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Effect of carboxymethyl cellulose addition on the properties of Si_3N_4 ceramic foams

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Abstract

The effect of carboxymethyl cellulose (CMC) addition on the preparation of Si_3N_4 ceramic foam by the direct foaming method was investigated. The addition of CMC in the foam slurry can reduce the surface tension, increase the viscoelasticity of foams, and improve their stability and fluidity. The foam ceramics show low shrinkage during drying owing to the CMC and the gelation of acrylamide monomers. The surface structure of dried foam is uniform, and there are no macropores and cracks on the surface. The sintered Si_3N_4 foam ceramics have very uniform pore distribution with average pore size of about 16 μm; the flexure strength is as high as 3.8–77.2 MPa, and the porosity is about 60.6–82.1%.

Keywords: Direct foaming method; Particle-stabilized foams; Si_3N_4 ceramics; CMC

1. Introduction

Direct foaming method is an easy, cheap and fast way to prepare high-porosity ceramics (~90%) with open or closed pores [1]. In this method, air bubbles are incorporated into a ceramic suspension to produce wet foams, and the suspension is subsequently consolidated by a setting reaction, dried and finally sintered into porous ceramics. Foam formation is accompanied by foam drainage and lamella rupture, and the coalescence of the bubbles depends on the stability of the lamella separation of the two bubbles approaching each other. The stability of the foam is governed by many factors [2], such as viscoelasticity of bulk solution, concentration of surfactant/proteins or particles, external forces, etc. Foam stability is very important for the preparation of high-quality foam ceramics.

In ceramic suspension, a surfactant, particle or protein can provide the necessary barrier against bubble coalescence. Partially hydrophobic particles can attach to gas–liquid interfaces to stabilize air bubbles in surfactant-free diluted suspensions [3,4]. A network or a dense layer of particles at the interface is responsible for foam stability, and the strong attachment of particles on bubble surface provides steric stabilization and prevents the coalescence of bubbles. Compared to conventional surfactant molecules that adsorb and desorb on relatively short time scales [1,5], particles adsorb irreversibly at the air–water interface, and this enhances resistance against bubble coarsening due to disproportionation, drainage and coalescence [6–10]. If the bulk solution is very viscoelastic or the thick film contains a large amount of particles, the bubbles are "kinetically" very stable and often do not coalesce [9]. This can be compared to a very viscous honey, where a number of bubbles are very stable and remain in the same position for a long period of time.

In order to improve the foam stability and avoid crack formation during drying, the wet foam has to be slightly strengthened before water evaporation either by adding organic binder or by chemically gelling the foam liquid phase, and this is conducive to overcome the capillary stresses and avoid differential shrinkage during drying [9,11,12]. The key factors affecting the foam stability are the surface tension of the foam solution, interface viscosity, solution viscosity, pressure, temperature, etc.

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The study of foam stabilization using Si_3N_4 as colloidal particles has not been reported, and the purpose of the paper is to investigate the improvement of foam stability by adding carboxymethyl cellulose (CMC) used as binder during the preparation of particle-stabilized Si_3N_4 foam ceramics.

2. Experimental procedures

2.1. *Preparation of Si_3N_4 foam ceramics by particle-stabilized foams*

During the preparation of Si_3N_4 foam ceramics by particle-stabilized foams, in the first step, the organic binder (carboxymethyl cellulose (CMC) or polyvinyl alcohol (PVA)), dispersant (1 wt%, ammonium salt of poly (acrylic acid)) and organic monomers were completely dissolved in deionized water by mechanical stirring; the pH value was set to 9.5, and the premix solution served as a dispersing medium for the Si_3N_4 ceramic powders. The next step was to add Si_3N_4 powders (mean particle size: 1 μm, α phase >94 wt%) and 6 wt% sintering additives (Al_2O_3 and Y_2O_3) into the premix solution to prepare suspension, which was rolled for 12 h, followed by adding short-chain amphiphiles (propyl gallate). The foaming of the suspension was carried out using a household mixer at full speed for 5–10 min; then thick foam was cast immediately into a mold, and foam drying was subsequently carried out in air. Finally, sintering was performed at a heating rate of 10 °C/min and 60 min holding time at 1750 °C, and the sintered Si_3N_4 foam ceramics were achieved. The processing route is shown in Fig. 1.

2.2. *Characterization*

The microstructures of Si_3N_4 foam ceramics were observed by scanning electron microscopy (Hitachi S-570 SEM). Pore size distribution of sintered body was measured by a high-pressure porosimeter (Autoscan 33, Quantachrome Corp., USA). The shear viscosity of foam slurry was measured using a Modular Compact Rheometer (MCR300, Paar Physica, Germany).

The porosity of sintered body was measured by the Archimedes displacement method with distilled water. The bulk density (ρ_0) and the true density (ρ) of the sintered bodies were determined by Archimedes' method in water and by water displacement method, respectively. The porosity (P) was calculated as follows:

$$P=\left(1-\frac{\rho_0}{\rho}\right)\times 100\% \qquad (1)$$

The room-temperature flexural strength of sintered Si_3N_4 foam ceramics was determined by three-point flexural test. The specimens were machined into test bars of $30\times4\times3$ mm^3, and the three-point flexural strength was measured on specimen bars of a span of 16 mm at a crosshead speed of 0.5 mm/min (Instron 1195; Instron, UK).

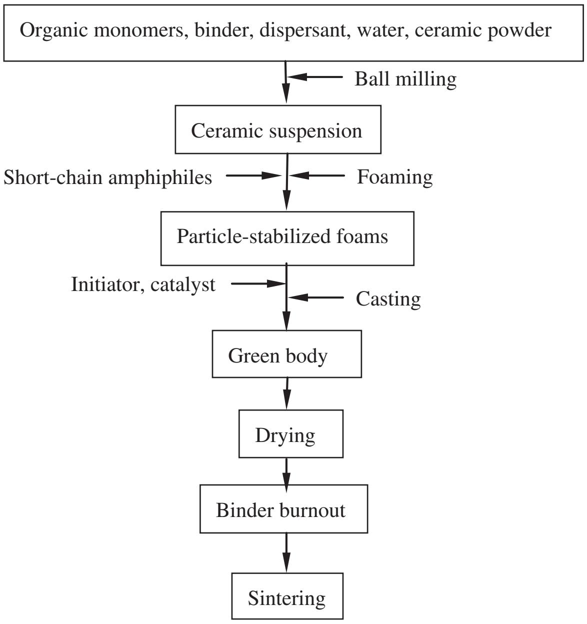

Fig. 1. Processing route for the production of foam ceramics by direct foaming method.

3. Results and discussion

3.1. *Influence of CMC on surface tension of water solution*

Surface tension is usually related to the adsorption of surfactant molecules at the air/water interface. Low surface tension can reduce the energy of the foam system, and it is conducive to the bubble stability. In the experiment, PVA, CMC and CMC+propyl gallate were separately added in water solution; surface tensions with different water-soluble polymers (PVA, CMC and CMC+propyl gallate) were determined, and they were 65 mN/m, 51 mN/m and 34 mN/m, respectively. The surface tension of pure water is 72 mN/m. The experimental results indicate that the surface tension is reduced more by adding CMC than adding PVA, and the lowest surface tension is obtained by adding CMC and propyl gallate.

3.2. *The influences of CMC on the rheological properties of Si_3N_4 particle-stabilized foams*

Fig. 2 shows the effects of CMC and PVA addition on the viscosity of Si_3N_4 foam slurry with 25 vol% solid loading, and the viscosity of slurry by adding CMC is greater than that of slurry by adding PVA. The high viscosity of foams can prolong the bubble relaxation times of gravity drainage and gas diffusion. The increase of slurry viscosity by adding CMC is conducive to form a very viscoelastic surface, increase the strength of foam membrane, reduce the drainage rate of liquid in foam membrane, and the gas permeability of foam membrane. This makes the coalescence (film rupture) difficult, and thus foam stability increases substantially [11].

3.3. Influences of CMC on stability of Si_3N_4 particle-stabilized foams

In order to improve the foam stability and avoid the crack formation during drying, the wet foam has to be slightly strengthened to overcome the capillary stresses and avoid differential shrinkage [11]. The Si_3N_4 foam stability with/without the addition of CMC is investigated, and the results are shown in Fig. 3.

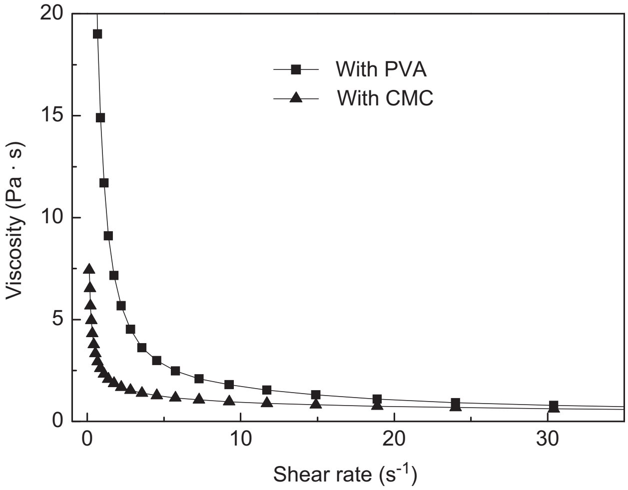

Fig. 2. Influence of CMC and PVA addition on the foam slurry viscosity.

Fig. 3(a) and (b) shows the wet and dried Si_3N_4 ceramic foams, respectively, obtained by adding PVA. The foam slurry with PVA addition has poor fluidity so it must be carefully filled into a mold and then slightly compressed to remove possible air pockets introduced during filling. In Fig. 3(b), the dried ceramic foams have some cracks and macropores on the surface, and air pockets in the foams are noticeable.

Fig. 3(c) and (d) shows the wet and dried Si_3N_4 ceramic foams, respectively, obtained by adding CMC. The foam slurry with CMC addition is sticky and is like a fine smooth paste with good fluidity, and the foam slurry can be cast immediately into a mold. In Fig. 3(d), the dried ceramic foam surface is uniform, and there are no apparent cracks on the surface.

Fig. 4 shows the dried large-size Si_3N_4 foam ceramics having little shrinkage obtained by adding CMC and the gelation of acrylamide monomers. The surface structure of dried foam is uniform, and there are no macropores and cracks. The main reasons of little shrinkage of the ceramic foams are as follows: the addition of CMC can increase the slurry viscosity; this can prolong the bubble relaxation times of the gravity drainage and gas diffusion during drying, and the dense particle layer around the bubbles

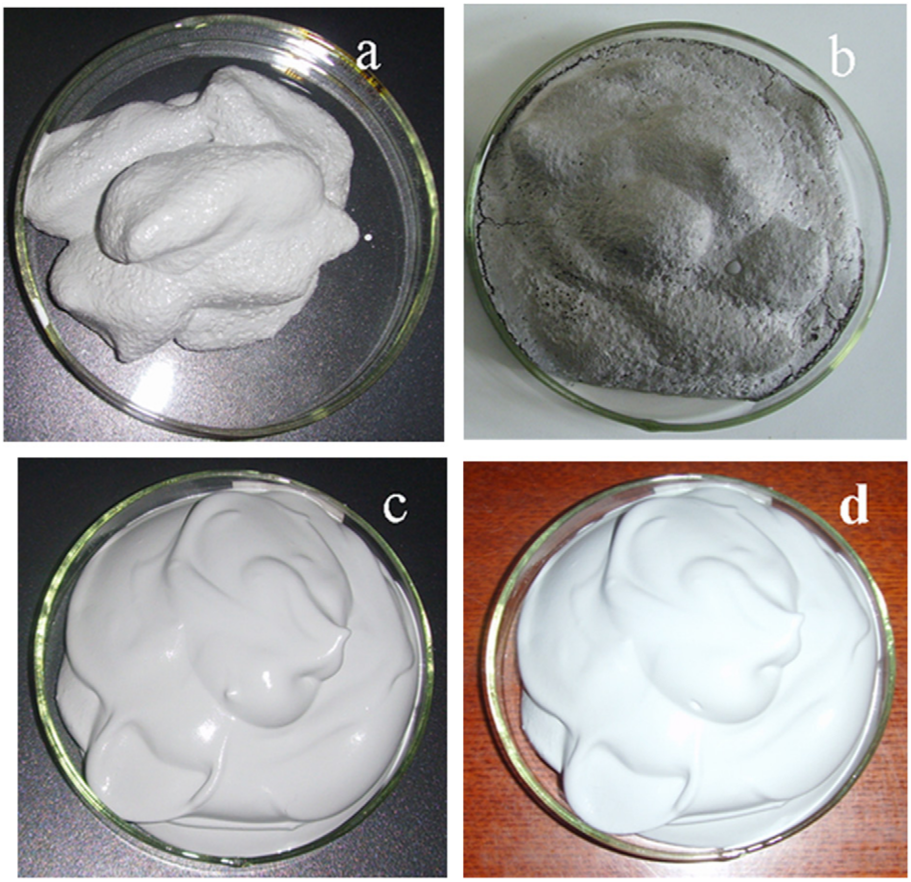

Fig. 3. Comparison of Si_3N_4 foams obtained by adding PVA ((a), (b)) and CMC ((c), (d)).

and gel in the bulk contribute to the enormous stability of the bubbles, and avoiding foam shrinkage.

3.4. The performances of Si_3N_4 foam ceramics produced by Si_3N_4 particle-stabilized foams

Fig. 5 shows the microstructures of sintered Si_3N_4 foam ceramics produced by particle-stabilized foams with PVA and CMC addition. Compared to the microstructure of Si_3N_4 foam ceramics produced by adding PVA, the pore size of foam ceramics produced with CMC is smaller, and the pore distribution is more uniform (see Fig. 5(b)).

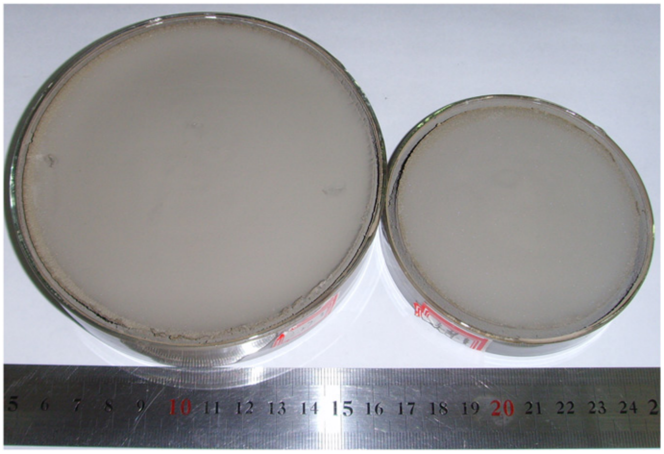

Fig. 4. Large size dried Si_3N_4 ceramic foams.

Fig. 6 shows the pore size distributions of sintered Si_3N_4 foam ceramics. In Fig. 6(a), the pore distribution of sintered Si_3N_4 foam ceramics produced by adding PVA exhibits three noticeable peaks of differential pore volume where pore diameters are 150.7 nm, 3902.8 nm and 11,884.3 nm, and the pore size centralizes mainly at 11884.3 nm, and this means that the pore distribution is very non-uniform. The median pore diameter is about 38.3 μm. Fig. 6(b) illustrates the pore distribution of Si_3N_4 foam ceramics produced by adding CMC. There is one peak of differential pore volume, which means that the pore distribution is very uniform, the median pore diameter shown here is about 10.1 μm, and the average pore size is about 16 μm.

As mentioned above, the addition of PVA cannot effectively prevent foams from coalescence (film rupture) and the Ostwald ripening (disproportionation)), and this finally results in the large pore size and non-uniform microstructures (see Figs. 5 and 6(a)) of Si_3N_4 foam ceramics. Reversely, CMC can effectively increase the stability of foam, and the stable foam structure can be kept throughout the preparation process of foam ceramics (foaming, drying and sintering, see Figs. 5 and 6(b)). Thus, the microstructures of Si_3N_4 foam ceramics are effectively improved by adding CMC.

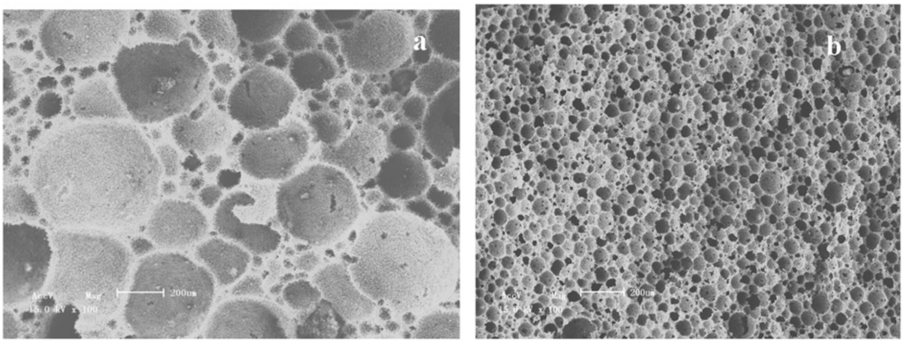

Fig. 5. Microstructures of Si_3N_4 foam ceramics by adding (a) PVA and (b) CMC.

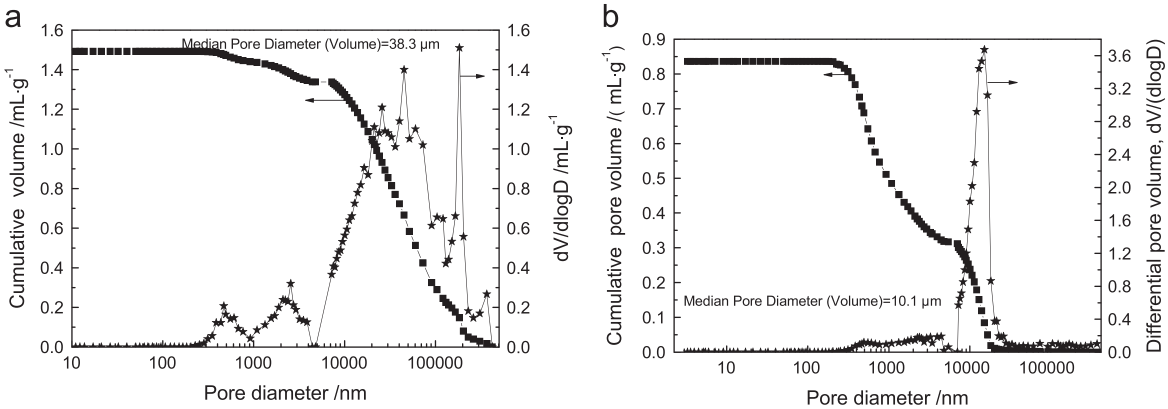

Fig. 6. Pore size distribution of sintered Si_3N_4 foam ceramics with (a) PVA and (b) CMC.

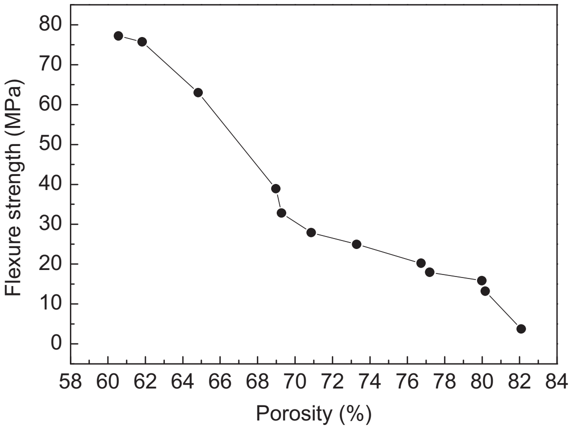

Fig. 7. Flexural strength and porosity of sintered Si_3N_4 foam ceramics.

Fig. 7 shows flexural strength and porosity of sintered Si_3N_4 foam ceramics by adding CMC. The results indicate that the flexural strength is in the range of 3.8–77.2 MPa when the porosity varies from 82.1% to 60.6%, and flexural strength monotonically decreases with the increase of porosity.

4. Conclusions

The effect of carboxymethyl cellulose (CMC) addition on Si_3N_4 foam ceramics preparation was investigated. The addition of CMC in water solution can reduce the surface tension; low surface tension is obtained by adding CMC and propyl gallate; the viscosity of slurry by adding CMC is greater than that of slurry by adding PVA, and this is conducive to increasing the stability of ceramic foams.

By adding CMC in foam slurry, it gains good fluidity. The foam ceramics have little shrinkage during drying obtained by adding CMC, the surface structure of dried foam is uniform, and there are no macropores and cracks. The sintered Si_3N_4 foam ceramics have very uniform pore distribution, the average pore size is about 16 μm, the flexure strength is as high as 3.8–77.2 MPa, and the porosity is about 60.6–82.1%.

Acknowledgments

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