size to many times the original size [9]

The new shaping technique has been presented: starch consolidation casting (SCC). This method based on the ability of starch to swell and finally gelatinize in water at elevated temperature (60–80 °C), so that ceramic green samples can be formed from suspensions in impermeable molds (usually metal molds) [7,10–18]. As the starch granules or particles swell they will also act as a binder adding strength to the consolidated body, which enables demolding prior to drying. After burn-out of the starch and sintering of the ceramic matrix a material is obtained with a porosity corresponding to the original amount, shape and size of the starch particles [8]. Today SCC has become a competitive shaping technique beside traditional slip casting with starch added as a mere pore former [7].

This work was intended to fabricate and investigate of porous alumina ceramics by starch consolidation casting (SCC) technique using different contents of alumina (as solid loading) and corn starch after sintering at different temperature (1400, 1500, 1600 and 1700 °C).

2. Materials and experimental methods

2.1. Starting materials

The starting materials used for preparation of the porous alumina ceramic samples are:

(1) A commercial calcined alumina (α-Al_2O_3) powder with mean particle size $\leq$10 μm, its chemical composition is given in Table 1.

Table 1
Chemical composition of the starting alumina powder, mass%.

Oxides	Calcined alumina
SiO_2	0.74
Al_2O_3	98.20
Fe_2O_3	0.41
TiO_2	0.23
CaO	0.27
MgO	0.07
Na_2O	0.10
K_2O	0.05
Cl^-	–
SO_3	–
LOI	–
Total	100.07

Table 2
Composition of the colloidal suspensions, mass%.

Sample	Alumina solid loading	Corn starch content	Polyethylene glycol	Water content
A	65	3	2	30
B	60	8	2	30
C	55	13	2	30

(2) Poly ethylene glycol (PEG of molecular weight 10,000) used as a dispersant agent and also required for obtaining the significant mechanical resistance before the final consolidation by sintering [19], it is supplied by Fluka.
(3) Native corn starch, commercially available in the market for use in cooking.

2.2. Experimental procedures

To prepare slurry, different amount of calcined alumina ranging from 65 to 55 mass% (as seen in Table 2) was added stepwise to a fixed amount of premix solution containing poly ethylene glycol (PEG) and de-ionized water followed by milling for 2 h using a mechanical mill then different contents of starch ranging from 3 to 13 mass% were added to the premix solutions that containing alumina thoroughly. After 1 h of mixing, the slurry was subjected to de-aeration to remove undesired entrapped bubbles. After that, they were poured into the molds, which heated in air (80 °C, 1 h) for the gelatinization process.

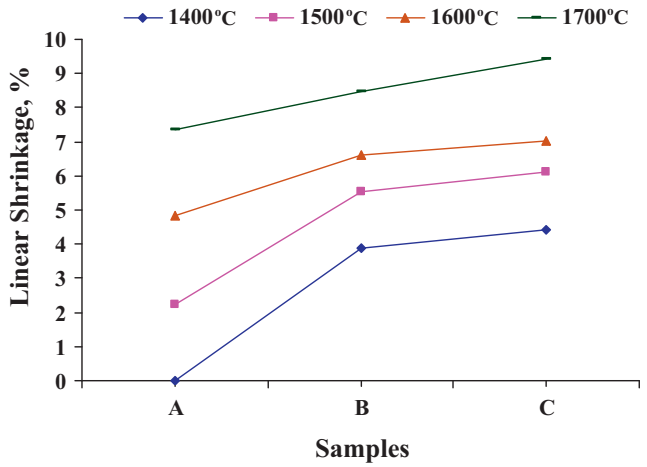

Fig. 2. Linear shrinkage of the porous alumina samples sintered at different temperatures 1400, 1500, 1600 and 1700 °C.

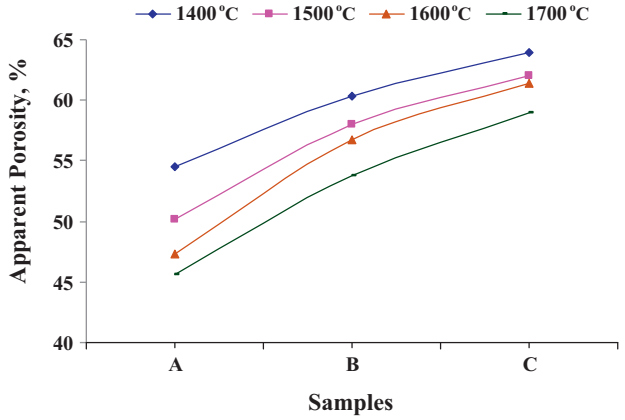

Fig. 3. Apparent porosity of the porous alumina samples sintered at different temperatures 1400, 1500, 1600 and 1700 °C.

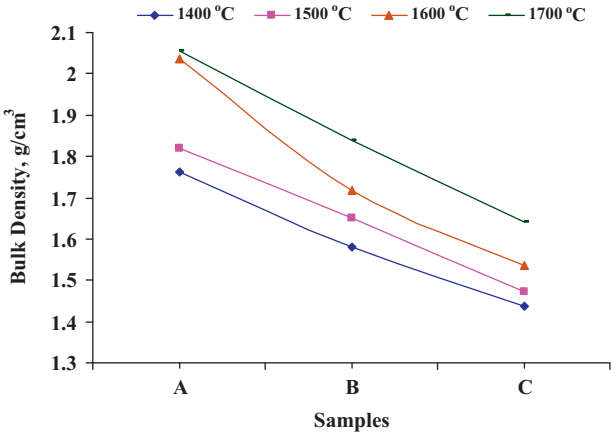

Fig. 4. Bulk density of the porous alumina samples sintered at different temperatures 1400, 1500, 1600 and 1700 °C.

The molds were covered to minimize evaporation of water before and during the solidification to prevent segregation phenomena and, hence, avoid uneven shrinkage and subsequent deformations during sintering. After the gelling step the samples were dried for 24 h at room temperature. After demolding, the green samples were fired at 600 °C with rate 3°/min for 1 h and subsequently sintered at 1400, 1500, 1600 and 1700 °C. Bulk density and apparent porosity of the sintered samples were measured by the Archimedes displacement technique following ASTM-C20 method. The linear shrinkage of the samples was determined by the length measurements before and after the sintering process. The pore size distribution of the sintered porous alumina ceramic samples fired at 1700 °C was measured using a mercury porosimeter (Pore Sizer, Micromeritics model 9320, USA). The obtained microstructure was examined using scanning electron microscope (SEM, Philips XL 30) of gold coated fractured samples. The volume resistivity of the sintered samples was measured using four-probe method. It was calculated from the measured resistance and thickness; both quantities was measured for each sample. A hydraulic testing machine was used for determinations of cold crushing strength of the sintered samples.

3. Results and discussion

3.1. Linear shrinkage

The linear shrinkage of the porous alumina samples sintered at different firing temperature 1400–1700 °C were given in Fig. 2. The linear shrinkage depends on the starch content and sintering temperature. Hence, the linear shrinkage may be due to loss of the added pore forming agent (i.e., corn starch) and sintering of the samples. The linear shrinkage after sintering was ranged from 0.00% (at 1400 °C) to 7.34% (at 1700 °C) and from 4.40% (at 1400 °C) to 9.44% (at 1700 °C) with increasing of corn starch addition from sample A (3 mass% starch) to sample C (13 mass% starch), respectively.

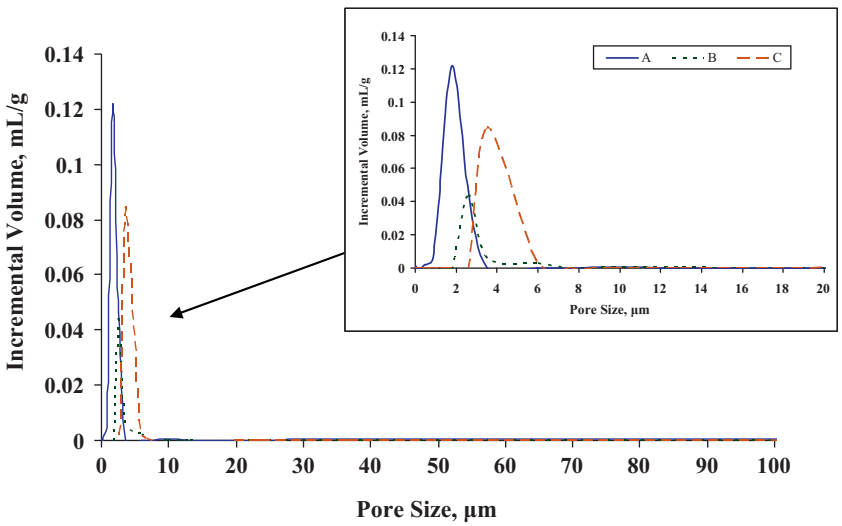

Fig. 5. Pore size distribution of the porous alumina samples sintered at 1700 °C.

3.2. Apparent porosity and bulk density

The influence of the starch content on the apparent porosity and bulk density of the porous alumina samples were shown in Figs. 3 and 4, respectively. The apparent porosity increases with increasing of corn starch content from sample A (3 mass% starch) to sample C (13 mass% starch) at the same firing temperature and decreases with increasing of firing temperature from 1400 up to 1700 °C. This is due to evaporate of corn starch when fired at a higher temperature and leave the open pores in the matrix of the sintered alumina samples, which lead to increase of apparent porosity with increasing of corn starch content. However, the increasing of firing temperature enhanced the sintering of samples as well as each alumina grains near from others resulting decreases the distance between alumina grains and alumina grain growth. Hence, the apparent porosity is decreased.

Bulk density estimated in Fig. 4 is dependent on the sintering temperature and starch contents of the original colloidal suspensions, as well as the solid loading of alumina content in the prepared green samples. In general, the bulk density increases with decreasing of corn starch content and increasing of alumina content, at the same firing temperatures. The bulk density of the samples fired at 1400 °C were present in the range of 1.76–1.44 g/cm^3 corresponding with apparent porosity of 55–64%, while at 1700 °C it is present in the range of 2.05–1.64 g/cm^3 corresponding with a porosity of 46–59%. For samples with the same starch content, the bulk density increases with increasing of firing temperature. This is due to eliminate of pores between particles and a fast grain growth during sintering. Finally, we should point out that the porosity of the sintered samples prepared by this formula is considerably high (46–64%), comparing with the work done by Panyathanmaporn et al. [20].

3.3. Pore size distribution

Fig. 5 shows the pore size distribution of the porous alumina samples sintered at 1700 °C. It is observed that the pore size increases with increasing of starch content from sample A (1.79 μm) to sample C (4.28 μm). With increasing of the amount of starch the number of contacts between the starch particles also increase, which results of a larger pore size [8].

3.4. Microstructure evaluation

SEM microphotographs of the cross sections of the porous alumina samples sintered at 1700 °C prepared with different amount of corn starch addition (3, 8 and 13 mass%) were shown in Fig. 6. It is evident that the pore size structures of the sintered alumina samples increased with increasing of corn starch addition from sample A (3 mass% corn starch) to sample C (13 mass% starch). This is due to increase of connected between corn starch particles with increasing of starch addition resulting increase of pore size structure. Generally, the open paths and channels among pores increase with increasing of starch addition. These results are in a good agreement with the pore size distribution of these samples which increases with increasing of starch addition, Fig. 5. A similar finding was also obtained by other researchers using starch consolidation method for preparation of porous ceramics [8,21–23].

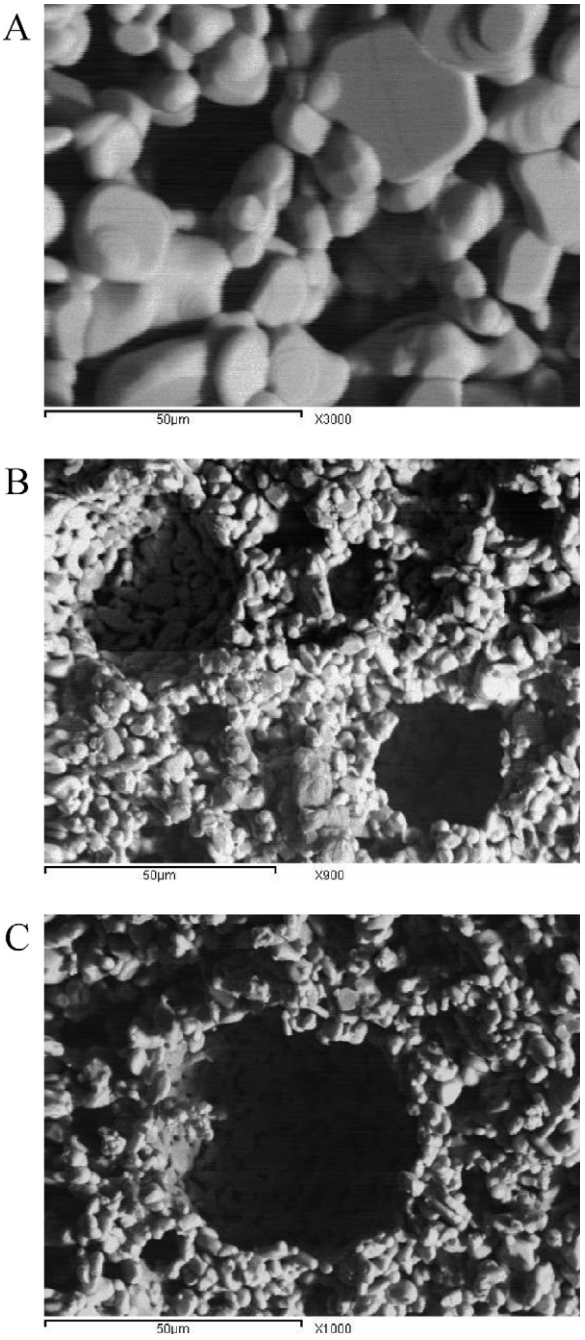

Fig. 6. SEM microphotographs of the porous alumina samples sintered at 1700 °C.

3.5. Volume electrical resistivity

The volume electrical resistivity of the sintered porous alumina samples measured at room temperature as a function of the starch content shown in Fig. 7. The high resistivity for all fired samples is due to the fact that the Al_2O_3 is a good insulator; the resistivity of alumina is 10^{12} Ω m [24]. Fig. 7

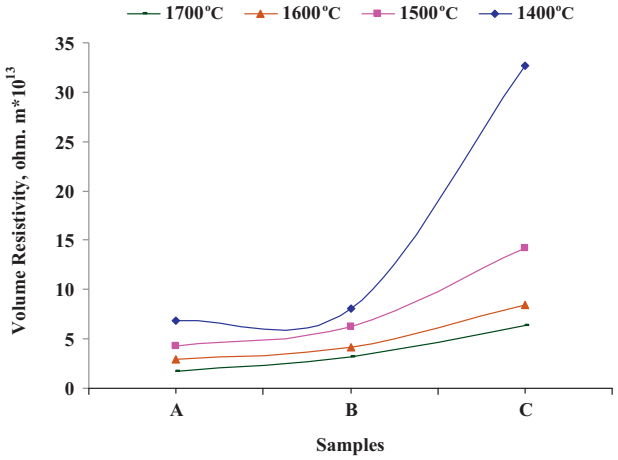

Fig. 7. Volume resistivity of the porous alumina samples sintered at different temperatures 1400, 1500, 1600 and 1700 °C.

shows that the resistivity decreases with either increasing in the firing temperature or the starch content. This is relative to the voids between the particles increase with increasing the starch content. According to Dietzmann et al. [25] an increarse in intergranular porosity also result in an enhancement of electrical resistivity.

3.6. Cold crushing strength

Fig. 8 shows the cold crushing strength of the porous alumina samples sintered at different firing temperatures 1400, 1500, 1600 and 1700 °C. The compressive strength exhibits higher value for the samples fired at 1700 °C comparing with those fired at 1400 °C. This change in the compressive strength with firing temperature is related to decrease of porosity and increase of sintering with increasing of firing temperature. Porosity has a significant role to influence the strength of sintered porous alumina samples. It is well known that the strength of the porous ceramics increases with decreasing of porosity [26–28]. Previous works indicated that changes of porous body strength as a result of grains grow up that led to the porous body had more contacting areas. It becomes the main reason for causing the change of porous alumina strength at that time [2]. Hence, porous alumina sample that has gone sintering

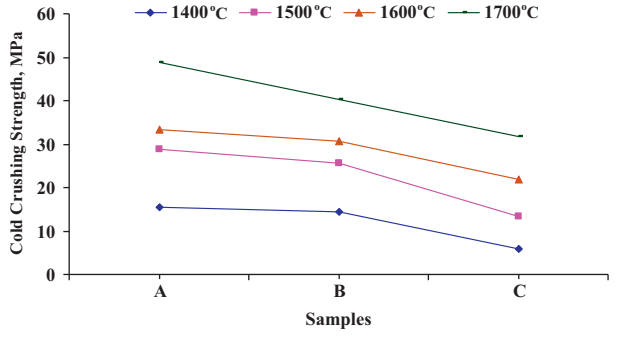

Fig. 8. Cold crushing strength of the porous alumina samples sintered at different temperatures 1400, 1500, 1600 and 1700 °C.

at 1700 °C gives the highest strength value (48.11 Mpa), which is almost three times higher than porous alumina sample sintered at 1400 °C with the strength value of 15.47 MPa.

4. Conclusions

In this investigation, corn starch was employed as a pore former for preparing of porous alumina ceramics. The influence of sintering on the mechanical, electrical, physical properties and microstructure of porous alumina are investigated. Porous alumina ceramics prepared by starch consolidation casting exhibit significantly higher open porosity at low starch contents. This indicates a highly interconnected pore space (large pore bodies connected by small pore throats), even with low little contents of starch. The process is based on body conformation from colloidal suspension which changes to gel in an oven at 80 °C. Sintered samples were prepared at 1400, 1500, 1600 and 1700 °C; technological studies showed that bulk density, apparent porosity, pore size, volume resistivity and mechanical properties of porous alumina ceramics were a function of starch contents and sintering temperature. The sintered samples were presented bulk density value in the range of 1.4–2.05 g/cm^3 and apparent porosity percent in the range of 46–64% as well as the pore size in the range of 1.79–4.28 μm depending on the starch content of the precursor suspensions and sintering temperature. These ceramic samples may have potential use in a wide range of applications due to an excellent combination of properties. Regarding the possible range of ceramic material to meet specific requirements regarding the pore structure, modifications can be done by adding other organic materials. To simplify the forming and further increase the control of component dimensions, binder (Latex, PEG, etc.) can be added to enhance the green machining properties.

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