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Short communication

Formation of 3D tubular cannel in fully densified zirconia ceramics by free-foaming method using superplasticity

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Abstract

Three-dimensional (3D) tubular cannels in fully densified zirconia ceramics have been fabricated by a newly developed solid-state free-foaming method using superplasticity. Three mole percent of yttria-stabilised zirconia (3YSZ) and α-SiC were used as foam matrix and foaming agent simultaneously. Dried pattern of 15 wt% (wt%) α-SiC slurry based on 10 wt% methyl cellulose buried into 3YSZ powder compacts and proper heat treatment at the sintering temperature causes successful fabrication of 3D cannel in zirconia ceramics.

Keywords: A. Sintering; E. Thermal applications; Superplasticity; 3YSZ

1. Introduction

Recently, ceramic materials have been intensively studied because of their specific physical, electrical, mechanical, optical or chemical properties, as well as their wide range of applications in various fields of research [1,2]. The mechanical characteristics of superplastic yttria-stabilised zirconia polycrystals have been analysed as a function of stress, temperature and grain size. 3YSZ ceramic materials exhibit high strength and toughness compared to other ceramics [3]. The evolution of the stress exponent with stress found in high-purity materials is similar to that observed in superplastic metals. Superplastic behaviour was first demonstrated in fine-grained partially stabilised zirconia by Wakai et al. [4].

Three-dimensional (3D) porous ceramic was developed by chemical synthesis due to demands in the ceramic research sector [5]. A new process for custom-made 3D porous ceramic scaffolds has been developed for bone replacement, with fully interconnected channel networks [6]. Porous ceramic with a structure containing 3D pore channels in a tetragonal zirconia polycrystal ceramic was fabricated using a combination of a Computer Numerically Controlled (CNC)-machining method and a slurry coating process [7]. Superplastic forming could be used for the fabrication of 3YSZ components with complex shape and controlled dimensionality. Various methods have been demonstrated for fabricating 3D inter-connective ceramics with engineered structures [8].

Porous ceramics are well-known to be thermal insulators, with low thermal conductivity, and they have been used, for example, in gas sensors and catalytic carriers. The unique combination of properties, such as chemical inertness, high-temperature resistance, low thermal conductivity, thermal shock resistance, low dielectric constant and high specific strength in ceramic foams, makes them suitable for many applications [9].

Ceramic microreactors can be used for applications in which metal or polymer systems are not suitable because special material properties (high thermal and chemical resistance) are required. However, the application of ceramic components often fails because of the time-consuming and costly manufacturing of components with patterning details. We have previously fabricated novel porous ceramics by expanding closed pores using superplastic deformation driven by gas pressure [10]. Closed gastight multiple pores are also introduced after full densification of the matrix [11], but production of refractory ceramic foams that possess a continuous, gastight 3D tubular cannel has not been previously possible.

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The present report attempts to explain the successful formation of 3D tubular cannels in fully densified zirconia ceramics using superplasticity via a cost-effective, solid-state, free-foaming method. Benefits of this method include not only producing 3D cannels in zirconia materials in a simple way, but also controlling the protuberances of ceramic foam by controlling the amount of foaming agent in the powder compacts. The advantages of simplicity and high thermal resistance will allow this method to be widely applied in industry.

2. Experimental

Approximately 8 g powder of 3YSZ (zirconia TZ-3Y; Tosoh, Tokyo, Japan) was used as a matrix to produce the ceramic foaming material. Zirconia slurry (2 wt%) was prepared by dispersing 3YSZ powder in 5 wt% methyl cellulose (MC) aqueous solution and mixing for 4 min with a MX-201 conditioning mixture (Thinky Co. Ltd., Tokyo, Japan). The zirconia slurry in a glass pot was kept refrigerated, below 15 °C, until use. Using the 3YSZ powder slurry based on MC, a green sheet was fabricated with a glass bar on a plastic thin paper and dried for 24 h in air. Various α-SiC (CY-15; Yakushima, Kakoshima, Japan) slurries were prepared: 5, 10, 15, 20 and 25 wt%, based on 5, 8, 10 and 12 wt% MC aqueous solutions (Fig. 1).

The foaming agent-containing slurry was placed onto the zirconia sheet in a straight line using copper stencils and was dried for 2 h in air. The high-temperature foaming agent alpha-silicon carbide (α-SiC) was used because of its known oxidative properties [12].

Initially, 10-mm-diameter (φ) core cylindrical powder compacts were fabricated by unitarily pressing (Riken P-18 press station; Riken Seiki Company Ltd., Tokyo, Japan) at 14 MPa using 3.5 g of 3YSZ powder. SiC liner in the zirconia sheet was used to surround the pellet to make a foaming agent pattern. This pellet was placed in a φ 18 mm steel die and surrounded by 8 g of 3YSZ powder and pressed again at 14 MPa under the same conditions (Fig. 2).

The resulting pellet containing a SiC 3D pattern was placed in a polyethylene bag and evacuated, followed by cold isostatic pressing under 100 MPa for 1 min just before heat treatment.

The calcination process was carried out at 500 °C, with a temperature increase rate of 500 °C/h, remaining at this temperature for 10 min to remove MC components from the compacts. Heat treatment was then conducted, at 1600 °C, at a rate of 800 °C/h, for 8 h, following a slow heating and cooling method that caused the formation of closed cannel pores.

3. Results and discussion

A continuous spiral protuberance was formed over the external position of the cylindrical sintered body, as shown in Fig. 3(a) and (b).

Just beneath the protuberance, a contiguous cannel of φ 1.5 mm was confirmed by examining the cross section. The cannel dimension was larger than the line width of the foaming agent (1 mm), indicating a pore expansion due to superplastic deformation. The pore wall was thought to be evenly developed toward the surface to form protuberances along the cannel. We believe that the new superplastically solid-state, free-foaming method introduced controlled 3D pores after densification.

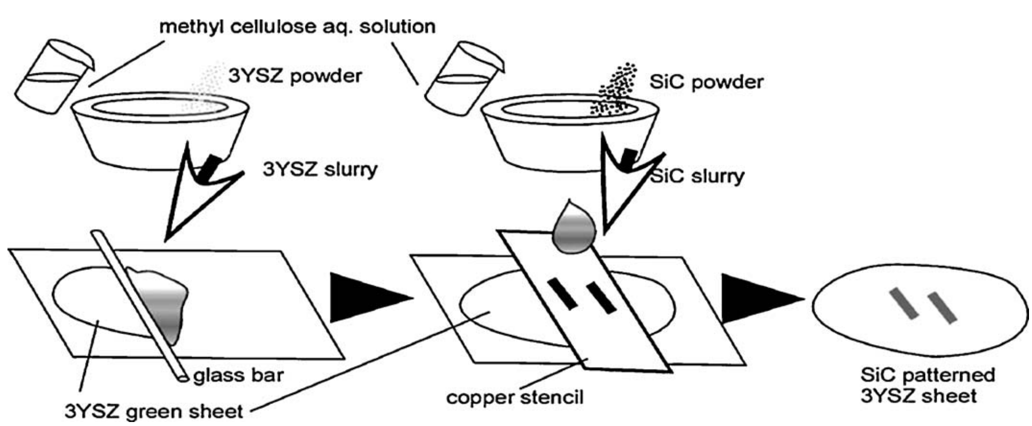

Fig. 1. Schematic illustration of preparation of 3YSZ based sheet and patterning of α-SiC slurry as foaming agent, respectively.

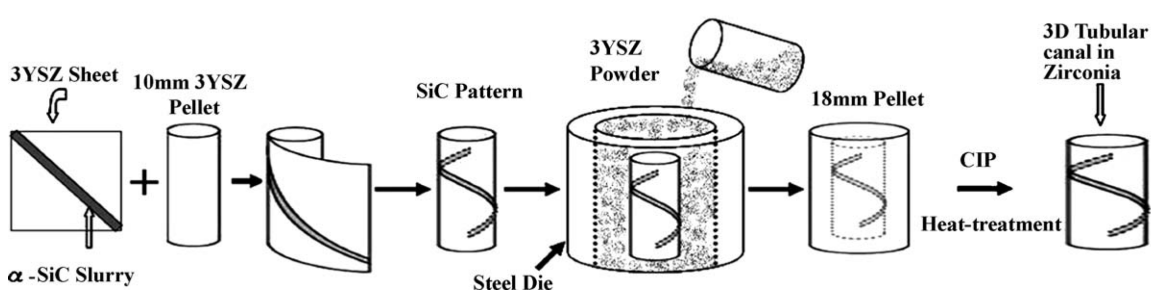

Fig. 2. Transformation of the SiC pattern into spiral tubular cannel in 3YSZ ceramics.

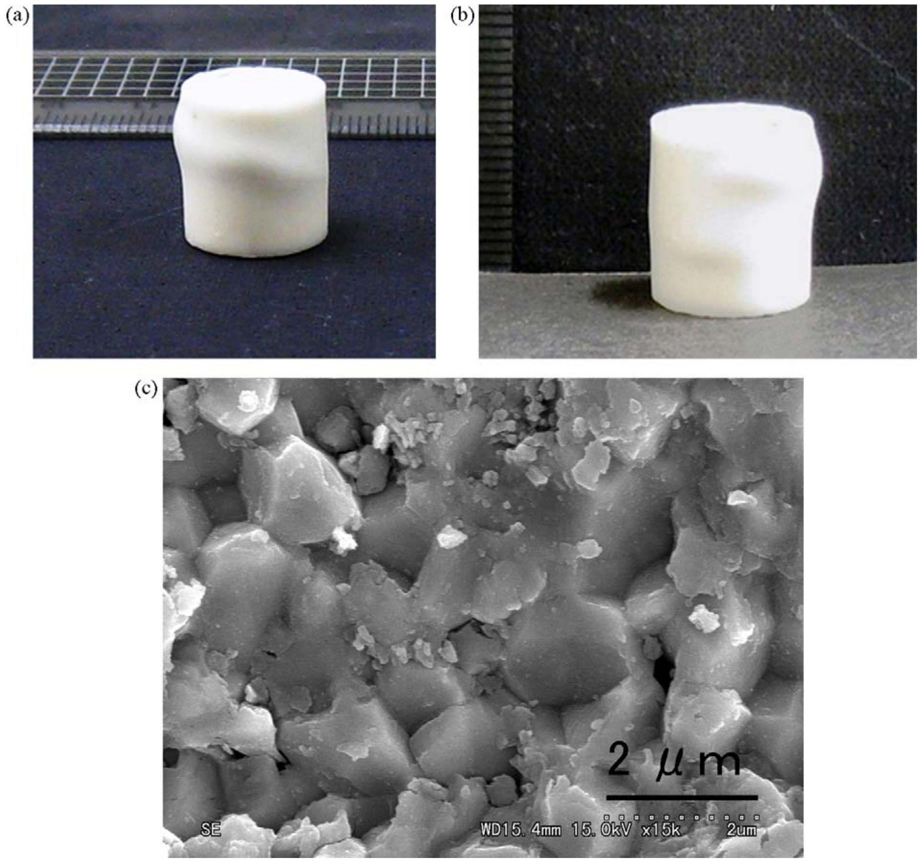

Fig. 3. 3D tubular cannel in zirconia ceramic materials (a) front view, (b) schematic view, (c) SEM photo on the fracture surface.

When the SiC concentration deviated from the optimum value (15 wt%), clear tubular cannels could not be obtained. Surface cracking was found due to heavily doped foaming agent in the matrix. By using a more lightly doped foaming agent than the optimum value, intermittent protuberances, suggesting an irregularly sized tubular cannel, resulted. According to Table 1, the results depended on the amount of gas formed based on the quantity of foaming agent used in the experiment.

Expansion of the components presumably arose due to superplastic deformation. Potential advantages of using a microreactor, with 3D tubular cannel porous zirconia materials rather than a conventional reactor, include better control of reaction conditions, improved safety and portability. Better control of reaction conditions refers to the ability to precisely control the temperature of the reactor, a direct result of the reactor's extremely high surface to volume ratio.

Decomposition of MC compound was conducted at 500 °C, smoothly carrying out the sintering process. A foaming processing is performed after sufficient sintering; consequently, the 3D tubular cannel pore is closed, with fully dense pore walls. The foaming of zirconia-based ceramics is believed to arise from the swelling of gas phases formed from the decomposition of SiC upon oxidation. The oxidation process

Table 1
Results and trial conditions to form 3D tubular cannel in 3YSZ ceramics.

MC wt% based on Aq.	SiC wt% based on MC aq.Sol.				
	5	10	15	20	25
5	▲	△	◎	◎	◎ ◆
8	▲	△ ◎	◎	◎	◎ ◆
10	△ ▲	△ ◎	⊛	◎ ◆	◆
12	△ ▲	△ ◎	◎ ◆	◆	◆

⊛ best stable condition; ◎ contiguous tubular canal; △ intermittence; ◆ crack; ▲ not found.

may proceed by two routes, depending on the concentration of oxygen in the atmosphere. The oxidation to form solid silica occurs before sintering:

$$SiC + 3/2\,O_2\,(g) \rightarrow SiO_2\,(s) + CO\,(g) \quad (1)$$

$$SiC + O_2\,(g) \rightarrow SiO\,(g) + CO\,(g) \quad (2)$$

The ambient oxygen concentration should be low after sintering. The products must be evaporated during foaming to solidify on cooling. In addition, perfect 3D tubular cannel pores were produced when 15 wt% α-SiC, based on 10 wt% MC aqueous solutions, was sintered at ambient temperatures.

The total strain that can be produced may depend on the density of the materials. The absence of changes in grain shape, even after several hundred percent of strain, along with the lack of dislocation activity inside the grains and a stress exponent of 3D, the standard value for superplasticity in metals indicate that grain boundary sliding (GBS) is the predominant mode of deformation [13]. In superplastic materials, the primary deformation mechanism is GBS and the rate of this process determines the macroscopic strain rate. Generally, GBS is agreed to be one of the major strain-contributing mechanisms of flow in superplastic deformation because its contribution to total strain typically exceeds 50% in ceramic materials.

During superplastic deformation, conventional plasticity also takes place (diffusion, intra-granular dislocation slip, IDS), but its contribution to the total strain remains limited. Superplasticity permits substantial shape flexibility and good dimensional accuracy. Because cavitations due to GBS must be accommodated by diffusion and/or dislocation processes for successive deformation, a short accommodation length, meaning a small grain size, is indispensable for attaining high strain-rate superplasticity. As shown in Fig. 3(c), the grain size was less than 2 μm, which is suitable for superplastic deformation.

Perfect 3D zirconia materials were reportedly produced when 15 wt% α-SiC slurry, based on 10 wt% MC, was buried in a 3YSZ matrix, initially at 500 °C for 10 min and later at 1600 °C for 8 h. By heat treatment at the sintering temperature, ceramic foam containing 3D tubular cannel closed pores, derived from the SiC pattern, were successfully fabricated. A superplasticity solid-state, free-foaming method has been developed to introduce pores after densification.

4. Conclusions

3D tubular cannels in zirconia were fabricated by a solid-state, free-foaming method using superplasticity following appropriate sintering. Due to the cost-effectiveness of fabrication, this material may be popular amongst scientists working with ceramics. The properties of high-temperature resistance, low thermal conductivity and high specific strength in 3D tubular cannel zirconia foaming material may be useful in several industries. In ceramic microreactors, it can be used for applications instead of metals because of its excellent chemical resistance. Sufficient sintering at 1600 °C for 8 h should exclude pores, leading to increased mechanical properties. Controlling the dimensions of cannel pores by controlling the amount of foaming agent used in this experiment revealed the value of this product.

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