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Porous YSZ ceramics by water-based gelcasting

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Abstract

Gelcasting, as a novel method to form ceramic bodies, has been successfully developed to fabricate porous YSZ ceramics with an open porosity of 33.1–50.3%, mean pore size of 0.66–0.98 μm and the nitrogen permeability of 215–438 m^3/m^2.bar.h. In order to further illustrate the features of this water-based gelcasting process to prepare porous ceramics, the same YSZ powders were blended with the same additives, and then cold pressed and sintered at the same conditions employed for gelcasting process. Compared with the cold pressed samples, the gelcast bodies exhibit higher open porosity, lower closed porosity, relatively larger pore size and thus higher gas permeability. Therefore, the developed gelcasting process is a very effective method to fabricate porous ceramics for filters or supports.

Keywords: Ceramics; Porous; YSZ; Water-based; Gelcasting

1. Introduction

Porous yttria stabilized zirconia (YSZ) ceramics are becoming increasingly important because of a variety of applications, such as separation media for liquid or gas filtration processes, thermal insulators and sensors [1]. In recent years, porous ZrO_2 based ceramics have been extensively used as supports for solid oxide fuel cells (SOFCs) [2–6].

According to their different applications, the fabrication process must be carefully controlled to meet the different performance required, such as pore size, porosity and microstructure. For example, a high sintering temperature is required to ensure the dense YSZ membranes as electrolyte in SOFCs. At the same time the YSZ support should have sufficient porosity to allow high gas diffusion rates on the basis of enough mechanical strength, and suitable average pore size. In general, YSZ membranes prepared by common techniques such as screen printing are heated to at least 1400°C to obtain a dense layer [2–3]. At this higher sintering temperature the YSZ support will become less porous for the transport of gases in spite of the addition of the pore-forming agents.

Gelcasting is a novel forming method for fabricating ceramic bodies by means of in situ polymerization through which a macromolecular network is created to hold the ceramic particles together. This process has several noteworthy features such as high solid loading of the suspension; controllable casting and solidification through the use of polymerizable organic monomers; low drying and sintering shrinkage for ceramic body from a dense suspension; and strong machinable green body for more complex shapes [7]. Commonly, this process is being used to form complex-shape, near-net-shape advanced ceramic materials in the electronics, automotive, and defence industries [8]. To date, however, there are less reports on employing the gelcasting method to fabricate porous ceramics.

In this paper, we have tried to develop this process to prepare porous ceramics and taken YSZ porous ceramics as example. At the same time, YSZ porous bodies were fabricated from the same ceramic powders and additives by cold pressing, a common technique for porous ceramics, as a comparison with the gelcasting process.

2. Experimental

Zirconia doped with 9 mol% yttria (YSZ) powders were prepared by a coprecipitation route in which oxalate was used as the coprecipitating agent. The resulting precipitate was vacuum-filtered, washed 5 times each with water and ethanol and then dried. The de-washing

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step with ethanol improves the sintering characteristics of the resulting oxide powders. After calcination at 900°C (300°C/h heating rate), the oxide powders were confirmed to be YSZ single phase with fcc structure by X-ray diffraction analysis.

The gelcasting process flow sheet is illustrated in Fig. 1. The amount of organic monomers, acrylamide (AM) and *N*,*N*′-methylenebis-acrylamide (MBAM), is 5 wt% of the dried solids. Some inorganics, e.g. carbon powder with the amount of 5–10 wt% of ceramic powders may be added as a pore-forming agent. The suspension obtained has at least a 50 vol% solid loading. As the gelled oxide bodies were demolded and dried, they were machined and finished to disks of Ø13×2 mm in size, and then sintered under the different sintering temperature from 1300 to 1650°C for 5 h.

To compare with this gelcasting process, the same YSZ powders were mixed with the same amount of the organic and inorganic additives excluding the catalyst TEMED, ball-milled, dried, and then cold pressed into the pellets with the same size of Ø13×2 m. The green bodies were heated at the same conditions mentioned above.

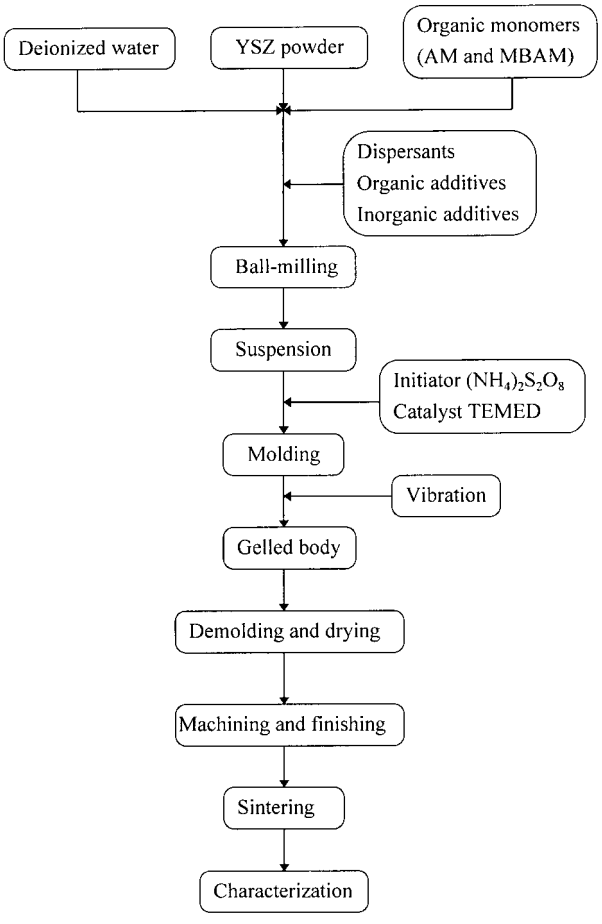

Fig. 1. The preparation process of YSZ porous ceramics by water-based gelcasting (AM: acrylamide; MBAM: *N*,*N*′-methylenebis-acrylamide; TEMED: *N*,*N*,*N*′*N*′-tetramethylethylenediamine).

The density, open porosity, and total porosity was determined on all sintered specimens using the Archimedes method with a theoretical density of 6.02 g/cm^3 for zirconia doped with 9 mol% yttria. The microstructures of all specimens were observed by SEM (a Hitachi X-650 Scanning Electronic Microscope). The average pore size and pore size distribution of the sintered porous samples were obtained by the bubble-point method and pure nitrogen gas permeation through the porous disks was measured in a permeation device.

3. Results and discussion

3.1. Pack characteristics of green bodies

During the gelcasting process as shown in Fig. 1, in order to minimize shrinkage and produce a high as-cast green density, a minimum loading of 50 vol% solids was selected and the dense suspension was made stable and well-dispersed by ball-milling and adding the dispersants. When adding the catalyst and molding in a vibrating table, the oxide ceramic powders were fixed in situ by gelation for a few minutes, so the gelled body with a homogeneous green structure can be obtained, and thus lead to a uniform shrinkage during sintering. As expected, Fig. 2 shows that the gelcast green bodies have almost the same axial shrinkage as the radial shrinkage. In contrast, the sintering shrinkage of the green pellets by cold pressing was not isotropic and the axial shrinkage rates were somewhat larger than the radial shrinkage rates. During die compaction, friction develops from the relative motion between die sidewalls and powder particles, between powder particles within the powder mass, and between powder particles and punch faces. Because of this friction, the local pressure within the premix powder mass caused by the upper punch load is not uniform, which results in density variations in the compact.

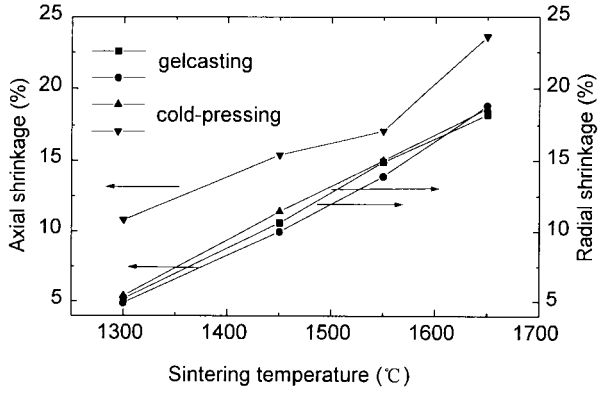

Fig. 2. Linear shrinkages of all samples sintered at the different temperatures.

In addition, as the organics are burned out, the relative packing density of the green body obtained by gelcasting is higher than that by cold pressing, and they are 32.4 and 39.3%, respectively. However, the linear shrinkage rate of the gelcast bodies, especially axial shrinkage rate, is lower than that of the pressed bodies. This is beneficial to their uniform shrinkage.

3.2. Structure parameters of sintered specimens

The effect of the sintering temperature on the porosity of the sintered YSZ ceramics is illustrated in Fig. 3. As the sintering temperature rises, all sintered specimens become increasingly dense. However, compared with the cold pressed samples, it is obvious that the sintered gelcasts have higher open porosity and lower closed porosity. At the higher sintering temperature of 1450–1550°C, the gelcasting process provides the porous ceramics with the open porosity of 33.1–50.3%, which is high enough to be used as filters or porous supports. By contrast, the open porosity of cold-pressed samples is only in the range of 19.1–30%, although the same amount and composition of the organics and inorganics were also added. On the other hand, the closed porosity of the gelcast samples is at least 30% lower than that of cold pressed specimens. This distinction is very important for the porous ceramics to be used as filters or supports. These significant results may be attributed to the formation of the polymeric network, which has been further studied.

The sintering temperature also has influence on the mean pore diameter and pore size distribution of the sintered samples, as shown in Figs. 4 and 5 . Comparatively speaking, they have the similar trend in the pore structure when the temperature is changed from 1450 to 1550°C. However, it is noted from Fig. 4 that for the gelcast samples, the mean pore diameter has a relatively obvious increase. This is because that as the sintering temperature increases, the growth of the particles leads to the formation of larger pores and elimination of smaller pores. This can be proved by the change of the pore size distribution of gelcasts illustrated in Fig. 5. Clearly, when the temperature is raised to 1550°C, the number of the pores with the diameter less than 0.7 μm significantly decreases and the pore distribution becomes narrower.

On the other hand, compared with the pressed samples, the results in Fig. 4 show that the average pore size of gelcast samples is larger than that of the cold pressed specimens, even for the samples with the same porosity. Fig. 6 is the surface SEM photographs of the gelcast sample sintered at 1550°C and the pressed pellet at 1450°C, respectively. Although their open porosities are about 30%, the average pore size of the former is bigger than that of the latter, which is 0.98 and 0.18 μm, respectively. In addition, it is found from Fig. 5 that the pore size distribution of the gelcasts is comparatively wider. However, it should be noted that the maximum pore sizes in the gelcasts are lower than 1.5 μm, smaller than the mean particle sizes (observed by SEM). This indicates that no flaws and cracks exist in the gelcast specimens. Since the same amount and composition of the ceramic powders and additives was contained in their green bodies, the distinctions for the gelcasting process have no relation with the additives.

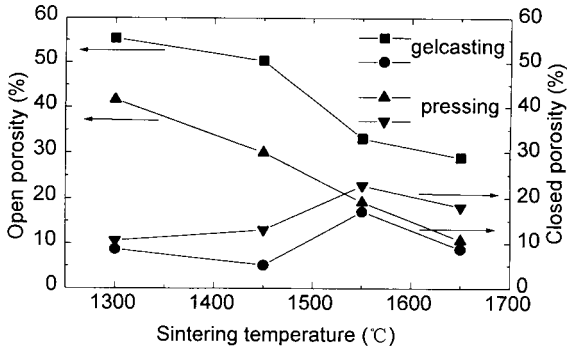

Fig. 3. Effect of the sintering temperature on the porosity of the sintered specimens.

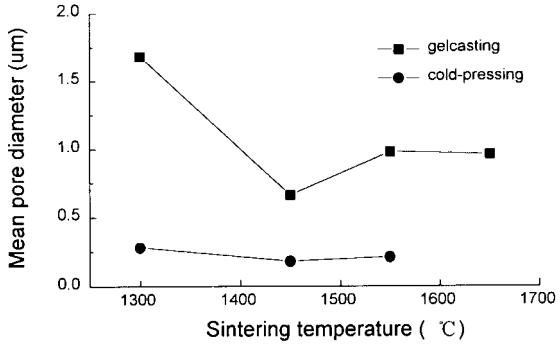

Fig 4. Influence of the sintering temperature on the mean pore size of the sintered samples.

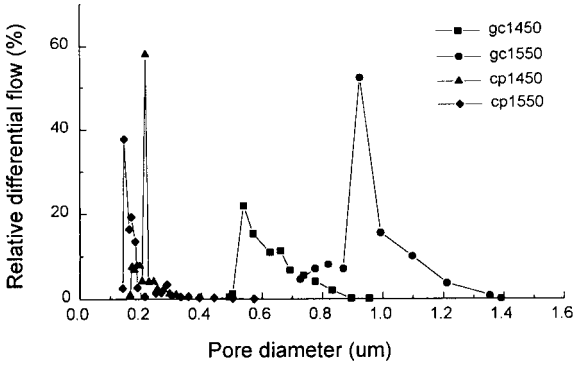

Fig 5. Sintering temperature vs pore size distribution of samples; gc1450 and gc1550: gelcasts sintered at 1450 and 1550°C, respectively; cp1450 and cp1550: cold-pressed samples at 1450 and 1550°C, respectively.

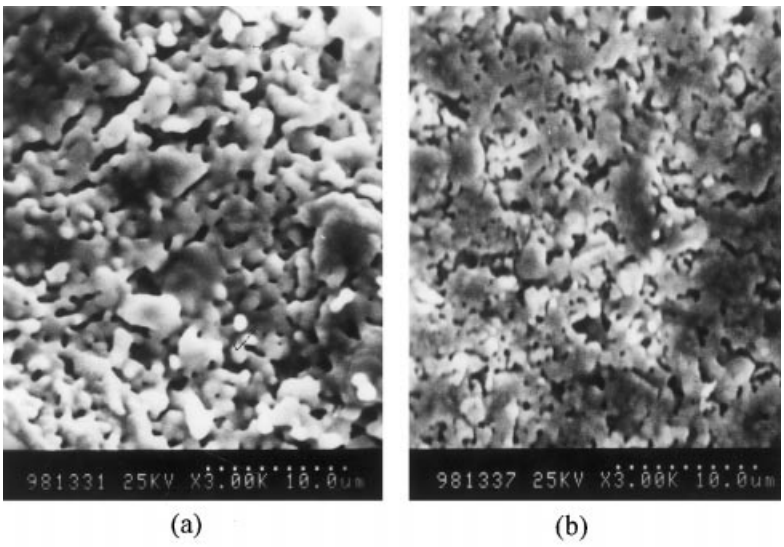

Fig 6. Scanning electron micrographs of surface of samples with the same open porosity; (a) gelcasts sintered at 1550°C (b) cold pressed samples sintered at 1450°C.

So we think that they may also be related to the polymeric network.

3.3. Gas permeation

The fluid flux of porous ceramics is commonly considered from the viewpoint of applications. In this study, nitrogen gas was used to measure and compare the gas permeation of the samples by these two different processes. Fig. 7 illustrates that nitrogen flux increases with pressure drop across all the porous specimens, and that the gas permeation for the gelcast disks is much larger than that for the cold pressed pellets. This is in agreement with the results of higher porosity and larger pore size for the gelcast samples mentioned above. As for the gelcast samples, the gas permeation of the sample sintered at 1550°C is larger than that sintered at

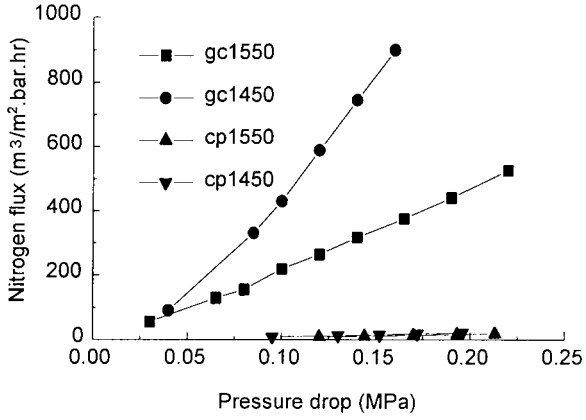

Fig 7. Nitrogen flux vs pressure drop through the porous YSZ disks; gc1450 and gc1550: gelcasts sintered at 1450 and 1550°C, respectively; cp1450 and cp1550: cold-pressed samples at 1450 and 1550°C respectively.

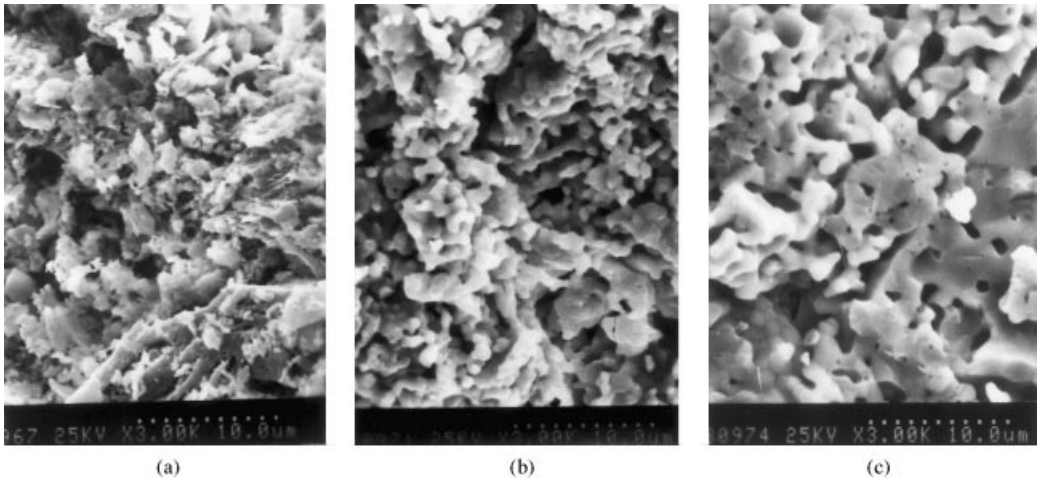

Fig 8. SEM of fracture surface of gelcasted YSZ ceramics sintered at the different temperatures; (a) 1300 (b) 1450 and (c) 1550°C.

1450°C. This is because the former has a larger pore size in spite of lower open porosity.

3.4. Microstructure development of the gelcasts

SEM photographs of fracture surface of the sintered gelcasts at 1300, 1450 and 1550°C for 5 h are shown in Fig. 8. When sintering progresses, highly reactive small particles prepared by coprecipitation grow fast. Fig. 8(b) indicates that the ceramic particles have bonded together at 1450°C, which provides for the mechanical strength of the compact. As the sintering temperature is extended to 1550°C, an obvious increase in interparticle bonding and changes in the amount and morphology of the porosity result in the continuous increase of the strength as shown in Fig. 8(c). In addition, it also shows that continued neck growth causes pore channels within the compact to be closed, leading to an increase in the isolated porosity. These changes in the microstructure are consistent with the results shown in Fig. 3.

4. Conclusions

1. As a novel method for ceramic bodies, the water-based gelcasting process has been successfully employed to fabricate porous YSZ ceramics.
2. The open porosity and mean pore size of porous YSZ ceramics obtained by gelcasting, which sintered at 1450–1550°C, are in the range of 33.1–50.3% and 0.66–0.98 μm, respectively. The nitrogen permeations are correspondingly in the range of 215–438 m^3/m^2.bar.h. This means that gelcast YSZ ceramics are suitable for use as porous ceramic filters for separation process or supports for catalytes or SOFCs fabrication.
3. In comparison with the conventional cold pressing process, the gelcasting process leads to ceramic bodies with higher open porosity, lower closed porosity, larger pore size and higher gas permeation, which proves that this gelcasting process is more suitable for porous ceramics.

Acknowledgements

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