

# The effect of membrane thickness on the co-sintering process of bi-layer ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membrane

Jun Feng, Minghui Qiu, Yiqun Fan, Nanping Xu\*

*Membrane Science & Technology Research Center, State Key Laboratory of Material-Oriented Chemical Engineering,  
Nanjing University of Technology, Nanjing 210009, China*

Received 14 March 2007; received in revised form 18 June 2007; accepted 23 June 2007  
Available online 30 June 2007

## Abstract

As a method for fabrication of multilayer structures, co-sintering process has attracted increasing attention due to its promising advantages. In this study, co-sintering process was applied to fabricate bi-layer ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membranes supported by rigid Al<sub>2</sub>O<sub>3</sub> substrates. Following our previous work, this paper focused on the effect of membrane thickness on the co-sintering process. Experimental results showed that thinner sub-layer membrane without defects was favorable to achieve good bonding between the membrane layers and the support after co-sintering. The thickness of the top-layer membrane should be not very thin. Otherwise the compressive stress caused by fast shrinkage of the top-layer membrane would be insufficient to promote the sintering of the sub-layer membrane during the co-sintering process. The suitable thicknesses for the sub-layer and the top-layer membranes have been determined, which were about 15 and 10 μm, respectively. The bi-layer ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membrane co-sintered at 1200 °C had the average pore size of about 0.28 μm and the pure water flux through the membrane was about  $2.82 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1} \text{ Pa}^{-1}$  ( $2.82 \times 10^3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ). The bi-layer ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membranes prepared by co-sintering process showed good performance in an oil–water separation.

© 2007 Published by Elsevier B.V.

**Keywords:** Co-sintering; Membrane thickness; Ceramic membrane; Zirconia

## 1. Introduction

As a method for fabrication of multilayer structures, the co-sintering process has attracted increasing attention due to simple preparation process and low production cost. The co-sintering technology has been widely applied in the preparation of electronic packages, especially for the low-temperature co-fired ceramics (LTCC) [1–3] and solid oxide fuel cells (SOFC) [4,5]. Up to date, a few researchers [6–8] have made efforts to introduce the economic co-sintering process in the preparation of ceramic membranes. Lindqvist and Liden [6] introduced the co-sintering process in the preparation of flat bi-layer α-Al<sub>2</sub>O<sub>3</sub> membranes. de Jong et al. [7] reported the fabrication of bi-layer α-Al<sub>2</sub>O<sub>3</sub> hollow fibers by the co-sintering process. In their co-sintering processes, two layers were co-sintered without additional rigid substrate. One of the layers acted as a supporting

layer and provided the mechanical strength for the whole membrane [6,7]. Considering shrinkage matching between two layers during the co-sintering process, the supporting layer could not be sintered sufficiently at the co-sintering temperature, which resulted in poor mechanical strength [6]. In our previous work, a modified co-sintering process was developed by the use of an additional rigid support to provide high mechanical strength for a membrane. In this process, two membrane layers were sequentially dip-coated on the rigid support and then co-sintered at a suitable temperature. The co-sintered membranes have been demonstrated having high mechanical strength [8].

Generally, the thermal mismatch of each layer and the developed stresses in each layer are key problems during the co-sintering process. Cai et al. [9,10] have investigated the stresses developed in Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> hybrid laminates during the co-sintering process. They calculated the stress values by correlating the difference in shrinkage rate between each layer, the layer thickness ratio and some corresponding physical properties such as elastic modulus and Poisson's ratio. The correlations have been widely used to calculate stresses caused by the thermal

\* Corresponding author. Tel.: +86 25 83587174; fax: +86 25 83300345.  
E-mail address: [npxu@njut.edu.cn](mailto:npxu@njut.edu.cn) (N. Xu).

mismatch during the production of various low-temperature co-fired ceramics [1,2] and multilayer ceramic laminates [11,12]. Suresh et al. [13] analyzed the stresses in layered structures by Finite-element simulation. They pointed that the distribution of stresses were not uniform across the multilayer structures. The maximal stress was at the interface between the co-sintered layers. Therefore, the effect of each layer thickness on the stress should be considered during the co-sintering process.

Our previous works [8] mainly dealt with the influence of the co-sintering temperature on the co-sintering of two  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> membrane layers supported on a rigid  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate without considering the effect of membrane thickness. It was found that moderate shrinkage mismatch between each layer was required to ensure the success of the co-sintering process, as the moderate mismatch would generate beneficial compressive stress in the sub-layer membrane. The present work is aimed to co-sinter two membrane layers on a rigid  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support using different materials, which are  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the sub-layer and ZrO<sub>2</sub> for the top-layer. Following the early work [8], this study focused on the influence of the membrane thicknesses on the co-sintering process.

## 2. Experimental

### 2.1. Membrane preparation

The procedure for the preparation of bi-layer ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membranes was similar to what we described in the previous paper [8]. Stable coating slurries for the sub-layer membrane and the top-layer membrane were prepared with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders (average particle size of 1.5  $\mu$ m, Aloca, USA) and ZrO<sub>2</sub> (Monoclinic) powders (average particle size of 0.6  $\mu$ m, Nanjing High Technology NANO Co., Ltd., China), respectively. Nitric acid (1 mol/L) and methylcellulose (MC) were added in the slurries as dispersion and binder, respectively.

The supports used were porous  $\alpha$ -alumina tubes made by the Membrane Science and Technology Research Center (Nanjing, China). Before use, the supports were cleaned with acetone and dried at 150 °C to remove surface dirt and grease. The treated support was first dipped into the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> slurry for 10–120 s and then taken out with a speed of about 15 cm/s. The wet membrane was dried overnight at room temperature and at 120 °C for 5 h. The as-made membrane was further coated with the ZrO<sub>2</sub> slurry using the similar procedure except for the coating time of 10–90 s. The supported bi-layer membranes were dried overnight at room temperature and at 120 °C for 5 h. Finally, the bi-layer membranes were, respectively, co-sintered at 1150, 1200 and 1250 °C for 2 h with the heating and cooling rates of 1 °C min<sup>-1</sup>. By adjusting the solid content in the coating slurry and soaking time during dip-coating, the membrane thickness varied from 15 to 30  $\mu$ m for the sub-layer Al<sub>2</sub>O<sub>3</sub> membrane and 3–10  $\mu$ m for the top-layer ZrO<sub>2</sub> membrane.

The bi-layer ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membranes were also prepared by the conventional method for comparison. During the conventional preparation process, the sub-layer and the top-layer membranes were sintered sequentially at 1300 and 1150 °C, which were the appropriate sintering tempera-

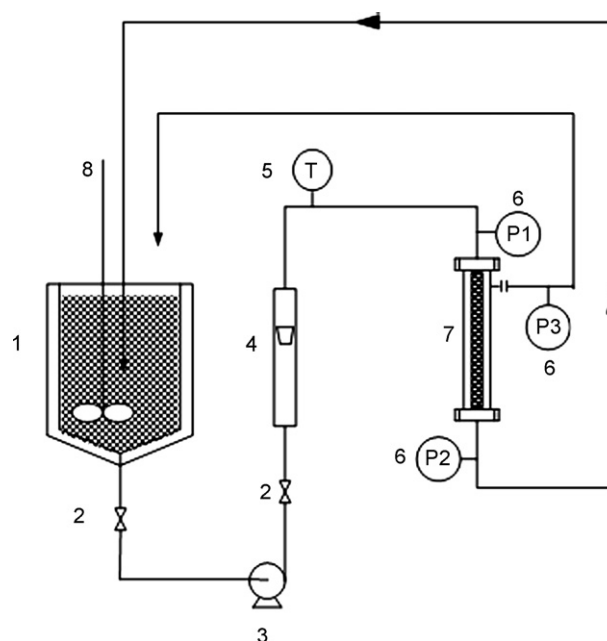


Fig. 1. Schematic of cross-flow filtration apparatus: 1, feed tank; 2, needle valve; 3, centrifugal pump; 4, flow meter; 5, temperature meter; 6, pressure gauge; 7, membrane module; 8, blade stirrer.

tures for each membrane layer, as revealed by experimental optimization.

### 2.2. Characterizations

A differential thermal dilatometer (DIL402C, Netzsch, German) was used to study the shrinkage behaviors of the membrane layers during sintering. The shrinkage rate, which is defined as  $\Delta l/l_0$ , was measured under temperature-rising conditions and the sample temperature was raised to 1300 °C at a heating rate of 1 °C/min.

Morphologies of the prepared membranes were examined by scanning electron microscopy (SEM) and the composition distributions over the membrane cross-section were determined by an energy dispersive X-ray spectrometer (EDS) (Quanta 200, Philip, USA).

The phase structure of the prepared membranes was identified by X-ray diffraction (XRD) (D8 Advance, Bruker, German) using Cu K $\alpha$  radiation with  $2\theta$  from 15° to 80°.

Average pore size and pore size distribution (PSD) of the membranes were measured by the gas bubble pressure method (GBP), which were performed following the American Society for Testing and Materials (ASTM) Publication (F316-80).

Pure water flux (PWF) of the membrane was measured in a cross-flow filtrating apparatus illustrated in Fig. 1. The apparatus was capable of operating at a variety of temperatures and pressures. PWF of the membrane was determined by collecting the permeation in a graduated cylinder and timing the collection period.

The separation performance of the prepared membrane was tested by the separation of oil–water emulsion using the same apparatus. These emulsion consisted of 5 g/L Drawing Oil of

Download English Version:

<https://daneshyari.com/en/article/638290>

Download Persian Version:

<https://daneshyari.com/article/638290>

[Daneshyari.com](https://daneshyari.com)