Ceramics International 43 (2017) 16283–16291

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Macro-porous dolomite hollow fibers sintered at different temperatures toward widened applications

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ARTICLE INFO

Keywords:
Membrane
Ceramic
Phase inversion
Dolomite
Hollow fiber

ABSTRACT

Ceramic hollow fibers from natural dolomite with different pore structures have been designed. The unique hollow fibers were produced by the phase inversion method and applying different sintering temperatures. The hollow fiber precursor presented coagulated polymers through the fiber thickness due to the high granulometric size of the used dolomite material (11.3–47.2 μm). The fiber sintered at 400 °C presented mechanical strength of 4.5 MPa and water permeability of 84.7 $L\,h^{-1}\,m^{-2}\,kPa^{-1}$. The increase in the sintering temperature up to 1250 °C resulted in fragile hollow fibers due to dolomite transformations that resulted in gas release and a significant mass loss of 33.7%. At 1350 °C, the liquid phase sintering mechanism occurred and the dolomite hollow fiber sintered at 1350 °C presented mechanical strength of 5.5 MPa and water permeability of 2219 $L\,h^{-1}\,m^{-2}\,kPa^{-1}$. Doloma dissolution in water was investigated and calcium concentration was increased from 0.72 (pure water) to 2.905 ppm for a contact time from 4 h between the fiber sintered at 1250 °C and pure water. However, this dissolution did not decrease the mechanical resistance of the fiber. These results suggest the potential of applying natural dolomite for producing low cost membranes or substrates. The hollow fiber sintered at 400 °C is suggested to be used as a proper separation medium, while the hollow fiber sintered at 1350 °C may be used as a substrate for the deposition of a separation layer to be used in gas separations. The high porosity of the fiber sintered at 1250 °C suggests its application as a support for the impregnation of functional materials. Thus, depending on the applied sintering temperature the dolomite membrane can be used in different applications.

1. Introduction

Porous inorganic membranes have been suggested for several applications mainly due to their advantages regarding to the membrane material that ensures better thermal, chemical and mechanical resistances compared to polymeric membranes. However, the high cost of the ceramic material (oxide-based materials) and the complexity of the membrane preparation process represent some drawbacks for the widespread use of ceramic membranes. In this sense, several studies have been recently presented to propose low cost materials based on minerals and industrial wastes for the production of inorganic membranes [1–9]. The use of these materials also enables the possibility of applying sintering temperatures lower than 1500 °C that are normally used to alumina-based membranes.

The material used for the membrane fabrication should ensure the required membrane properties in terms of mechanical resistance, permeability and selectivity. Dolomite is a mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$) with varied amounts of impurities including SiO_2, Al_2O_3 and Fe_2O_3. This mineral is used as refractory brick, for magnesia production, as an ingredient in the production of glass, bricks, and ceramics, and in several other applications [10]. Dolomite decomposition occurs from 900 °C, in which a mixture of CaO and MgO (doloma) is produced with CO_2 liberation. Due to this release of CO_2, Liu et al. [11] and Zhou et al. [12] proposed the incorporation of dolomite into coal fly ash and kaolin, respectively, to improve the membrane porosity. However, the use of pure dolomite for the production of ceramic membranes was not yet reported. The effect of the applied sintering temperature on the characteristics of the based-dolomite membrane should be investigated since the material is susceptible of several transformations under heating treatment, including the gas release and the liquid phase sintering mechanism [13].

Ceramic membranes can be fabricated by different methods including slip casting and extrusion, but these methods result in a limited range of structures. As well as polymeric membranes, ceramic hollow

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http://dx.doi.org/10.1016/j.ceramint.2017.08.214
Received 7 July 2017; Received in revised form 30 August 2017; Accepted 31 August 2017
Available online 05 September 2017
0272-8842/

fibers can also be produced by the phase inversion method, in which the asymmetric pore size distribution is obtained in one-stage [14]. Additionally, ceramic membranes can be configured in the hollow fiber geometry, which presents the main advantage of improving the membrane area related to the filtration module volume.

In order to tackle the challenge of producing low cost inorganic membranes for broadened applications, we propose the fabrication of ceramic hollow fibers by the phase-inversion method using natural dolomite powder as raw material. The effect of applying different sintering temperatures (400, 1250 and 1350 °C) on the membrane properties was evaluated so that hollow fibers sintered at different temperature may be toward different applications. For the dolomite hollow fiber membranes, the lower temperature of 400 °C was selected in order to observe the effect of achieving the polymer melting point. The other temperatures (1250 and 1350 °C) were selected to observe the membrane characteristics as consequence of dolomite phase changes. Pure alumina hollow fibers were also produced for comparisons.

2. Material and methods

2.1. Material

Dolomite powder was supplied by HMX Chemical Specialties (Brazil). Aluminum oxide powder (alumina, Al_2O_3, alpha-phase, 99.9% (metal basis), surface area 6–8 $m^2 g^{-1}$) with particle size lower than 1 μm were purchased from Alfa Aesar. Polyethersulfone (PESf, Verdal 3000P, Solvay), dimethyl sulfoxide (DMSO, Vetec, Brazil) and Arlacel P135 (Croda, Brazil) were used as binder, solvent and additive, respectively, to form the ceramic suspension.

2.2. Hollow fiber preparation

Hollow fibers were produced by the phase inversion/sintering technique following the methodology described by Kingsbury and Li [14]. The ceramic suspension was prepared firstly dissolving the additive (Arlacel) in the solvent (DMSO) followed by the addition of the required amount of the ceramic powder. Pure alumina or pure dolomite was used as ceramic material. The ceramic suspension was agitated in a ball mill for 48 h. The polymer (PESf) was then added to the ceramic suspension and this final ceramic suspension was agitated for further 48 h. The final composition of the ceramic suspension was as follow: 60 wt% of dolomite or alumina, 33.6 wt% of DMSO, 0.4 wt% of Arlacel and 6 wt% of PESf.

Prior to extrusion, the ceramic suspension was degassed using a vacuum pump at 850 mmHg for complete air removal from the suspension (for approximately 2 h). The suspension was then extruded through a tube-in-orifice spinneret (OD 3 mm, ID 1.2 mm) to a water bath with an air gap of 5 cm. Pure water was used as internal and external coagulants. Flows of ceramic suspension and of internal coagulant were controlled at 7 and 15 mL min^{-1}, respectively, using two individual pumps (Harvard Apparatus, model XHF). The hollow fiber precursors were left into the coagulant bath for 48 h to complete phase inversion, and then were manually cut to the required length, washed with water to remove the solvent completely, straightened and dried at room temperature for 48 h.

After that, the fibers were sintered in a tubular furnace (Carbolite, model TZF 15) at different temperatures. Dolomite hollow fibers were sintered at 400, 1250 and 1350 °C, while alumina hollow fibers were sintered only at 1350 °C, both without controlling the sintering atmosphere. The literature suggests the sintering of alumina membranes at 1300–1350 °C [15,16], although later studies have suggested even higher temperatures. The reduction in the sintering temperature is favorable to increase the membrane permeability and to decrease the membrane cost. The temperature was increased at a ramp of 1 °C min^{-1} with a dwelling of 5 h at the target temperature of 400 °C. The temperature was then reduced to room temperature at the rate of 2 °C min^{-1}. For the higher temperatures the following ramps were programmed: from room temperature to 300 °C at the rate of 2 °C min^{-1}, from 300 to 600 °C at the rate of 1 °C min^{-1} with a dwelling of 60 min (for polymer removal), and from 600 to the target temperature (1250 or 1350 °C) at the rate of 9 °C min^{-1} with a dwelling of 5 h. The temperature was then reduced to room temperature at the rate of 2 °C min^{-1}.

2.3. Characterizations

The particle size distribution of the dolomite powder was determined using a laser particle size analyzer (Malvern, Mastersizer 2000). Thermogravimetric analyses (TGA-DTA) of the dolomite material were performed in a thermobalance (Shimadzu, model DTG-60H) under nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10 °C min^{-1} from 30 to 1200 °C. Chemical composition of the dolomite material was examined by X-ray fluorescence spectrometry (XRF, Oxford, model 51-ADD0048). The loss on ignition (LOI) was calculated as a weight percentage after drying a sample of dolomite powder at 900 °C for 5 h. The crystalline phase of the starting material (dolomite) and of the sintered samples were characterized by X-ray diffraction (XRD) in a Shimadzu diffractometer (model XDR600) with an X-ray tube containing a copper anode (Cu-Ka wavelength), at a scan rate of 2° min^{-1}, 2Θ ranging from 10° to 80° with step of 0.02°, voltage at 40 kV and current at 30 mA. Morphological analyses were carried out using a scanning electron microscopy (SEM, Carl Zeiss, model EVO MA 10). Energy dispersive spectroscopy (EDS, Oxford, model 51-ADD0048) was used to perform quantitative microanalysis of the prepared hollow fibers.

The produced hollow fibers were characterized in terms of their mechanical strength, water permeability and porosity. Water permeability through the produced hollow fibers was measured at room temperature (approximately 25 °C) and at different transmembrane pressures. For these water flow measurements, the module with the hollow fiber was connected to an automatic pumping system (Convergence Inspector Minus) and dead-end filtrations were carried out. The three-point bending test was performed to measure the mechanical strength of the fibers using a Instron Model 9600 equipment coupled with a 5 kN cell and using hollow fibers with length of 30 mm. The mechanical strength (σ_F) of each individual hollow fiber was calculated using Eq. (1) [17]:

$$\sigma_F = \frac{8F\,L\,D}{\pi(D^4 - d^4)} \quad (1)$$

where F is the measured force at which the fracture occurred and L, D and d are the length, and the outer and inner diameters of the fiber, respectively.

Dissolutions of calcium and magnesium from the produced fibers in water were investigated. The fibers were kept in water for up to 56 h at the proportion of 4 fiber pieces of 4 cm each one in 10 mL of deionized water. After the required time, concentrations of calcium and magnesium in water were measured by ion chromatography. Analyses were conducted in an ion chromatograph equipped with a conductivity detector (Metrohm model 881 compact IC pro) and a cation exchange column (Metrosep C4, 250 mm length, 4.0 mm ID). Isocratic elution was performed using dipicolinic and nitric acid solutions at 1.7 and 0.7 mmol L^{-1}, respectively. Flow rate was 0.9 mL min^{-1} and the oven temperature was set to 40 °C. Linear calibration was performed using multielementary solution with calcium and magnesium analytes at concentrations from 0.1 to 2 ppm. Values of mechanical strength of the fibers after contact with water were also evaluated.