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Investigation of reinforcement of porous alumina by nickel aluminate spinel for its use as ceramic membrane

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ABSTRACT

This paper reports the reinforcement of porous alumina ceramics by forming nickel aluminate spinel phase in an alumina matrix via the reaction between nickel (II) oxide and alumina. X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, three-point bending test and mercury porosimetry were used to characterise the porous ceramic samples. The highest bending strength of 146 MPa was achieved in the porous alumina with 14.7 wt% $NiAl_2O_4$ and a porosity of 30.5%. A decrease in bending strength and increase in porosity was observed in porous alumina with over 14.7 wt% $NiAl_2O_4$. The appreciable bending strength and porosity made $NiAl_2O_4$ reinforcement a promising method for fabricating ceramic membranes with improved toughness in different geometries including hollow fibre membranes.

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 because of their attractive properties and instantaneous response to system variations [1]. In particular, porous ceramic membranes are suitable to be used in extreme conditions which could not be achieved by traditional polymer membranes, such as high temperature, highly acidic or basic feed [2]. The advantages of ceramic membranes include high thermal and chemical stability, insensitivity to swelling and ease of cleaning. For instance, alumina that is the most economical ceramic was proved to be far more stable than common stainless steel 316 in strong acid. [3]

However, brittleness is the major obstacle for the large scale application of ceramic membranes especially hollow fibre ceramic membranes, as most of the separation processes involve significant trans-membrane pressure. The brittleness of ceramic membranes also leads to difficulty in assembly of membrane modules. Studies on the improvement of the bending strength of ceramic hollow fibre membranes were carried out on the adjustment of raw particle size, which traded-off porosity of the membrane for its bending strength.[4]. Nickel reinforcement was tried with the sample prepared in inert gas atmosphere and proved to effectively strengthen fully dense alumina [5], while the toxicity of nickel makes this particle reinforcement method unfriendly to human and the environment [6]. The formation of eutectic mixture with gadolinium aluminium perovskite ($GdAlO_3$) in the alumina matrix changed brittle fracture of pure alumina to plastic deformation [7] but its raw material gadolinium oxide is of a very high cost. Fibre reinforcements were applied and showed the excellent strengthening effect on ceramic materials so far, which in comparison with particle reinforcement, have complicated preparation processes in general, such as difficulty of fibre dispersion and oxidation of many types of fibres when sintered in air [8,9].

In this study, the reinforcement of porous alumina by the formation of nickel aluminate spinel ($NiAl_2O_4$) was investigated. The boundary strengthening effect in the matrix of the ceramic materials was a result of the stress field created by the difference in thermal expansion between alumina and $NiAl_2O_4$. The formation of $NiAl_2O_4$ has been used in waste treatment, where the toxic metal nickel is transformed into $NiAl_2O_4$ by its reaction with alumina [10,11]. This stable and non-toxic aluminate showed even stronger reinforcement of dense alumina than nickel particles [5]. It is necessary to study the effectiveness of $NiAl_2O_4$ reinforcement in porous ceramics. The sample preparation process was simple in comparison with other ceramic reinforcement as nickel oxide particles could be evenly distributed in alumina precursor by thorough mixing and sintering could be carried out in air without unfavourable reactions. In this paper, the relationship between bending strength and microstructure of nickel aluminate spinel reinforced porous alumina was investigated.

2. Experimental

2.1. Materials

Alumina powder of an average particle diameter of 1 μm (SLS Lapidary Product PP4) purchased from Shell-Lap Supplies Pty Ltd.

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(SA, Australia) was used as a raw material for the preparation of porous ceramics. Nickel (II) oxide powder was synthesised by the air-calcination method described by Xiang's group [12]. Nickel carbonate, basic hydrate (BNC) (99.9% trace metal basis) purchased from Sigma-Aldrich 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 0.3 to 0.45 μm.

2.2. Preparation of porous alumina/nickel oxide ceramics

Alumina and nickel oxide powder were weighed and mixed in the required ratios. The powder mixtures were dry ball-milled at 30 rpm for over 48 h to achieve a homogeneous mixture. One gram of the powder mixture was then dry-pressed in a rectangular die of dimension 50 mm × 5 mm for the shaping of a bar with a thickness of 2 mm. The bars were heated up at a rate of 5 °C/min and sintered at 1500 °C and 1600 °C for 5 h. The sample precursors contained 0, 2.5, 6.4, 12.7 and 19.1 wt% of NiO.

2.3. Characterisation

X-ray diffraction was used for identifying the phase present in the samples. X-ray diffraction analysis was carried out in a Philips 1130 diffractomer with a scan range 10–90° and a step size of 2°. Microstructures of the cross-section surface of samples were observed under a Jeol 7001F scanning electron microscope (SEM) at various magnifications. The cross-section cutting surfaces of the bars were obtained by manual snapping at room temperatures. All samples were coated with a platinum layer of 1.5 nm thick and SEM images were taken at 30 kV. 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 mechanical strengths of the samples were determined by the three-point bending strength method. The three-point bending test was carried out with an Instron Micro Tester 5848 with a load cell of 2 kN (Instron Calibration Laboratory, U.K.). The tested sample was placed on a span of 18 mm and was extended under a crosshead speed of 0.25 mm/min until fracture occurred. Three runs for each sample were performed. The bending strength, σ_F, of each sample was calculated from the equation [13].

$$\sigma_F = \frac{3FL}{2bt^2}$$

where F is the force measured at the fracture point of the hollow fibre, L is the span, which was kept at 18 mm, and b is the width and t is the thickness of the rectangular bar.

The porosity and pore size distribution of the samples were determined by mercury intrusion with an Auto Pore III analyser (Particle and Surface Science Pty. Ltd.). The samples were first manually broken into pieces and dried and degassed to a pressure below 0.05 mbar at 350 °C. One gram of degassed samples was transferred to the chosen sample holder, which was then pressurised from 38.6 mbar up to 4.2×10^6 mbar for mercury intrusion. The porosity and pore size distribution were evaluated by the intrusion pressure and volume of mercury.

The nitrogen permeance of the samples with a thickness of 2 mm was determined by the pressure rise method, and calculated by

$$Permeance = \frac{N}{\Delta PA}$$

where N is the flowrate of nitrogen gas (mol/s) measured by a MKS 628D Baratron pressure transducer. ΔP is the transmembrane pressure difference (Pa) and A is the area on the sample that the gas passed through. The gas flow area, A, of the pure Al_2O_3, 14.7 wt % $NiAl_2O_4$ and 28.8 wt% $NiAl_2O_4$ sample was 23.7 mm^2, 31.5 mm^2 and 24.0 mm^2, respectively. Three readings of N were taken for each ΔP applied for each sample and the average value of N was taken to calculate the permeance.

3. Results and discussions

3.1. Phase identification

The X-ray diffraction patterns of samples containing different amount of NiO and sintered at different temperatures are shown in Fig. 1. Only peaks of alumina and $NiAl_2O_4$ were shown in the XRD patterns. The absence of NiO peaks indicated that NiO fully reacted with alumina into $NiAl_2O_4$ in all samples at both temperatures. This agreed with the NiO–Al_2O_3 binary phase equilibrium diagram presented by Phillips et al. [14], which stated at the temperatures 1500 °C and 1600 °C, when the NiO content is below 58 mol% and 57 mol% respectively, $NiAl_2O_4$ and Al_2O_4 are the only phases present at equilibrium state. The NiO content in the sample precursors ranged from 0 to 24.4 mol% fell into this two-phase range. By stoichiometry, the compositions of the final products were calculated and the results are summarised in Table 1.

3.2. Bending strength

Fig. 2 shows the bending strength of the $NiAl_2O_4$ reinforced porous alumina sintered at different temperatures and Fig. 3 shows their porosities.

At both sintering temperatures, the formation of $NiAl_2O_4$ increased the bending strength of the porous alumina up to 14.7 wt%, and then the bending strength decreased with the increase in $NiAl_2O_4$ content. The change in bending strength corresponded with that in porosity, with the porosity of 14.7 wt% $NiAl_2O_4$ reaching the minimum. There was an average of 10% drop in porosity when the sintering temperature was raised from 1500 °C to 1600 °C. As seen in Fig. 3, the sintering temperature is an important factor that controls the porosity of porous ceramics

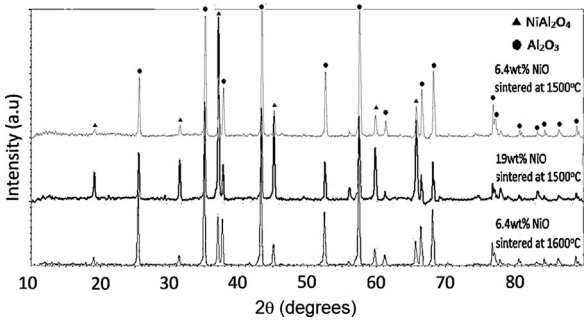

Fig. 1. XRD patterns of samples with 6.4 wt% NiO in precursor sintered at 1500 °C, with 19 wt% NiO in precursor sintered at 1500 °C and with 6.4 wt% NiO in precursor sintered at 1600 °C.

Table 1
Compositions of sintered samples by stoichiometry in weight percentage and mole percentage.

Sample	1	2	3	4	5
Al_2O_3 wt%	100	94.0	85.3	71.2	57.8
Al_2O_3 mol%	100	96.6	91.5	83.4	75.6
$NiAl_2O_4$ wt%	0	6.0	14.7	28.8	42.2
$NiAl_2O_4$ mol%	0	3.4	8.5	16.6	24.4