Electrostatic Formation of a Ceramic Membrane with Fine Pores†

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Abstract

A new method for forming a ceramic membrane was devised. Ultra-fine particles synthesized by thermally activated CVD (Chemical Vapor Deposition) were deposited on the surface of a porous ceramic supporter by electrostatic force and sintered in an inert gas atmosphere. The ceramic membrane made by this method is available for ultrafiltration because it has very fine pores of about 0.04 micro-meter in diameter but a large porosity.

1. Introduction

A new process for producing ceramic membranes with fine pores, using ultra-fine particles prepared by a vapor-phase reaction (thermal CVD process) has been developed, with studies on its effectiveness being carried out†−3). The principle of this method is as follows: CVD ultra-fine particles are electrically charged directly after being produced, deposited onto a surface of a porous ceramic substrate in the DC-field to form a particle layer, and are sintered to form a membrane with fine pores. This new method was named "Electrostatic Formation of a Ceramic Membrane (EFCM)", and it is being investigated further.

It is very important to successfully develop this method of forming ceramic membranes with fine pores because of its extensive applications, including water treatment under high pressure and high temperature, separation or condensation of organic solutions, cleaning of high temperature gases containing corrosive components, etc., while the present polymer membranes are not always suited to these specific processes.

This paper describes the principle of the Electrostatic Formation of a Ceramic Membrane (EFCM), the structure and results of basic performance tests of the membrane as a separation membrane in the case of forming a membrane from silicon nitride ultra-fine particle coating on the outside of porous ceramic tubes.

2. Experimental Apparatus and Principles of Electrostatic Formation of a Ceramic Membrane (EFCM)

Figure 1 shows a schematic diagram of the

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experimental apparatus for producing a membrane from ultra-fine silicon nitride particles. It consists of a reactor and membrane-forming section, with a quartz tube (1) contained within (42 mm ID). The reactor consists of four coaxial quartz tubes within a quartz tube (1). In a membrane-forming section, a corona-discharging electrode (3) and a DC electrode (4) are installed to charge the ultra-fine particles from the reactor and make them migrate. Power supplies (5) and (6) supply high-frequency high voltage (about 20 kHz, 20 kV) and high DC voltage (about 5 kV), respectively. An AC-corona discharging system is adopted for stable corona generation even under high temperature and in a complex gas composition, and monopolar ions are produced by supplying the DC voltage to this system.

The ultra-fine particles prepared in the reactor are carried down like a thin cylinder with sheath gas (inert gas such as nitrogen or argon) which flows from the inner and outer inlet. Reaching the forming section, they are charged with the same polarity in the corona area close to the discharging electrode, migrate toward the center electrostatically in the supplied DC-field, deposit on the outer wall of the substrate (a porous ceramic tube) installed on the central axis and form a layer of the accumulated particles. The substrate can be moved up or down and rotating slowly to be coated with a uniform layer. The particle layer is then sintered directly into an asymmetric ceramic membrane without being taken out of the apparatus. The porous substrate used in this study is sintered alumina tubes with an outer and inner diameter of 10 and 7 mm, respectively, and its nominal mean pore size is 10 μm.

For preparing the ultra-fine particles of silicon nitride as the forming material of the membrane, silicon-tetrachloride and ammonia gas are used. This reaction is carried under excess ammonia; therefore, ammonium-chloride deposits as the by-product following the reactions:

\[
3\text{SiCl}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{HCl}
\]
\[
12\text{HCl} + 12\text{NH}_3 \rightarrow 12\text{NH}_4\text{Cl}
\]

Ammonium-chloride, however, does not deposit on the substrate surface when the membrane forming section is kept above its sublimation temperature of 340°C \(^4\).

3. Membrane Formation

3.1 Size and size distribution of the particles prepared by CVD

It is expected that the pore size of the membrane prepared by sintering the deposited particle layer would depend on the size of the constituent silicon nitride particles, and it is necessary to prepare particles as fine as possible for forming a membrane with fine pores. The size of the particles prepared by thermal CVD process depends on the concentration of the reactive gases and the reaction temperature essentially; therefore, it is necessary to select the optimum condition for preparing particles.

The ultra-fine particles of silicon nitride prepared at 1200°C are considered to be amorphous like \(^4\).

Fig. 2 TEM photograph of Si\(_3\)N\(_4\) particles synthesized by thermally activated CVD (temperature: 1200°C, concentration of SiCl\(_4\): 1.4%, NH\(_3\)/SiCl\(_4\) = 6)

Fig. 3 Size distribution of the particles of Fig. 2 measured with centrifugal photo extinction method

Figures 2 and 3 show a TEM photo of the silicon nitride particles prepared in these experiments and the size distribution of these particles measured by the photo extinction centrifugal sedimentation method, respectively. These
particles were synthesized under the following reactive conditions: the concentration of silicon-tetrachloride in the reactor was 1.4% by volume, the ratio of ammonia to silicon-tetrachloride was 6 and the reaction temperature was 1200°C. As being observed in Fig. 2, the particles are of uniform diameter of several tens of nm, and the weight medium diameter is 0.07 μm according to Fig. 3. It should be noted that the photo extinction centrifugal sedimentation method does not give an absolutely correct size distribution, because it has some problems remaining to be solved including several factors such as the extinction coefficient, but we can get a significant information regarding the relative size distributions of the other particle groups. Figure 4 shows the effects of the silicon-tetrachloride concentration on the average particle size determined by the photo extinction centrifugal sedimentation method, where the weight-average particle size is plotted against the silicon-tetrachloride concentration in the reaction zone (the ratio of ammonia to silicon-tetrachloride was fixed at 6). It is shown that the average particle size decreases as the silicon-tetrachloride concentration decreases.

3. 2 Electrostatic deposition

Figure 5 presents a photo of the substrate coated with the electrostatically deposited particles before sintering. The upper photo is the alumina substrate coated with the particles; it is difficult to be observed because both the particles and substrate were white in color. To avoid this difficulty, the middle one shows the particles which are deposited on a quartz tube. The lower one shows the test pieces for the electromicroscope. The white part is the deposit layer in the middle one. It is observed that the particles are deposited uniformly over the tube's surface. The length and thickness of the deposited particle layer can be controlled by the movement distance of the substrate, and the velocity of movement of the substrate and the concentration of the particles prepared, respectively.

3. 3 Structure of the sintered membrane

To form a better membrane, it is necessary to sinter the particle layer to provide as a
in sintering ceramic materials, the temperature, time of reaction, rate of temperature rise, the atmosphere and the sintering aids must be controlled. In these experiments, the deposits were sintered under various trial and error conditions and the membrane structures examined by SEM analysis mainly. The silicon nitride particles prepared in these experiments could be sintered at 1200 ~ 1300°C in nitrogen. This is a much lower temperature than that normally associated with production of the structural silicon nitride materials. For this reason, these particles are considered very small and amorphous, or the deposit layer is very thin. As this is a very interesting phenomenon, it is necessary to study it in more depth in future.

**Figure 7** presents a cross-sectional SEM photo of the membrane. It is an asymmetric, dense membrane with a thickness of approximately 20 μm, covering the 1.5 mm thick alumina substrate. **Figure 8** shows a SEM photo of the membrane with its surface structures. This membrane was sintered at 1200°C for 2 hr in nitrogen. A very peculiar membrane with a three-dimensional network is observed. Such structures have resulted presumably from the characteristic structures of the electrostatically deposited particle layer shown in **Fig. 6**. A membrane with this structure has a large porosity similar to a fiber filter; therefore, is advantageous in keeping the pressure drop very low when it is utilized as the separation membrane.

The pore size of the membrane shown in **Fig. 8** is several micrometers, determined from the photo, and can be directly applied for various industrial purposes including microfiltration (MF). On the other hand, there is also a strong need for a membrane with smaller pores. To control the size of the ultra-fine particles synthesized as the material for the membrane is one of the major factors that can be used to control the pore size in this membrane forming method. One of the factors to control the particle size is the reactant gas concentration as shown in **Fig. 4**. The membrane shown in **Fig. 8** is made from the particles prepared with a silicon-tetrachloride concentration of 1.4%, while with a fairly reduced concentration of 0.21% in **Fig. 9**. The pore size of the membrane shown in **Fig. 9**, determined from the micro-photo, is 1 μm or less, and it is about one-tenth of the membrane shown in **Fig. 8**. Although the size of these particles is not measured, it is considered to be much smaller than that of the particles in **Fig. 8**, and estimated to be 0.04 μm from **Fig. 4**. (It has to be noted that this particle size is characterized using the photo extinction centrifugal sedimentation method.) These results have indicated that the pore size of the membrane can be controlled to some extent by controlling the size of the
deposited (or prepared) particles. On the other hand, in these experiments, decreasing the reactant gas concentration with change the number concentrations of the produced particles; therefore, the concentration of the depositing particles is expected to be one of the factors to control the pore size of the membrane. It is, however, not known how the structures of the deposited particle layer are affected by these factors, nor how the structures of the sintered membrane are affected by that of the deposited particle layer. At present, the effects of reactant gas concentration, reaction temperature, electrostatic depositing conditions and sintering conditions are being quantitatively investigated.

4. Basic Characteristics of the Membranes

The membranes prepared by the method “Electrostatic Formation of a Ceramic Membrane (EFCM)” have characteristic structures; therefore, they are expected to be used for a wide variety of industrial applications. These ceramic membranes are highly heat- and chemical-resistant, and they are sufficiently porous to allow fluids to pass at a very low pressure drop. Some of the expected applications of these membrane are, therefore, utilizing them as the filters for high-temperature gas cleaning and for the separation of organic solutions.

![Figure 10](image1.png)

**Fig. 10** Gas pressure drop of the ceramic membrane

Figure 10 shows the gas pressure drops across the substrate and that coated with the membrane shown in Fig. 8. They have almost the same magnitude of resistance to gas permeation, though the pore size of the membrane is about 1/10th the size of the alumina substrate (nominal pore size is 10 μm). This is due to the fact that the ceramic membrane layer is much thinner than the substrate (20 to 1500 μm), and the membrane has a porous and three-dimensional network structure.

![Figure 11](image2.png)

**Fig. 11** Water flux of the ceramic membrane

Figure 11 shows similar experimental results in case of water flow at various temperatures. The decrease in the water flux caused by forming the membrane is about 10%, and its resistance may be seen to be very low. It is also noted that water flux increases with temperature, these membranes are suitable for treatment of water as well as for separation of organic solutions at high temperatures.
Figure 12 shows the results of the separation tests of the membranes shown in Figs. 8 and 9 using the mono-dispersed polystyrene latex systems of various particle sizes (latex concentration is 100 ppm or less). The separation capacity corresponds to the pore size distribution of each membrane and agrees well with the results of observing by SEM photos. Both membranes have a sharp separation efficiency; in particular, the efficiency of the membrane shown in Fig. 9 is 0.04 μm at a 50% rejection, and this is high enough to be used for ultrafiltration (UF).

4. Conclusions

This paper has discussed the principle of the Electrostatic Formation of a Ceramic Membrane (EFCM), and the characteristics and basic properties of the ceramic membranes prepared by this method.

The membranes prepared by this newly developed process are characterized by a three-dimensional network structure and very high porosity; therefore, they allow various fluids to pass through them at a very low pressure drop. These characteristics are unique for these membranes.

The pore size of the membrane can be controlled to some extent by controlling the size of the ultra-fine particles used as the material of the membrane. One membrane prepared in this study has micropores of 0.04 μm on the average.

The separation efficiency of the membrane (this corresponds to its micropore distribution) is fairly sharp, it is suitable for various applications including ultrafiltration (UF), and now other application areas are under studying. We are also investigating the effectiveness of the electrostatic formation of a ceramic membrane applying for ultra-fine particles of materials other than silicon nitride, such as titanium dioxide and alumina.

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