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## Characterized microstructure of porous $\text{Si}_3\text{N}_4$ compacts prepared using the pyrolysis of polysilazane

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### Abstract

The present paper describes the feasibility of controlling pore sizes of porous-fired  $\text{Si}_3\text{N}_4$  compacts prepared using the pyrolysis of polysilazane, for developing a  $\text{Si}_3\text{N}_4$  membrane manufacturing technique. Attention has been paid to the microstructure of these compacts in order to identify the main parameter governing the evolution of polysilazane-to-ceramic direct conversion. A volumetric shrinkage, stemming from the pyrolysis of polysilazane and the following crystallization of pyrolyzed polysilazane, have been shown to be of prime interest in the control of pore-size determination. A porosity of ~35% was achieved in the fabrication of compacts, the pore-size distribution of which was controlled in the range 1–1000 nm, with polysilazane additions of 80–200 vol%. Also demonstrated was the effect of firing temperature on pore-size distribution. The bending strength of the processed specimens was equivalent to that of Vycor glass, indicating the feasibility of an application in the preparation of microstructured membrane system.

**Keywords:** Ceramic membrane; Pyrolysis; Silicon nitride; Pore-size distribution

### 1. Introduction

Recently, microporous ceramic membranes have been attracting a good deal of attention resulting from the important applications of such membranes in separation industries where their organic counterparts fail to function [1,2]. Silicon nitride membranes do offer potential advantages, particularly in high-temperature gas separation and catalytic applications, because of their unique combination of better high-

temperature mechanical properties and resistance to oxidation and thermal shock [3]. For making use of these characteristics, pure  $\text{Si}_3\text{N}_4$  has to be densified. Owing to the covalent nature of the Si–N bond,  $\text{Si}_3\text{N}_4$  ceramics processed without sintering aids, and high temperatures and pressures are porous bodies normally. When  $\text{Si}_3\text{N}_4$  ceramics prepared with additives are used under high-temperature conditions, the additives form a second phase and commonly impair the mechanical and physical properties of the original  $\text{Si}_3\text{N}_4$ .

New processing routes are in progress to fabricate pure  $\text{Si}_3\text{N}_4$  ceramics by using thermal decomposition

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of organo-substituted polysilazanes. These routes enable high-yield pure  $\text{Si}_3\text{N}_4$  to be synthesized without additives [4,5]. Since the pyrolysis products show some blistering of the solid, reasonably so, due to the release of gaseous by-products during pyrolysis [6,7], polysilazanes cannot be directly transformed into dense  $\text{Si}_3\text{N}_4$  ceramics.

Nevertheless, the fact that  $\text{Si}_3\text{N}_4$  porous bodies can be prepared using the pyrolysis of polysilazane reasonably supports an application in the preparation of  $\text{Si}_3\text{N}_4$  membrane system. A major concern is therefore to develop a technology to form well-tailored microstructures by controlling the gas release during pyrolysis.

The objective of the present study is to develop a fabrication technology of  $\text{Si}_3\text{N}_4$  membrane system with well-controlled microstructures, based on the pyrolysis mechanism of polysilazane. Wakeman et al. [8] were able to prepare a ceramic membrane, the pore size of which was 100 nm or less, by pyrolytically decomposing a methylsilazane precursor immersed into a sialon microfilter. The present paper discusses the feasibility of controlling pore sizes of porous  $\text{Si}_3\text{N}_4$  compacts by adequate control of the amount of polysilazane doped and the firing conditions. Emphasis is laid on the microstructure of these compacts in order to identify the main parameter governing the evolution of polysilazane-to-ceramic direct conversion and the deformation of the original porous structure. In the proposed process, polysilazane is capable of serving as a binder for  $\text{Si}_3\text{N}_4$  powders, thereby insuring the stability of the processed compacts, either thermal or chemical.

## 2. Experimental procedure

Fig. 1 shows the sequence of steps in preparing porous  $\text{Si}_3\text{N}_4$  compacts. The starting materials were  $\text{Si}_3\text{N}_4$  (SN-E10, Ube Ind., with an average diameter of 300 nm) and polysilazane (SILACERAM-NCP-201, Chisso, with an average molecular weight of 1250) powders. The polysilazane used had been synthesized according to the recipe proposed by Seyferth et al. [7], with some modifications. In conventional method, KH-catalyzed polymerization of  $(\text{CH}_3\text{SiH}_2\text{NH})_n$  cyclic oligomers obtained by ammonolysis of methylchlorosilane  $(\text{CH}_3\text{SiHCl}_2)$  results in  $(\text{CH}_3\text{SiH}_2\text{NH})_n(\text{CH}_3$

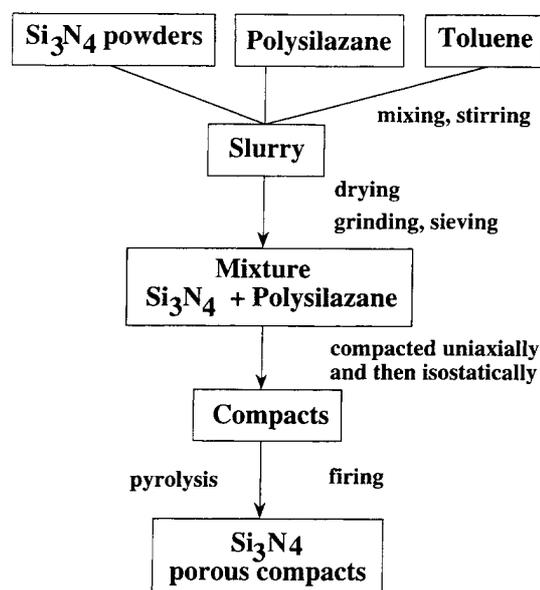


Fig. 1. Preparative procedure of microporous  $\text{Si}_3\text{N}_4$  compacts by thermal decomposition of polysilazane.

$\text{SiH}_2\text{NCH}_3)_b(\text{CH}_3\text{SiN})_c$  polymers, which are unstable and sensitive particularly to hydrolysis by moisture in air. In our process, the addition reaction of tetramethyldisilazane  $((\text{CH}_3)_2\text{SiH})_2\text{NH}$  to the  $(\text{CH}_3\text{SiH}_2\text{NH})_n$  oligomers, with KH in tetrahydrofuran, was applied in order to prepare the stable polysilazane. KH and solvent were then completely removed by the appropriate workup, leaving the product in the form of a pale-yellow powder, which was found to contain  $-\text{CH}_3\text{SiH}_2\text{NH}-$  and  $-(\text{CH}_3)_2\text{SiH}-$  units. It should be noted that the SILACERAM in common organic solvents is stable on prolonged storage at room temperature and that it provides a high yield of ceramic product on pyrolysis. In this study, we used polysilazane dissolved in toluene.

The  $\text{Si}_3\text{N}_4$  powder was added to toluene-containing thick syrups of polysilazane in  $\text{Si}_3\text{N}_4$ /polysilazane mixtures with volumetric ratios of 100/80, 100/120, 100/160 and 100/200. These mixtures contained solid polysilazane in the range 20–38.4% by weight. The mixture was ultrasonically dispersed for 5 min and then dried at room temperature to form a friable cake. The cake was ground into powder using a motor and pestle, followed by further heat treatment at  $60^\circ\text{C}$  in vacuum for 20 h. Subsequently, the annealed product was ground again and then was screened to  $<250\ \mu\text{m}$ .

These prepared powders were compacted isostatically at 296 MPa after uniaxial compression in a die (20 mm in diameter) at 5 MPa. It should be noted that, in this compaction process, polysilazane is capable of serving as a binder for ceramic powders. The compacts were dewaxed by heating to 550°C at a constant heating rate of 0.1°C min<sup>-1</sup> and then calcined to 800°C at a rate of 3°C min<sup>-1</sup>. The temperature of the calcination process was determined from the result of thermal gravimetric analysis (TGA).

The fabricated compacts were fired isothermally for 4 h at temperatures of the range 1000–1800°C, according to the predetermined temperature–time conditions. Firing temperature was widely changed in order to observe the effects of temperature on the microstructure of a processed compact. Specimens from pure Si<sub>3</sub>N<sub>4</sub> powders were also prepared following the same recipe to compare the pore-size distributions with those prepared from the mixtures.

The porous structure of the processed specimen was characterized by mercury-penetration porosimetry. Nitrogen-adsorption experiments were also carried out for the sample with micropores (≤3 nm). XRD and SEM were used for phase identification and morphology observation, respectively. Finally, several specimens were subjected to measurements of bending strength in which 3×4×36 mm<sup>3</sup> test specimens were employed.

### 3. Results and discussion

The influence of firing temperature on pore-size distribution is shown in Fig. 2 where the cumulative pore volume is plotted against the pore size, for the specimen prepared without polysilazane. It has been found that the pore-size distribution had maximum pore size up to 110 nm and underwent no significant change with varying firing temperature in the range 800–1450°C. This result implies that the characteristic porous structure in the specimens prepared from pure Si<sub>3</sub>N<sub>4</sub> powders should be dominated by the pore volume and pore size, fabricated in green compacts. On firing at 1800°C, the mean pore size of 1 μm was observed. This was caused by grain growth of Si<sub>3</sub>N<sub>4</sub> particles and was verified by SEM analysis.

While in cases where polysilazane was doped as ceramic precursor, pore size is strongly dependent

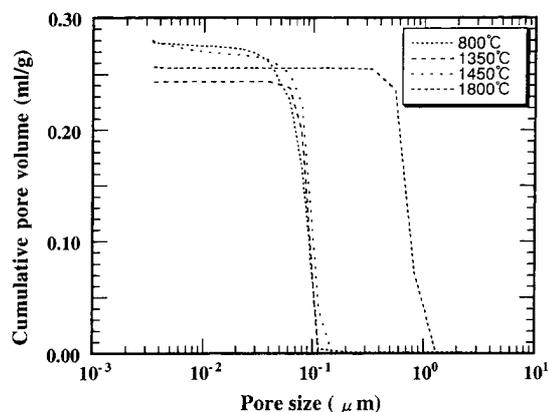


Fig. 2. Effects of firing temperature on pore-size distribution of the 0 vol%-Si<sub>3</sub>N<sub>4</sub> compact.

both on the firing temperature and the amount of polysilazane, as demonstrated in Fig. 3. It is clearly shown that the pore volume is slightly reduced according to the amount of doped polysilazane. In cases where polysilazane was oversaturated, the specimens fired at temperatures as below as 1450°C have smaller pores than those shown in Fig. 2.

Fig. 3(a) shows the result for the 80 vol%-specimen, the pore-size distribution of which underwent no significant change with varying temperature compared to the other specimens. Macropores contained in the green compact probably remained in the fired specimen, that was caused by the unsaturated doping of polysilazane along the grain boundaries in Si<sub>3</sub>N<sub>4</sub> matrices. It is also found that the grain growth starts at ~1450°C, resulting in an increase in the mean pore size. When larger amounts of polysilazane (Si<sub>3</sub>N<sub>4</sub>/polysilazane volumetric ratios of 100/120, 100/160, and 100/200) were used, the pore-size distributions of the specimens were obviously affected by firing temperature. Fig. 3(c) shows the result for the 160 vol%-specimens fired at different temperature. It is found that the specimen has a feasibility of controlling pore sizes ranging 10–600 nm under firing temperature ranging 1350–1800°C, with the pore volume remaining almost constant. These pores are suspected to be caused by volumetric shrinkage of polysilazane, which filled the grain boundaries of Si<sub>3</sub>N<sub>4</sub> and then crystallized during the firing process. This is probably explained by the fact that the specimen fired at 800°C, when polysilazane starts to crystallize, has an extremely small pore volume.

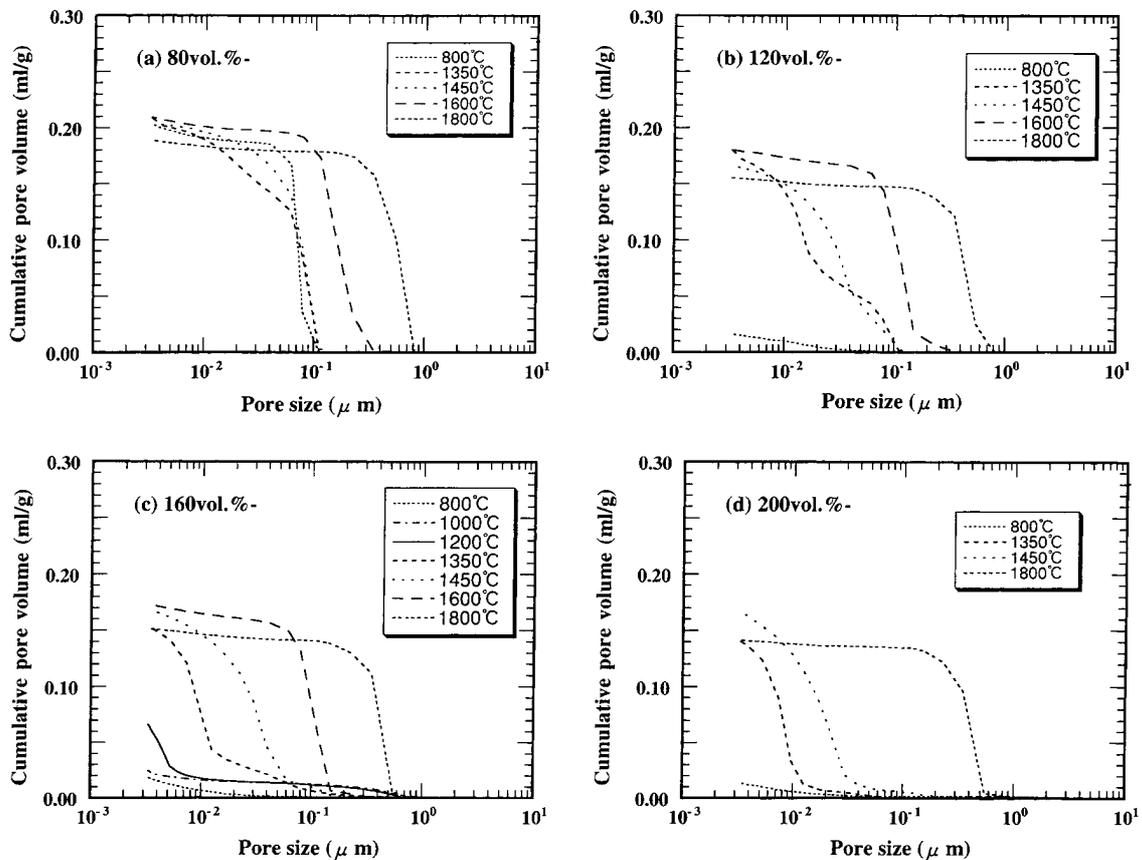


Fig. 3. Effects of firing temperature on the pore-size distribution of the polysilazane-doped compact.  $\text{Si}_3\text{N}_4$ /polysilazane volumetric ratios are: (a) 100/80, (b) 100/120, (c) 100/160, and (d) 100/200.

In order to demonstrate the difference in morphology of the fired compacts, examples of microstructures of the specimens, fired isothermally at temperatures ranging 550–1800°C, are shown in Fig. 4. In cases where polysilazane is contained, the specimens have microstructures, different from specimens without polysilazane. As the firing temperature was increased, polysilazane was allowed to serve as a binder and to evolve mesopores in  $\text{Si}_3\text{N}_4$  matrix. It is observed under the SEM that the grain boundaries grow at 1800°C in both cases, with or without polysilazane, and that polysilazane may bridge or cover silicon nitride particles, leading to the formation of more extended network structures. The specimens containing polysilazane with different  $\text{Si}_3\text{N}_4$ /polysilazane ratios showed similar morphological variations.

The extent of network structure may depend on the amount of polysilazane as well as firing temperature.

From the results of XRD analysis for the 160 vol%-specimens, it was concluded that a continuous transition from the amorphous phase to crystalline  $\alpha$ - $\text{Si}_3\text{N}_4$  occurred at 1300°C, and that mixtures of mainly the  $\beta$ -phase and residual  $\alpha$ -phase were found at  $\geq 1450^\circ\text{C}$ . The complete transformation from the  $\alpha$ -phase to the  $\beta$ -phase occurred at  $\geq 1500^\circ\text{C}$ , from which extensive grain growth would be suspected. Owing to the strong dependency of grain growth on temperature, the firing temperature should be an important factor which dominated pore-size distributions in the fired products.

The thermal-decomposition process was studied by thermogravimetry, using a 160 vol%-specimen. At a

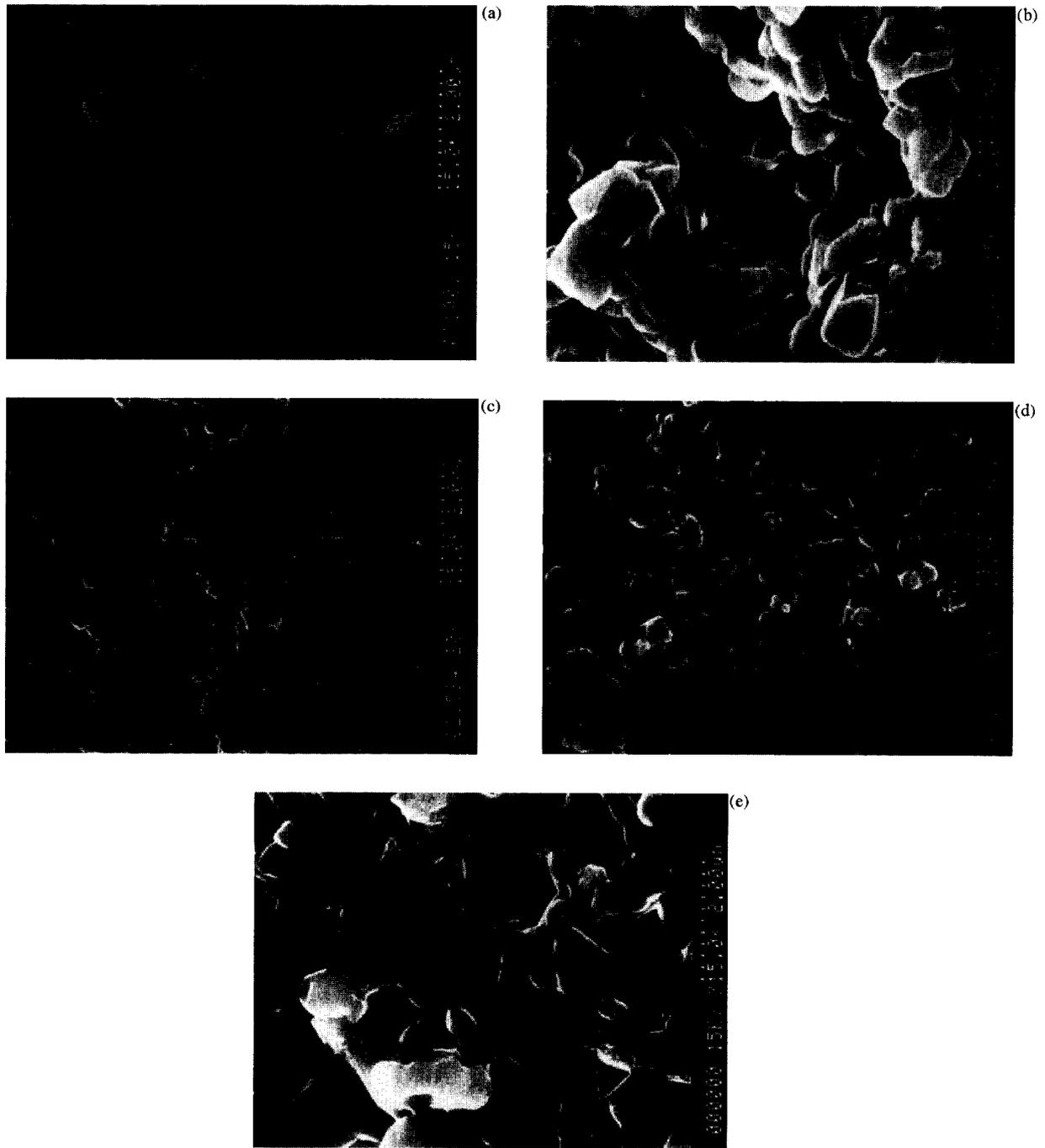


Fig. 4. SEM images of fired, porous  $\text{Si}_3\text{N}_4$  compacts: (a) polysilazane 0 vol%, fired at 1450°C; (b) polysilazane 0 vol%, fired at 1800°C; (c) polysilazane 200 vol%, fired at 550°C; (d) polysilazane 200 vol%, fired at 1450°C; and (e) polysilazane 200 vol%, fired at 1800°C.

constant heating rate of  $5^{\circ}\text{C min}^{-1}$  (from room temperature to  $1000^{\circ}\text{C}$ ), the decomposition proceeded smoothly and asymptotically with no inflections in the weight loss vs. temperature graph. Weight loss began at  $80^{\circ}\text{C}$  and was virtually complete at  $800^{\circ}\text{C}$ , amounting to 12% of the initial weight. The weight loss in the range  $800\text{--}1000^{\circ}\text{C}$  was  $\ll 1$  wt%. During the pyrolysis of polysilazane at temperatures exceeding  $200^{\circ}\text{C}$ , the reaction of Si–H and N–H groups takes place with the simultaneous loss of  $\text{NH}_3$  and  $\text{H}_2$  leading to the formation of trisilylated nitrogen bridges ( $\text{NSi}_3$ ) between the polymeric molecules [4,9]. When the temperature is raised, the main gaseous decomposition products evolved are  $\text{CH}_4$  and  $\text{H}_2$ . It has been suggested that gas absorption occurs at temperatures  $>400^{\circ}\text{C}$ , resulting from the reaction between polysilazane and  $\text{N}_2$  in the atmosphere. It should be noted that the gas release during the pyrolysis step causes foaming and crack formation [6,7]. In the present process, however, the gaseous reaction products can be removed without the formation of cracks, owing to the open porosity present in the compacted green samples.

The relative change in length in the temperature range  $550\text{--}1800^{\circ}\text{C}$  can be taken from Fig. 5, where the linear shrinkage is plotted against the volumetric ratio of doped polysilazane. The shrinkage gradually increases with increasing amount of polysilazane. The 0 vol%- and 80 vol%-specimens fired at  $1800^{\circ}\text{C}$  shrink by 1.2% and 2.0%, respectively, stemming

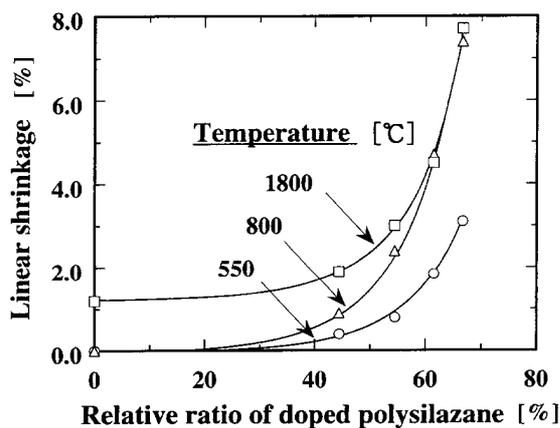


Fig. 5. Linear shrinkage of processed compacts during heat-treatment in the temperature range  $550\text{--}1800^{\circ}\text{C}$ , in  $\text{N}_2$  atmosphere.

from densification induced by the sintering process. While in cases where oversaturated amounts of polysilazane were used, variation in the shrinkage showed a relation similar to that observed for the specimens fired at  $800^{\circ}\text{C}$ .

Amorphous  $\text{Si}_3\text{N}_4$ , derived from pyrolysis of polysilazane starts to crystallize into the  $\alpha$ -phase at  $1300^{\circ}\text{C}$ , which increases with increasing temperature, as could be confirmed by XRD. This process seems to be accompanied by the formation of micropores, since the density of the amorphous phase is lower than that of the  $\alpha$ -phase and substantial shrinkage does not occur during the process. The  $\alpha$ -phase precipitates along the grain boundaries in  $\text{Si}_3\text{N}_4$  matrices, resulting in the size reduction of open pores due to densification of large crystalline grains. When the firing temperature is raised to  $1800^{\circ}\text{C}$ , no significant difference in mean pore size of the specimens of  $\text{Si}_3\text{N}_4$  and polysilazane-doped  $\text{Si}_3\text{N}_4$ , resulting from the extensive grain growth would be expected.

When the compact was fired at  $1450^{\circ}\text{C}$ , the pore volume as well as the median pore size has a tendency to decrease with increasing amount of polysilazane. The 200 vol%-specimen, for instance, has a median pore size of  $\sim 15$  nm, while the 0 vol%- and 80 vol%-specimens, 100 nm and 90 nm, respectively. The specimens with oversaturated polysilazane, however, do not have a significant difference in pore volume. For the compacts fired at  $1800^{\circ}\text{C}$ , the decrease in the median pore size was observed with increasing amount of polysilazane. The median pore size is considerably larger than those of the specimens fired at temperatures  $<1600^{\circ}\text{C}$ . This is obviously a result of the extensive grain growth of  $\text{Si}_3\text{N}_4$ , suggesting that advanced grain growth rate should be expected with a larger amount of polysilazane. On firing at  $1800^{\circ}\text{C}$ , the specimen has a more extended network structure and large pores, as could be confirmed by SEM.

As demonstrated in Fig. 3(c), it should be noted that the 160 vol%-specimen, fired at temperatures  $<1200^{\circ}\text{C}$  obviously has pores smaller than 3 nm which is the lower limit measurable by mercury porosimetry. Fig. 6 shows the effects of the firing temperature on the mean pore size measured by the nitrogen-adsorption method for the 160 vol%-specimens. The median pore size was determined from the peak value taken from the pore-size distribution diagram. Also plotted are the data measured by mercury porosimetry for the

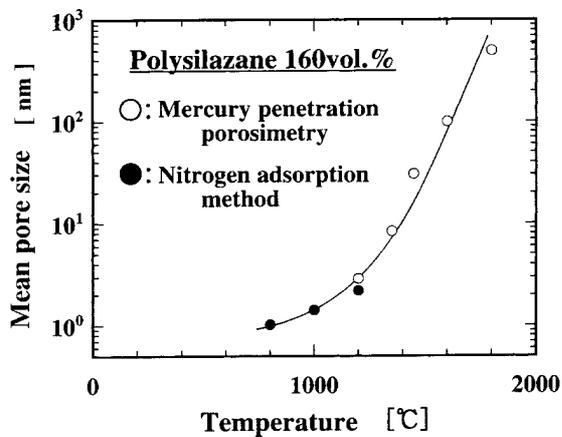


Fig. 6. Effects of firing temperature on the mean pore size measured by nitrogen-adsorption method for the 160 vol%-specimen.

specimens fired isothermally at temperatures  $>800^{\circ}\text{C}$ . It is found that the median pore size gradually decreases with decreasing firing temperature and takes values of 2.2, 1.6 and 1.0 nm for the specimens fired at 1200, 1000 and  $800^{\circ}\text{C}$ , respectively. These results suggest a feasibility to control the pore size ranging from one to several hundreds of nanometers by an adequate control of the firing temperature as well as the amount of doped polysilazane.

Asymmetric membranes usually consists of a thin top-layer responsible for separating components, and a porous ceramic-support with single or multiple layers for imparting the required mechanical strength to the membrane composite. In all cases, the top-layer must be defect-free and has preferably a narrow pore-size distribution, whose indispensability sets severe demands on the quality of the intermediate layer and the support. It should be noted that the support system including intermediate layers can have different morphologies and microstructures. In most cases, these composite membranes have a gradually decreasing pore size on their feed sides. In the proposed process, it is quite feasible to provide processing steps for preparing porous support with a gradual change in pore size through the membrane/support system. The result again implies that the process conditions which enable pore size to be tailored in the order of nanometer should be applicable in the development of separation layer of membrane as well as membrane-support systems. In the fabrication process of micro-

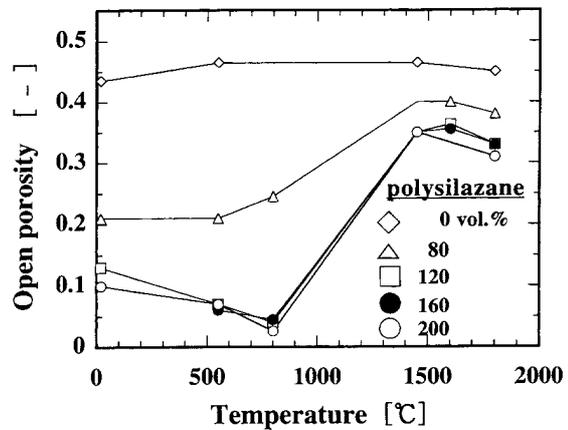


Fig. 7. Open-porosity changes with change in firing temperature for compacts derived from different amounts of polysilazane.

porous structure, the amorphous  $\text{Si}_3\text{N}_4$  was derived from pyrolysis of polysilazane crystallizes along the grain boundaries of the original  $\text{Si}_3\text{N}_4$  particles, thereby insuring the stability of the processed membrane system, either thermal or chemical. Further work is in progress to address the details of the mechanism of polysilazane-to- $\text{Si}_3\text{N}_4$  direct conversion and the micropore formation, as well as the important issues related to the ceramic membrane-system processing involved.

Open-porosity changes with change in firing temperature are shown in Fig. 7 for the specimens containing different amounts of polysilazane. The open-porosity was determined from the observed pore volume, taking into account the pore volume stemming from the apparently macroscopic defects ( $\geq 10 \mu\text{m}$ ). The porosity of a green compact increases with a decrease in the amount of polysilazane. This is reasonably explained by the insufficient amount of polysilazane required to fill the pores in the  $\text{Si}_3\text{N}_4$  matrices. The specimens prepared from pure  $\text{Si}_3\text{N}_4$  have a porosity of 45%, irrespective of the firing temperature. For these specimens, the grain growth would make the pore size increase at temperatures  $>1600^{\circ}\text{C}$ . Because of the unsaturated doping, the porosity of the 80 vol%-specimen increased with increasing temperature and a leveling-off occurred, with cure slopes giving indications of approaching an upper limit of 40%. Whereas for the specimens prepared with oversaturated polysilazane, which constitutes matrices in the compacts, the porosity was  $\sim 10\%$

in the green compacts and declined to 5% at 800°C where the pyrolysis of polysilazane is nearly complete. This decrease in porosity should be caused by the volumetric shrinkage of polysilazane during pyrolysis process, as demonstrated in Fig. 5. When the firing temperature is raised furthermore, the porosity increases to 35% at 1600°C. The maximum value of the porosity does not seem to depend on the oversaturated amount of polysilazane in the range 120–200 vol%.

The compacts processed at 1450°C currently has mechanical strengths upto 46 MPa, which were determined at room temperature in four-point bending tests. The bending strength gradually increased with an increase in the amount of doped polysilazane. Although the bending strength of the processed specimens is half of that of the reaction-bonded Si<sub>3</sub>N<sub>4</sub>, with a porosity similar to the present material (information provided by Showa Denko Co., Tokyo) it is almost the same as that of the Vycor glass widely used as membrane substrates or supports. This result indicates that the porous Si<sub>3</sub>N<sub>4</sub> compacts structured with polysilazane are applicable in the preparation of membrane systems. From the measurement of pore-size distribution, several specimens contained some macroscopic pore >5 μm, which were apparently defects stemming from the shrinkage and gas release during the pyrolysis of polysilazane. The higher mechanical strength of the processed specimens would be expected by optimizing the processing steps.

#### 4. Conclusions

Porous, fired Si<sub>3</sub>N<sub>4</sub> compacts with an open porosity, as high as 35%, have been prepared from a mixture of Si<sub>3</sub>N<sub>4</sub> powders and polysilazane. In the preparation process, the pores effective for gas separation can be controlled by pyrolysis of polysilazane.

Green compacts shrink linearly until the pyrolysis of polysilazane is virtually complete at 800°C, followed by the crystallization of the pyrolyzed polysilazane along the grain boundaries in Si<sub>3</sub>N<sub>4</sub> matrices. The size reduction of open pores due to the formation of network structure is expected, which insures the feasibility of controlling pore sizes.

In cases where polysilazane is oversaturated, the pore-volume-changes with amount of polysilazane are

less significant, indicating a small change in the open porosity after sintering at different temperatures. Whereas firing temperature shows a strong dependency on pore-size distribution, mean pore size decreases, reasonably so, to the nano-order with increasing firing temperature.

It is possible to vary the median pore size in the range 1–1000 nm, under the process conditions: adequate control of the firing temperature and the amount of doped polysilazane.

It has been demonstrated that the processed porous Si<sub>3</sub>N<sub>4</sub> compacts have a bending strength equivalent to that of the Vycor glass. This result should make it possible to prepare the porous Si<sub>3</sub>N<sub>4</sub> compacts applicable in the development of membrane systems.

#### References

- [1] R.S.A. de Lange, J.H.A. Hekkink, K. Keizer and A.J. Burggraaf, Formation and characterization of supported microporous ceramic membranes prepared by sol-gel modification techniques, *J. Membrane Sci.*, 99 (1995) 57–75.
- [2] R.J.R. Uhlhorn, M.H.B.J. Huis in't Veld, K. Keizer and A.J. Burggraaf, Synthesis of ceramic membranes, Part I Synthesis of non-supported and supported γ-alumina membranes without defects, *J. Mater. Sci.*, 27 (1992) 527–537.
- [3] K.S. Mazdiyasi and C.M. Cooke, Synthesis, characterization, and consolidation of Si<sub>3</sub>N<sub>4</sub> obtained from ammonolysis of SiCl<sub>4</sub>, *J. Am. Ceram. Soc.*, 56(12) (1973) 628–633.
- [4] R. Riedel, G. Passing, H. Schonfelder and R.I. Brook, Synthesis of dense silicon-based ceramics at low temperatures, *Nature*, 355 (1992) 714–717.
- [5] D. Seyferth and H. Plenio, Borasilazane polymeric precursors for borosilicon nitride, *J. Am. Ceram. Soc.*, 73(7) (1990) 2131–2133.
- [6] D. Seyferth, G.H. Wiseman and C. Prud'homme, A liquid silazane precursor to silicon nitride, *J. Am. Ceram. Soc.*, 66(1) (1983) C-13–C-14.
- [7] D. Seyferth and G.H. Wiseman, High-yield synthesis of Si<sub>3</sub>N<sub>4</sub>/SiC ceramic materials by pyrolysis of a novel polyorganosilazane, *J. Am. Ceram. Soc.*, 67(7) (1984) C-132–C-133.
- [8] R.J. Wakeman, J.L. Henshall and S.G. Ng, Modification of sialon microfilters by pressureless sintering, pyrolysis of organometallic precursors and nitridation of thin films, *Trans. I. Chem. E.*, 74(A) (1996) 329–339.
- [9] T.Q. Liu, O. Sakurai, N. Kieda, M. Kato and N. Mizutani, Preparation of spherical Si<sub>3</sub>N<sub>4</sub> particles from polysilazane by ultrasonic pyrolysis technique, *J. Ceram. Soc. Japan*, 97(10) (1989) 1321–1325.