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Mechanical and electrical properties of superplastically foamed titania-based ceramics

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Abstract

Ceramic monofoams based on titania were fabricated using superplastic deformation driven by the evolution of gas from a foam agent. Titania-based polyfoam with porosities of up to 25% can be fabricated by dispersing only 1 mol% of foam agent (silicon carbide). When the mechanical strength of superplastically foamed titania was compared with that of fully densified titania and conventionally fabricated porous titania, the superplastically foamed ceramics retained 70% of the mechanical strength of the dense ceramics, while that of the conventional porous ceramic decreased to 40%. Niobium-doped semiconducting titania polyfoam was also fabricated. The electrical resistivity and affect of ambient humidity were similar to those of the dense ceramics.

Keywords: Superplastic deformation; Titania porous ceramics; Mechanical strength; Electrical resistivity; Humidity

1. Introduction

The present authors have fabricated new ceramic foams utilizing their superplastic deformation after sintering [1]. Contrary to this new ceramic foams, conventional porous ceramics have been manufactured using partial sintering [2] in which the compaction pressure is adjusted or a pore-forming agent is incorporated [3] in solid-state processing, and the precursor liquid foaming method has been used to process porous ceramics derived from liquid precursor [4]. In any case, pores are incorporated in conventional porous ceramics before sintering, which results in insufficient sintering [5]. Since the sintering process inevitably excludes pores, sintering must be terminated at an early stage to maintain the high porosity, or the porosity should be sacrificed to obtain strong inter-grain bonding. In short, the conventional pore-incorporation method followed by sintering cannot attain both high porosity and strong inter-grain bonding simultaneously.

When the pores are introduced after melting the inorganic materials, both the inter-grain bonding and porosity increase, similar to analogous foams based on polymers, metals, and glass. Such processing cannot be applied to refractory ceramics practicably because their melting points are extremely high. To overcome this problem, we utilized the superplasticity around the sintering temperature far below the melting point, to introduce pores into the fully densified ceramics [1,6].

Compared to conventional porous ceramics, high levels of gas, heat, and sound insulation, as well as structural reliability, can be expected with our porous ceramics based on the fully densified sintered body. Compared to the melting method, our ceramics have the advantage of high fracture toughness because of their polycrystalline nature and improved heat insulation due to the reduced inner pressure after solidification of the foam agent gas. Moreover, our method involves low-temperature processing.

Superplasticity has been reported in various ceramics derived from small starting powders, including silicon nitride [7] and superconductive YBCO [8]. In addition to the first successful fabrication of superplastic foam based on 3 mol% yttria-stabilized zirconia (3YSZ) [1,6,9], we have already fabricated superplastic foams based on 8 mol% yttria-stabilized zirconia (8YSZ) with dispersed silica or alumina [10]. This material shows oxide ion conduction and is more stable in terms of the thermal history. We also fabricated alumina-based foams,

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a more widely used ceramics, by dispersing 3YSZ or MgO [11,12].

In addition to their thermal and mechanical properties, the electrical properties of our porous ceramics are expected to differ from those of conventional ceramics. For example, the contact resistance or inter-grain resistance of conventional porous ceramics tends to become large because the inter-grain bonding is usually small due to insufficient sintering. The specific surface area of conventional porous ceramics is large, and it is easily affected by the ambient environment, such as humidity or adsorbed oxygen.

In contrast to conventional porous ceramics, the inter-grain resistance of our ceramics is comparable to that of dense ceramics because our ceramics foam is based on fully densified ceramics. In addition, since closed pores predominate in our porous ceramics, the humidity dependence of the electrical resistivity is thought to be the same as that for dense ceramics.

In this study, we used titania ceramics, for which the ambient humidity affects the electric resistivity, and attempted to fabricate ceramics foam utilizing superplastic deformation. We also evaluated their mechanical and electrical properties and compared them to those of dense and conventional porous titania ceramics.

2. Experimental

2.1. Fabrication of titania monofoam

To demonstrate ceramic foaming following the sintering process, we fabricated macroscopic single foams (monofoams) using a method similar to the one we have reported elsewhere [1,6,9–12].

Titania powder (rutile, CR-EL; Ishihara Sangyo, Nagoya, Japan) was used as the matrix. Silicon carbide was chosen as a high-temperature foam agent that reacts and evaporates at high-temperatures [1]. First, 0.1 g of silicon carbide powder (Grade-UF; Ibiden, Aichi, Japan) was pressed into a pellet in a ϕ10-mm die under 30 MPa. Approximately 4 g of alumina-based powder was weighed. Half of the alumina-based powder, the compressed silicon carbide powder, and the remaining half of the alumina-based powder were put in a ϕ20-mm steel die and pressed uniaxially at 30 MPa for 1 min, and then hydrostatically at 200 MPa for 1 min. The resultant powder compacts were heated to between 1300 °C and 1500 °C at a rate of 800 °C/h, kept at that temperature for 8 h, and then cooled.

2.2. Fabrication of titania polyfoam

To incorporate many pores, foam agents were dispersed in the starting matrix powder before powder compaction. By holding the temperature at near the sintering temperature, sintering followed by foaming gave rise to polyfoam (porous ceramics). As a matrix material, n-type semiconducting titania doped with pentavalent niobium was also prepared.

First, 1 mol% silicon carbide powder was added to the titania matrix powder and mixed in ethanol with a planetary ball mill using zirconia balls. Four grams of the powder mixture were pressed uniaxially in a ϕ20 steel die under 30 MPa, followed by hydrostatic pressing under 200 MPa. The powder compacts were heated to between 1300 °C and 1500 °C at 800 °C/h, and kept at that temperature for 8 h.

As a semiconducting matrix, 1 mol% Nb_2O_5 (guaranteed grade; Kojundo Kagaku, Tokyo, Japan) was added to the powder mixture of the matrix and foam agent, and then subjected to the same compaction and heating treatment. A lower temperature is preferable for semiconducting titania ceramics to avoid the effect of anisotropic grain growth, which starts at relatively lower temperatures compared to pure titania ceramics.

As references, dense, conventional porous ceramics were fabricated using titania both with and without niobium. Even with added niobium, the titania powders without a foam agent become theoretically dense when using the same compaction and heating conditions as those described for the titania foam. Conventional porous ceramics were fabricated via insufficient sintering by lowering the sintering temperature to 1000 °C for 2 h.

The resultant samples were named after the composition and processing conditions: A, dense; B, superplastically foamed; and C, insufficiently sintered for titania without niobium. A', B', and C' indicate niobium-doped titania.

2.3. Evaluation

For the ceramics monofoams, the pore wall density and macroscopic pore fraction (porosity) were evaluated as follows. First, the apparent density of the monofoam was measured using an Archimedes method to obtain the sum of the pore wall porosity and macroscopic pore porosity. Then, part of the pore wall was cut from the monofoam, and the pore wall porosity was obtained from the apparent density using an Archimedes method. The macroscopic pore fraction was obtained from these values.

For polyfoam, rectangular bars (11 mm × 3 mm × 3 mm) were cut from the pellets. The bulk density was calculated from the volume and weight of the specimen to attain total porosity. Then, the open pore porosity was obtained by subtracting the closed pore porosity determined using an Archimedes method from the total porosity.

The mechanical strength was measured by the three-point flexure test. Rectangular bars (11 mm × 4 mm × 0.8 mm) were cut from the polyfoam pellets and subjected to the three-point flexure measurement (SV-950; Marubishi Kagaku, Tokyo, Japan) with a span length of 9 mm and crosshead speed of 2 mm/min. Ten measurements were made for each batch sample.

The electrical resistivity of the semiconducting samples (A', B', and C') was measured. Rectangular bars (11 mm × 4 mm × 0.8 mm) were cut from each ceramic disk and subjected to four-probe DC electric measurement. Approximately 40 nm-thick Pt electrodes were sputtered on the disk and silver wires were attached using conductive paste. This sample was then placed in a glass tube inserted in an electric furnace, as shown in Fig. 1. The temperature dependence of the resistivity

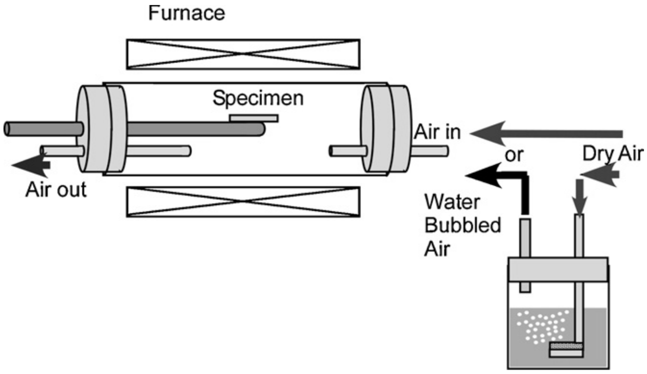

Fig. 1. Sample setup to evaluate the temperature dependence of electrical resistivity in dry and humid atmosphere.

was measured from room temperature to 150 °C and back to room temperature.

The influence of ambient humidity was evaluated by measuring the resistivity in both dry and humid atmospheres. Compressed dry air was introduced into the glass tube to make a dry atmosphere (relative humidity ~20%). A humid atmosphere (relative humidity (RH) ~80%) was obtained by streaming water bubbled air, as shown in Fig. 1.

Powder X-ray diffraction (XRD, Multiflex; Rigaku, Tokyo, Japan) was used to evaluate the lattice parameters. High-purity silicon powder (RSRP-43275G; Rigaku) was mixed into the ground sample as an internal standard. The diffraction data were acquired using a step scan with a sampling step of 0.02° for 10 s.

Microstructure was observed using field emission electron microscopy (S-4300; Hitachi, Tokyo, Japan). Grain size distributions were measured from the thermal etched cross-sectional view using the code method.

3. Results and discussion

3.1. Titania monofoam

Titania matrix monofoam was fabricated successfully without using additives, although the macroscopic porosity was smaller than that of 3YSZ analog. Fig. 2 shows side views of titania foams treated at 1300°C, 1400°C, and 1500 °C. The foam height increased with the heating temperature according to the increasing strain rate or strain limit, which is a supporting evidence of super plasticity. The total porosity and pore wall porosity of titania monofoams treated at each temperature are listed in Table 1. The relative pore wall densities all exceeded 95% of the theoretical value, indicating the gas tightness needed for pore expansion [1]. The total porosity increased with temperature.

Table 1
Porosity and shell wall relative density of titania-based monofoam

Sintering temperature (°C)	Porosity (%)	Shell wall density (%) (relative to theoretical)
1300	11	96
1450	14	96
1500	19	95

Superplasticity has not been reported in titania ceramics for which the grain growth is known to be large [13,14]. In this study, the superplastically foaming method was adapted to titania ceramics without using an additive to suppress the grain growth. The grain size of titania ceramics heated after 8 h exceeded 50 μm, which is substantially larger than that (~2 μm) of 3YSZ, which was previously reported to show the largest superplastic deformation. The deformation rate probably decreased drastically with grain growth after the large deformation rate at an early stage, halting pore expansion. Under these conditions, the macroscopic pore porosity of titania-based foams is thought to be small.

3.2. Titania polyfoam

In our preliminary experiment, the porosity was as large as 25% using only 1 mol% of foam agent. Then, the sintering conditions for conventional porous ceramics were adjusted to make one with a porosity of 25%. The total and closed pore porosities are listed in Table 2 for titania ceramics A–C.

Using the superplastically foaming method, closed pores predominated with a porosity of 25%. Even with the same porosity, almost all of the pores were open when made using the conventional insufficient sintering method. Fig. 3 shows the SEM surface photos on A–C. Open pores are predominant in C as expected by the porosity measurement. Inter-grain bonding seems strong in B while several open pores can be observed.

The average mechanical strength of dense (A), superplastically foamed (B, porosity ~25%), and conventionally fabricated porous (C, porosity ~25%) ceramics are listed in Table 2. The mechanical strength of the conventionally fabricated porous ceramics was only 40% that of the dense ceramics, while the superplastically foamed ceramics retained 70% of the mechanical strength of the dense one, although the total porosities of B and C were similar. This probably occurred because strong inter-grain bonding comparable to that of the dense ceramic was realized with the complete sintering followed by pore expansion in the superplastically foamed

Fig. 2. Side view of the titania monofoams heated at 1500 °C (left), 1450 °C (middle) and 1300 °C.

Table 2
Total porosity, open porosity and bending strength of three kinds of titania-based ceramics

	Total porosity (%)	Open porosity (%)	Bending strength (MPa)
A: dense	–	–	162
B: superplasticity foamed	24.2	7.72	110
C: conventional porous	26.5	23.8	63.3

ceramics, while the inter-grain bonding of conventional porous ceramics was weak due to insufficient sintering.

3.3. Niobium-doped titania polyfoam

The results for the ceramics doped with niobium are listed in Table 3. Similar to titania without a dopant, the open porosity of superplastically foamed titania (B') was considerably smaller than that for the conventionally fabricated porous ceramics (C'), while the total porosities were similar. Since the sintering temperature for sample C' (1000 °C) was lower than those for A' and B' (1300 °C), the solid solutions were compared by measuring the lattice parameters. In all of the samples, the niobium solution increased the lattice parameters, which were almost identical, probably because 1 mol% niobium was within the solution limit, even at 1000 °C. We postulate that all of the added niobium dissolved in the titania lattice of these samples.

Table 3
Total porosity, open porosity and lattice parameters for three kinds of Nb-doped titania-based ceramics

	Total porosity (%)	Open porosity (%)	Lattice parameters (nm)	
			a	*c*
A': dense	–	–	0.4593	0.2956
B': superplasticity foamed	25.6	6.53	0.4593	0.2957
C': conventional porous	29.1	26.9	0.4592	0.2957
*: dense undoped titania			0.4583	0.2952

For the three semiconducting samples, the temperature dependence of the electric resistivity was measured both in dry (RH ~20%) and humid (RH ~80%) atmospheres, as illustrated in Fig. 4. In the dry atmosphere, the resistivities of samples A' and B' were on the same order, while that for sample C' was considerably greater. In conventionally fabricated porous ceramics (C'), the inter-grain resistivity is large due to the small contact area ascribed to the insufficient sintering. In contrast, in our superplastically foamed porous ceramics, the matrix morphology including the inter-grain arrangement would be identical to that of a dense sintered body due to the completion of sintering in both cases.

At a higher ambient humidity, the resistivity of sample C' decreased drastically, probably due to proton conduction through the adsorbed water [15,16]. The specific surface area of

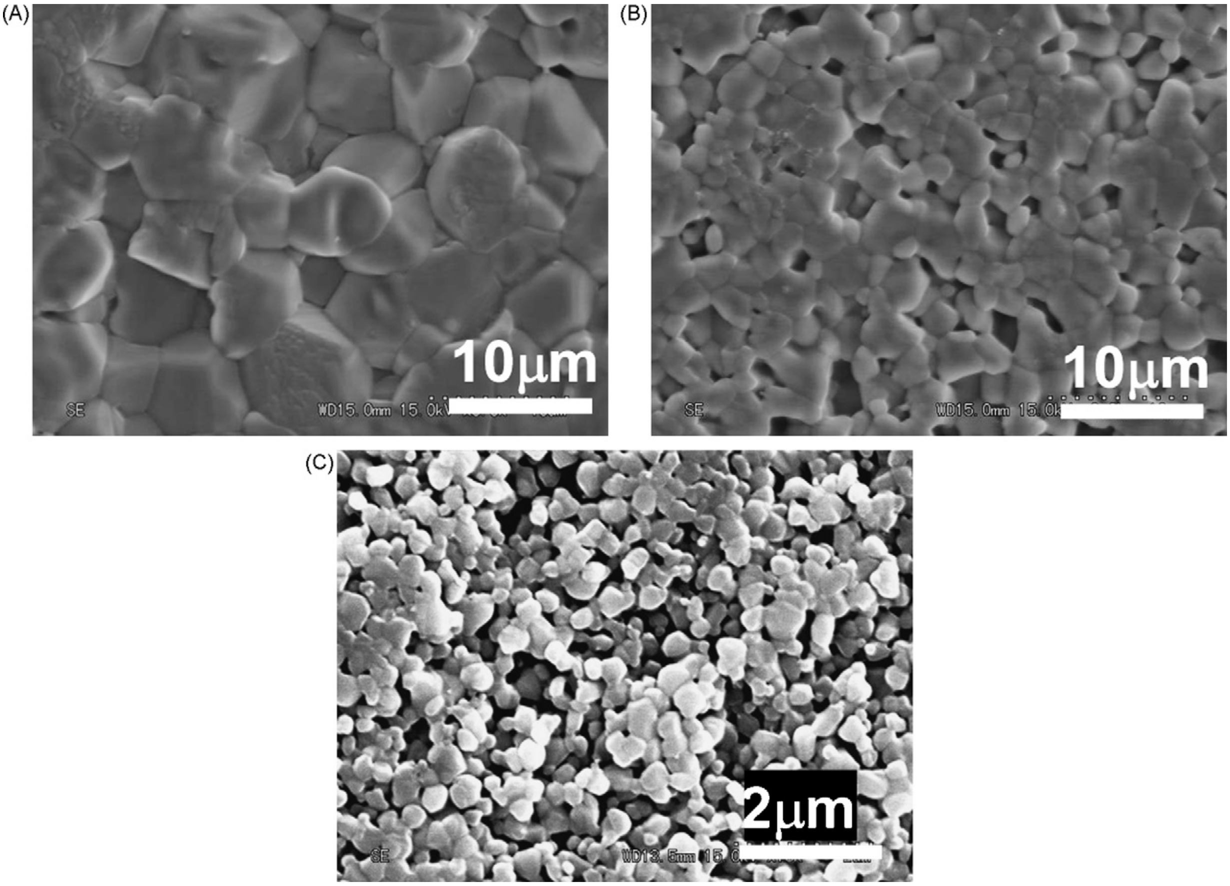

Fig. 3. SEM surface photo of (A) fully densified, (B) superplastically foamed, and (C) conventionally fabricated porous, titania ceramics.

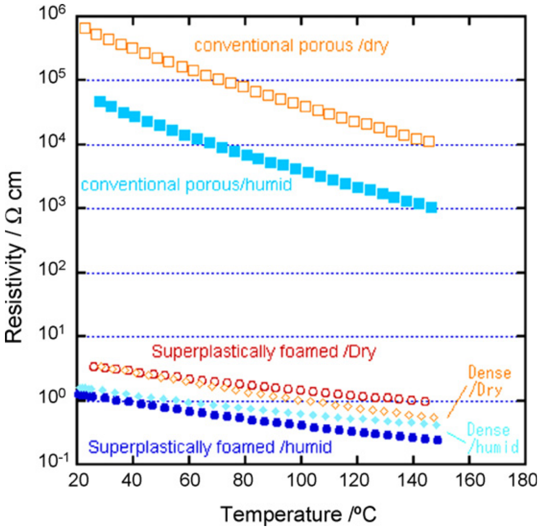

Fig. 4. Temperature dependence of electrical resistivity of (A') fully densified (B') superplasitically foamed, and (C') conventionally fabricated porous, titania ceramics doped with niobium.

dense ceramics is much smaller than that of conventional porous ceramics. As a result, the effect of the ambient humidity is smaller than for conventional porous ceramics. Since closed pores predominated in the superplastically foamed ceramics, the effect of ambient humidity was similar to that on dense ceramics. With the superplastically foaming method, we can control the weight and permittivity of a ceramic resistor without it being affected by the ambient humidity.

4. Conclusion

Titania monofoam was also fabricated without additives or a superplasticity-facilitating agent, although the macroscopic pore porosity was smaller than that of zirconia-based ceramics.

Titania-based polyfoam with porosities of up to 25% can be fabricated by dispersing only 1 mol% of foam agent (silicon carbide). Under the same processing conditions, titania without the foam agent densified almost fully. When the mechanical strength of superplastically foamed titania was compared with that of fully densified titania and conventionally fabricated porous titania, the superplastically foamed ceramics retained 70% of the mechanical strength of the dense ceramics, while that of the conventional porous ceramic decreased to 40%.

Niobium-doped semiconducting titania polyfoam was also fabricated. The electrical resistivity and affect of ambient humidity were similar to those of the dense ceramics.

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