Cost-effective utilization of mineral-based raw materials for preparation of porous mullite ceramic membranes *via in-situ* reaction method

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ABSTRACT

Porous mullite ceramic membranes were prepared via *in-situ* synthesis method using abundant natural minerals including coarse bauxite and fine kaolin powders. Thermal sintering behavior of the green sample shows that a unique dimension expansion appears during the sintering process due to the anisotropic growth of mullite crystals. The XRD analysis suggests the ceramic membrane is mainly composed of mullite phase when sintering above 1450 °C. The SEM images confirm that with an increase in sintering temperature, mullitization reaction firstly occurs in kaolin agglomerations, and then bauxite-derived alumina reacts with silica-containing phase by a solution-precipitation mechanism to form an interlocked framework of elongated secondary mullite. Both maximum and average pore sizes increase with increasing sintering temperature. The growth of mullite whiskers has a positive impact on the improvement of porosity and mechanical strength of ceramic membranes. Even after sintering at 1500 °C, the sample shows the highest open porosity of 31.6% and good biaxial flexural strength of 100.2 MPa.

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1. Introduction

Porous ceramic membranes have attracted great attention during last decades and applied in many industrial processes due to their superior properties such as excellent mechanical strength, chemical resistance and thermal stability (Studart et al., 2006; Smid et al., 1996). Alumina is considered as the popular membrane material of commercialized porous ceramic membranes. However, some drawbacks of porous alumina membrane, e.g. high raw material price and poor alkaline resistance, can be magnified when it is used in strong alkaline media separation and some economical environmental applications (Bayuseno et al., 1999; Chen et al., 2008; Dong et al., 2011). Thus, development of the cost-efficient ceramic membrane resistant to thermal shock and corrosion has gained more attention in scientific community.

Mullite ($3Al_2O_3 \cdot 2SiO_2$) has become a potential candidate for porous ceramic membrane application due to high strength and creep resistance, low thermal expansion coefficient, and good chemical and thermal stability. Porous mullite ceramic membranes have been extensively studied and used in the fields of catalyst carriers, filters and ceramic supports for filtration membranes (Abbasi et al., 2012; Liu et al., 2013; Zhao et al., 2010). Low-cost mullite-based ceramic can

be synthesized using kaolin or high-aluminum coal fly ash (Abbasi et al., 2012; Chen et al., 2000; Park et al., 2007). However, a serious problem is that the mullite ceramic from only silica-rich kaolin or fly ash is generally dense after high-temperature sintering due to the existence of excess SiO_2. Commonly, pure alumina and its precursors are added to react with the redundant SiO_2, which is expected not only to form secondary mullite but also to create porous structure at a wider temperature range by prohibiting sintering densification (Chen et al., 2008; Li et al., 2012). Here, the substitution of natural alumina-rich bauxite mineral for alumina can further reduce the cost of raw materials of ceramic membrane.

The mullite powers are not readily sinterable because of the low diffusion rates of the aluminum and silicon species (Jung and Park, 2001). Therefore, the porous mullite ceramic membranes derived from the conventional solid-state-particles sintering method will show the low mechanical strength when sintering temperature is not so high to maintain a porous structure. The growth of mullite crystal may be faster in a crystallographic direction parallel to the c-axis than in any other, resulting in a high degree of orientation (Kim et al., 2009). The produced mullite whiskers may interlock each other in *in-situ* synthesis process of ceramic membrane. This interlocked porous structure constructed by mullite whiskers may enhance the mechanical strength (Li et al., 2012). In this work, the porous mullite ceramic membrane was prepared *via in-situ* reaction using coarse bauxite and fine kaolin powders

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as starting materials. The effect of sintering temperature on phase composition, shrinkage percentage, microstructure, pore property and mechanical strength were studied in detail.

2. Materials and methods

2.1. Synthesis

The commercial bauxite (Ruiyuan Abrasive Sandblasting Factory, Henan, P.R. China) and kaolin (China Kaolin Clay Co. Ltd., Jiangsu, P.R. China), based on the chemical compositions of mullite ($3Al_2O_3 \cdot 2SiO_2$), were ball-milled and mixed at 300 rpm for 10 h in a roller grinding machine. The mass ratio of powder to zirconia ball to alcohol is 1:3:2. The obtained suspensions were dried in an oven at 100 °C for 3 h. After that, the mixed powders were mixed with 1 wt.% polyvinyl alcohol (PVA, molecular weight of 1750 ± 50, solved into 5 wt.% aqueous solution) of the total powders to facilitate dry-pressing process and form a crack-free sample. The green disk membranes with a diameter of 20 mm were produced by the dry-pressing method under an applied pressure of 200 MPa, and then sintered at 1300–1600 °C for 2 h, with a heating rate of 3 °C/min and 2 °C/min before and after 1300 °C respectively, and a cooling rate of 5 °C/min after dwelling at the highest temperatures.

2.2. Characterization

The particle size distributions of bauxite and kaolin as well as their mixture were detected by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK) using water as dispersing medium. The element composition of the bauxite and kaolin was determined by quantitative X-ray fluorescence spectrum analysis (Axios-Advanced, PANalytical Corporation, Netherlands). Open porosity was measured by the Archimedes method with water as liquid medium. The sintering shrinkage behavior of green bars with a dimension of 7 mm × 4 mm × 3 mm was measured in air using a high-temperature dilatometer (Netzsch DIL 402C, Germany) with the same heating and cooling program as green disk membranes. The diameters of disk membranes before and after sintering were examined using a vernier caliper and the radial shrinkage percents (S) were given according the following equation:

$$S = \frac{L - L_0}{L_0} \times 100\% \tag{1}$$

where L_0 and L are the sample diameters before and after sintering, respectively.

The microstructure of porous membranes was observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) at an accelerating voltage of 5 kV. Phase compositions of the raw materials and sintered samples were analyzed using an X-ray diffractometer (DX-2700, China) with Cu Kα radiation at a wavelength of λ = 0.154 nm, generated by 30 mA and 40 kV voltage. The scanning speed was 10°/min from 5°–70° with a step size of 0.03°. A semi-quantitative X-ray diffraction analysis by the Reference Intensity Ratio (RIR) method was employed to determine the phase contents.

A pore size analysis instrument (PSDA-20, Nanjing Gaoqian function materials Co. Ltd., China) was applied to determine the pore size distribution and pore parameters. The pore diameter D was calculated according to the Washburn equation:

$$D = -\frac{4\gamma \cos\theta}{\Delta P} \tag{2}$$

where γ is surface tension of GQ-16 (16 dynes/cm), θ is contact angle between the wetting liquid and the pore surface, and ΔP is the transmembrane pressure.

The biaxial flexure test was employed according to ISO 6872 (ISO-Standards, 1998). The disk specimens with diameters of 17–23 mm and thicknesses of 1.4–1.6 mm were used to a biaxial flexural strength test. Flexural strength was measured using the universal materials testing machine (AGS-X, Shimadzu Corporation Ltd., Japan) and six specimens were tested to obtain the average flexural strength and standard deviation. The biaxial flexural strengths were given according to the equation:

$$S = \frac{P}{t^2} \left\{ (1 + v) \left[0.485 \ln\left(\frac{a}{t}\right) + 0.52 \right] + 0.48 \right\} \tag{3}$$

where S is the flexural strength (MPa), P is the maximum load (N), a is the radius of three-ball support circle (mm), v is the Poisson's ratio, and t is the thickness of the disks.

3. Results and discussions

3.1. Powders characterization

Table 1 lists the chemical composition in oxides weight percentages (wt.%) of bauxite and kaolin. The main constituents of bauxite are Al_2O_3 (84.98 wt.%) and the major impurities are SiO_2 (7.36 wt.%), TiO_2 (4.57 wt.%), and Fe_2O_3 (1.27 wt.%). Besides, there are a minor amount of other oxides such as alkali and alkali-earth metal oxides. The kaolin is mainly composed of SiO_2 (45.51 wt.%) and Al_2O_3 (34.58 wt.%). Except for alkali and alkali-earth metal oxides such as K_2O, CaO and Na_2O in kaolin, there are also small amount of co-existing Fe_2O_3 and TiO_2. The ignition loss of kaolin is about 15.2 wt.%, significantly larger than that of bauxite. This is mainly due to the removal of structural water and organic substances, and the pyrolysis of carbonate, sulfate, sulfide, etc.

Fig. 1 shows the phase compositions of bauxite and kaolin raw materials according the powder XRD analysis. It can be seen that the bauxite presents the main crystal phase of corundum (Al_2O_3, hexagonal, PDF#10-0173) with minor of mullite ($3Al_2O_3 \cdot 2SiO_2$, orthorhombic, PDF#15-0776) and aluminum titanate (Al_2TiO_5, orthorhombic, PDF#41-0258). No peaks of other phases are observed, because of the impurities are very little (see Table 1) and most of them are probably incorporated into the crystal structure of mullite or corundum (Zhou et al., 2008). Phase analysis study of kaolin indicates that the major crystalline phase is kaolinite (monoclinic, PDF#29-1488) with a small amount of quartz (SiO_2, hexagonal, PDF#46-1045) and unknown phase.

The particle size and size distribution of powders play an important role in sintering property and pore structure of porous ceramic membranes. The particle size distributions of kaolin, bauxite and their mixture are shown in Fig. 2. The bauxite particles distribute in range from 2 μm to 70 μm with average size of 19.48 μm. The particle sizes of kaolin concentrate on 2–8 μm and the average particle size is 5.82 μm. The particle size distribution curve of mixed powders shows two main peaks located at ~4.5 and 10 μm, which respectively correspond to kaolin and bauxite. Moreover, the kaolin particles show better dispersion uniformity than bauxite particles in mixed powders. The peak of bauxite in mixed powders shifts to left, indicating that the ball milling causes a slight breakage of powder particles.

3.2. Sintering behavior

The sintering shrinkage behavior of the green rectangular sample was investigated from room temperature to 1580 °C using the dilatometric analysis. Length shrinkage rate (dL/Lo) as a function of heating time is shown in Fig. 3. In the temperature range of 486–565 °C, the obvious shrinkage (about 0.6%) occurs due to the transformation of kaolinite to metakaolinite according to the following reaction:

$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \text{ (kaolinite)} \rightarrow Al_2O_3 \cdot 2SiO_2 \text{ (metakaolinite)} + 2H_2O.$