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Effect of valeric acid on the agglomeration of zirconia particles and effects of the sintering temperature on the strut wall thickness of particle-stabilized foam

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Abstract

Highly porous zirconia ceramics were prepared utilizing a particle-stabilized direct foaming technique in which the hydrophilic characteristic of zirconia particles was altered by the in situ adsorption of valeric acid on its surface. These surface modified zirconia particles are irreversibility adsorbed at the air/water interface and create an armor coating around the bubbles to stabilize them. In this study, the foamability and stability of zirconia foam were investigated by varying the valeric acid concentration, and zirconia foam with a foam volume of approximately four times the colloidal system volume was successfully prepared. The sintered foam has cell size ranging from 50 to 150 μm and the pore structure was characterized by mercury porosimetry. The effects of the sintering temperature on the grain size, strut wall thickness, and tetragonal phase were studied and correlated with an increase in the mechanical strength to 3.5 MPa with porosity of more than 90%.

Keywords: Particle-stabilized foams; Porous ceramics; Zirconia foam; Colloidal chemistry

1. Introduction

Macroporous ceramics with a tailored pore structure are versatile materials, which offer a wide range of applications, including high temperature filtration,[1] orthopedic implants,[2] thermal insulations,[3] supports for catalytic reactions[4] and diesel particulate filters.[5] Several techniques for manufacturing macroporous ceramics have been investigated by many researchers such as replica, sacrificial templates and direct foaming methods.[6] Among ceramics, zirconia is one of the best engineering ceramics, but the use of pure zirconia is limited by its spontaneous phase transformation from tetragonal to monoclinic upon cooling at temperatures between 1200 °C and 1000 °C. To avoid this phase transformation, the crystal structure of zirconia can be retained as tetragonal at room temperature with an addition of 3 mol% yttria. This is referred to as partially stabilized zirconia (PSZ). PSZ is one of the ceramics, which has been used for advanced and structural applications such as solid oxide fuel cells,[7] in orthopedic applications due to its biocompatibility,[8] and as oxygen sensors and high temperature pH sensors[9] due to its high ionic conductivity and thermal stability. PSZ exhibits good strength and fracture toughness due to the stress induced phase transformation from the tetragonal to monoclinic phase.[10]

In recent years, several researchers have investigated the preparation of porous zirconia ceramics by various processing routes. Kroll et al.[11,12] developed highly efficient enzyme functionalized porous zirconia microtubes for bacteria filtration in water treatment. Lashtabeg et al.[13] studied the synthesis of macroporous YSZ using polystyrene spheres as templates and the effects of sintering temperatures on pore size, particle size and pore wall thickness were examined, whereas Hu et al.[14] proposed a novel decompress freezing process for the ultra-high porosity of zirconia ceramics and attained a porosity of more than 93%. Recently Liu et al.[15] used mono-dispersed PMMA micro-balls as a pore forming agent and studied the properties

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of porous YSZ foams. The particle-stabilized direct foaming method is an easy, inexpensive and rapid method for preparing highly porous ceramics with open or closed pores.[6] In this technique, ceramic particles are in situ partially hydrophobized by adsorbing a short chain surfactant on their surfaces after which air bubbles are incorporated into the ceramic suspension. These partially hydrophobic particles are irreversibly adsorbed at the air/water interface, and the stability of the wet foam is attributed to this adsorption. Gonzenbach et al.[16–18] was the first who used short chain amphiphile with an aim of the in situ hydrophobization of originally hydrophilic ceramic particles in an aqueous solution, and his work triggered many studies of particle-stabilized foams using different ceramic systems.[19–22]

Previously, we elucidated the effect of the process conditions on the microstructure of particle-stabilized alumina foam by varying the valeric acid concentration, solid loading and stirring speed.[23] Afterward, we successfully manufactured zirconia toughened alumina (ZTA) foam with ultra-low density using a particle-stabilized direct foaming technique.[24] Although colloidal particles have been widely used for foam stabilization purposes,[19–22] no one has reported zirconia foam prepared using valeric acid as an amphiphile. The aim of this study was to manufacture ultra-low density zirconia foam via a direct foaming technique and the in situ hydrophobization of particles using valeric acid. The effect of the valeric acid was fully exploited on the foamability and foam stability. In addition, the effects of the sintering temperature on the strut wall thickness, grain size and the presence of tetragonal phase were investigated. These effects on the compressive strength of ultra-low density foam are also discussed.

2. Experimental procedure

Commercially available zirconia (doped with 3 mol% yttria, LOT Number 120212, Heshan Huawang Zirconium Materials Co. Ltd., China) having an average particle size of 0.15 μm and a BET surface area of 9.31 m^2/g was used for the synthesis of the zirconia foam. Initially, aqueous colloidal suspensions were prepared with 50 vol% solid loading and 2 N HCl was used for the electrostatic dispersion of the particles. This was followed by ball milling for 24 h with a rotational speed of 60 rpm. Zirconia balls having a diameter of 5 mm were used as a grinding media and ball to powder volume ratio was 2:1. After the ball milling process, valeric acid (99% pure, LOT Number 78097MJV, Sigma–Aldrich, USA) was diluted in water to obtain a final solid loading of 35 vol% and was added drop wise for the in situ hydrophobization of the zirconia particles. The final pH of the slurry was adjusted to 4.7 with the help of 1 N NaOH solution and foaming was carried out for 5 min using a direct driven digital stirrer (Model SL1000D, Voltage AC 220 V, Wattage DC 50 W, Global Lab, Korea) at a speed of 1000 rpm. The specimens were prepared by using perspex molds having a diameter of 50 mm and height 80 mm, followed by drying for 24 h in humidity and temperature controlled chamber at 20 °C with the humidity set to 90%. After 24 h, the temperature was increased to 30 °C under the same humidity conditions and kept under this condition for further 24 h. After drying the specimens, sintering was carried out at 1480, 1530, and 1580 °C at a heating rate of 1 °C/min and a dwell time of 2 h.

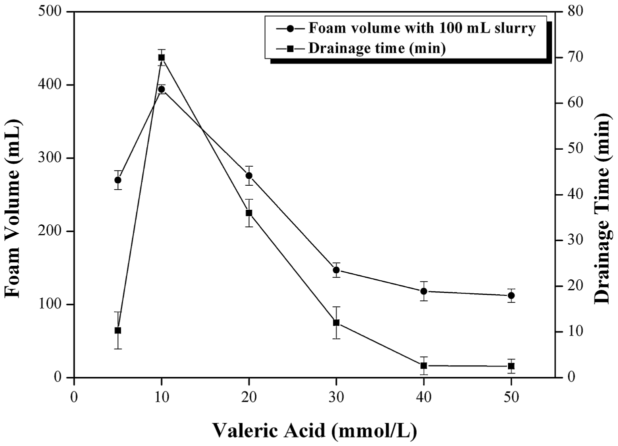

Fig. 1. Foam volume and drainage time of zirconia foam prepared with 35 vol% solid loading as a function of the valeric acid concentration.

The IEP of zirconia powder was determined by measuring the zeta potential at different pH using Beckman Coulter Delsa™ Nano C Particle analyzer, USA. For the zeta potential measurement, dilute suspensions containing 0.2 g/L of zirconia particles were prepared in distilled water and their pH was adjusted using diluted NaOH and HCl solutions. The pH of the dilute zirconia suspensions was varied from 4 to 11 and measured by using a pH meter (Mettler Toledo, InLab® Expert Pro, USA). The volume of the zirconia foam was measured with a volume of 100 mL of slurry, which is referred to as foamability. After foaming process, the foam was transferred to a graduated container and foam volume was measured. Foamability refers to how easily foam is formed and it measures the ability of a colloidal system to form a foam in the presence of in situ partially hydrophobized particles. To investigate the stability, foams were immediately transferred to a graduated glass cylinder and the time needed for 5 mL of liquid to drain from 50 mL of foam was recorded to evaluate the foam stability; this measured time is called the drainage time. The ability of foam to withstand a spontaneous collapse or breakdown from external/internal causes is denoted the foam stability. The microstructures of fractured surfaces of specimens were observed using SEM (JSM-5800, JEOL, Tokyo, Japan), and the average grain size and cell size of the sintered foams were analyzed using the ‘Image J’ software package. The pore size distribution and cumulative pore area of the sintered foams were measured using mercury porosimetry (AutoPore IV9510, Micromeritics USA). The bulk density of the resulting ceramic foam was calculated from the mass-to-volume ratio of the specimens. The porosity was determined from the bulk density to the theoretical density ratio. For a compression test, five specimens of each composition with dimensions of 10 mm × 10 mm × 10 mm were prepared. The compression test was carried out using a universal testing machine (Model 4206, Instron Corporation, USA) with a crosshead speed of 0.5 mm/s. The XRD patterns were determined to identify the phases by means of an X-ray diffractometer (D/max-2200 PC, Rigaku Co. Ltd., Tokyo, Japan) operated at 40 kV and 30 mA with a