Nickel aluminate spinel reinforced ceramic hollow fibre membrane

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ABSTRACT

Ceramic hollow fibre membranes are suitable for application in many industrial processes that involve harsh conditions such as high temperatures and concentrated organic solvents because of their high thermal and chemical stability. The major limitation of ceramic hollow fibre membrane is the brittle nature of ceramic materials, which leads to difficulty in large scale production and failure in pressurised processes. This paper presents the reinforcement of alumina (Al_2O_3) hollow fibre membrane by nickel aluminate spinel ($NiAl_2O_4$). The ceramic hollow fibre membrane was fabricated by the widely used phase inversion method. The $NiAl_2O_4$ phase was formed by the reaction of nickel (II) oxide (NiO) with Al_2O_3 during sintering. A maximum flexural strength of 156 MPa was achieved by the $NiAl_2O_4/Al_2O_3$ hollow fibre membrane containing 16.4 wt% of $NiAl_2O_4$, which was 2.3 times of that of the pure alumina sample. The 16.4 wt% $NiAl_2O_4/Al_2O_3$ hollow fibre membrane had a porosity of 46.8%, a mean pore size of 330 nm determined by a gas bubble pressure method, and a pure water flux of 597 L/m^2 h bar at a testing pressure of 2 bar. $NiAl_2O_4/Al_2O_3$ hollow fibre membrane could achieve a flexural strength comparable to higher-cost yttria stabilized zirconia and silicon nitride hollow fibres within the porosity range of 46.8–55.2%.

1. Introduction

Membrane systems are currently applied in a wide range of processes such as water desalination, waste treatment, filtration, distillation, gas separation and catalytic reactions. Polymers are the common and low-cost material for membrane fabrication, but polymeric membranes become unstable and tend to fail under harsh conditions such as high temperatures, highly acidic or basic environment [1]. By contrast, ceramic membranes show much better durability under these harsh conditions. The advantages of ceramic membranes include high thermal and chemical stability, insensitivity to swelling and ease of cleaning. In terms of geometry, hollow fibre membranes made the highest compactness in comparison with flat sheet, disc and tubular membrane systems because of their highest surface area to volume ratio [2,3].

The brittle nature of ceramic materials, however, is an obstacle for large-scale production and application of ceramic membranes. This problem is even more significant with the hollow fibre geometry because of their small diameters and thin membrane walls. Apart from cracking under high operating pressure, brittleness of the hollow fibre membranes also leads to difficulty in being assembled into as well-configured and orientated modules to

achieve the desirable performance [4]. To date, there have been some studies on the strengthening of porous ceramic hollow fibre membranes. For instance, addition of nanoparticles into micro-sized powder in the preparation of ceramic hollow fibre membrane favoured mechanical strength, at the same time greatly reduced the porosity of the ceramic hollow fibre membrane [5,6]. The same densification effect was observed in the high temperature sintering of ceramic hollow fibre membrane [7]. Some studies focused on modifying the formation of hollow fibre precursors by the phase inversion method have resulted in ceramic hollow fibre membranes with significantly improved mechanical properties; these included the use of sintering additive [8] and addition of non-solvent in a ceramic-binder slurry [9].

Nickel aluminate spinel ($NiAl_2O_4$) was introduced to effectively reinforce dense alumina ceramic [10]. Such a reinforcement mechanism lies in the boundary strengthening effect in the matrix of alumina as a result of the stress field created by the difference in thermal expansion between alumina and $NiAl_2O_4$. Note that $NiAl_2O_4$ was formed by the solid reaction between nickel oxide (NiO) and alumina [11,12]. This reaction has been widely used in waste treatment, where the toxic metal nickel is oxidised into NiO then transformed into $NiAl_2O_4$ [13,14]. The resulting aluminate is stable, non-toxic and has a density of 4 g/cm^3 [15] which is close to that of alumina (3.983 g/cm^3). In our previous work, porous alumina with the inclusion of $NiAl_2O_4$ was prepared by dry pressing of mixed Al_2O_3 and NiO powder, and subsequent sintering. The resulting porous ceramic showed greatly improved flexural strength

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[16], which proved the feasibility of the corresponding strengthening mechanism in porous alumina ceramics.

In the present work, $NiAl_2O_4/Al_2O_3$ hollow fibre membranes were fabricated using the phase inversion method, and the $NiAl_2O_4$ reinforcement effect was investigated for the purpose of developing toughened ceramic hollow fibre membranes for practical applications. The ceramic hollow fibre membranes prepared had an asymmetrically porous structure, and significantly enhanced flexural strength. They can tolerate a higher applied pressure for a more efficient separation in pressure-driven microfiltration processes.

2. Experimental

2.1. Materials

Alumina powder of a particle diameter $< 1\,\mu m$ (alpha phase, 99.98% metals basis, APS powder, surface area 10 m^2/g) purchased from Alfa Aesar, A Johnson Matthey Company was used as a raw material for the preparation of ceramic hollow fibre membrane. Polyethylsulfone (PESf) (E6020P, BASF) was used as a binder in hollow fibre extrusion. 1-Methyl-2-pyrrolidone (NMP) purchased from Sigma-Aldrich Australia was used as a solvent of the powder, polymer and additive. Nickel (II) oxide powder was synthesised by the calcination of nickel carbonate as described by Xiang and co-workers [17]. Nickel carbonate, basic hydrate (BNC) (99.9% trace metal basis) purchased from Sigma-Aldrich Australia was a source of nickel. The BNC powder was placed in a crucible and heated in open air at 500 °C for 2 h. The resulting NiO powder was black in colour, with particle sizes of 0.30–0.45 μm.

2.2. Preparation of ceramic hollow fibre membranes

The well-known phase inversion method was used to prepare ceramic hollow fibre membranes. The alumina suspension was prepared by mixing 15 g of alumina powder and 1.8 g of PESf in 13.2 g of NMP. Different amounts of NiO were added into the alumina suspension for different samples. The addition of NiO powder gave a slight variation of total powder loading in the slurries, which ranged from 50.0 wt% to 51.8 wt%. The ratios of Al_2O_3:NiO were 1:0, 1:0.0086, 1:0.022, 1:0.047, 1:0.067, 1:0.072, 1:0.075 and 1:0.106 by mass; these ratios were calculated by stoichiometry on the basis of complete reaction of NiO with Al_2O_3 to form $NiAl_2O_4$, aiming at achieving final $NiAl_2O_4$ loadings of 0, 2.02 5.15, 10.62, 14.78, 15.83, 16.42 and 22.62 wt%, respectively.

The slurry was ball-milled at 30 rpm for over 48 h to achieve a homogeneous mixture, followed by degassing at room temperature for 1 h. The degassed slurry was then transferred to a stainless steel chamber with a tube-in-orifice spinneret where it was extruded into hollow fibre precursors. A schematic diagram of the extrusion process is shown in Fig. 1. The outer and inner diameters of the orifice were 2.8 mm and 1.4 mm, respectively. Nitrogen gas was used to pressurise the chamber for the extrusion process at room temperature. Tap water was used as both internal and external coagulant. Since water is miscible with the solvent NMP, during the extrusion process NMP rapidly exchanged with the water from both sides. With NMP being removed, the slurry was solidified, resulting in PES-containing hollow fibres that are precursors of ceramic hollow fibres. The same coagulants were used internally and externally to minimise the difference of phase inversion rate towards the inner and outer wall of the hollow fibre membrane, in order to avoid long finger-like pores extending through either side of the hollow fibre [9]. Long finger-like pores in hollow fibre membranes do not favour flexural strength. The internal coagulant flowrate was kept at 3 mL/min. The air gap was
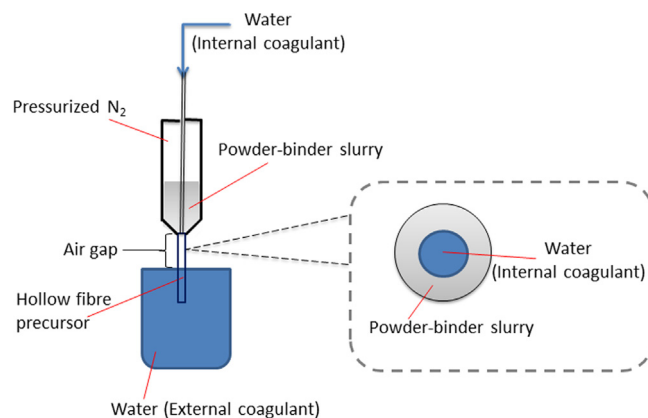

Fig. 1. Schematic diagram for hollow fibre extrusion by the phase-inversion method.

kept as 1.3 cm through the extrusion process. The hollow fibre precursors were left in room-temperature tap water for 24 h for complete solvent exchange. A detail study on the effect of extrusion process on the morphology of ceramic hollow fibre membranes was presented by Kingsbury et al. [7].

The hollow fibre precursor was heated to 580 °C in air at a heating rate of 3 °C/min and was held for 3 h in a furnace to remove the polymer binder. They were then sintered at 1500 °C for 5 h. The samples were left in the furnace to be cooled naturally to room temperature to prevent cracking due to a sudden temperature change.

2.3. Membrane characterisation

X-ray diffraction (XRD) was used to identify the phases present in the samples. The XRD analysis was carried out in a Rigaku MiniFlex 600 with a scan range 10–90° and a step size of 2°. Structures of the cross-sectional surface and outer surface of the hollow fibre membranes were observed using a JEOL 7001F scanning electron microscope (SEM) operating at 30 kV at various magnifications. The cross-sectional surfaces of the hollow fibres were obtained by manual snapping at room temperature. All samples were sputter-coated with a 0.5 nm platinum layer. The elemental distribution of nickel and hence $NiAl_2O_4$ in the cross section of the samples was analysed by energy-dispersive X-ray spectroscopy (EDS). EDS scan was taken at 15 kV.

The flexural strengths of the samples were determined by the three-point bending strength method. The three-point bending tests were carried out with an Instron Micro Tester 5848 with a load cell of 2 kN (Instron Calibration Laboratory, United Kingdom). The sample was placed on a span of 18 mm and was loaded at a crosshead speed of 0.25 mm/min until fracture occurred. Five runs for each sample were performed. The bending strength, σ_F, of each single hollow fibre was calculated using the following equation [5]

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

where F is the force measured at the fracture point of the hollow fibre. L is the span, which was kept at 18 mm. D and d are the outer and inner diameters of the hollow fibre, respectively.

The porosity and pore size distribution of the samples were determined by mercury intrusion with an Auto Pore III analyser (Micromeritics, USA). The samples were manually broken into pieces and then dried and degassed to a pressure below 0.05 mbar at 350 °C. The degassed samples were cooled to room temperature, and then transferred to the chosen sample holder, which was then pressurised from 38.6 mbar up to 4.2×10^6 mbar for mercury intrusion.