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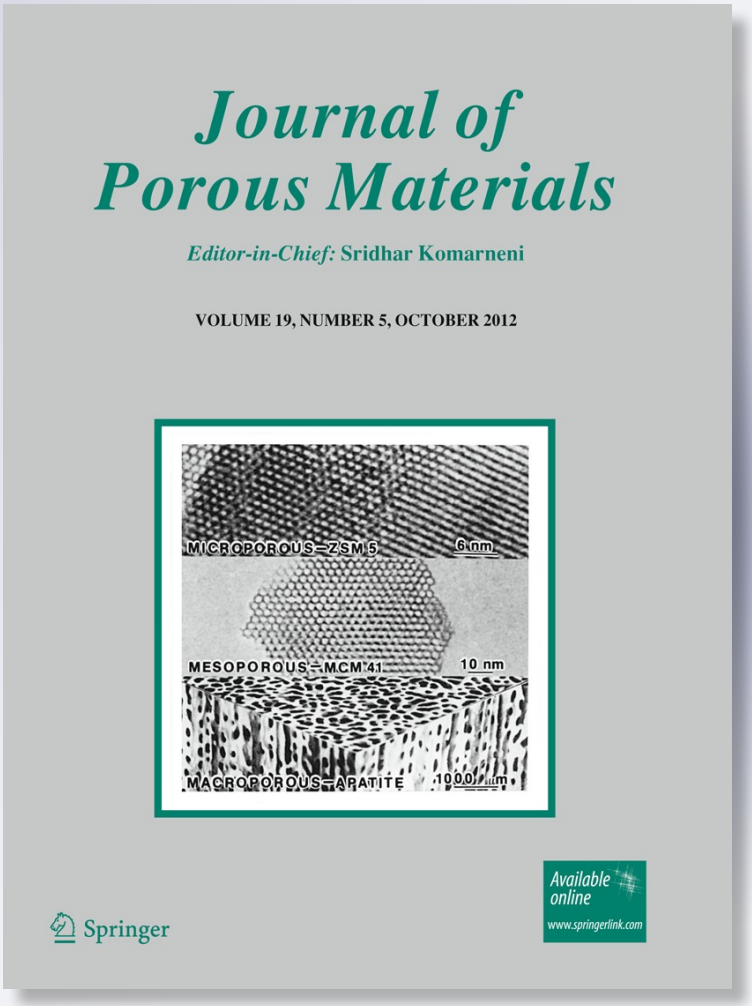


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# The comparison of macroporous ceramics fabricated through the protein direct foaming and sponge replica methods

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**Abstract** The macroporous ceramic samples fabricated using the sponge replica and protein direct foaming methods were compared in terms of porosity, density, compressive strength and microstructure. The egg white protein was applied in both fabrication methods as the binder or foaming agent. The samples fabricated using the protein direct foaming method were stronger and more uniform pore structures in the similar porosity. This result was supported through the Weibull modulus analysis and the scanning electron microscope microstructure observation.

**Keywords** Protein direct foaming · Sponge replica · Homogeneity · The Weibull modulus

## 1 Introduction

The advantages of using macroporous ceramics include their low density, high surface area, high porosity, and good wear resistance [1–5]. Depending on their nature and structure, an increasing number of researches have appeared over the last few decades, especially using natural polymers. Since late 1990s', egg white protein was reported as an additive to facilitate the macroporous ceramic processing. Tuck et al. [6] first reported that the porous alumina was made from blending alumina powder into the egg white protein solution by a domestic food mixer. Then Lemos et al. [7] extended the foaming capability of egg white protein to make porous hydroxyapatite bioceramics. Dhara et al. [8] further investigated the foaming processing using fresh egg whites and concluded that several parameters could influence the overall porosity and foam microstructure. These parameters included ceramic solid-loading, egg white protein-water ratio, foaming time and sintering temperature. In our early work, the foaming ability of the egg white protein based slurry was also compared with whey protein based slurry in terms of morphology, pore size distribution and mechanical strength [9]. Macroporous ceramics could be obtained through specific manufacturing processes.

Each fabrication method was best suited for producing a specific range of cell sizes, cell sizes distribution and overall amount of porosity. However, there were not too many researches on the comparison egg white protein direct foaming with other macroporous ceramic fabrication methods. In this work, an environmentally-friendly protein system—egg white protein—was investigated to fabricate macroporous ceramics to take the advantage of the well-known foaming and gelling capabilities of egg white protein. The conventional sponge replica method [10] was employed and compared in terms of porosity, density, compressive stress, Weibull modulus, and microstructure.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10934-011-9528-z) contains supplementary material, which is available to authorized users.

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## 2 Experimental

### 2.1 Raw materials

Alumina (Alcoa CT 3000 SG, USA) and titania (Tronox TR-HR-2, Germany) powders were used for the fabrication of macroporous ceramics. Darvan 821A (RT Vanderbilt Inc., USA) was used as an electrosteric dispersant. Egg white protein (Danish pasteurised spray dried, Lactosan-Sanovo (UK) Limited) was employed as a binder and foaming agent. As a defoamer, 1-octanol was purchased from Sigma-Aldrich. Distilled water was used as a solvent.

### 2.2 Porous ceramic sample preparation

All samples began from the carefully prepared slurries. Concentrated ceramic slurries were created by adding a predetermined amount of Darvan 821A to distilled water, followed by addition of the 40 wt% solid loading ceramic powders. There are two kinds of ceramic powders, alumina and 50 vol%$Al_2O_3$–50 vol%$TiO_2$ composite, used in this work. The slurry was ball milled for 24 h with 10 mm diameter zirconia balls as the grinding media in the same weight as the slurry. After 24 h, a well-dispersed slurry without flocculation was obtained.

For protein direct foaming method, a well-dispersed slurry was mixed with egg white protein powder for 1 h. The formed slurry in a water-proof polypropylene bottle was put upside-down at a ball milling machine for 20 h agitation of 100 rpm, and uniform air bubbles could be achieved afterwards. Then the slurry was placed into a mould and set by a simple drying consolidation in an oven at 40 °C overnight. The green samples were sintered at 1,600 °C and soaked for 120 min.

For the sponge replica method, the 10 wt% egg white protein powder was added to the dispersed slurries and mixed for 1 h. At the same time, 1-octanol was added to remove air bubbles generated during milling. Then, the slurries were further degassed in vacuum for 10 min after milling. The prepared slurries were de-aired using a defoamer in order to achieve the fully dense struts. As a starting material for the sacrificial template, the commercial polyurethane sponge (Sydney Heath & Son Ltd., UK) with 45 ppi (pore per inch) was cut to the appropriate rectangular shape for replica porous ceramics. The sponge was impregnated within the ceramic slurries and then put into a universal testing tube to extract surplus slurry in a centrifuge machine (MSE, DJB Labcare Ltd, Newport Pagnell, UK). Then, the centrifuged samples were impregnated in the same slurry again. This dipping-and-coating cycle was repeated three times. The coated sponge was then dried at 40 °C overnight. The samples were sintered at the same 1,600 °C for 120 min. Repeating the above infiltration process 2–5 times reduced the overall porosity of the porous structure.

### 2.3 Physical characterisation

The open porosity of the porous samples was measured using the traditional Archimedes method [11, 12]. Samples of 10 × 10 × 5 $mm^3$ were cut with an Accutom-5 (Struers, UK) for compressive tests using a uni-axial mechanical tester (Lloyd Instruments LR5 K, UK). The crosshead speed was 0.5 mm/s. The compressive strength data were analysed using Weibull distribution. The specimens viewed in an SEM (Cambridge 90B Stereoscan, UK) to observe the microstructure of macroporous ceramics.

## 3 Results and discussion

### 3.1 Density and porosity

The main issue in porous ceramics fabrication is how to control overall porosity. The greatest advantage of the sponge replica method is that overall porosity can be easily controlled [13, 14]. According to Table 1, as the infiltration time increased, the overall porosities decreased and bulk densities increased proportionally.

Taking the theoretical density of $Al_2O_3$, 3.96 g/$cm^3$, $TiO_2$, 4.2 g/$cm^3$, the composite (50 vol% $Al_2O_3$–50 vol% $TiO_2$) density was calculated as 4.076 g/$cm^3$, which was used as a reference to calculate the apparent porosity of each composite porous ceramic. As the infiltration time increased, the bulk densities increased, and the porosities decreased proportionally. Increasing infiltration time deposited more slurry distribution on struts, and the bulk ceramic regained more mass, which contributed to the density increase and porosity decrease.

In contrast, the porosity of the direct foaming method was controlled through the controlled viscosity, which could be determined by the egg white protein concentration as shown in Fig. 1. Studart et al. [2] concluded that the

**Table 1** Total porosity and density data of sponge replica samples

| Materials | Infiltration times | Porosity (%) | Density (g/$cm^3$) |
|---|---|---|---|
| $Al_2O_3$ | 1 | 90 | 0.39 |
| | 3 | 86 | 0.54 |
| | 4 | 78 | 0.86 |
| | 5 | 71 | 1.16 |
| 50 vol%$Al_2O_3$–50 vol%$TiO_2$ Composite | 3 | 84 | 0.64 |
| | 4 | 77 | 0.93 |
| | 5 | 71 | 1.2 |

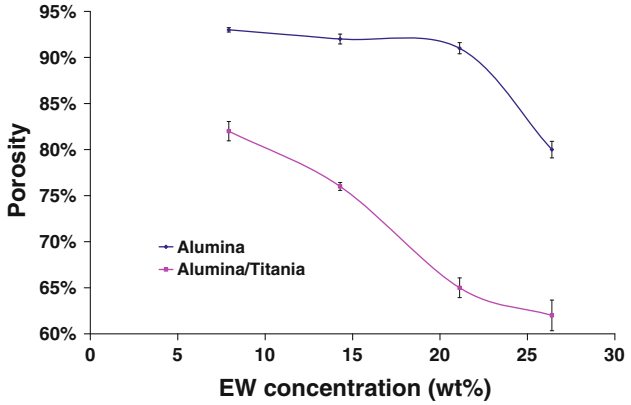


**Fig. 1** Porosities change of direct foamed samples with the egg white protein solution concentration

total porosity acquired from this method is proportional to the amount of air incorporated into the slurry or liquid medium during the foaming process. In this work, the viscosity of the slurry increased when the amount of egg white protein in the slurry increased. When the viscosity increased, the total amount of air incorporated into more viscous slurry was less than that incorporated into less viscous slurry. Therefore, fewer pores formed from more viscous slurry. This phenomenon was observed from both ceramic materials used in the direct foaming investigation. As shown in Fig. 1, when the concentrations of egg white protein increased, the porosities of the resulting ceramics decreased. Also in Fig. 1, at corresponded egg white protein solution concentrations, porosities of alumina samples were higher than those of $Al_2O_3/TiO_2$ composite samples. This was related to the solution viscosity difference of two ceramic powders used here. Titania powder generated higher solution viscosity than that generated by alumina powder. Therefore, the solution viscosity of $Al_2O_3/TiO_2$ composite was higher than that of alumina at the same egg white protein concentration. Hence, the macroporous $Al_2O_3/TiO_2$ composite samples fabricated through corresponded solutions were less porous than alumina samples.

### 3.2 Compressive testing

For the sponge replica method, the samples were infiltrated 4 or 5 times, resulting in similar porosities for alumina (78–71%) and the $Al_2O_3/TiO_2$ composite (77–71%) as shown in Table 1. However, the compressive strength was quite low for the $Al_2O_3/TiO_2$ composite samples, e.g. $0.16 \pm 0.07$ MPa for 77% porosity and $0.23 \pm 0.07$ MPa for 71% porosity (Table 2). At similar porosities, the alumina samples were approximately 10 or 20 times stronger (Table 2). The compressive strength was $1.58 \pm 0.07$ MPa for 77% porosity and $4.52 \pm 0.75$ MPa for 71% porosity.

**Table 2** The compressive strength (with SD) of sponge replica samples

| Materials | Porosity (%) | Compressive strength (MPa) |
|---|---|---|
| $Al_2O_3$ | 86 | $0.19 \pm 0.08$ |
| | 78 | $1.58 \pm 0.07$ |
| | 71 | $4.52 \pm 0.75$ |
| 50 vol%$Al_2O_3$–50 vol%$TiO_2$ Composite | 77 | $0.16 \pm 0.07$ |
| | 71 | $0.23 \pm 0.07$ |

**Table 3** The compressive strength (with SD) of protein direct foaming samples

| Materials | Porosity (%) | Compressive strength (MPa) |
|---|---|---|
| $Al_2O_3$ | 93 | $1.36 \pm 0.23$ |
| | 92 | $1.61 \pm 0.42$ |
| | 91 | $2.19 \pm 0.4$ |
| | 80 | $12.97 \pm 3.76$ |
| 50 vol%$Al_2O_3$–50 vol%$TiO_2$ Composite | 82 | $0.70 \pm 0.13$ |
| | 76 | $1.04 \pm 0.25$ |
| | 65 | $5.54 \pm 1.83$ |
| | 62 | $6.76 \pm 1.22$ |

The difference in compressive strength between the alumina and composite samples resulted in inherent strength difference between alumina (2,945 MPa) and titania (680 MPa) raw materials. Titania replaced 50% of the alumina volume in the composite samples. Similar results were observed for the protein direct foaming method (Table 3).

Using the protein direct foaming method (Table 3), compressive strength increased as porosity decreased for both testing materials. The compressive strength of the alumina samples increased from $1.36 \pm 0.23$ MPa to $12.97 \pm 3.76$ MPa when the porosity decreased from 93 to 80%, respectively. Due to the inherent strength difference between alumina and titania, the direct foamed samples made from alumina were much stronger than those made from the $Al_2O_3/TiO_2$ composite at similar porosity. Even though the highest compressive strength of the $Al_2O_3/TiO_2$ composite samples reached $6.76 \pm 1.22$ MPa at 62% porosity, they were still weaker than the alumina samples with the higher porosity (80%).

### 3.3 Weibull modulus analysis

Room-temperature compressive strength as a function of porosity is presented as a Weibull distribution in Figs. 2, 3, 4 and 5, where $P$ is the survival probability at a given stress, $\sigma$ is the applied stress, and *Weibull M* is the Weibull modulus. Due to the limited number of samples available,

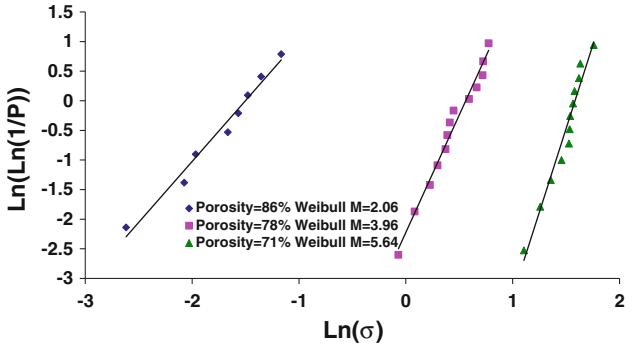


**Fig. 2** Weibull distribution of compressive strength change of the sponge replica $Al_2O_3$ samples infiltrated 3, 4, and 5 times to porosity of 86, 78 and 71%, respectively

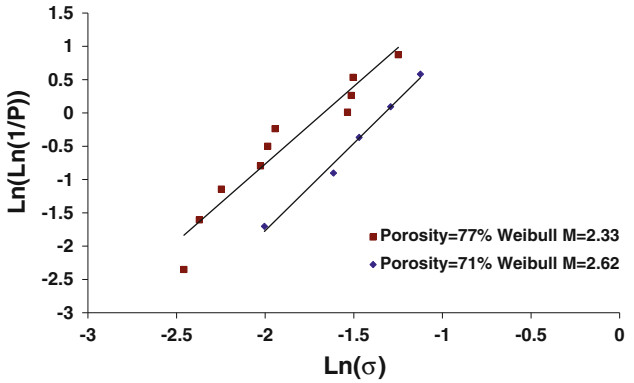


**Fig. 3** Weibull distribution of compressive strength change of the sponge replica $Al_2O_3/TiO_2$ composite samples infiltrated 4 and 5 times to porosity of 84 and 71%, respectively

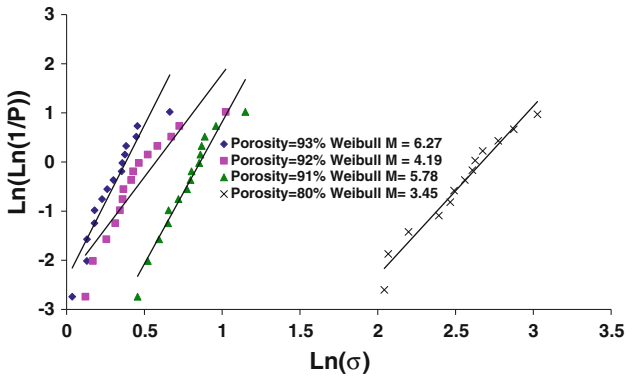


**Fig. 4** Weibull distribution of compressive strength change of the protein direct foamed $Al_2O_3$ samples

the Weibull data obtained do not represent true material parameters; they are only used for comparison purposes.

The sponge replica method can be used to reduce the overall porosity by increasing the infiltration time; the compressive strength proportionally increased with the

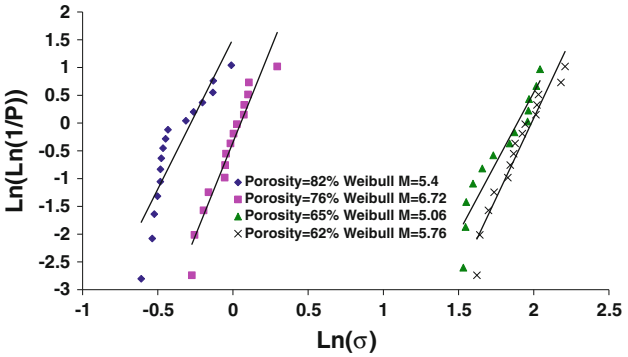


**Fig. 5** Weibull distribution of compressive strength change of the protein direct foamed $Al_2O_3/TiO_2$ composite samples

decreasing porosity [15]. The strength gained from the ceramic mass deposition and the reliability, indicated as the Weibull modulus in Figs. 2 and 3, increased simultaneously. When a sample was immersed in the slurry, the struts were coated with the ceramic particles. The more infiltration cycles used the more particles that were coated, which filled the defects left from the last infiltration to improve mechanical properties and reliability. Repeating this infiltration process, the samples resulted in more uniform stress distribution, which was directly linked to a higher Weibull modulus. Higher Weibull modulus means less probability that brittle ceramics will fail; i.e., more even distribution of defects in products is essential for advanced ceramic materials.

For the protein direct foaming method, the Weibull moduli of both samples had independent porosity relationships (Figs. 4, 5). For the porous structure, the ultimate fracture strength was related to the strut strength as well as the pore size and distribution. All samples fabricated using the protein direct foaming method had the higher Weibull modulus than the ones fabricated using the sponge replica method at the similar porosity. The higher Weibull modulus indicated the more homogenous porous structure, which was more reliable with uniform struts and cell walls. Due to the nature of fabrication methods, the inevitable defects would be left in struts of samples fabricated using the sponge replica method. However, the ceramic particles could be evenly attached to bubble surfaces between air and water, which were stabilised with the egg white protein. Under the balance of particle gravity and surface tension, the ceramic particles agglomerated at the bubble joint area and then finally formed the struts after sintering. A homogeneous porous structure could be achieved using the protein direct foaming method through careful balance of entrapped air bubbles and ceramic solid-loadings. Therefore, the struts formed in the protein direct foaming method were denser and much uniform than that formed in sponge replica method.

### 3.4 Microstructure

Figure 6 illustrated the typical morphology of the macroporous ceramics fabricated using two different methods. These pictures showed that the microstructures significantly differed, which implied the mechanical differences between the samples as discussed previously. The left side of Fig. 6 showed a low-density, open-cell, net-like structure; while the right side showed a spherical shell-like structure interconnected by small windows on large pore walls. The former structure was a replica of the polyurethane sponge which was used as support in sponge replication processing; the latter was formed by well-distributed ceramic particles at the air bubble interface, which was generated by the amphiphilic egg white protein during direct foaming.

Examination of the SEM micrograph demonstrated the existence of two types of pores in the sponge replica samples: 800–1,000 μm interconnected cell windows (Fig. 6, left) and voids inside the struts after burnout of the polymer sponge (see arrow in Fig. 7, left). These voids could not be completely removed even after several infiltrations. Voids only became smaller, as the slurry was limited in the spaces that it could fill; they contributed to a deterioration of mechanical properties. There were still some average 5 μm cavities in the struts because of incomplete densification during sintering. Long cracks could be found on struts in the first coated samples because of the thermal expansion difference between the polymer and ceramic powders during the initial pyrolysis of the sponge.

The microstructure of protein direct foaming samples was much more uniform (see Fig. 7, right). The pores were of regularly spherical shape with interconnected windows on the pore walls. Some closed pores were also present, and the fraction of closed pores increased as the foam density increased. The pore walls and the struts were dense, with no macroscopic cracks or defects observed after sintering. Therefore, it could be concluded that the protein direct foaming method produced a stronger porous structure than the sponge replica method at similar porosities.

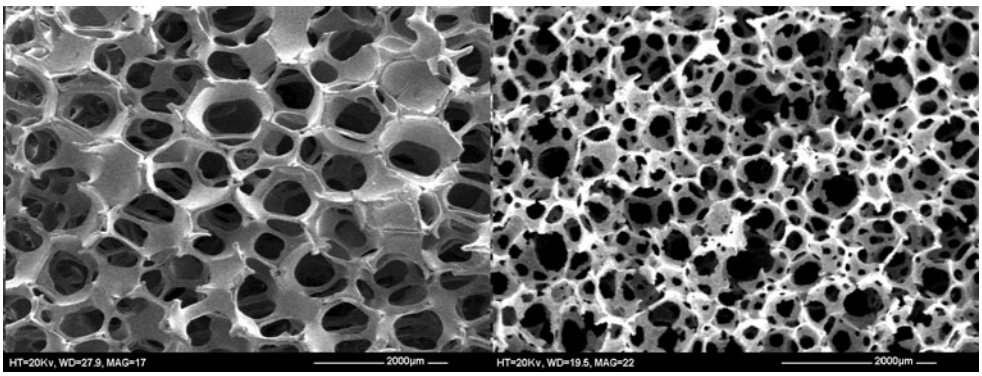


**Fig. 6** Examples of cellular structures obtained by sponge replica (*left*) and protein direct foaming (*right*) for alumina samples. The sponge replica sample had a density of 0.35 g/cm$^3$ at 91% porosity. The protein direct foaming sample had a density of 0.42 g/cm$^3$ at 89% porosity

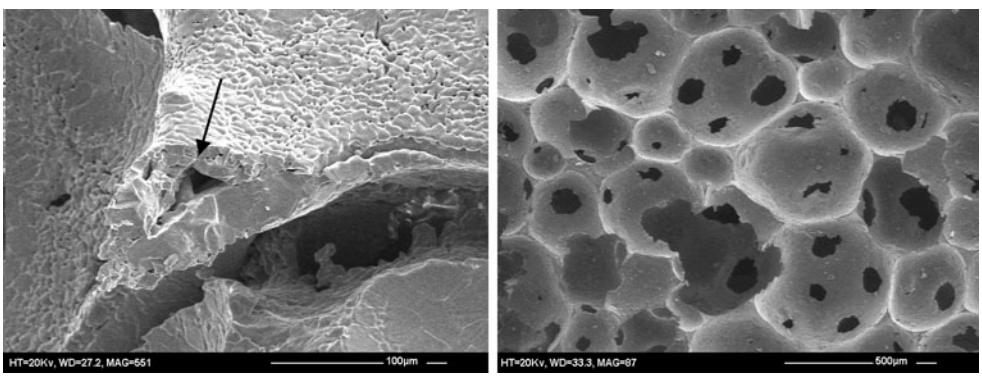


**Fig. 7** *Left* A void (the *arrow* pointed) in the *triangle area* of the strut of a sponge replica sample. *Right* The closer view of sample of protein direct foaming alumina with 78% porosity

## 4 Conclusions

Using the sponge replica and protein direct foaming methods, different porous ceramics were fabricated from two materials. In terms of mechanical properties, porous $Al_2O_3$ ceramics were much stronger than porous $Al_2O_3$/$TiO_2$ composites under similar processing conditions. At similar porosity, samples made from the protein direct foaming method were stronger than those made from the sponge replica method, which also had a less homogenous structure as indicated by the lower Weibull modulus. The mechanical properties of the porous ceramics depended on their microstructures. The sponge replica method produced an open-cell, net-like structure with inevitable voids within struts. On another hand, the protein direct foaming produced dense struts and uniform spherical pores with small windows.

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