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Controlled fabrication of porous Al_2O_3 ceramic by *N*,*N*′-dimethylformamide-based gel-casting

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Alumina ceramic with controlled porosity and small pore sizes of <3 μm can be successfully fabricated via a novel and facile *N*,*N*′-dimethylformamide-based gel-casting technology without using any pore-forming agents, and its drying process can be completed within 10 h by simple heating. When regulating the content initially and changing the processing conditions, the porosity can be controlled between 82% and 29%, as the compressive strength of the porous ceramic remarkably varied from 3.8 to 79 MPa.

Keywords: Porous material; Ceramic; Gel-casting; Microstructure; Mechanical property

Porous materials have received much attention for the special pore structure that endows them with a unique set of properties, such as low bulk density, low thermal conductivity, high surface area, and high permeability [1–3], making them promising candidates for a variety of applications. One kind of porous material, aerogel, is widely considered for use in many applications, such as thermal insulation [4], high-energy particle detectors [5], drug carriers [6], catalysts [7], catalyst supports [8], and nuclear waste storage [9]. Practical applications of aerogel have been slow though, because it is usually brittle, hygroscopic, hard of bulk integrity and cannot withstand high temperature [10,11]. Materials that are strong, lightweight, and high-temperature-resistant are much in demand, requiring components with these properties carefully designed and manufactured accordingly.

Porous ceramics are increasingly found to have significant impact in applications because they integrate the advantages of porous materials and ceramics inherent to their structure. Many techniques have been developed to fabricate porous ceramics [12–15]. In particular, gel-casting, a fast in situ consolidation colloid-forming process, promising for the manufacture of structural ceramics with various shapes, recently became a focus in the field of porous ceramic preparation due to its near-net-shape, low monomer content and homogeneous structure obtained after debinding and sintering [16–18]. Up to now, there have been three main ways to prepare porous ceramics through the gel-casting technique; that is, by combining it with foaming techniques, or replica methods, or the addition of a sacrificial phase [19–22]. The products obtained by the first two ways bear a high porosity, usually composed of large pores even up to several hundred micrometers. The pore size decides on the diameter of the sacrificial phase in the third way, which is reported to include PMMA, graphite, flour, starch, etc. Small pores could be obtained by decreasing the pore size of the foreign combustible organic material; however, the porosity is usually lower than 50%, mainly because significant shock occurs caused by the decomposition of organic material in the heating process. The difficulty in acquiring small pores with high porosity prevents the gel-casting technique from becoming a universal production process.

We realize that aerogel is formed through sol–gel technology by network growth from an array of discrete colloidal particles or by the simultaneous hydrolysis and polycondensation of an organometallic precursor. When the pore liquid is removed from the interconnected solid gel network and the network does not collapse, then a low-density aerogel is produced [23]. So the successful fabrication of aerogel is achieved with small pore size and high porosity in the absence of extra pore formers.

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Inspired by this conception, it would be worthwhile to devote much effort to the preparation of porous ceramics in an elaborately formed pore structure like aerogel by manipulating gel-casting technology, which would well overcome the shortcomings in the previous report.

Herein, we demonstrate porous ceramic with controlled porosity and small pore sizes of <3 μm can be fabricated by a developed gel-casting technology. This novel gel-casting technique induced pores by evaporation of solvent, without using any pore-forming agents. To accomplish this, alumina/*N*,*N*′-dimethylformamide (DMF) slurries with various alumina contents (10, 20, 30, 40 vol.%) were mixed and gelled, followed by drying treatment at 120 °C for 10 h. The pore structure (e.g. porosity, pore size) and compressive strengths of the samples can be regulated by adjusting the treatment process.

In a typical experiment (see Supporting information for details), commercially available α-Al_2O_3 and DMF were used as the ceramic material and the vehicle, respectively. Acrylamide (AM) and *N*,*N*′-methylenebisacrylamide (MBAM) were employed as monomer and cross-linker. Polyacrylic acid (average molecular weight of 5000 Da) was added as dispersant. The polymerization reaction was initiated by the addition of $(NH_4)_2S_2O_8$.

First, alumina/DMF slurries with various alumina contents, ranging from 10 to 40 vol.% in intervals of 10 vol.%, were prepared by vigorous stirring and ultrasonic vibration at room temperature (25 °C). After the initiator solution was added, the prepared slurries were then poured into cylindrical molds and capped. Then they were put in an oven for 30 min at 60 °C to accomplish the gelation. After that, the samples were cooled naturally to room temperature. Then the solid products were transferred from the molds and dried at a temperature of 120 °C. DMF, unlike common solvents such as water, can be completely removed after 10 h and no obvious shrinkage occurred. The organic additives were burned out at 600 °C, having been held for 60 min at both 262 and 400 °C. Subsequently, separate samples were sintered for 2 h at either 1200, 1300, 1400, 1500, or 1600 °C.

The fabricated samples were characterized by evaluating their pore structures (e.g. pore size, porosity, pore morphology) using scanning electron microscopy (SEM), a laser scanning confocal microscope, and a mercury porosimeter. The porosities were calculated by the difference between the bulk densities and the skeletal true densities. The compression strength of the sintered bulks was performed in the light of GB/T 1964–1996, employing a universal testing machine. Each data entry was the average of at least 5 samples.

The conceptual basis of our strategy can be appreciated by considering a graphic sheet (Fig. 1a). First, low concentrated suspension is employed that makes the solvent occupy much space. Then gelation occurs which results in ceramic particles being partitioned into many “rooms” in a “multi-storey building”. After heat treatment and sintering, the loosely immobilized particles directly form into porous ceramics in the absence of any pore-forming agents.

To put these ideas into practice, an appropriate medium, which can satisfy the requirement of gel-casting and at the same time be feasible in practice, is extremely critical. The merits of our chosen solvent, DMF, are the following. First, it bears excellent solvent power, having the same element and similar chemical structure with the organic material used in gel-casting. This can make the monomers dissolve well and disperse in it. Moreover, DMF contains no α-hydrogen, so the chain transfer reaction takes place less readily. In addition, the surface tension of DMF is 36.2 mN m^{-1} at 25 °C, almost one-half that of water (71.81 mN m^{-1}), thus ensuring that there is limited shrinkage during green-body drying when used as a vehicle of ceramics slurry. The polymerization of acrylamide in DMF was corroborated by DSC and FT-IR experiments (shown in Figs. S1 and S2). Plenty of pores and perfect pore structure were observed in Figure 1d and e. This architecture was achieved in two processes. First, gel skeleton frame was formed in a polymeric state (Fig. 1b), which can lock the alumina powders into the “multi-storey building”. Then, the organic framework was removed by heating, leaving behind the ceramic particles loosely ar-

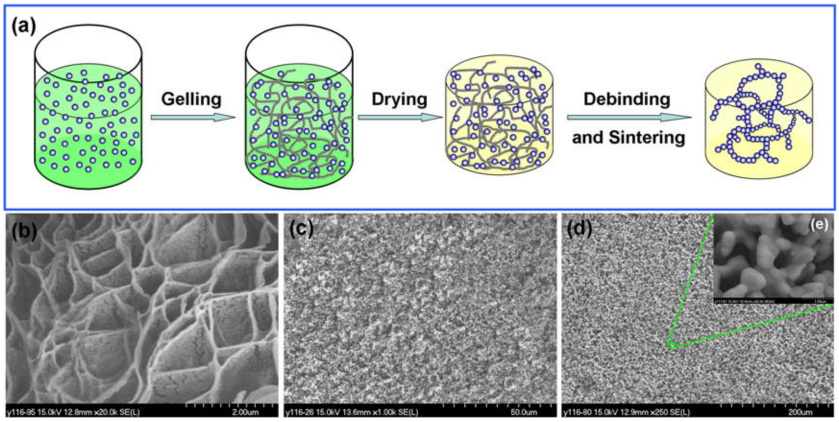

Figure 1. (a) Schematic illustration of the formation of porous ceramic by DMF-based gel-casting. (b–e) SEM images of the fabricated porous alumina ceramic, where (b) shows an acrylamide gel prepared in DMF solvent, (c) is the microstructure of green body after debinding, (d) and (e) show the microstructure of porous alumina ceramic sintered at 1400 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)