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Fabrication of ice-templated tubes by rotational freezing: Microstructure, strength, and permeability

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ABSTRACT

We demonstrate a facile and scalable technique, rotational freezing, to produce porous tubular ceramic supports with radially aligned porosity. The method is based on a conventional ice-templating process in a rotatory mold and demonstrated here with yttria-stabilized zirconia (YSZ). We investigated the effects of solid loading, freezing temperature, and volume of the slurry on the microstructure, strength (o-ring test and four-point bending), and air permeability. The results show that pore volume and pore size can be controlled by the solid loading and freezing temperature respectively, and overall tube thickness can be adjusted by the volume of slurry initially poured into the mold. Decreasing pore size and pore volume increases the mechanical properties but decreases the air permeability. These tubes could be particularly interesting as tubular membrane supports such as oxygen transport membranes.

1. Introduction

Porous ceramic membranes are increasingly used in technologically important applications such as energy production (solid oxide fuel cells, oxygen and proton transport membranes) [1–4], solid-liquid filtration [5,6], and gas separation [7]. These membranes usually have an asymmetric configuration where a membrane layer is deposited on top of a porous substrate. The membrane layer provides the selectivity required for the process, while the porous support provides the mechanical stability. Besides strength, porous supports must also exhibit a high permeability to facilitate the evacuation of the fluid and thus minimize detrimental effects such as concentration polarization or exaggerated pressure gradients that compromise the overall performance of the membrane [8].

Typically, tubular porous substrates are prepared by extrusion [9,10], slip casting [11], centrifugal casting [12], or isostatic pressing [13]. However, these techniques rely on increasing the total pore volume and pore size to achieve the required permeability at the expense of mechanical properties. Therefore, it is necessary to explore other strategies such as an optimized pore shape or reduced tortuosity to simultaneously improve permeability and strength.

Nowadays, the method to obtain unidirectional macroporous materials most conventionally used is extrusion. However due to technical limitations is not possible to produce materials with a high pore volume content (>50%) and reduce the pore size below 100 μm [14]. On the other hand, direct replication of wood has successfully been demonstrated as a feasible technique, although the large number of steps and the microstructural variability among samples remain as important drawbacks to overcome. Alternatively, in the last decade ice-templating (or freeze-casting) has emerged as a popular shaping route to produce macroporous materials with a tailored pore morphology and aligned porosity. The technique is based on the freezing of a colloidal suspension and the segregation of ceramic particles between the crystals. Afterwards, the solvent crystals are removed by sublimation and the green body is sintered to consolidate the structure. The final porosity is thus a direct replica of the solvent crystals [15].

The mechanical and gas flow properties of ice-templated monoliths have been extensively evaluated [16–24]. However the literature on ice-templated tubes is scarce. Moon et al. [25] used an external metallic mold with a central PTFE rod to induce the thermal gradient required to align the porosity. They studied the effect of solids loading and freezing temperature on the microstructure and the feasibility of depositing an external dense layer. Liu et al. [26] used a similar set-up to evaluate the impact of solids loading, pore size, and particle size on compressive strength, nitrogen flux, and water flux. However, the difficulties demolding the tubes after

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solidification is drawback of this set-up that limits further industrial development. Moon et al. [27] overcomes this issue combining ice-templating with co-extrusion, however the resultant porosity is not radially aligned.

In this work, we propose a novel method based on a rotational freezing to produce ice-templated tubes. We investigate the impact of pore volume, size, and tube thickness on mechanical properties using an o-ring test and four-point bending. Furthermore, we studied the effect of the same morphological parameters on permeability to assess the applicability of these materials as a membrane supports.

2. Experimental procedure

2.1. Sample preparation

Ceramic suspensions were prepared by mixing distilled water with 0.75 wt.% of dispersant (Prox B03, Synthron, Levallois-Paris, France), 3 wt.% of organic binder PVA (PVA2810, Wacker, Burghausen, Germany), and 3 mol% yttria-stabilized zirconia (TZ-3YS, Tosoh, Tokyo, Japan). All the percentages are referred to the total solids loading of the slurry. After a first mixing step with a magnetic stirrer, the slurry was ball milled at 800 rpm for a minimum of 18 h to ensure a good homogenization. Afterwards, it was deaired during 10 min and poured in a tubular cooper mold.

The set-up used to ice-template tubes consists of a cryothermostat (Model CC 905,Hubert, Offenburg, Germany), freezing liquid (SilOil M90.055.03, Hubert, Offenburg, Germany), metallic container, tube-shape mold, and a rotating system. The tube filled with slurry was attached to the rotational clamp and the speed set at 70 rpm. The silicon oil was pumped in the container with a preset temperature (−80 °C or −30 °C) until it achieved a steady flow. The system was left under rotational freezing for a minimum of 5 min. The next steps were similar to the regular ice-templating process and detailed elsewhere [17]: demoulding, freeze-drying (Free Zone 2.5 Plus, Labconco, Kansas City, Missouri, USA), and sintering. Tubular specimens were sintered in air at 1400 °C for 3 h with a heating and cooling rate of 5 °C/min. A previous step at 500 °C for 5 h with the same heating rate was used to ensure a proper organic burn-out.

The process was repeated with variations of the solid loading of the initial slurry (50 wt.%, 55 wt.%, and 65 wt.%), temperature of the freezing liquid (−30 °C and −80 °C), and volume of slurry initially poured into the mold (16, 18, and 20 ml). The final dimensions of the tubes in all tested conditions were: 150 mm length (L) and 10 mm of external diameter (D_{ext}).

2.2. Sample characterization

Micrographs of the ice-templated tubes were taken with a scanning electron microscope (Nova NanoSEM 230, FEI, Hillsboro, USA) at 10–15 kV. Total pore volume P(%) was calculated based on the relative density measured geometrically with respect to that of fully dense TZ-3YS (ρ_{ysz} = 5.8 g cm^{-3}). P(%) measurements were performed in a minimum of five rings per tube, and two tubes per condition. The average pore size was measured by mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics, Norcross, USA) with an applied pressure up to 0.31 bar.

Mechanical properties of ice-templated tubes were characterized by two different tests: (1) four-point bending on half tubes, and (2) o-ring test. All the experiments were conducted with a universal testing machine (Shimadzu model AGSX, Kyoto, Japan), equipped with a 10 kN load cell at a crosshead speed of 0.2 mm/min.

1 Samples were cut with a slow-speed saw first in the radial direction and then in the longitudinal direction with a final length (L) ≥ 55 mm, and external diameter (D_{ext}) = 10 mm. The spacing between the outer supports was adjusted to S_1 = 40 mm whereas the span between the inner supports was S_2 = 20 mm. A minimum of three samples per condition were tested.

The maximum stress (σ_{max}) at the middle point between the two inner supports was calculated based on the approximation proposed by Kwok et al. [28]. Tests were considered invalid when the crack propagated outside the inner supports. When the test crack pattern resulted in a successful test, the maximum stress was calculated by:

$$\sigma_{\max} = \frac{Pay_c}{I} \quad (1)$$

where P is the maximum load, a is the distance between the load and the support, y_c is the distance between the middle point and the centroid of the specimen cross section along the radial direction, and I is the second moment of inertia of the cross section. For a semi-circular annulus, y_c and I are expressed as:

$$y_c = R - \frac{4}{3\pi}\frac{R^3 - {R_i}^3}{R^2 - {R_i}^2} \quad (2)$$

and

$$I = \frac{\pi}{8}(R^4 - {R_i}^4) - \frac{8}{9\pi}\frac{(R^3 - {R_i}^3)^2}{R^2 - {R_i}^2} \quad (3)$$

where R and R_{int} are the external and internal radius respectively.

2 Eight tubes were sliced in the radial direction with a slow-speed saw leaving specimens with an external diameter (D_{ext}) = 10 mm, height (h) = 4 mm, and ring thickness (t) ≈ 2 mm. Tests were performed with a piece of alumina supporting the samples to avoid the rotation and distribute evenly the load through the surface.

The maximum stress (σ_{max}) is located on the inner diameter of the ring and was determined by:

$$\sigma_{\max} = 1,8\frac{Pr_a}{ht}\left(1 + \frac{t}{3r_a}\right) \quad (4)$$

where P is the maximum load, t the tube thickness, h the width of the ring, and r_a the average radius $(r_{ext} - r_{int})/2$.

Gas permeability was evaluated using custom built equipment to measure the air pressure drop across the tubes. A preliminary test was performed to assess the tightness of the system. Synthetic air was passed through the tubular samples which were held by a silicon ring. The specimens exhibited one closed side, 120 mm length (L), and 10 mm external diameter (D_{ext}). The air flow studied ranged between 0 and 25,000 ml/min (0–0.25 m/s) and was controlled by an electrovalve. Two sensors were placed before and after the tube to record the inlet (P_i) and outlet pressure (P_o).

3. Results and discussion

3.1. Microstructure control

Fig. 1 schematically depicts the process that occurs during the rotational freezing. First, the tube rotation spreads the slurry evenly across the inner surface of the mold. Then, the freezing oil is pumped into the container and the slurry in contact with the mold solidifies almost instantly. The freezing rate at this initial stage is very high due to the high heat transfer between the copper mold and the slurry. Afterwards, the velocity of the solidification front undergoes an abrupt decrease, until it reaches a steady rate.

The ice-templated tubes exhibited two different pore morphologies, random (area in contact with the copper mold) and lamellar porosity, similarly to that reported in unidirectional frozen ice-templated monoliths [29]. The external layer with random porosity is generated when the velocity of the solidification front is too high