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# Protein foaming method to prepare $Si_3N_4$ foams by using a mixture of egg white protein and whey protein isolate

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**Abstract**

Structure and properties of $Si_3N_4$ foams prepared by using egg white protein or whey protein isolate were compared. Pores of $Si_3N_4$ foams prepared by using egg white protein are generally closed, while pores prepared by using whey protein isolate are generally open. However, layered structure is found in the $Si_3N_4$ foams prepared by using whey protein isolate. Further, a combinational usage of egg white protein and whey protein isolate was employed to prepare $Si_3N_4$ foams. It is indicated that the addition of egg white protein when using whey protein isolate as foaming agent can avoid the formation of layered structure in the product. However, the size and number of windows on the walls decrease with the addition of egg white protein. Moreover, it is indicated that the combinational usage of egg white protein and whey protein isolate has certain advantage over using either of them especially when solid content is high.


*Keywords:* A. Sol–gel process; B. Porosity; D. $Si_3N_4$; E. Functional applications

## 1. Introduction

Ceramic foams with controllable pore structure have great potential in applications such as catalyst supports, hot gas filters and biomaterials [1,2]. During the past decades, varieties of methods [3], including replication and foaming, have been employed to prepare ceramic foams. Schwartzwalder and Somers [4] reported the replication of polymeric sponges as a typical manufacturing technique for producing macro-porous ceramics. However, the natural defect of this method is the low mechanical properties of the products. In comparison with the replication method, foaming method bears some striking advantages and can be used to produce ceramic foams with high overall performance. Recently, Tian and Ma [5,6] have successfully developed a kind of direct foaming method (self-blowing) to fabricate ceramic foams with open porosity of 40–75% by using silicone resin. In addition, some natural substances, such as protein [7,8] and starch [9–11], have also been used to prepare ceramic foams. Moreover, there is an increasing attention to prepare ceramic foams by using protein, with the consideration of its environmental friendliness and low expenditure.

For the protein foaming method, the commonly used proteins are egg white protein [12–15] and bovine serum albumin [7]. However, natural defect of these proteins in preparing ceramic foams is that pores prepared by using these proteins are generally closed, especially when the solid content is high. To control the pore structure of the products, some natural additives, such as starch [12,14], sucrose [16] and egg yolk [15,17], which act as pore former or increase the stability of foamed slurry, are used in the preparation. However, great efforts are still needed to well control the pore structure and improve the performance of the products. Whey protein isolate has a comparable [18,19] or higher [20,21] foaming capacity and a potential to replace egg white protein as a foaming agent. However, it is rarely used in preparing ceramic foams due to its low foaming stability [22,23]. Recently, we have reported the preparation of $Si_3N_4$ foams by simultaneously using egg white protein and fish collagen [24]. It is indicated that the combinational usage of different kinds of proteins is a practical way to control the pore structure of ceramic foams prepared by

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the protein foaming method. However, it is scarce to find any other studies about this issue. Moreover, a substitution of the fish collagen or egg white protein is necessary due to the existence of proteins which have high foaming ability than egg white protein and fish collagen. In this research, whey protein isolated was chosen to substitute the conventionally used egg white protein in the protein foaming method and a mixture of egg white protein and fish collagen was substituted by a mixture of whey protein isolated and egg white protein. Further investigation on the pore structure of the product indicates that the mixture of whey protein isolated and egg white protein has some advantages in preparing $Si_3N_4$ foams with high overall performance over using either of them.

## 2. Experiments

### 2.1. Materials

$Si_3N_4$ powder used here was purchased from Fidone Special Ceramics Materials Co., Ltd. with $d_{50}$ of 0.7 μm and α-$Si_3N_4$ content >92%. 5 wt% $Y_2O_3$ with the purity of 99.9% (Sinopharm Chemical Peagent Co., Ltd., China) was used as sintering additive. D3005 (Rohm and Hass, Germany) was selected as dispersant to stabilize $Si_3N_4$ powder in protein–water suspension. Whey protein isolate used here was American Hilmar WPI 90, with the purity >89%. Egg white protein (Purchased from Jilinjinyi food production Co, Ltd., China) was derived from egg white solution by wiping of water and sugar, with the purity of >78%.

### 2.2. Preparation of foamed slurry

Slurries were firstly prepared by dispersing $Si_3N_4$ powder in distilled water with the solid content of 40–60 vol%. Density of $Si_3N_4$ powder was taken as 3.4 g/cm$^3$ in the solid content calculations. $Y_2O_3$, D3005 and whey protein isolate were added with $Si_3N_4$ powder simultaneously. Then, the slurries were mixed together by ball-milling in a 250 ml bottle for 24 h at the rate of 100 rpm. After that, egg white protein (when using a mixture of egg white protein and whey protein isolate) was added into the slurries for foaming. In foaming process, the bottle was tumbled about an axis perpendicular to the height of it.

### 2.3. Preparation of ceramic foams

The as-generated foamed slurry was casted in cylindrical molds, which was covered with oil before the casting process for the convenience of demolding. Thermal consolidation process has been detailed elsewhere [25]. After consolidation, the as-generated green bodies were cooled to room temperature. The gelled bodies were subsequently dried in the drying oven. Then the proteins were removed by burnout at the temperature of 600 °C for 1 h with a heating rate of 1 °C/min in air. Finally the green bodies were sintered at the temperature of 1700 °C for 1 h in the protection of $N_2$.

### 2.4. Characterization

Open porosity was measured by the Archimedes method. The $Si_3N_4$ foams were finally cut into a dimension of $10 \times 10 \times 10$ mm$^3$ for compressive tests using a mechanical tester (CTM 9100 produced by Xieqiang Co., Ltd., China) at the crosshead speed of 0.5 mm/min. Three to five specimens were used to determine the average compressive strength. The pore structure was characterized by scanning electron microscopy (SEM, JSM-6700F).

## 3. Results and discussions

### 3.1. Structure and properties of $Si_3N_4$ foams prepared by egg white protein or whey protein isolate

Pore structure of $Si_3N_4$ foams prepared by either egg white protein or whey protein isolate is shown in Fig. 1. In this paper, the samples are denoted by using "vol", "E" and "W" for solid content, egg white protein addition and whey protein addition, respectively. For example, the $Si_3N_4$ foam 50vol-E2W6 represents the $Si_3N_4$ foam prepared by 2 wt% egg white protein and 6 wt% whey protein isolate at 50 vol% solid content. As shown in Fig. 1, pores of the $Si_3N_4$ foam 45vol-E8W0 are generally in the size of 100–250 μm and regular in shape with one or two small windows on the walls. For the $Si_3N_4$ foam 50vol-E8W0, the pores are generally in the size of 50–150 μm and regular in shape. These pores are generally closed for no window can be observed on the walls. Moreover, the pores are isolated by the dense part, which indicates the poor foaming ability of egg white protein at this solid content. As shown in Fig. 1(b and e), the cross-section of the $Si_3N_4$ foam 50vol-E8W0 is evidently different from that of the $Si_3N_4$ foam 50vol-E0W8. Layered structure (a foam part and a dense part) is found in the $Si_3N_4$ foam 50vol-E0W8. As shown in Fig. 1(c), no pores can be found in the dense part, while numbers of big pores, generally in the size of 300–500 μm can be clearly observed in the foam part, as shown in Fig. 1(f). The pores are generally open with three or more big windows on the walls, which forms 3D interconnective pore structure.

Preciously, great efforts have been spent on investigating the discrepancy in foaming and interfacial properties between whey protein isolate and egg white protein [20,21,26,27]. As reported before, these two kinds of proteins have different chemical composition. The major constituent of egg white protein is ovalbumin [28], while the major constituent of whey protein isolate is β-lactoglobulin [29]. These two components have different chemical and physical properties, for instance the molecular weight of ovalbumin is about 43 kDa, about twice as much as the molecular weight of β-lactoglobulin [21]. The comparisons of the foaming and interfacial properties of whey protein isolate and egg white protein indicate that the high foaming stability of egg white protein was attributed to the exceptional properties of ovalbumin [20,21,30]. Due to the higher molecular mass of ovalbumin, egg white protein can form a much thicker interfacial network, which can prevent the bubble coalescence and drainage more efficiently than whey protein isolate.