Processing and properties of glass-bonded silicon carbide membrane supports

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ARTICLE INFO

ABSTRACT

Porous SiC membrane supports were fabricated from SiC and glass frit at a temperature as low as 850 °C in air by a simple pressing and heat-treatment process. The effects of the initial SiC particle size and frit content on the porosity, flexural strength, and air permeation of the membrane supports were investigated. During heat-treatment, the glass frit transformed to a viscous glass phase, which acted as a bonding material between SiC particles and as a protecting layer for severe oxidation of SiC particles. The porosity of the porous SiC membrane supports could be controlled within a range of 37–46% with the present set of processing conditions. The typical flexural strength, permeability, and specific air flow rate of the porous membrane supports fabricated using 23 μm SiC particles with 15 wt% glass frit were 75 MPa, 4.2×10^{-13} m^2, and 32.4 L/min/cm^2, respectively.

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1. Introduction

Water is a key element in our daily lives, and membrane filtration for water treatment is one of the most promising methods for cleaning and recycling water. Among the membranes commercially available and/or under development, SiC membranes have attracted attention due to their set of unique properties: low thermal expansion coefficient, high thermal conductivity, excellent thermochemical and thermomechanical stability, and biocompatibility [1–10]. The structure of the SiC microfilters consist of membrane supports (porous media) and a surface layer (so-called membranes). The quality of SiC membranes, which is hampered by the presence of pinholes and microcracks, is strongly dependent on the porosity and microstructure (pore size, pore shape, pore size distribution of SiC grains) of the membrane supports [11]. Thus, preparation of membrane supports with tailored microstructural characteristics is a key factor for producing high quality filters.

Most of the previous research on SiC membranes focused on (1) the processing of a disk or tube-type SiC support by a partial sintering method and subsequent coating of SiC membranes on the SiC supports with polymeric precursors (mostly allylhydrido polycarbosilane) [1–3,12–15], (2) processing of ultrafiltration membranes on commercial SiC microfiltration or macroporous supports (mostly from LiqTech International A/S (Ballerup, Denmark)) [8,16], and (3) processing of SiC hollow fiber membranes and characterization of their mechanical properties and permeability [10].

Various processing methods, including partial sintering [1,5,10,17], recrystallization [18], and bonding techniques [19–27], have been reported for processing SiC membrane supports. Partial sintering and recrystallization techniques require high temperatures ≥ 1500 °C for processing if SiC powder is used as a starting material because of its strong covalent bonding [1,5,17,18]. Possible routes to reduce the processing temperature are to use preceramic polymers as a precursor for SiC [5,6,28] and the use of bonding materials [19–27]. Mullite ($3Al_2O_3 \cdot 2SiO_2$) [19,21,29], silica (SiO_2) [22,23], silicon oxycarbide (SiOC) [24,25], sodium borate [26], cordierate [27], and glass frit [30,31] were investigated as bonding materials for porous SiC ceramics. However, open-cell SiC supports prepared from preceramic polymers showed poor mechanical strength compared to powder-processed SiC membrane supports [28,32]. In contrast, porous SiC supports prepared with bonding materials showed relatively better mechanical properties [22,24,25]. Among the above bonding methods, the glass-bonding technique has not been investigated extensively although it provides several benefits for processing SiC membrane supports, such as ease of porosity and pore size control, and cost-effectiveness. Only a few previous works were found in the literature and are summarized as follows:

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(1) Chae et al. [30] prepared glass-bonded porous SiC using SiC powders, a glass frit, and glass microbeads as raw materials and characterized the flexural strength of the porous ceramics. The typical flexural strengths of glass-bonded porous SiC ceramics were 19–23 MPa at 46–49% porosity.

(2) Wang et al. [31] prepared glass-bonded porous SiC for vacuum chuck applications. By adjusting the particle size of SiC powders and glass frit content, the porosity of the porous SiC ceramics could be controlled within the range of 32–65%. The air permeability and adsorbability were investigated for the glass-bonded porous SiC ceramics.

However, mechanical properties and chemical durability of glass-bonded porous SiC membrane supports have been rarely investigated. This paper investigated the effects of SiC particle size and glass frit content on porosity, flexural strength, and air permeation of glass-bonded porous SiC membrane supports. The chemical durability of glass-bonded porous SiC ceramics in acid and alkali solutions was also investigated.

2. Experimental procedure

Commercially-available SiC powders with particle sizes of 10 μm, 23 μm, 35 μm (Sinxing Advanced Materials, Hong Kong), and 65 μm (Showa Denko K.K., Tokyo, Japan), and a glass frit bonding material (Korea Ceramics Co. Ltd., Gwangju-shi, Gyeonggi-do, Korea) were used as the starting powders. The chemical composition of the glass frit material was as follows: 73.2% SiO_2, 10.6% B_2O_3, 6.4% Al_2O_3, 6.3% Na_2O and 3.5% other materials. The weight fraction of the glass frit was 10, 15, 20, and 25 wt%. To prepare a batch consisting of SiC and glass frit, the SiC powder, glass frit, and organic binders (polyethylene glycol and polyvinyl alcohol, 5 wt% with respect to ceramic powders) were mixed by ball milling using SiC media in distilled water in a polypropylene jar for 24 h. The mixture was dried, sieved, and uniaxially pressed at an applied pressure of 40 MPa. The samples were sintered at 850 °C for 2 h with a heating rate of 3 °C/min in air without an applied pressure. The number after SC denotes the particle sizes of the SiC powders, e.g., SC10 and SC65 represent the SiC membrane supports prepared from 10 μm and 65 μm SiC powders, respectively.

The bulk densities of the SiC membrane supports were calculated from the weight-to-volume ratios of the samples. The porosities of the SiC membrane supports were measured using Archimedes' method. The crystalline phases in the sintered specimens were characterized by X-ray diffraction (XRD; D8 Discover, Bruker AXS GmbH, Karlsruhe, Germany) of the crushed powders using Cu Kα radiation.

The fracture surface morphology was observed using scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan). For the flexural strength measurements, bar-shaped samples were cut to a size of $3 \times 4 \times 35$ mm^3 and bending tests were performed at a constant crosshead speed of 0.5 mm/min using a three-point bending fixture with a span of 30 mm.

The open porosity and pore size distribution of SiC membrane supports were measured using mercury porosimetry (AutoPore IV 9500, Micromeritics, Norcross, GA, USA). The air flux of some selected specimens was measured by capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., Ithaca, NY, USA). The specimens (25 mm in diameter and 3.5 mm thick) were fitted between O-rings in the bottom of the chamber and the bottom of the chamber was inserted for capillary flow porosimetry. The flux was then measured automatically by sensors while incrementally changing the pressure of the regulator. The gas permeability (α) was com-
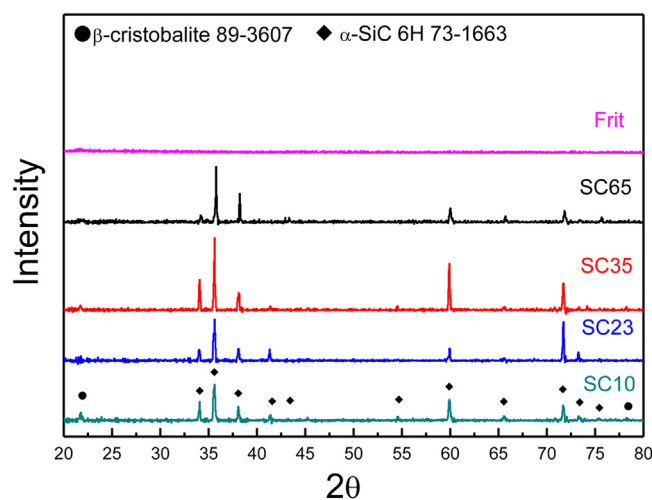

Fig. 1. XRD patterns of the glass frit and SiC membrane supports sintered at 850 °C for 2 h in air: SC10, SC23, SC35, and SC65 denote membrane supports prepared from SiC powders with particle sizes of 10 μm, 23 μm, 35 μm, and 65 μm, respectively, containing 15 wt% glass frit.

puted from the measured flow rate and pressure difference using Darcy's law,

$$\Delta p/L = \eta \cdot Q/A \cdot \alpha \tag{1}$$

where Δp is the pressure drop from the entrance to the exit of the sample, L is the thickness of the sample, Q is the flow rate of air through the sample, η is the viscosity of air, A is the cross-sectional area of the sample, and α is the permeability.

The chemical stability of the glass-bonded SiC membrane supports (SC10) with 15 wt% glass frit was evaluated by placing samples in glass bottles filled with a pH solution of 3 or 11, respectively. The pH 3 and 11 solutions were prepared using nitric acid and ammonia solution with distilled water, respectively. The bottles were stored at room temperature for 63 days. The strength of the samples subjected to acid or base solution was compared with an identical unexposed sample (SC10). The glass frit composition in the neck areas after 63-days exposure in an acid or base solution was analyzed using energy dispersive spectroscopy (EDS, JSM-6010PLUS/LA, JEOL, Tokyo, Japan) and compared to that of the identical, unexposed sample.

3. Results and discussion

XRD analysis was performed to identify the phases present in the SiC membrane supports sintered with 10–25 wt% glass frits at 850 °C for 2 h in air. XRD patterns of the SiC membrane supports sintered with 15 wt% glass frit are shown in (Fig. 1). Those of the other supports with 10, 20, and 25 wt% glass frit were almost the same for corresponding specimens in Fig. 1. The glass frit was an amorphous material with no crystallization product after heat-treatment at 850 °C for 2 h and furnace cooling. All membrane supports consisted of α-SiC (6H) and a trace of SiO_2 (β-cristobalite), which is an oxidation product of SiC powders from sintering in air. The intensities of the β-cristobalite peaks increased with decreasing SiC particle size because of the accelerated oxidation of finer powders at the sintering temperature.

Fig. 2 shows the typical microstructures of the SC10 specimens with 10–25 wt% glass frit. The microstructures show well-developed pore structures in all specimens. Most of the pores originated from the inter-particle spaces in the green compact. Comparison of Fig. 2(a) and (d) clearly shows that the addition of more glass frit produced thick bonding areas and the filling of smaller pores. The glass-bonding phase in the present specimen is