Superplastically foaming method for inclusion of closed pores in fully densified ceramics

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Porous ceramics incorporate pores to improve material properties, including thermal insulation, while maintaining inherent ceramic properties such as corrosion resistance and high mechanical strength. Conventional porous ceramics are usually fabricated by insufficient sintering that excludes pores; thus, it must be terminated in an early stage to maintain high porosity. The premature termination leads to degraded strength and durability. We developed a superplastic-foaming method to fabricate ceramic foams in the solid state. In this method, the inserted foam agent evaporates after full densification of the matrix at the sintering temperature. Closed pores expand by superplastic deformation driven by the gas pressure. The pores are introduced after sintering the solid polycrystal. Then, only closed pores are introduced, improving the insulation of gas, sound and heat. The pore walls are fully densified for high mechanical strength. Compared to the melt-foaming method, this technique is practical because the fabrication temperature is far below the material’s melting point, and it does not require moulds. In addition, the size and location of the pores can be controlled by the amount and position of the foam agent.

Key-words : Superplasticity, Dense pore wall, Closed pore, Pore patterning

1. Introduction

Porous materials that contain isolated pores are frequently used as thermal insulators because their thermal conductivity is very low. Expanded polystyrene, a typical foamed plastic, is produced through evaporation of a foaming agent when polystyrene is softened by heat. Similarly, metal foams can be formed by foaming softened metals.

However, the production of porous ceramic materials is quite different. In particular, the sintering process of many ceramics takes place at temperatures well below their melting points. Methods involving limited sintering or pore-forming inclusions are usually used. In both processes, open pores are formed, resulting in large surface areas on which exchange with ambient gases can occur, making such porous materials useful in gas sensors or as catalytic carriers. However, a high-porosity or pore-volume fraction is incompatible with a high ratio of closed pores, which is necessary when a high degree of thermal insulation is required. Furthermore, any increase in porosity reduces the strength of porous ceramics, which commonly occurs when sintering is insufficient.

Recently, the production of porous ceramics via a liquid intermediate has become popular. In this process, air bubbles are introduced into the precursor slurry or gel. The liquid components evaporate prior to solidification. Although the resultant porous ceramics have a higher porosity, the closed-pore ratio and intergrain bonding are similar to those obtained by solid-state methods.

Glass can be foamed by exploiting the plastic deformation that occurs above its softening temperature. For refractory ceramics, however, the formation of porous ceramics above their melting points (2720°C in the case of zirconia ceramics) has not been practicable. The plastic deformation that occurs below the melting temperature is thought to be extremely limited, and the production of refractory ceramic foams that possess a gastight pore shell has not been possible until now.

We demonstrate that ceramic foam can be produced from a well-known refractory zirconia ceramic using gas pressure to expand the dense shell formed after sintering (Fig. 1). Because this ceramic shell is gastight, a high level of structural reliability and mechanical strength can be expected, despite the large pore volume. In other words, foaming after sintering results in high structural reliability and a high closed-pore fraction. We refer to this method as solid-state foaming or superplastic-foaming because the processing is carried out in the solid phase using superplasticity as the deformation process.

Superplasticity is defined as the ability of a specific material to exhibit substantially large elongation until it fractures under relatively low stress. Application of superplasticity would allow ceramic components with complex shapes to be produced by plastic processing, similar to metallic materials.

Superplasticity occurs below the melting point (Tm) of a material up to a temperature of 3/5Tm. The temperature at which superplasticity occurs for ceramics is high because of their high melting point. The processing time can be reduced by operating at higher temperatures, but this has disadvantages. For example, available die and clamp media may be limited or reaction may occur between the clamp media and ceramics.

Theoretical analysis of superplastic phenomena in ceramics has been conducted to overcome these problems. Practical methods for achieving high-speed superplasticity and for reducing processing damage have been obtained, but the current superplastic properties have not been used in practical applications.

Ceramic foam can be produced using any material that exhibits superplasticity. The method presented here is the first practical
application of superplasticity in ceramics because it requires only prolonged sintering and does not rely on an external force during processing. Furthermore, conventional porous ceramics are dominated by open pores and have limited efficiency in sound insulation, and their electrical resistance fluctuates with ambient humidity. This paper reviews superplasticity in ceramic materials for technological applications. In addition, an overview of our superplastic-foaming method is discussed.

2. Demonstration of solid-state foaming of ceramics

2.1 Fabrication of ceramic monofoam

To demonstrate that ceramic foam could be fabricated using only ceramic powder at the sintering temperature, composite powder compacts were heat-treated. Typical compacts combined 3 mol% yttria-stabilised zirconia (3YSZ) and silicon carbide (SiC) as follows (Fig. 1).3)

Approximately 4 g of 3YSZ powder (TZ3Y, Tosho, Tokyo, Japan) was used as the matrix to create the macroscopic ceramic foam. The high-temperature foaming agent was 0.1 g of silicon carbide powder (Grade-UF, Ibiden, Aichi, Japan) compressed into a pellet in a φ10-mm die under 30 MPa. Half of the 3YSZ powder was placed in a steel φ20-mm die, followed by the pressed SiC pellet, and the remaining 3YSZ powder was added. The blend was compressed uniaxially at 30 MPa for 1 min before heating at a rate of 800 to 1600°C/h and maintaining this temperature for 2 to 8 h.

Figure 1 shows the zirconia-based ceramic foam produced by heating the compacted composite SiC/3YSZ powder for 8 h. Based on the foam size (especially height), the foaming followed the sintering process. The density of the external shell of the foam was measured to be >99% of the theoretical value for 3YSZ. This represents the degree of gastightness expected for the outer shell and supports the conclusion that the foaming followed densification. The total porosity of the ceramic foam shown in Fig. 1 exceeded 30%.

2.2 Gas evolution

The foaming of the zirconia-based ceramics was likely due to swelling of gas formed from the decomposition of silicon carbide upon oxidation, which can proceed via two routes depending on the concentration of oxygen in the atmosphere:20)

\[
\text{SiC} + 3/2\text{O}_2(g) \rightarrow \text{SiO}_2(s) + \text{CO}(g) \quad (1)
\]

\[
\text{SiC} + \text{O}_2(g) \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (2)
\]

In the present study, we assumed that oxidation proceeded via route (2) because the ambient oxygen concentration should have been low after sintering, and the pressure on the inner shell increased.

2.3 Superplastic deformation

The expansion of the cell was presumably due to superplastic deformation reported for 3YSZ.18) The ceramic foaming process was evaluated using silica-dispersed 3YSZ, which has enhanced superplasticity.21) The height of the ceramic foam increased,3) suggesting that the expansion resulted from superplastic deformation.

Compared to the melting method, our ceramics had 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 involved low-temperature processing.

2.4 Ceramic foams from a diverse matrix and foaming agents

In addition to the first successful fabrication of superplastic foam based on 3 mol% yttria-stabilised zirconia (3YSZ),3-5) we previously fabricated superplastic foams based on alumina,6) 8 mol% yttria-stabilised zirconia (8YSZ)7) and titania.9) In contrast to 3YSZ, the deformation speed of these materials from commercial powders was not high enough to relieve the inner gas pressure. Additives were necessary to prevent fracture, namely silica or alumina for 8YSZ, magnesia and spinel for alumina.
and silica for titania. By dispersing the additives, the porosities increased due to improved deformation speed and limit, similar to the 3YSZ matrix.

We investigated the applicability of several nitride powders as foaming agents in superplastic-foaming ceramics.13) Ceramic monofoams were fabricated successfully using AlN and Si3N4 as foaming agents. In contrast, when BN was used as a foaming agent, we could not fabricate well-developed ceramic foams due to cracks and fractures. When the quantity of foaming agent was increased, the porosity increased to a certain amount, then became saturated. With equal amounts of Si3N4, the porosity from the dispersed foaming agent was higher than that obtained from a monolithic compact without mixing, which was similar to the SiC foam agent.

3. Superplastic-foamed porous ceramics

3.1 Fabrication and characterisation

The fabricated ceramic foams had a monofoam structure consisting of a macroscopic closed pore in a pellet. In contrast, typical porous ceramics contain a significant amount of pores. Thus, a more productive method that includes numerous foaming agents in the matrix powder is required for practicable applications.

We used a granular coating method in which cyclic patterning of foaming agents was readily fabricated in the matrix powders. After compaction followed by sintering, superplastic-foamed porous ceramics containing numerous closed pores were fabricated (Fig. 2).8),11),14),16) Three composite granules with different core sizes were fabricated, as shown in Fig. 3.

First, spherical core granules composed of foam agent powders were fabricated by ball-milling fine β-SiC powders. Core/shell-structured granules with various matrix powder-coating layers were fabricated by dry-coating in a ball mill. The resulting composite granules were ~800 μm in size with a foaming agent core (~250 μm). These composite granules are referred to as a.

Next, 10 wt % β-SiC powders were dispersed in 1 wt % methylcellulose aqueous solutions to produce low-viscosity slurries. By spraying the slurries on the 3YSZ powder and then ball-milling with 3YSZ, composite granules with a core size of 10 μm were fabricated and are referred to as b.

Finally, the composite granules (b) were crushed in a planetary ball mill to produce flakes with cores less than 3 μm in size. These powder mixtures with cores partially connected to matrix 3YSZ powder granules are referred to as c.

These three composite granules (a–c) were pressed uniaxially in φ20-mm steel die under 30 MPa and then pressed hydrostatically under 200 MPa. The resulting powder compacts were heated at 1600°C for 8 h to sinter them after foaming.

From the three kinds of powder granules, porous ceramics with porosities of 25–35% were fabricated by changing the ratio of foam agent to matrix. Unlike conventional methods for fabricating porous ceramics, our method achieved both dense pore walls and high porosity, simultaneously. Furthermore, the size and location of the pores were controlled by the amount and location of the foam agent in the powder compact.

Figure 4 shows optical and scanning electron micrographs of a cross section of superplastic-foamed porous ceramics from respective granules in which the sample name a, b, and c correspond to the core size, as defined previously. In each case, all of the pores were roughly spherical and surrounded by a dense wall. The average pore diameters measured from the cross-sectional views were (a) 387, (b) 104 and (c) 4.24 μm. All of the pores were larger than those of the respective foam agent granules, indicating their expansion.8)

3.2 Mechanical strength

Three-point bending strengths were measured using rectangular bars cut from the three kinds of superplastic-foamed porous ceramics. These data are shown in Fig. 5, in addition to those for dense and conventionally fabricated porous ceramics. The porosity was 27% for the porous samples in Fig. 5. The conventional porous ceramics had an average strength of 274 MPa, corresponding to 25% of that for dense ceramics, which is consistent with reported values.22)

The average mechanical strengths of the three kinds of superplastic-foamed porous ceramics were 285 (a), 362 (b) and 520 MPa (c). The strength of c was close to half that of the fully...
The mechanical strength of superplastic-foamed porous ceramics increased with decreasing pore size. These results suggest that the mechanical strength would be governed by the initial crack size closely related to the pore size because the pore wall densities were almost full in all superplastic-foamed samples.

The strength data for superplastic-foamed porous ceramics are plotted against porosity in Fig. 6. Data for conventional porous ceramics in which the porosity was controlled by the compaction pressure are also plotted for comparison. In the latter case, the strength decreased substantially for a small amount of pores; it was half as large as that of the dense ceramic with a porosity of only 10%. Then, strength decreased monotonically with porosity.22),23)

In contrast to these conventional porous ceramics, the mechanical strength of the superplastic-foamed porous ceramics increased with decreasing pore size. These results suggest that the mechanical strength would be governed by the initial crack size closely related to the pore size because the pore wall densities were almost full in all superplastic-foamed samples.

The strengthening or toughening of ceramics is usually accomplished by incorporating other materials into the matrix. This increases the randomness of the material system, leading to a large expenditure of energy that separates and purifies the material for recycling. In addition, possible reactions between dispersoids and the matrix may affect the properties of the composite.

### 3.3 Electrical properties

To develop a high-frequency dielectric substrate, we investigated methods to fabricate a porous alumina-based substrate that contained only closed pores and was insensitive to ambient humidity.14)–16) Figure 7 shows the relationship between the porosity ($\rho$) and relative permittivity ($\varepsilon_r$) in the superplastic-foamed porous ceramics formed from composite granules with different constituent matrices. The dielectric constant decreased monotonically with the porosity. Figure 7 also shows two theoretical plots based on the logarithmic mixture rule.

Compared to the 3YSZ-dispersed matrix, the spinel-dispersed alumina had low relative permittivity at all porosities. This is partly attributable to the low permittivity of the dispersoid, spinel. In addition, data for the spinel-dispersed sample agreed well with the theoretical line, while the 3YSZ-dispersed sample decreased...
but did not follow the logarithmic mixture rule. In other words, the porosity dependence of the permittivity in the former was larger than that in the latter, contributing to the decrease in permittivity. This difference in porosity dependency is attributable to the pore alignment, as concluded from our previous work.\(^{13,14}\)

**Figure 8** shows the change in the dielectric constant before and after submersion in water for the superplastic-foamed, conventional porous and fully densified ceramics. 0YZ + spinel was dispersed into the matrix in both the porous and fully densified ceramics\(^{15,16}\) because it enhanced the superplasticity while maintaining the permittivity. The degree of porosity for superplastic-foamed and conventional porous ceramics was \(\approx 30\%\). The dielectric constant for the three types of porous ceramics was approximately 5.5, or about half that of fully densified ceramics, regardless of the fabrication method.

After submersion in water, the dielectric constant of conventional porous ceramics increased by more than one order of magnitude, while the increase for dense ceramics was marginal. Because the pores in the conventional porous ceramics with a porosity exceeding 30% should be open, residual water increased the dielectric constant substantially. Such porous ceramics, even those with a lowered dielectric constant, are not suitable for practical use because the dielectric constant is likely to increase under conditions that cause sweating.

In contrast, the change in the dielectric constant in our superplastic-foamed porous ceramics before and after water submersion was negligible, similar to what was seen in the fully dense ceramic. Because the introduced pores were all closed, no water penetrated the inner pores, resulting in a dependence that was identical to that for dense ceramics.

### 4. Patterning

#### 4.1 Pore patterning using the superplastic-foaming method

The deformation speed of superplasticity in ceramics is very low compared to polymers and metals; thus, long processing times at high temperatures have been required. Our superplastic foam required 4 h to reach a stable state, even with the simplest processing system.

Alternatively, if quasi-steady strain was maintained for a certain time, then the size of the pores could be controlled by terminating the gas evolution or by controlling the amount of foam agent required for saturation with a desired strain. Furthermore, if the location of the foam agent was controlled at the powder compaction stage, the resultant pores would sit at the desired place.

Based on this concept, we fabricated continuous hollow paths in dense ceramics with no further processing [Fig. 9(a)].\(^{14,15}\) We also fabricated model ceramics containing several isolated closed pores derived from the foam agent pattern [Figs. 10(a) and 10(b)]. This figure shows clearly the protuberances corresponding to the closed pores. This is thought to be a versatile technique for forming patterned closed pores in ceramics without using conventional processing such as cutting, polishing and joining. It does not require an expensive moulding apparatus; thus, it provides a cost-effective processing method.

#### 4.2 Three-dimensional patterning

The pattern discussed above was two-dimensional; however, such procedures can easily be expanded to three-dimensional patterning. Figure 9(b) shows a schematic for the production of spiral channels in a ceramic body.\(^{17}\)

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. Next, 10-mm-diameter (\(\phi\)) core cylindrical powder compacts were fabricated by unitary pressing using 3YSZ powder. A SiC liner in the zirconia sheet was used to surround the pellet and create a foaming agent pattern. This pellet was placed in a \(\phi18\)-mm steel die, surrounded by 3YSZ powder and pressed again under the same conditions.

The resulting powder compact containing a SiC-3D pattern was CIPed, followed by calcination to remove organic 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 channel pores.

A continuous spiral protuberance was formed over the external position of the cylindrical sintered body, as shown in Fig. 10(c). Just beneath the protuberance, a continuous channel of \(\phi1.5\) mm was confirmed by examining the cross section. The channel 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 have developed evenly toward the surface, forming protuberances along the channel. We believe that the new superplastic solid-state, free-foaming method controlled three-dimensional pores after densification.
5. Conclusions

We demonstrated a method for fabricating ceramic model foams by expanding once-sintered dense shells using superplastic deformation of 3YSZ-, 8YSZ- and alumina- and titania-based ceramics. A granular coating method was applied to produce porous ceramics via the superplastic-foaming method based on 3YSZ. Favorable mechanical properties were demonstrated based on the fully densified matrix. In contrast to conventional methods for fabricating porous ceramics, our method selectively introduced only closed pores with high porosity. The affect of ambient humidity on the dielectric property was almost identical to that of the fully densified matrix, whereas the dielectric constant decreased with increasing porosity, similar to conventional porous ceramics. By using the superplastic-foaming method, the figure, size and location of the closed pores were controlled. We also demonstrated the formation of controlled dots and continuous tubular pores with three-dimensional shapes.

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