



Effect of starch addition on microstructure and properties of highly porous alumina ceramics[☆]

Sa Li, Chang-An Wang*, Jun Zhou

State Key Lab of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

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Abstract

Porous alumina ceramics with ultra-high porosity were prepared through combining the gel-casting process with the pore-forming agent technique. Porosity and pore size distribution of the sintered bulks were evaluated with and without adding starch, respectively. In particular, the influences of starch addition on the properties, including thermal conductivity and compressive strength were studied. It was found that the incorporation of starch increased the nominal solid loading in the suspension and subsequently promoted the particle packing efficiency. The porosity is raised with increasing starch content from 0 to 30 vol%, which brings the decrease in thermal conductivity, whereas the compressive strength isn't seriously degraded. The further higher starch addition (40 vol%), however, would deteriorate the performance of the alumina porous ceramics. It is believed that the appropriate starch amount (lower than 30 vol%), working as a pore-forming agent, suppresses the driving force of densification without affecting the connections of neighboring grains while excessive starch amount would lead to the collapse of the porous structure.

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1. Introduction

Porous ceramics have attracted increasing interest due to their applications as separation media for molten metal, hot gases, a variety of liquid filtration processes and as catalyst supports, bone scaffolds, and electrodes in fuel cells [1–4]. A number of techniques have been developed to fabricate porous ceramics, including the direct foaming method, the sacrificial template method and the gel-casting method [5–10]. Each of these methods has its own merits and drawbacks. For example, reticulated porous ceramics produced by the polymer foam replication method can have ultra-high porosity with large interconnections; however, these materials often have poor mechanical properties because of the defects generated during the pyrolysis of the polymer foam. In addition, this

method is only suitable for generating ceramics with relatively large pores with a size of several hundreds of microns, or even millimeter scale. Tape casting with pore-forming fugitive phases is also a commonly used method, owing to its simple processability, yet it is difficult to optimize the pore structure using this method. Since each technique has its own inherent advantages and disadvantages, many attempts have been made to combine those methods to fabricate samples with some mechanical and structural properties that cannot be attained by either method. Ramay et al. prepared porous hydroxyapatite scaffolds by combination of the gel-casting and polymer sponge methods, which provided a better control over the microstructure of scaffolds and enhanced their mechanical properties [11]. Mao and co-workers produced porous ceramics with tri-modal pores by foaming and starch consolidation [12]. The resulting materials consisted of a hierarchical structure with large-sized cells, moderate-sized pores in cell wall and small-sized voids among grains. However, the integration of gel-casting and pore former agents is rarely reported.

For more than decades, preparation of porous ceramics using starch as pore-forming agent is attracting more and more attention because of its chemical purity and easy burnout without any residue as well as good body-forming ability

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*Corresponding author. Tel./fax: +86 10 62785488.

E-mail addresses: wangca@tsinghua.edu.cn, wangca@mail.tsinghua.edu.cn (C.-A. Wang).

[13–15]. Lyckfeldt and Ferreirab reported starch consolidation casting as a new shaping technique that utilized the ability of starch to swell and gelatinize in water at high temperature [16]. Starch worked as pore-forming and body-forming agents simultaneously in the starch consolidation casting process. However, starch granules generally change their size as well as the shape due to its swelling in the aqueous suspension, and therefore it becomes difficult to determine the characteristics of the pores of the final porous ceramics. In this study, we report a novel technique that integrates gel-casting with pore-forming agents by adding starch into alumina/TBA slurries. Microstructure including pore morphology, and pore size distribution was characterized. Thermal and mechanical properties were also investigated. An explanation was given to clarify the mechanism of starch addition working in the processing as well.

2. Experimental procedure

As starting materials, Al_2O_3 powder (about 1 μm average diameter, Shanghai Chemical Regent Co., China) was used. Tert-butyl alcohol (TBA, Beijing Yili Chemical Co., Beijing, China) was used as shaping solvent and pore forming agent in the gel-casting process. Commercially available wheat starch was used as pore former agent and binder. Experiments were carried out using the as-received starch, without any subsequent processing. The average size of the spherical granule of starch was approximately 10 μm . A premix solution of monomers and cross linker was prepared in TBA with a concentration of 14.5 wt% of acrylamide (AM, $\text{C}_2\text{H}_3\text{CONH}_2$) and 0.5 wt% N,N'-methylenebisacrylamide (MBAM, $(\text{C}_2\text{H}_3\text{CONH})_2\text{CH}_2$). Initiator and catalyst for gelation reaction were ammonium persulfate (APS) and N,N,N,N-tetramethylethylenediamine (TEMED), respectively. All chemicals used in this study are of analytical grade. The TBA-based gel-casting technique typically consists of preparing a liquid suspension (slurry), molding, drying, binder removal and sintering. Different amounts of starch added to the stabilized Al_2O_3 suspension were measured as a volume fraction of ceramic powders, ranging from 0% to 40%. Slurries with 15 vol% solid loading, including Al_2O_3 powders, starch, TBA, and acrylamide (AM) were prepared by ball milling for 5 h. To adjust the suspension to a proper flow ability during casting, selected citric acid solution was added into the slurries. After ball milling, initiator and catalyst were mixed into the slurry. The slurries were poured into molds and dried at 52 °C in nitrogen atmosphere. During the drying procedure, the polymerization of AM took place and the TBA gradually volatilized. Green bodies were then produced and finally sintered at 1450 °C for 2 h.

Thermal gravimetric-differential scanning calorimetry (TG-DSC) analysis was performed using SDT Q600 (TA-Instruments) with air flow at a heating rate of 10 °C/min from room temperature to 1450 °C. Microstructure was observed using scanning electron microscope (SEM, JSM 6700 F, JEOL, Tokyo, Japan). Pore size distribution was analyzed by mercury intrusion porosimetry (AutoPore-IV9510, Micromeritics Instrument Corp., United States). Porosity was obtained from the ratio of the bulk density,

measured from the samples' mass and dimensions, to the theoretical one of this Al_2O_3 material (3.98 g/cm³). Three samples were examined to determine the average porosity. Linear shrinkage was obtained through recording the image changes on a sintering point testing device with screen display machine (SJY, Xiangtan Instrument and Meter Factory). A cubic sample with a dimension of 1 × 1 × 1 mm³ was heat treated from 50 to 1450 °C and the heating schedule was the same with the green body. Then we measured the size change and calculated the linear shrinkage based on a series of images got at a interval of 30 s during the sintering process. Thermal conductivity at room temperature was measured on 5 × 5 × 3 mm³ machined specimens, using Thermal Transport Option (TTO) of Physical Properties Measurement System (PPMS, Model 6000, Quantum Design, USA). For the compressive strength measurements, samples with 6 mm diameter and 12 mm height were loaded with a cross head speed of 0.05 mm/min (Instron 3369, Instron Corp.). Five specimens were used to obtain average values and standard deviations.

3. Results and discussion

In order to produce the desired porous ceramics without generating any defects, the organic phases (the starch and polymer) must be completely removed before sintering the alumina green bodies. To establish a heating schedule, TG/DSC analysis was carried out and the result is shown in Fig. 1(a). As revealed, the green body would go through weight reduction at two stages: a remarkable loss of about 30 vol% occurred at about 380 °C, and a following decrease continued at about 520 °C. The organic components were completely degraded at a temperature of < 600 °C. This result is confirmed by the DSC curve. A negligible amount of organic phases remained after the heat treatment. Based on this result, the optimized heating schedule for the sintering could be determined in Fig. 1(b). Samples were heated from 120 to 600 °C at a rate of 0.5 °C/min and maintained at this temperature for 2 h to remove the organic phases completely. Thereafter, the samples were sintered at 1450 °C for 2 h, followed by furnace cooling.

Fig. 2(a) and (b) respectively represents the SEM micrographs of the green bodies and the sintered compacts without adding any starch. Interconnected pores, which arise from the detachment of the solvent TBA during the drying process, are observed in the green body and amorphous materials exist between the spherical particles, which are polymer binders. Fig. S1(a, b and c) shows SEM micrographs of the original wheat starch granules, the wheat starch milled in TBA and water for 5 h, respectively. The mean granular size was approximately 10 μm before milling. When dissolved in water, starch would absorb water and generate fibrous structure (Fig. S1(c)). Such phenomenon has been applied in the starch consolidation, in which starch works as a body-forming agent to connect the ceramic powders together. However, after ball milling in TBA, the original large starch granules turn to regular small spherical particles with a diameter of about 2 μm . Fig. 1S(d) represents the micrograph of the mixture of alumina particles and starch granules after milled in the TBA for 5 h.

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