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Preparation of crack-free ZrO_2 membrane on Al_2O_3 support with ZrO_2–Al_2O_3 composite intermediate layers

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Abstract

To develop porous alumina supported MF ZrO_2 membranes, ZrO_2–Al_2O_3 composite intermediate layers are considered in order to decrease stress creation during the processing and avoid cracks formation. The relation between distortion stress and sintering shrinkage was experimentally studied. And the cracks formation mechanism was qualitatively evaluated and discussed. Finally, crack-free YSZ membrane with pore size of 0.16 μm on the two ZrO_2–Al_2O_3 intermediate layers possessing a gradient composition was successfully prepared and characterized.

Keywords: Ceramic membrane; Preparation; ZrO_2–Al_2O_3; Composite layer; Crack-free

1. Introduction

On meeting the requirements of separation process for caustic media application, ceramic membrane with high corrosive resistance is required. Zirconia exhibits excellent surface properties and high chemical stability [1,2] that makes zirconia membranes very suitable for the applications in caustic media or oily wastewater treatment [3,4]. Zirconia membranes are usually fabricated on commercially available alumina or carbon supports. In this multilayer structure, cracks often exist due to the mismatch stress between adjacent layers. The stress can be originated from the thermal expansion mismatch [1,5] or difference in sintering rates for the top layer and the support [6]. As a common idea, an intermediate Al_2O_3/ZrO_2 layer with gradient composition can be considered to introduce in order to decrease the mismatch stress. For example, stress has been reported in constrained densification of symmetric and asymmetric Al_2O_3/ZrO_2 laminates [6–9]. The sintering procedure for the laminate materials is well understood, however, it cannot be applied directly to the membrane fabrication by dip-coating. The reasons are: (1) the support is a rigid because the firing temperature for the membranes is much lower than that for the support, and the membranes are too thin to make the support deform; (2) the induced stress created during supported membrane formation is larger than that between the laminates because the relative deformation of the membrane is larger; (3) the contact degree between membrane and support continuously changes before they sinter together. Thus, the stress in processing cannot be avoided for the composite membrane preparation. Little attention, however, is given to that how to reduce the mismatch sintering stress [10–13].

In this work, ZrO_2–Al_2O_3 composite membranes are introduced as intermediate layers between top YSZ membranes and alumina supports. The intermediate layers have a gradual change in composition and pore size. The change in composition reduces the sintering stress by smooth the sintering shrinkage difference of the adjacent layers. The particles size change ensures zirconia membrane has an appropriate pore size.

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2. Experiment procedures

The 8 mol% yttria stabilized zirconia (YSZ) powders (commercial, $d_{50} = 0.8\ \mu m$) and α-alumina powders (commercial, $d_{50} = 2.4\ \mu m$) were mixed by ball milling. The composite powders were denoted as ZA-M, where M represented YSZ bulk fraction.

The composite powders were made into the rectangular bars by cold-pressed at 200 MPa to measure the sintering shrinkage with the thermal dilatometer (NETZSCH DIL 402C, Japan). The sintering temperature is up to 1500 °C at heating rate of 10 °C/min.

The discs were also made by cold-pressed in which any two of the composite powders above had the same thickness. The discs were baked at 1300 °C for 2 h subsequently and the deformation was observed.

For preparing ZA-M particle suspensions, ZA-20, ZA-80 or ZA-100 powders were mixed with polyacrylic acid (PAA) by ball milling and adjusting pH with ammonia. Membrane was fabricated by dip-coating on 19-channel tubular α-alumina support. The support is 25 cm length with porosity of 40% and mean pore diameter of 2.89 μm. After dried at the room temperature, ZA-20 layer was sintered at 1400 °C for 2 h at heating and cooling rate of 1 °C/min. ZA-80 layer then was fabricated on the ZA-20 layer, and the ZA-100 layer was the top layer with a similar procedures.

Microstructure of the membrane was observed with scanning electron microscopic (Hitachi X-650, Japan) and element distribution was observed with EDX (XL30ESEM, Britain). Pore size distribution of the specimens was determined by bubble point method and the pure water flux was measured on a cross-flow filtration apparatus with trans-membrane pressure of 0.1 MPa.

For examining the corrosion resistance of the membranes, the composite membrane was dipped in 20 wt.% H_2SO_4 and 10 wt.% NaOH at 100 °C for 1 h to measure the effect of the caustic media on the membrane. After H_2SO_4 or NaOH washed out by distilled water, pore size distribution was measured again.

3. Results and discussion

3.1. Description on relationship of crack shape and sintering stress

Cracks formation is unavoidable if the stress is high enough. Fig. 1 shows typically the shape of cracks in ZA-80 and ZA-100 samples prepared on alumina support. The crack in ZA-80 is perpendicular to the membrane and transverse on a random cross-section, whereas, the crack in ZA-100 grows along the interface between the membrane and the support. The following parts explain why the crack shapes are different.

In dip-coating process, particles deposited on the support and form wet membrane. The particles are rearranged to try making a close compact. Assuming only two particle sizes, the sintering process of the wet membrane on a rigid support is schematically illustrated in Fig. 2. The fine particles are tumbled in the concave surface of the support. The compact pattern depends on the wet membrane formation mechanism [2]. If capillary colloid filtration is a dominating factor, more fine particles could move to the interface because the current schlep off fine particles; while film coating is the leading factor, less fine particles could move comparing to that in the membrane. However, quite a few fine particles are still blocked in the interstice of the coarse ones for both mechanisms (Fig. 2a).

In drying process, all the particles are rooted by dispersant, denoting that the relative situation might not change, although their distance decreases after water leaving off.

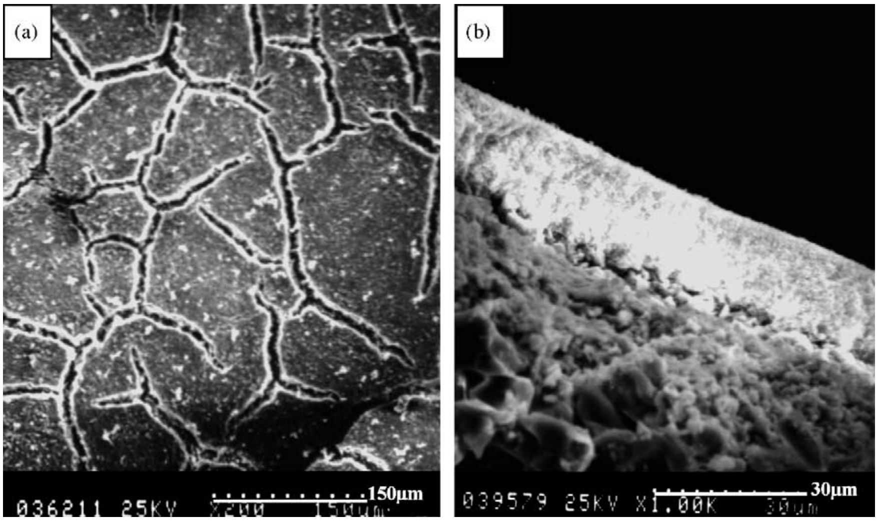

Fig. 1. Shape of cracks in (a) ZA-80 membrane, (b) ZA-100 membrane on alumina support.