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Oxidation-bonded SiC membrane for microfiltration

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ABSTRACT

Porous SiC is a proven viable material for microfiltration membranes, but its application has been limited by high fabrication cost. In this study, the oxidation bonding technique was used for the first time to fabricate SiC microfiltration membrane. The study was divided into two parts: optimization of the slurry used to dip coat the SiC particles over a porous SiC ceramic support and controlling the oxidation behaviour of SiC with respect to temperature. The oxidation behaviour during different thermal treatments was related to pore morphology and ultimately the membrane permeance. By coating the clay-bonded SiC support with oxidation-bonded SiC and sintering the coating at 1100 °C for 1 h, we prepared a defect-free microfiltration membrane with pure-water membrane permeance of $> 210\ \mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$, an average pore size of 93 nm, and a narrow pore-size distribution.

1. Introduction

Porous silicon carbide (SiC) has emerged as an essential ceramic material because of its unique characteristic properties such as high mechanical strength, strong chemical resistance, high thermal conductivity, low thermal expansion coefficient, and high thermal shock resistance. It is used in many industrial applications such as water filtration [1–7], diesel particulate filters [8], high-temperature/high-voltage semiconductor electronics [9], vacuum chucks [10], hot gas filters [11], porous burners [12], and molten metal filters [13].

A water-filtration membrane made of SiC possesses some excellent properties [14] as the surface of SiC matrix has a low water contact angle [15], which makes it highly hydrophilic, and as a result, the material shows high water permeability. Moreover, owing to the characteristic negative charge on the material surface [16], the ability to reduce deposition of foulants is highly increased. Conventionally, porous SiC ceramics are fabricated by heating powder compacts in an inert atmosphere. Owing to the highly covalent character of the SiC bond in SiC, high sintering temperatures (above 2000 °C) are required to achieve sufficient neck growth between the particles, thus limiting the practical application of porous SiC ceramics.

The oxidation of SiC is an important phenomenon that has been studied extensively during the past several decades [17–23]. Many studies have been carried out on the oxidation behaviour of SiC, and it has been reported that SiC-based materials generally exhibit two different oxidation regimes: active and passive oxidation. The oxidation behaviour depends on the oxidizing conditions such as the oxidizing species, temperature, total pressure, and partial pressure of the oxidant. Passive oxidation occurs at high oxygen partial pressures and very high temperatures, and a protective SiO_2 layer is formed according to the reaction

$$SiC_{(s)} + 1.5\,O_{2(g)} \rightarrow SiO_{2(s)} + CO_{(g)} \tag{1}$$

In contrast, active oxidation, which is observed at low oxygen partial pressures and high temperatures, a non-protective oxide film is formed because of significant SiO vapour formation:

$$SiC_{(s)} + O_{2(g)} \rightarrow SiO_{(g)} + CO_{(g)} \tag{2}$$

Passive oxidation leads to weight gain, while active oxidation leads to weight loss [24]. Active oxidation reduces the strength of a sample, whereas passive oxidation leads to the formation of a coherent silica layer over the silicon carbide surface, thereby improving its performance in several applications.

It is known that the passive oxidation of SiC is controlled by the diffusion of oxygen molecules (or oxygen ions) through the oxide thin film [25–29]. At temperature above 600 °C in air, SiC will react with air to form a silica-rich surface layer. Several studies showed that the oxidation of SiC above 1000 °C follows a parabolic rate law, which indicates that the oxidation process is controlled by diffusion [27–33]. At low temperature (< 1300 °C), the oxidation process is dominated by the transport of molecular oxygen, whereas at higher temperature (> 1300 °C), the contribution of the transport of ionic oxygen is high [33–36].

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The oxidation phenomenon is well studied for SiC in powder or completely dense unicrystalline form. The first study on the porous preform based on oxidation-bonded SiC was carried out by Shi et al. [37]. Their study involved heating a SiC powder compact in air instead of an inert atmosphere, which led to the formation of a passive silica layer on the surface of the SiC particles. This silica layer was found to bind SiC particles together. They also reported that when the temperature was increased, the amount of oxidation-derived silica, mass of the specimens, and particle size also increased. The increase in the particle size was attributed to the development of the low-density silica layer on the SiC particle surface.

After the publication of the work by Shi et al. [37], continued research was carried out by She et al. to prove the validity of the oxidation-bonding mechanism [38–41]. In this series of work, porous SiC specimens with controlled microstructure were fabricated by changing the sintering temperature, particle size, and pore former, and using alumina as an additive. Furthermore, Chun et al. [42] and Dey et al. [43] prepared porous SiC specimens by coupling the oxidation-bonding technique with the use of microbeads and petroleum coke as pore formers, and Liu et al. [44] uses starch and carboxy-methyl cellulose as pore forming agent. In all of these studies, the specimens were isotropic in nature and the applications were limited to electronic packaging, aerospace industry, catalytic support, filters for hot gas or molten matter, coal gasification, and combustion. None of the above studies on porous SiC material based on oxidation-bonding mechanism was focused on the utilization of an oxidation-bonded SiC membrane in the form of a thin coating over a porous support.

In this study, an oxidation-bonded SiC membrane was first fabricated by heating the coating made by dip coating in slurry having pure silicon carbide powder in an oxidizing atmosphere. This was done in order to evaluate and control the bonding phase in form of oxide film formed on the surface of the silicon carbide. In other words, a reliable ceramic membrane for water treatment was produced by controlling the formation of a rigid oxide layer resulting from passive oxidation.

A particularly important point is that a slight volume expansion occurred during the oxidation process, and this phenomenon was effective in inducing the rearrangement of particles in the coating. This is in contrast to the generation of defects such as surface cracks by the shrinkage occurring during sintering of the coating. Since fine SiC powder is more sensitive to the oxidation reaction, a systematic study like ours is necessary. Moreover, by using the oxidation-bonding method and a lower sintering temperature, it is possible to prepare cost-effective ceramic membranes.

2. Experimental procedures

For the preparation of clay-bonded SiC support layers, α-SiC (average particle size: 6.7 μm) from Dalian Zhengxing Abrasive Co., China, and kaolin (average particle size: 2.1 μm) from Sigma-Aldrich, USA, were used in concentrations of 92 and 8 wt.%, respectively. To extrude the clay-bonded flat-tubular porous SiC support layers, 25 wt.% of methyl cellulose (Sigma-Aldrich, USA) was added as an organic binder, and 25 wt.% of distilled water was added as a solvent. The resultant mixtures were aged in sealed bags for 48 h at 25 °C temperature and then extruded by a double-screw extruder (KTE-50S, Kosentech, Korea).

In our earlier study [45], an extruded clay-bonded flat-tubular porous SiC support layer was prepared. In comparison with the disk type samples, the structure of the extruded support, allows both sides of the support as membrane thus increasing the effective surface area of the membrane. Also, this type of structure allows easy surface cleaning from outside as well. The extruded structure was used as it gives increased surface area, with high strength. As shown in Fig. 1(a), it had a flat tubular morphology (width: 50 mm, height: 4 mm, length: 200 mm) and 16 inner holes (width: 2 mm, height: 2 mm). After extrusion, the specimens were dried for 24 h at 25 °C temperature. To burn off the organic binder, the dried specimens were heat-treated at 400 °C for 4 h and then sintered at 1400 °C for 1 h. Fig. 1(b) shows the cross-sectional morphology of the clay-bonded SiC support; it had an interconnected porous network with high open porosity of 47%, an average pore size of 1.80 μm, and pure-water permeability of 5.5×10^3 L m^{-2} h^{-1} bar^{-1} (LMH bar^{-1}).

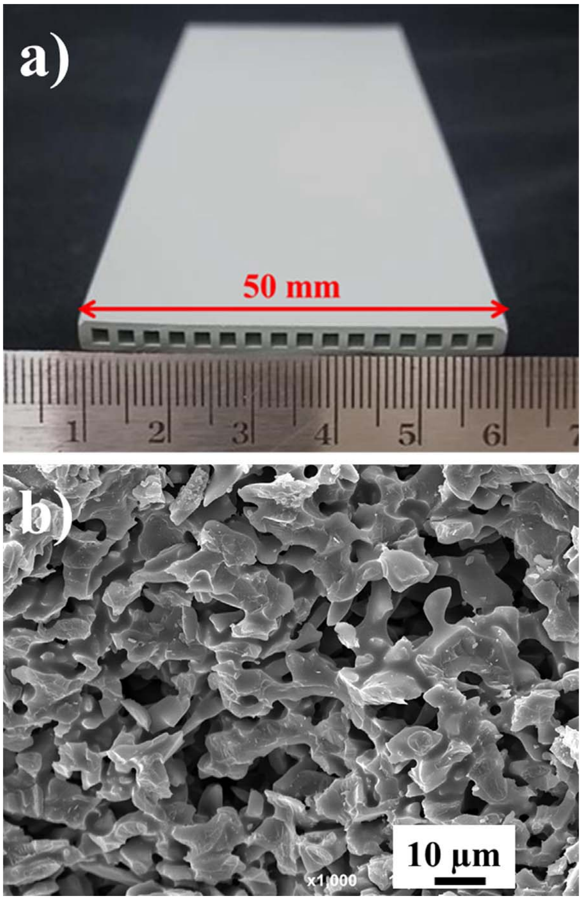

Fig. 1. (a) Macroscopic view and (b) SEM micrograph of a cross section of the extruded and sintered clay-bonded flat-tubular porous SiC support layer.

The dip-coating method was used to prepare an oxidation-bonded SiC active layer over the clay-bonded flat-tubular porous SiC support. For coating, the inner holes were first sealed by masking tape, in order to coat only outside surface. Then SiC slurries with concentration varying from 2 to 10 wt.% were prepared from SiC powder (UF-15-A, average particle size: 0.55 μm, specific surface area: 15 m^2 g^{-1}) produced by H.C. Starck Ceramics GmbH, Germany (Table 1). De-ionized water and iso-propyl alcohol (IPA) from Samchun Chemicals, Korea, were used as solvents, and polyvinyl alcohol (PVA; M_W:

Table 1
Slurry composition for dip coating of SiC on clay-bonded flat-tubular porous SiC support layer.

Sample	Slurry composition [a]				
	Powder	Solvent		Binder	
	SiC	H_2O	IPA	PVA	PEG
S2	2	64	32	1	1
S4	4	62.7	31.3	1	1
S6	6	61.3	30.7	1	1
S8	8	60	30	1	1
S10	10	58.7	29.3	1	1

[a] 0.5 wt.% of Darvan-CN was also added as a dispersant.