Journal of Membrane Science 489 (2015) 90–97

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Effects of sintering atmospheres on properties of stainless steel porous hollow fiber membranes

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ARTICLE INFO

Article history:
Received 20 January 2015
Received in revised form
9 April 2015
Accepted 15 April 2015
Available online 24 April 2015

Keywords:
Hollow fiber
Stainless steel
Membrane
Sintering atmosphere
Hydrogen

ABSTRACT

Stainless steel (SS) is one of excellent materials for fabrication of hollow fiber membranes because of its good mechanical property. Phase inversion technique is a promising method for preparation of SS hollow fibers. The sintering step is critical for controlling the quality of SS hollow fibers by removal of organic additives and activation of particle binding. In this work, we prepared SS porous hollow fiber membranes by combined dry-wet spinning and sintering technique. The influence of sintering atmosphere (air, CO_2, N_2, He and H_2) on microstructure and properties of SS hollow fibers were investigated extensively. It was found that air and CO_2 could lead to metal oxidation while inert atmospheres (He and N_2) caused carbon remaining in SS hollow fibers. By contrast, H_2 atmosphere was effective in removing organic additives without metal oxidation. High mechanical strength could be achieved for the hollow fiber membranes sintered in H_2 atmosphere. At 1100 °C for 1 h, the as-sintered SS hollow fiber showed high bending strength of >200 MPa and nitrogen permeance up to 9.5×10^{-5} mol s^{-1} m^{-2} Pa^{-1}.

1. Introduction

Inorganic hollow fiber membranes have attracted great attention in last decades due to their excellent thermo-chemical resistance and high surface area/volume ratio for membrane modules. Ceramic hollow fiber membranes constructed with alumina [1–4], yttria-stabilized zirconia [5,6] or titania [7] have been successfully prepared by phase inversion methods such as dry spinning, wet spinning and dry-jet-wet spinning. The mechanical property of low fracture load and high brittleness is the main obstacle for industrial applications of ceramic hollow fiber membranes [1–3]. To address the issue, metal materials are considered as candidates for producing hollow fiber membranes, which could provide high mechanical strength and toughness. Furthermore, the metal membranes can be easy to seal by welding or brazing.

In the past decade, flat and tubular porous stainless steel membranes have been commercially fabricated by a couple of companies such as GKN, Mott and Pall [8,9]. These membranes were used as supports or particle filters for gas and liquid separations [8,10,11]. There are very limited reports working on the preparation of metal hollow fiber membranes. In 2011, Luiten-Olieman et al. [12] first reported porous stainless steel hollow fiber membranes. The membranes were prepared with dry–wet spinning, which produced an asymmetric structure with sponge-like region and finger-like voids. The membranes showed a permeance up to 0.1 mmol m^{-2} Pa^{-1} s^{-1} and a bending strength of ~1 GPa. Michielsen et al. [13] also prepared stainless steel hollow fiber membranes using a phase-inversion robotic fiber deposition, which produced a sponge-like structure without any macro-voids. The sintered membranes showed a 3-point bending strength up to 333 MPa at a sintering temperature of 1300 °C.

In preparation of inorganic hollow fiber membranes with phase inversion methods, sintering treatment on green fibers is an important step to remove organic additives and activate particle binding. Generally, air atmosphere is used for sintering treatment on ceramic hollow fibers. For metal membranes, oxygen-free atmosphere should be used to avoid metal oxidation. It was reported that inert gases such as nitrogen and argon were adopted to protect stainless steel hollow fibers during the sintering processes [12,13]. However, it seems difficult to remove organic binder completely from the hollow fibers in the inert atmospheres. It is well known that carbonization of polymer would occur at elevated temperatures. The remaining carbon in the metal hollow fibers has negative effects on toughness and corrosion resistance.

In this work, stainless steel porous hollow fiber membranes were prepared by dry-wet spinning method. We aimed to reveal the effect of sintering atmospheres (air, CO_2, N_2, He and H_2) on the properties of as-sintered stainless steel hollow fibers. CO_2 and H_2 were used as sintering gases with the purpose of consuming carbon by reaction. The properties such as porosity, nitrogen permeance, pore size and bending strength were investigated extensively in order to optimize sintering conditions.

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http://dx.doi.org/10.1016/j.memsci.2015.04.021
0376-7388/

2. Experimental

2.1. Materials

Stainless steel powders (SS, 316L, d50 = 8.11 μm, Antai Technology Co., Ltd.), polyethersulfone (PESf, BD-5, Bei-Shi-De synthetic plastics company), N-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd.) and deionized water were used as fiber material, binder, solvent and additive, respectively. Deionized water and tap water were used as the internal and external coagulants, respectively, for the gelation of the extruded hollow fiber precursors. The gases used for sintering and permeation experiments were purchased from Nanjing Shangyuan industrial gas company. All the gases have the purity of $>99.999\%$.

2.2. Preparation of hollow fiber membranes

PESf was slowly added in NMP under constant stirring ($\sim$300 rpm) for 60 min. A certain amount of SS powders was then added into the solution while kept stirring for 24 h to ensure the SS powders dispersed uniformly. Deionized water was used as an additive to modulate its viscosity [1,12]. The spinning suspension had a mass ratio of SS:PESf:NMP:H_2O = 0.71:0.07:0.2:0.02. The suspension was transferred to a gas-tight stainless container for air bubble removal under vacuum at room temperature. After degassing, the spinning suspension was pressurized to 0.1–0.3 MPa by the use of compressed nitrogen. The spinning process was carried out by extruding the suspension through a tube-in-orifice spinneret into an external coagulant. The spinneret had an inter diameter/ outer diameter of 1.2 mm/3.0 mm. The air gap between the spinneret and the coagulant bath was kept at 50 mm. The injection rate of internal coagulant (deionized water) was kept at 20 mL/min. The hollow fiber precursors were left in the external coagulant (tap water) overnight for complete solidification.

The hollow fiber precursors were sintered in an atmosphere furnace (WN-17M-G100, Nanjing ProEnergy Furnace Co., Ltd.). Five gas environments including air, carbon dioxide, nitrogen, helium and hydrogen were used for sintering. The gas flow rate was controlled at 200 mL/min unless otherwise stated during the sintering process. The sintering temperature was first increased to 600 °C and then held for 1 h to remove the organic polymer binder. After that, the fibers were sintered at 1100 °C for 1 h. The heating and cooling rate was controlled at 1 °C/min. The final hollow fiber membrane samples were used for characterizations.

2.3. Characterizations

The morphologies of the hollow fiber membranes were observed by a scanning electron microscopy (SEM, S4800, Hitachi). The element compositions of the membranes were analyzed by an energy dispersive X-ray spectrum (EMAX, X-Steam 7, Horiba). The crystal phases were determined by X-ray diffraction (XRD, MiniFlex 600, Rigaku) with a Cu Kα radiation source in the 2θ range of 20–80°. Single component permeation of pure nitrogen through a SS hollow fiber membrane was measured at room temperature under a pressure-driven mode. One end of the membrane was blocked with sealant while the other end was connected to a rotor flowmeter for measurement. The feed side was operated at 2 atm while the permeate side was kept at atmospheric pressure. The gas permeance ($\overline{P}$) was calculated from the following equation:

$$\overline{P}=\frac{Q\,\ln(D/d)}{\pi L(D-d)\Delta p} \tag{1}$$

where Q, D, d, L and Δp are the nitrogen permeation rate (mol/s), the outer diameter (m) and the inner diameter (m) of the hollow fiber, the hollow fiber length (m), and the trans membrane pressure difference (Pa), respectively.

The pore size distribution was measured with a mercury porosimeter (PoreMater GT60, Quantachrome Instruments) and the mean pore size was measured with a homemade gas bubble pressure instrument. Archimedes method was employed to measure the porosity of SS hollow fibers. Thermogravimetric spectra of samples were recorded by a thermogravimetric analyzer (TG, 209F1, Netzsch) under different atmospheres including air, carbon dioxide, nitrogen, helium and hydrogen at a heating rate of 10 °C/min over a temperature range of 30–800 °C. The species generated from sintering processes were monitored by a mass spectrometry (MS, Ametek LCD/Dycor).

The mechanical strength of the sintered hollow fibers was measured with three-point bending test using a universal testing machine (CMI6203, Shenzhen Xin-San-Si Co., Ltd.). The bending strength (σ_F) was calculated from the following equation [4,13]:

$$\sigma_F=\frac{8FLD}{\pi(D^4-d^4)} \tag{2}$$

where F is the measured force at which fracture takes place; L is the effective length (0.04 m) of the hollow fiber.

3. Results and discussion

3.1. Morphology study

Fig. 1a and b shows SEM images of a SS hollow fiber membrane before sintering treatment. It can be seen that the green hollow fiber has an outer diameter of 2.5 mm and thickness of 0.5 mm. An asymmetric structure consisting of sponge-like region and finger-like voids were observed, which is a typical structure for the hollow fibers prepared by dry – wet spinning method. The finger-like structure originated from inner surface, which occupied about 1/2 of the cross-section. The sponge-like structure was located at the outer region of the cross-section. During the spinning process, the finger-like voids were generated due to fast exchange between solvent (NMP) and no-solvent (water) while sponge-like structure was formed due to slow exchange. The as-generated structure of hollow fibers was related with the viscosity of hollow fiber precursor [1]. High viscosity up to phase boundary of instantaneous demixing would lead to a sponge-like structure. In this work, the precursor with solid content of 71 wt% and water content of 2 wt% had a viscosity of 20.0 Pa s, which could eliminate small finger-like voids at the outer edge. After passing through air gap, the outer surface of hollow fiber precursor had an increased viscosity due to solvent evaporation and moisture effect, which resulted in a slow diffusion for nonsolvent from outer side in coagulation bath. Comparatively, the inner surface contacted with the internal coagulant directly when the outer surface exposed to air. A fast phase separation could occur on the inner side of hollow fiber precursor with formation of finger-like voids [1,12,14].

Fig. 1c – l shows the SEM images of SS hollow fiber membranes sintered at 1100 °C for 1 h under different atmospheres (air, CO_2, N_2, He, H_2) with the flow rate of 200 mL/min. Obvious shrinkage was found after sintering treatment, however the general structure consisting of sponge-like region and finger-like voids were still observed. Table 1 presents the shrinkages in both radial and axial directions of hollow fiber membranes sintered in different atmospheres. The shrinking was mainly due to removal of organics and bonding of metallic particles during the sintering process. The shrinkages of the fibers prepared in air and CO_2 were found to be obviously smaller than those in other atmospheres. The hollow fibers sintered in H_2 atmosphere showed largest shrinkage. The results suggested that the formed structure could be variable with