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Preparation of high open porosity ceramic foams via direct foaming molded and dried at room temperature

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Abstract

Herein an alternative approach was considered for addressing one difficulty of ceramic foams that the foam slurry with a high content of bubbles which were obtained via direct foaming, cannot maintain well for a long time at room temperature. It is fascinating that the foam slurry mentioned above could stably mold and dry at room temperature, based on an animal protein as foaming agent, kaolin, talc powder and alumina as raw materials, alpha-tricalcium phosphate prepared via co-precipitation as curing agent, and hydrophobic activated carbon powders as stabilizing agent. Effects of the calcination temperatures, the contents of alpha-tricalcium phosphate and activated carbon powder on microstructures, crystal phases, compressive strength and open porosities of ceramic foams were studied systematically. The results indicated that ceramic foams with a high open porosity and uniform pore distribution and sizes sought for application in catalysts supports, could be produced by adjusting these parameters.

Keywords: Direct foaming; Alpha-tricalcium phosphate; Hydrophobic activated carbon powder; Room temperature drying

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1. Introduction

Ceramic foams, one of the most important materials, have been widely used in a range of fields, namely filters, catalysts supports and bone scaffolds, due to their characteristics of high permeability, high porosity and specific surface area.[1–3] In these extensive applications, microstructural features of ceramic foams, for instance, the morphology, porosity, and pore size, are crucial factors that dominate the functional properties of the final product. Ceramic foams were advantageous in terms of great property of low density,[4] controllable microstructure,[5–8] widely adjustable strength,[9,10] high temperature resistance[11,12] and chemically inert composition. Direct foaming which is one of the most versatile among the methods to fabricate ceramic foams, offers a simple, low-cost and effective way to produce ceramic foams by incorporation of air bubbles into a suspension of powders, and the pore structure of ceramic foams can be effectively controlled. However, the foam slurry cannot exist steadily for a long time at room temperature, derived from the thermodynamically unstable bubbles. Especially the foam slurry system with a high content of bubbles is prone to collapse and crack at room temperature, which will seriously affect the performance of the final product. To date, freeze drying[13,14] and gelfoaming[15] have been proposed to deal with the problem. However, freeze drying is not suitable for mass production, also with a shortcoming of high cost. Gelfoaming which uses a large number of organic monomers and crosslinking agents, suffers from high cost and environmentally hazardous behavior owing to the burning out of organics. In this work, a novel method was considered for addressing this difficulty. Ceramic foams with a high open porosity and uniform pore distribution and sizes, were prepared via direct foaming, based on an animal protein (cattle hoof shell protein) as foaming agent, kaolin, talc powders and alumina as raw materials, alpha-tricalcium phosphate (α-TCP) prepared via co-precipitation as curing agent, and hydrophobic activated carbon powder as stabilizing agent.

Among animal protein foaming agents, egg white protein (EWP)[16] and whey protein isolate (WPI)[17] are the most frequent. Problems arising in Europe in the 1990s, due to the presence of animals in the feed chain of beef cattle, have raised

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Table 1
The mass ratios of chemicals to synthesize cattle hoof shell foaming agent.

Chemicals	Mass ratios
Cattle hoof shell powder	63
Sodium bisulfite	2.5
Distilled water	630
Calcium oxide	6.7
Acetic acid	Several drops
Sodium dodecyl benzene sulfonate	7.8
Triethanolamine	3.2

socio-economic concerns and questions regarding the use of the blood collected in slaughterhouses.[18] Remadnia et al.[18] has used atomized bovine hemoglobin derived from animal blood as foaming agent to manufacture cementitious concrete composites. However, it is rarely reported that cattle hoof shell was used as a foaming agent to prepare ceramic foams. Concerning a foam stabilizing agent, particles are the most popular.[8,19–21] Vivaldini et al.[19] has analyzed why foams containing colloidal hydrophilic particles are unstable, and Mishra et al.[21] has prepared porous silica tiles, involving the use of partially hydrophobized silica powder particles for stabilization of foams. To the best of our knowledge, hydrophobic activated carbon powder was firstly used in the present work as a foam stabilizing agent.

2. Experimental

2.1. Synthesis of cattle hoof shell foaming agent

The cattle hoof shells were immersed and boiled in dilute alkali solution for 4 h, and then dried in an oven for 24 h at 60 °C. The previously dried samples were crushed, followed by ball-milling for 12 h with a rotational speed of 180 rpm and a medium of zirconium ball to aim powder particles with ca. 10 μm in diameter. To produce the liquid of protein foaming agent, $NaHSO_3$ and cattle hoof shell powders were added to distilled water at 80 °C for 4 h. The temperature was controlled by a water bath. Then the reaction mixture was heat-treated for 6 h at 100 °C after the addition of CaO. After that, the mixture was cooled and filtered, following acetic acid was added to adjust pH to 7. Finally, sodium dodecyl benzene sulfonate and triethanolamine were added to the solution, stirred gently. Table 1 summarizes the mass ratios of chemicals to synthesize cattle hoof shell foaming agent.

2.2. Preparation of alpha-tricalcium phosphate (α-TCP)

Alpha-tricalcium phosphate (α-TCP) was prepared via co-precipitation by controlling Ca/P in molar ratio 3/2. A solution of $Ca(NO_3)_2 4H_2O$ was slowly added to the mixed solution of NH_4HCO_3 and $(NH_4)_2HPO_4$ at a water bath 37 °C, followed by using concentrated ammonia water to adjust pH to 7. Presoma powders were obtained after vacuum filtration, washing the precipitate exhaustively with anhydrous ethanol, and drying. The presoma powders were firstly calcined at 1260 °C for 1 h and then taken out from the furnace immediately, following simultaneously agitated to cool down to room temperature. Eventually, fine particles of α-TCP were produced by planetary ball milling for 3 h with a rotational speed of 180 rpm and media of anhydrous ethanol and zirconium ball.

2.3. Fabrication of ceramic foams

The mixture of kaolin, talc powders and alumina, α-TCP and activated carbon powders were mixed uniformly in the proportions given in Table 2. Then a certain amount of polyvinyl alcohol (PVA, 1788 ± 50) solution and a mixed solution which consisted of Na_2HPO_4, NaH_2PO_4 and citric acid, were added to gain ceramic slurry, following stirred evenly. Foams were prepared with cattle hoof shell foaming agent and distilled water via direct foaming. Ceramic foam slurry system was obtained by adding ceramic slurry to foams, agitated homogeneously. Subsequently, ceramic foam slurry was poured into a cylindrical mold which was coated a fine layer of petrolatum previously, to form a cylinder-shaped, followed by drying at room temperature to gain ceramic foam green body. The samples were demolded during the drying process. The calcinations of ceramic foam green bodies were carried out at 1050–1150 °C with 25 °C in interval for 2 h in air, followed by cooling down to room temperature in furnace. The weight/volume details of chemicals to fabricate ceramic foams are shown in Table 2. During the suspension preparation, some points deserved to be mentioned are given below.

Alpha-tricalcium phosphate was chosen for curing agent based on our previous work.[22] A mixed solution of Na_2HPO_4, NaH_2PO_4 and citric acid was added to promote the hydration reaction of α-TCP. Consulting the reports[8,19–21] that particles have been used as foam stabilizing agents, the hydrophobic activated carbon powder was used as a foam stabilizing agent owing to its advantages of hydrophobicity, low density, porous surface

Table 2
The weight/volume details of chemicals to fabricate ceramic foams.

Chemicals	Solid weights (wt.%)/Liquid volumes (vol.%)	Ratios/concentrations
α-TCP	3, 5, 10, 15, 20	
Activated carbon powders	3, 5, 10, 15, 20	
Kaolin, talc powder and alumina	$100 - W_{\alpha\text{-TCP}} - W_C$	In mass ratios 19/8/3
Polyvinyl alcohol (PVA) solution	36.35	9.1 wt.%
Mixture of Na_2HPO_4, NaH_2PO_4 and citric acid solution	36.35	0.2 M, 0.2 M and 6.7 wt.%, respectively
Cattle hoof shell foaming agent	9.1	
Distilled water	18.2	

$W_s/V_l = 15/11$, where, W_s, V_l is the total weight of the solids (g), the total volume of the liquids (ml), respectively.