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Preparation of Si_3N_4 ceramic foams by simultaneously using egg white protein and fish collagen

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Abstract

Fish collagen, a kind of fibrous protein, and egg white protein were selected as foaming agent to prepare ceramic foams by protein foaming method. Ceramic foams with open porosity of 84.8–86.9%, average pore size of 216–266 μm and compressive strength of 8.7–13.7 MPa were fabricated. Studies of fish collagen addition on the influence of open porosity, pore size distribution and mechanical property of ceramic foams were investigated. In comparison with single addition of 8 wt% egg white protein, the combinational addition of 2 wt% fish collagen and 6 wt% egg white protein results in 23% increase in average pore size. In addition, the introduction of fish collagen decreases the count of small pores. Moreover, with the introduction of fish collagen, pores become regular in shape.

Keywords: B: Porosity; D: Si_3N_4; Protein foaming

1. Introduction

Ceramic foams have variety of potential applications in hot gas filters, catalyst supports and biomaterials, due to their excellent chemical stability, good wear resistance and biocompatibility [1–5]. During the past years, many routes [6] have been developed to prepared ceramic foams, including polymeric foam impregnation and direct foaming. Polymeric foam impregnation is a typical method to fabricate ceramic foams with high open porosity and interconnectivity. However, natural characteristic defect of this method is low mechanical property of the product [7]. Compared with polymeric foam impregnation method, direct foaming method can be used to produce ceramic foams with good mechanical property in a wide range of porosity. Protein foaming is a representative direct foaming method by using protein as foaming agent and binder. When adding protein into ceramic slurry through a mixing process, protein will absorb on air–water interfaces and stabilize air bubbles in the slurry to generate slurry foam [8]. When heating the slurry foam to a certain temperature, protein will gel by denaturing and form 3D network to stabilize the pore structure of slurry foam. Protein foaming method has a serial of advantages. For example, it can be used to produce high performance ceramic foams with widely controllable pore size, porosity and relatively high mechanical property. In addition, it is environmentally friendly [9–11].

Protein is traditionally categorized as fibrous and globular protein according to its molecule conformation [12]. However, for protein foaming method to fabricate ceramic foams, the most widely used proteins are globular proteins, such as egg white [10,13,14], whey protein [10] and bovine serum albumin [15]. Some researchers suggested that fibrous protein, for example fish collagen derived from skin or scale of fish, also had good foaming ability [16]. Nevertheless, preparation of ceramic foams by fish collagen is scarce. In the present work, we reported a novel protein foaming method by simultaneously using egg white protein and fish collagen as foaming agent and binder. Moreover, we studied fish collagen addition

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on the influence of pore structure, open porosity, pore size distribution, compressive strength of the produced ceramic foams.

2. Experimental procedures

Three steps were undertaken in this experiment to prepare ceramic foams. Firstly, powder of Si_3N_4 ($d_{50}=0.7$ μm, α-$Si_3N_4>92\%$, Fidone Special Ceramics Materials Co., Ltd., China) and sintering additive were dispersed in distilled water at a volume ratio of 30 vol% based on distilled water. Y_2O_3 (99.9%, Sinopharm Chemical Peagent Co., Ltd., China) was selected as sintering additive and the addition was 5 wt% based on the weight of Si_3N_4 powder. Dispersant D3005 from Rohm and Hass was selected to modify the rheological behavior of slurry with the content of 0.34 wt% (based on solid content). The powders mixed together in distilled water were ball-milled for 20–24 h at the rate of 100 rpm to obtain well-dispersed slurry. Then egg white protein powder (derived from egg white solution by wiping of water and glucide in it, Jilinjinyi food production Co, Ltd., China) and fish collagen powder (Derived from skin of tilapia, Zhenlu Co. Ltd., China) were added into the slurry with the total content of 8 wt% (based on the weight of slurry). For comparison, ceramic foam prepared by adding 6 wt% egg white protein was also prepared. Continuously, the slurry was ball-milled for another 2 h at the rate of 100 rpm. In this process, the bottle was tumbled about an axis perpendicular to the height of bottle [10,13]. All the conditions were kept the same for comparison. It should be mentioned that the samples were denoted by using letter "F" and "E" for fish collagen addition and egg white protein addition, respectively. For example, "F1E7" denotes for 1 wt% fish collagen and 7 wt% egg white protein.

The generated slurry foams were poured into PTFE mold and gelled at the temperature of 80 °C. Two hours were taken to finish the coagulation of the slurry foam. The gelled bodies were subsequently dried at ambient temperature for 24 h and finally dried at 60 °C in the drying oven for approximate 5 h. Burnout of protein was undertaken in air at 600 °C for 1 h with a heating rate of 1 °C/min. Finally sintering of Si_3N_4 ceramic foams were undertaken in a gas pressure furnace (high-multi 5000, Fujidempa Kogyo Co. Ltd.) at the temperature of 1700 °C for 1 h in the protection of N_2.

Open porosity and density were measured by Archimedes method. The ceramic foams were finally cut into a dimension of $10\times10\times10$ mm^3 for compressive tests using a mechanical tester (CTM 9100, Xieqiang Co., Ltd., China) at the crosshead speed of 0.5 mm/min. The pore structure was characterized by scanning electron microscopy (SEM, JSM-6700F). Pore size distributions of as-sintered ceramic body were evaluated through the measurement of the pore size in the SEM micrographies.

3. Results and discussion

Open porosity and average pore size with different protein addition are shown in Fig. 1. As shown in Fig. 1, the introduction of fish collagen has a significant influence on average pore size. In comparison with single addition of 8 wt% egg white protein, combinational addition of 2 wt% fish collagen and 6 wt% egg white protein results in average pore size increasing from 216 μm to 266 μm, about 23%. Moreover, compared with single addition of 6 wt% egg white protein, ceramic foams prepared by adding 2 wt% fish collagen and 6 wt% egg white protein also illustrate 17% increase in average pore size. However, with the increasing addition of fish collagen, the rate of this increment decreases. Average pore size illustrates no obvious change when increasing fish collagen addition from 2 wt% to 3 wt%. Open porosities of ceramic foams prepared here are generally in the range of 84–87%. In contrast to average pore size, introduction of fish collagen has no significant effect on open porosity. The highest open porosity was obtained by adding 1 wt% fish collagen and 7 wt% egg white protein. However, open porosity decreases at increasing fish collagen addition. Therefore, it can be indicated that small addition of fish collagen has significant influence on average pore size but slight influence on open porosity. However, with the increasing addition of fish collagen, these influences become unobvious.

Pore structure of ceramic foams prepared with and without fish collagen is presented in Fig. 2. As shown in Fig. 2b, pores of ceramic foam prepared by single addition of 8 wt% egg white protein are not uniform in size and regular in shape. Some big pores with the size of 400–600 μm can be observed. In comparison with 8 wt% egg white protein addition, pores of ceramic foams prepared by adding 6 wt% protein addition are more regular in shape and uniform in size. Moreover, some regularly spherical pores can also be observed in Si_3N_4 foams prepared by introducing fish collagen. Some small windows are also observed on the walls of pores. As for

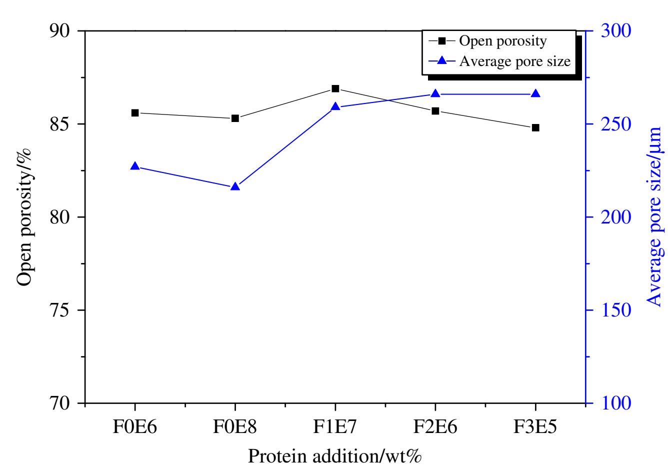

Fig. 1. Open porosity and average pore size of ceramic foams with different content of fish collagen and egg white protein.

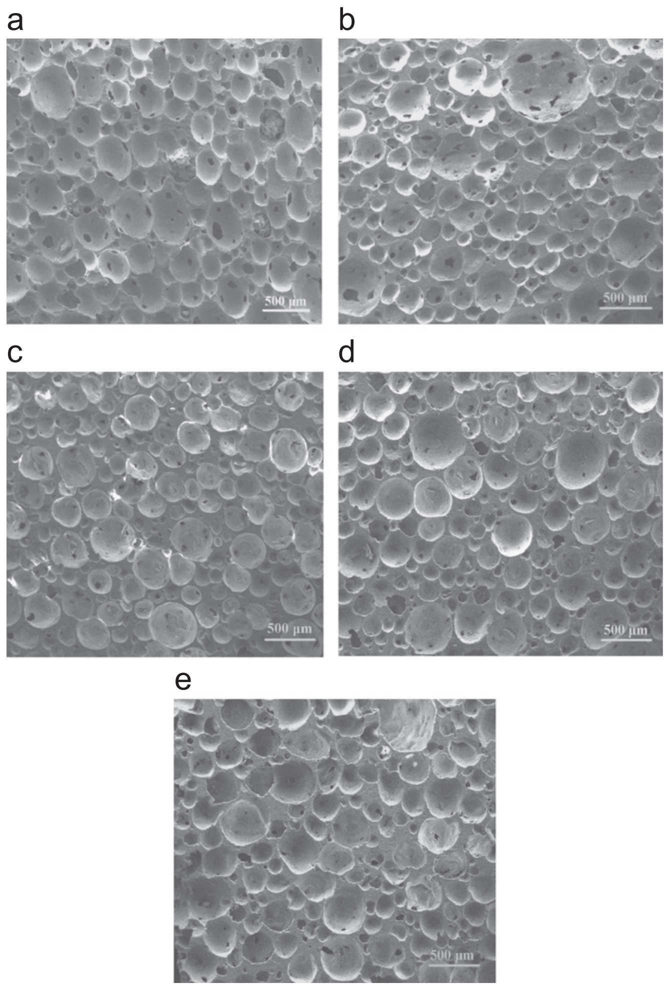

Fig. 2. Pore structure of ceramic foams prepared by adding different content of fish collagen and egg white protein; (a) F0E6, (b) F0E8, (c) F1E7, (d) F2E6 and (e) F3E5.

ceramic foams, these windows provide good interconnectivity and hence increases open porosity.

Pore size distributions of the produced ceramic foams are illustrated in Fig. 3. 244 pores from two or three SEM micrographies are measured to calculate average pore size. To be representive, pores in measurement are optionally selected. It is obvious that pores of ceramic foams prepared with or without fish collagen are generally in the size of 100–500 μm. However, addition of fish collagen has a significant influence on the pore size distribution. For ceramic foams with single addition of egg white protein, percentage of pores between 100 μm and 150 μm is nearly 20%, while only 10% of pores are in the size of 100–150 μm after the introduction of fish collagen. It can be indicated that the introduction of fish collagen decreases the count of small pores. Moreover, as shown in Fig. 3, for sample without fish collagen, most of the pores are in the size of 100–250 μm. However, for the samples foamed by adding fish collagen, the pore size mainly concentrates at 150–350 μm. To some extent, this can account for the significant increment in average pore size. Therefore, it can be concluded that the introduction of

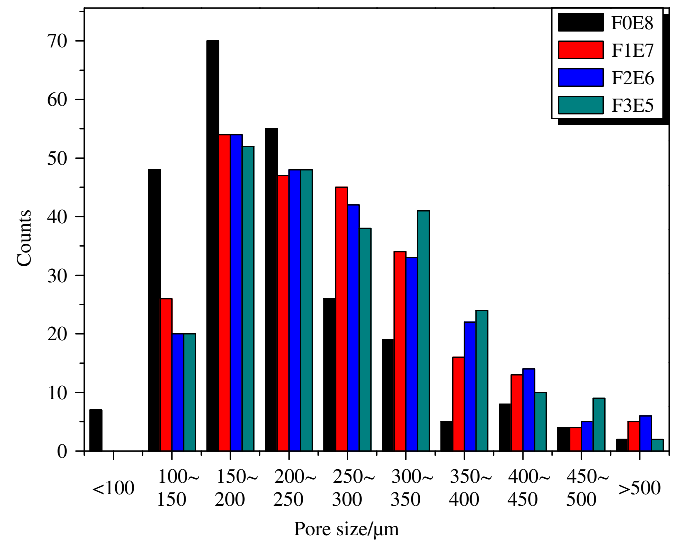

Fig. 3. Pore size distribution of ceramic foams prepared by adding different contents of fish collagen and egg white protein.

fish collagen may depress the formation of small pores resulting in decreasing count of small pores and hence increasing in average pore size.

Since all the conditions in this research were kept the same, the significant change of pore size may affect the special structure and properties of fish collagen. For protein foaming method, the final pore structure of ceramic foams is largely determined by the slurry foaming process. During this process, protein will (1) diffuse to air–water interface and further absorb on it and (2) interact between different protein molecules to form continuous viscoelastic film [17,18]. For effective foam formation, protein should be capable of migrating and interacting rapidly to form encapsulating films around the bubbles [17,18]. Compared with globular structure of egg white protein, the fibrous structure of fish collagen may accelerate the diffusion process, thereby enhancing foam formation.

Mechanical property of as-fabricated ceramic foams with different fish collagen addition was illustrated in Fig. 4. Compressive strength of Si_3N_4 foams prepared here are in the range of 9–14 MPa. Variety of factors may affect compressive strength of ceramic foams, such as porosity, pore size and strut of pores. In comparison with total 8 wt% protein addition, compressive strength of ceramic foam prepared by adding 6 wt% protein is obviously low. For ceramic foams prepared by adding fish collagen, the highest compressive strength was obtained by adding 2 wt% fish collagen and 6 wt% egg white protein. However, compressive strength of ceramic foams prepared by adding 1 wt% and 3 wt% fish collagen is evidently lower than 8 wt% egg with protein.

4. Conclusions

Egg white protein and fish collagen were used to fabricate ceramic foams. Ceramic foams with open porosity of 84.8–86.9%, average pore size of 216–266 μm and compressive

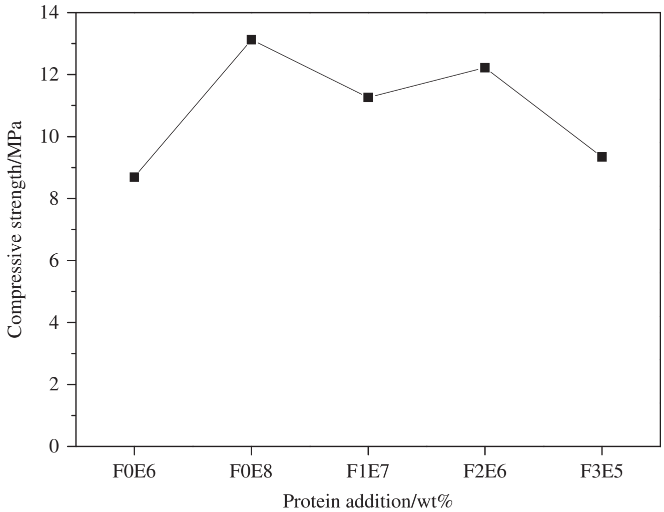

Fig. 4. Compressive strength of ceramic foams prepared by adding different contents of fish collagen and egg white protein.

strength of 9.3–13.7 MPa were prepared. Studies of fish collagen addition on the influence of open porosity, pore size distribution and compressive strength of ceramic foams were investigated. It is suggested that small addition of fish collagen leads to significant increase in average pore size. Moreover, pores become regular in shape when adding fish collagen. In addition, the introduction of fish collagen may depress the formation of small pores resulting in increasing in average pore size.

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