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Short communication

# Annealing effects on the pore structures and mechanical properties of porous alumina via directional freeze-casting

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ABSTRACT

The effects of the annealing methods and annealing temperatures on the pore structures and mechanical properties of porous alumina were investigated. The amorphisation behavior and solidification behavior of the sucrose solutions during annealing were discussed. The pore morphology of porous alumina changed noticeably after uniform annealing. As annealing temperature increased from −25 °C to −5 °C, the pore morphology of porous alumina changed gradually from irregular lamellar channels to circular channels. After directional annealing, the pore morphology of porous alumina was similar to that after uniform annealing; however, the uniformity of pore channels and the density of pore walls were increased. During directional annealing at −15°C, the compressive strength of porous alumina reached 58.8 MPa, which was 35% higher than that of unannealed porous alumina.

## 1. Introduction

Porous ceramics prepared via freeze-casting can achieve higher compressive strength than porous ceramics prepared using other methods because of their directional pore channels [1,2]. The former has a wide range of applications in bone implant materials, high-temperature filtration, and fuel cells [3,4]. The mechanical properties of this type of porous ceramics mainly depend on their porosity, pore size, and pore distribution [5,6]. Porosity is primarily determined based on the solid content of the slurry [7], whereas pore size and pore distribution are closely related to the preparation process [8,9]. At present, many studies have focused on controlling the pore size and pore distribution of porous ceramics [10–12], such as by inducing the electric field and magnetic field in the freeze-casting process [13,14] and by adding inorganic salts and glycerol to the slurry [15,16]. Changing the freezing temperature is the most effective means to adjust the pore size of porous ceramics [17]. The supercooling degree of the slurry and the nucleation ratio increase as freezing temperature decreases, and thus, small directional crystals can be obtained [18]. However, certain solvents are crystallized in situ instead of demonstrating directional growth when the freezing temperature is too low [19], which decreases the porosity of porous ceramics.

In the pharmaceutical field, ice crystals that formed during the freezing process of the liquid exhibit different shapes and uneven size and distribution, thereby resulting in considerable flow resistance during the drying process and low drying efficiency [20]. To solve the above-mentioned problems, a sucrose solution was used and the annealing process was performed before drying. In this manner, the drying rate can be improved because annealing can change the morphology and distribution of ice crystals, and consequently, the morphology of the amorphous matrix [21,22]. Annealing is also used to eliminate residual stress, reduce deformation and crack tendency, and refine grains during metal heat treatment [23]. Therefore, if the annealing process is introduced into the freeze-casting process to fabricate porous ceramics, then the morphology of solvent crystals can be changed, thereby changing the pore structure and mechanical properties of porous ceramics.

In the current study, sucrose solutions were used as the freezing medium for the alumina slurry. The frozen slurry was annealed after directional freezing, which led to the softening and redistribution of the sucrose solutions. Consequently, the pore structure of the porous alumina was changed. The effects of the annealing methods and annealing temperatures on the pore structures and mechanical properties of porous alumina were investigated. The amorphisation behavior and solidification behavior of the sucrose solutions during annealing was discussed. The compressive strength of porous alumina was also tested. The result of this study provides an important reference for improving the mechanical properties of porous ceramics.

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## 2. Experimental procedures

### *2.1. Materials and methods*

Alumina powder (GW-1, Zhengzhou Dengfeng Materials Co. Ltd., Zhengzhou, China) was used as the starting material, and distilled water was used as the freezing medium. Sucrose (AR, Alfa Aesar, Massachusetts, U.S.) was used as the additive for annealing. Carboxymethyl cellulose (CMC, Tianjin Fuchen Chemical Reagents Factory, Tianjin, China) and sodium polyacrylate (PAAS, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as the binder and dispersant, respectively.

Alumina powder was mixed with 2 wt.% PAAS, 1 wt.% CMC, and 20 wt.% sucrose in distilled water. Then, the resulting mixture was ground with a ball mill for 24 h to obtain alumina slurry (with a solid content of 20 vol.%). The slurry was injected into cylindrical molds and frozen directionally using a −75 °C cold source for 3 h. After the slurry was completely frozen, it was annealed at −5 °C, −15 °C, and −25 °C, and then refrozen at −75 °C. The refrozen slurry was dried in a freeze-dryer (TRID 2.5 L, LABCONCO FreeZone®, Kansas, U.S.) for 24 h. Finally, porous alumina was obtained after being sintered at 1600 °C for 2 h. The heating and cooling rates were 5 °C/min.

Sucrose is a non-reductive disaccharide that exhibits amorphous transition but not crystallization during cooling. It is an effective, and in fact, the most commonly used protective agent for freeze-drying [24]. The amorphous transition temperature ($T_g'$) of sucrose solution is −32.5 °C [20], and the annealing temperature is generally higher than $T_g'$. Accordingly, −5 °C, −15 °C, and −25 °C were selectedas the annealing temperatures in this study. Annealing methods were divided into uniform annealing and directional annealing (Fig. 1). In uniform annealing, the frozen slurry was sealed and then placed in a liquid cold source (i.e., low-temperature ethanol) for annealing and refreezing. In directional annealing, annealing and refreezing were directed from the cold source toward the top.

### *2.2. Characterization*

The morphology of porous alumina was characterized using a scanning electron microscope (JSM 6390 A, JEOL, Japan). The lamellar spaces of porous alumina were determined by measuring the cross-section of the samples in the SEM images with SmileView (Software, JEOL, Japan). A total of 100 pore channels were tested in this manner to obtain the lamellar spacing distribution. Viscosities of the saturated sucrose solution with different freezing temperature were measured with a viscometer (SNB-2, Shanghai Nirun Intelligent Technology Co., Ltd., Shanghai, China). A differential thermal analyzer (DSC-204, NETZSCH, Germany) was used to measure the thermal changes of the ceramic slurry with the sucrose solution during the freezing and annealing processes. The heating and cooling rates were 1 °C/min under the protection of argon. The open porosity of porous alumina was measured based on the standard ASTM C20 (Standard Test Methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick). The compressive strength of porous alumina was measured on cylindrical samples with Φ7 × 11 mm using a computer servo to control the material testing machine (HT-2402-100KN, Hungta, Taiwan). Ten samples were tested to obtain an average value.

## 3. Results and discussion

When the frozen slurry was heated to over $T_g'$ for annealing, the molecules in the vitreous body could be moved and rotated. Amorphous transition occurred from a non-equilibrium glass state to a softened state [25]. The mobility of molecules increased with an increase in temperature. After refreezing, the softening part was refrozen, but the structure was rearranged. A liquid cold source was used for uniform annealing. The morphologies of porous alumina obtained at different annealing temperatures are shown in Fig. 2. When the annealing temperature was −25 °C, lamellar pore channels were maintained, but several large channels were observed. The lamellar spaces between pore walls were uneven, and a large number of small pores were distributed between lamellar channels from the longitudinal section (Fig. 2d–f). Viscosities of the saturated sucrose solution with different freezing temperature were measured (Fig. 3). The sucrose solution showed a rubbery state and no fluidity when the temperature below −20 °C, and the viscosity value could not be performed. After continuously heated to −15 °C, the rubbery state was changed to viscous state. The deformation of the sucrose molecular was gradually increased with fluidity. The viscosity of the sucrose solution was 1681 mPa·s. The viscosity was reduced to 194.5 mPa s at −5 °C. The viscosity of sucrose solution was decreased with the increasing temperature in annealing. Therefore, it is inferred that the softening degree and fluidity of alumina frozen body were increased with the high temperature. Sucrose molecules were easy redistribute in melting state and changing the pore morphology in high annealing temperatures. The annealing temperature at −25 °C was close to $T_g'$, the viscosity of the softened amorphous body was high (unable to be measured), and molecular activity was limited. Inadequate annealing caused the softening part to gather only near the original position. After refreezing, several large frozen bodies were formed. When the annealing temperature was −15 °C, small and uniform lamellar pores (about 20 μm) were observed and several bridges were found in the pore channels. The mobility of sucrose molecules was increased, and annealing was sufficient. The decreased viscosity of the softened sucrose solution was beneficial for redistribution. When the annealing temperature was increased to −5 °C, the pore size of porous alumina was evidently increased to about 40 μm, and some of the pores were circular. The viscosity of the softened sucrose solution was low (194.5 mPa·s), molecular mobility was active, and the driving force of diffusion was increased. After refreezing, circular pores were formed due to the minimum surface

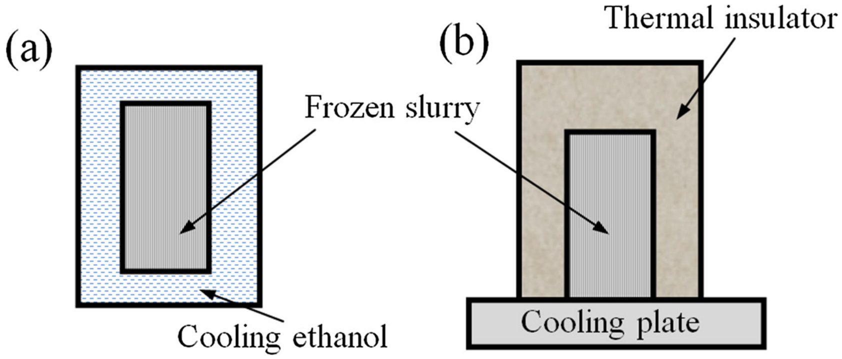

**Fig. 1.** Schematic of annealing methods for slurries with sucrose solutions after freezing: (a) uniform annealing and (b) directional annealing.