

# Processing of SiC Ceramics with High Reliability Using Chemically Modified Polycarbosilane as a Compaction Binder

Yuichi SAWAI, Yuji IWAMOTO, Sachiko OKUZAKI,\* Yoshiyuki YASUTOMI,\*

Koichi KIKUTA\*\* and Shin-ichi HIRANO\*\*

Synergy Ceramics Laboratory, Fine Ceramics Research Association, 2-4-1, Mutsuno, Atsuta-ku, Nagoya-shi 456-8587

\*Department of Energy Devices, Hitachi Research Laboratory, Hitachi Ltd., 7-1-1, Omika-cho, Hitachi-shi 319-1292

\*\*Graduate School of Engineering, Nagoya University, 1, Furo-cho, Chikusa-ku, Nagoya-shi 464-8603

## 化学修飾ポリカルボシランを用いた高信頼性 SiC セラミックスの作製

沢井裕一・岩本雄二・奥崎幸子\*・安富義幸\*・菊田浩一\*\*・平野眞一\*\*

ファインセラミックス技術研究組合シナジーセラミックス研究所, 456-8587 名古屋市熱田区六野 2-4-1

(財)ファインセラミックスセンター内

\*(株)日立製作所日立研究所エネルギー素子研究部, 319-1292 日立市大みか町 7-1-1

\*\*名古屋大学大学院工学研究科, 464-8603 名古屋市千種区不老町 1

Chemically modified polycarbosilane containing organofluoric groups, PCOCF, was synthesized and used as a compaction binder for SiC ceramics. The powder fluidity and the powder packing property were evaluated by measuring angle of repose, tap density, green density and pore size distribution of both the binder coated powders and the compacts. The PCOCF coated SiC powder showed improved fluidity and packing property, owing to the organofluoric side chains of PCOCF. Thus, the PCOCF coating was found to be the most effective among other binders to lubricate the SiC particles, which results in a higher compaction under the same loading conditions. The compact of PCOCF coated SiC powder contains only homogeneously dispersed small pores, and therefore, the mechanical strength of the sintered body can be improved, the scatter in bending strength values being also significantly reduced due to the PCOCF coating.

[Received February 8, 1999; Accepted August 23, 1999]

**Key-words :** SiC, Polycarbosilane, Powder packing, Powder fluidity, Pore size distribution, Scatter in strength value

### 1. Introduction

Engineering ceramics, such as SiC, Si<sub>3</sub>N<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>, have high fracture strength and low fracture toughness due to the strong covalent bonding or ionic bonding. The strength of ceramics is sensitive to the size of defects in contrast to metals due to its low fracture toughness. The strength of ceramics has been known to depend strongly on flaw size in ceramic material even if produced through the same process, i.e., the scatter in the strength value of ceramics is generally large. This is one of the reasons to limit in commercial applications of ceramics.

The microstructural control is one of the ways to improve the reliability of ceramics. Strengthening leads to high allowable stress. Toughening leads to enhance the fracture strength when the increase in the size of fracture origin is prevented. Toughening has been achieved in ceramic composites by nano-particles,<sup>1)-5)</sup> whiskers<sup>6)-8)</sup> or fibers<sup>9)-11)</sup> dispersion. It is, however, difficult to toughen the monolithic ceramics without any dispersants.

The fracture strength often decreases due to the increase in defect size.<sup>3),12)</sup> Thus it is effective to decrease total amount of defects and the defect size for improving the reliability of the monolithic ceramics. Basically, an important method to decrease the size of defects in ceramics is to fabricate well-densified powder compacts as well as the microstructural control.

Polycarbosilane (PC) is the most typical polymeric precursor for SiC-based ceramics<sup>13),14)</sup> and can be chemically modified to yield binary ceramic systems such as SiC-TiC,<sup>15),16)</sup> SiC-ZrC<sup>17)</sup> and Si-Al-C-O systems.<sup>18)</sup> If the polymeric SiC precursor is applied as the compaction binder for SiC ceramic powder compacts, the precursor derived functions are introduced to SiC ceramic powder and powder compacts, leading to the high quality of the

monolithic SiC ceramics. Such a functional binder can be designed flexibly by chemical modification technique. The authors have reported on the chemical modification of PC and its application as a compaction binder of SiC powders. PC was chemically modified with the fluoroalkylmethyldimethoxysilane. The modified PC, named as "PCOCF" acts as a coating material with excellent oxidation resistance in wet air.<sup>19)</sup>

The objective of this study is to apply PCOCF for the compaction binder of the SiC powder to decrease total amount of defects and the defect size in the green compacts, and to decrease the scatter in the strength value of the sintered one. This paper describes properties of the PCOCF coated SiC powder, pore size distribution of the compacts, and mechanical properties of the sintered bodies.

### 2. Experimental procedure

PCOCF was synthesized by modifying PC (Nippon Carbon Co., Ltd., Type UH, Mn=2600) with fluoroalkylmethyldimethoxysilane (Toshiba Silicone, TSL-8231 : CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>3</sub>(OCH<sub>3</sub>)<sub>2</sub>). The chemical processing of PCOCF is described in the reference.<sup>19),20)</sup>

The PCOCF coated SiC powder (denoted PCOCF/SiC) was fabricated as follows. Calculated amount of toluene solution of PCOCF was mixed with SiC powder (Showa Denko, α-SiC, DU-A1, 0.47 μm) and 0.5 mass% of boron (B, Mitsuwa Pure Chemicals, 0.85 μm) by a glass mortar for 1.5 h. The mixed slurry was then dried and sieved through a 60 mesh screen. In this way, 1, 3, 5 and 10 mass% PCOCF coated SiC powders were prepared. On the other hand, one of the typical compaction binders for SiC powder is phenol, and phenol (Mitsubishi Co., Novolac type) coated SiC powder (denoted phenol/SiC) was also prepared by the same way as the PCOCF coating using

ethanol solvent.

Evaluation of powder properties was carried out by measuring the angle of repose of the powder on a spatula as well as measuring the tap density of loosely accumulated powder. The angles of repose of the PCOCF/SiC powder and the phenol/SiC powder were determined by a restricted-pile method as shown in Fig. 1. A spatula (120 × 22 mm) and a sieve of 0.21 mm mesh were used. The powder was passed slowly through the sieve onto the spatula. After the spatula was buried under the powder, the saucer was removed and the limit accumulation angle,  $\theta_1$ , was measured. Next a small weight (50 g) was dropped from the height of 160 mm onto one end of the spatula to knock off the loose surface powder, and the second limit accumulation angle,  $\theta_2$ , was measured. These measurements

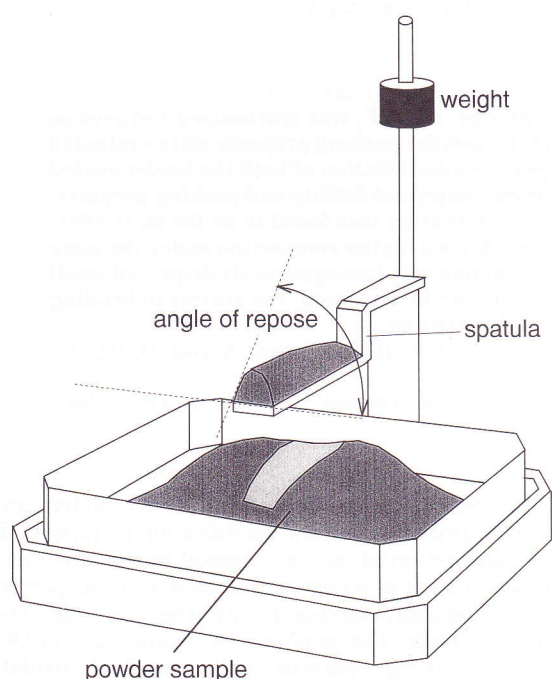


Fig. 1. Experimental system to measure the angle of repose.

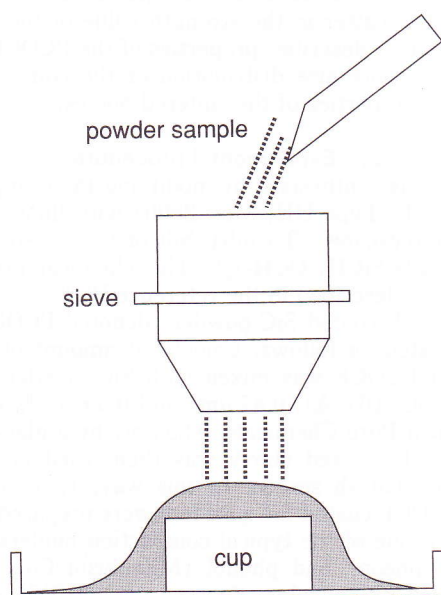


Fig. 2. Experimental system to measure the tap density.

were carried out four times.

The tap densities of the powders were determined using a cup (100 ml) and a sieve of 0.21 mm mesh as shown in Fig. 2. The powder was dropped from the height of 220 mm, passed slowly through the sieve into the cup. After the cup was buried under the powder, the loose surface powder was removed, and the weight of the powder in the cup, i.e., 100 ml, was measured. These measurements were carried out four times.

Cylindrical green compacts of PCOCF or phenol coated SiC powders were prepared by uniaxial pressing into pellets (15 mm in diameter and 3 mm in thickness) at a pressure of 30 MPa. Relative densities of the green compacts were evaluated as a function of binder content. The green densities were calculated by measuring the volume and the weight of the green compacts. Relative density was calculated using the theoretical density of SiC ( $3.21 \text{ g} \cdot \text{cm}^{-3}$ ) and that of PCOCF or other binders ( $1.1 \text{ g} \cdot \text{cm}^{-3}$ ). Pore size distributions of all samples were obtained by a mercury porosimetry (Auto Pore 3, Shimadzu Corp., Tokyo, Japan), under a pressure up to 413 MPa ( $6 \times 10^4$  psi). A contact angle of  $130^\circ$  was used to calculate pore radius.

The green compacts for hot pressing ( $40 \times 50 \times 10 \text{ mm}$ ) of 1, 3, 5% PCOCF or 3% phenol coated SiC powders were prepared under the same compaction conditions described above. The green compacts were placed in a graphite die and heat-treated in a graphite resistance heating furnace (Model High Multi 10000, Fujidempa Kogyo, Osaka, Japan). Heat treatment consists of three steps such as, (1) heating to  $1000^\circ\text{C}$  at the rate of  $100^\circ\text{C}/\text{h}$  for pyrolyzing, (2) heating to  $1500^\circ\text{C}$  at the rate of  $600^\circ\text{C}/\text{h}$  and holding for 1 h for the reduction of the surface oxide of SiC powder, and (3) heating to  $2050^\circ\text{C}$  at the rate of  $600^\circ\text{C}/\text{h}$  and holding for 15 min at a hot pressing pressure of 30 MPa. Heat treatment was carried out in an ambient argon atmosphere. Apparent density of hot press sintered compacts was measured by the Archimedes' method. Four-point bending strengths were determined using a four-point rupture test on  $3 \times 4 \times 40 \text{ mm}$  bar samples of which surfaces and edges were polished with diamond powder ( $0.5 \mu\text{m}$ ). The fracture toughness was determined by the single-edge-pre-cracked beam (SEPB) method.

### 3. Results and discussion

#### 3.1 Properties of PCOCF coated powder

The angles of repose of the powder samples on a spatula,  $\theta_1$  and  $\theta_2$ , are summarized in Fig. 3. Both of  $\theta_1$  and  $\theta_2$  of the

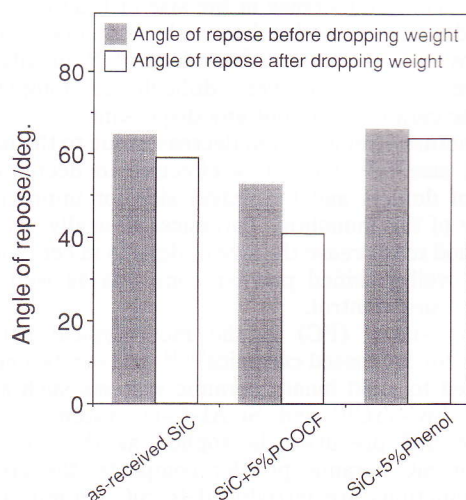


Fig. 3. Angles of repose of powder samples.

PCOCF/SiC powder are smaller than those of the as-received powder and the phenol/SiC powder. The difference ( $\theta_1 - \theta_2$ ) of the PCOCF/SiC powder is larger than that of the as-received powder and the phenol/SiC powder.

The tap densities of the powder samples are summarized in Fig. 4. The tap density of the PCOCF/SiC powder is higher than those of the as-received powder and the phenol/SiC powder. This result also suggests the improvement of powder fluidity by the PCOCF coating, leading to the highly dense accumulation, while the phenol coating conducts no improvement in the powder fluidity.

### 3.2 Properties of PCOCF coated powder compacts

Figure 5 shows the relationship between the binder content and the relative green densities of the binder coated SiC powder compacts under the same loading condition of 30 MPa. The relative green density of the PCOCF/SiC compact is higher than those of the phenol/SiC compact and the other binders/SiC compacts.

Figure 6 shows a comparison of the pore size distributions of the green compacts of the PCOCF(5%)/SiC powder and the phenol(5%)/SiC powder. The peak position of pore size distribution of the PCOCF/SiC compact is observed at about  $0.07 \mu\text{m}$ , which is smaller than that of phenol/SiC compact. The pore size distribution of the

PCOCF/SiC compact is sharper than that of the phenol/SiC compact. Those results indicate that the PCOCF coating does lubricate the SiC particles better than phenol, which results in higher compaction under the same loading condition.

Figure 7 shows a comparison of the pore size distributions of the compacts pyrolyzed at  $1000^\circ\text{C}$ . No significant change in the peak position can be observed for each sample. The PCOCF converts to SiC phase in high yield (75 mass%) by heating,<sup>19)</sup> while only the half of phenol is burn-

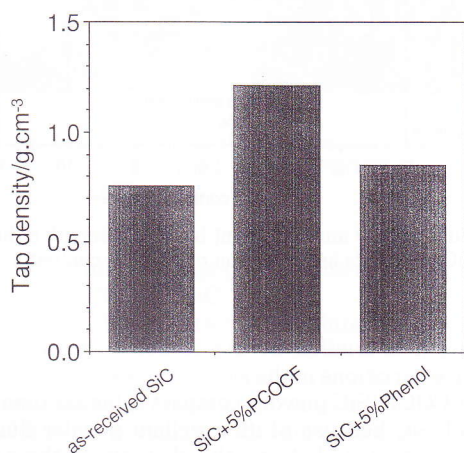


Fig. 4. Tap densities of powder samples.

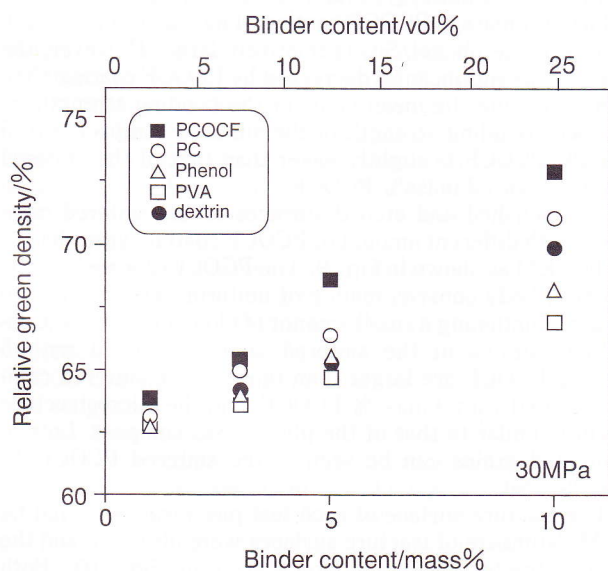


Fig. 5. Relationship between binder content and relative green density.

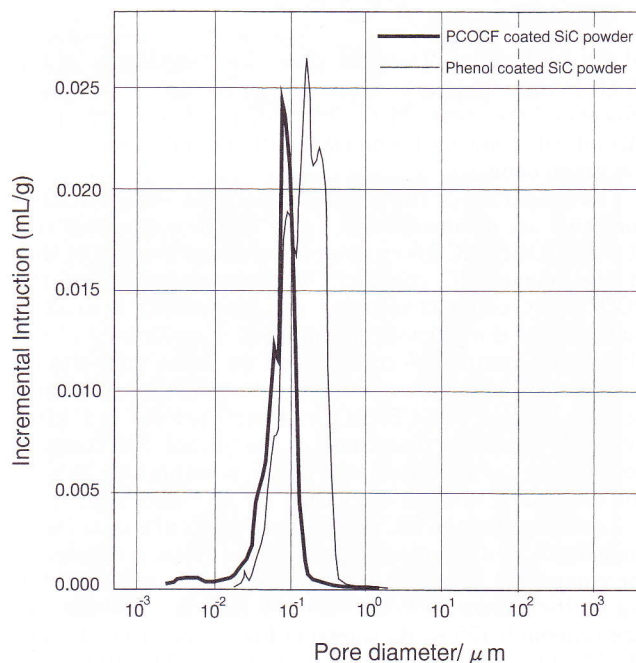


Fig. 6. Pore size distributions of the PCOCF/SiC compact and the phenol/SiC compact (green compacts).

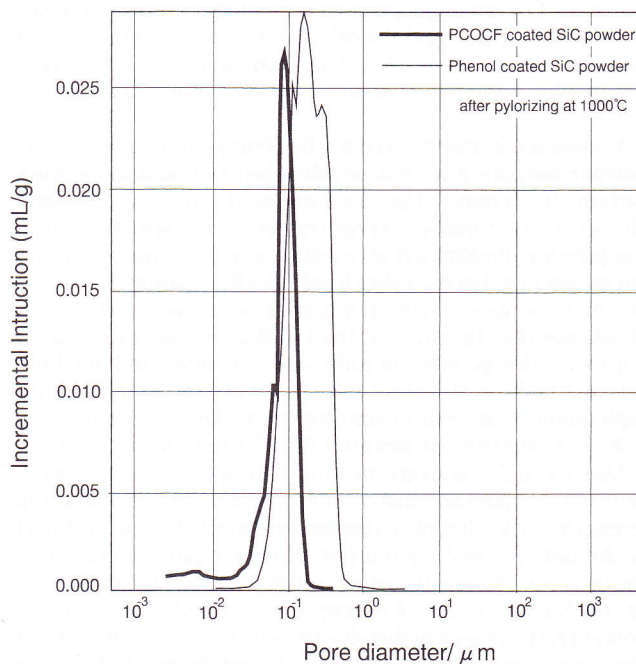


Fig. 7. Pore size distributions of the PCOCF/SiC compact and the phenol/SiC compact (compacts after heat treatment at  $1000^\circ\text{C}$  for 1 h).

Table 1. Properties of Green Compacts and Pyrolyzed Compacts

|                                  | green compact |             | pyrolyzed compact |             |
|----------------------------------|---------------|-------------|-------------------|-------------|
|                                  | SiC+5%Phenol  | SiC+5%PCOCF | SiC+5%Phenol      | SiC+5%PCOCF |
| mean pore size/ $\mu\text{m}$    | 0.119         | 0.058       | 0.151             | 0.059       |
| green density/ $\text{gcm}^{-3}$ | 1.850         | 1.950       | 1.809             | 1.856       |
| porosity/%                       | 37.25         | 34.75       | 39.05             | 36.02       |
| relative density/%               | 63.2          | 65.5        | ---               | ---         |

ed out by heating. Thus the pore size distribution of the PCOCF/SiC compact after pyrolysis is still sharp. However, the pore size distribution of the pyrolyzed phenol/SiC compact becomes slightly broader than that of the green compact.

The properties of the green compacts and the pyrolyzed compacts are summarized in Table 1. The mean pore size of the PCOCF/SiC green compact is about the half of that of the phenol/SiC compact. The green density of the PCOCF/SiC compact is larger, i.e., its porosity is smaller, than that of the phenol/SiC compact. The density of the phenol/SiC compact decreases, and the mean pore size increases after pyrolysis. However, the changes in those properties of the PCOCF/SiC compact before and after pyrolysis is smaller than those of the phenol/SiC compact because the ceramic yield of PCOCF is as high as 75%,<sup>19)</sup> and it is the advantage of PCOCF for its binder use.

Assuming that the SiC particles are uniform spheres with diameter  $r_0$  and are closest packed, the relative density of the compact is 74%, i.e., the volume fraction of binder filling up the gaps is 26 vol% (about 9 mass%), and the gap size is about  $0.155 r_0$ . As shown in Fig. 5, a relative density of 74%, i.e., near-closest packing is achieved by 10 mass% PCOCF coating, while the relative densities of the green compacts using phenol and the other binders are lower than 70%. The measured gap size of the PCOCF/SiC compact, i.e., the average pore diameter is  $0.058 \mu\text{m}$  as shown in Table 1. The average particle size of the as-received SiC powder is  $0.47 \mu\text{m}$ , and the calculated gap size of the closest packed compact is  $0.155 r_0 = 0.07 \mu\text{m}$  which agrees reasonably with the measured average pore diameter of  $0.058 \mu\text{m}$ .

Phenol is commonly used as the compaction binder of SiC powder because it assists powder compaction and supplies carbon to remove the surface oxide of SiC powder. However, the phenol coating conducts no improvement in the powder fluidity and 50 mass% of the phenol is burned out by heating. On the other hand, PCOCF contains free-carbon and can also supply carbon to remove the surface oxide of SiC powder. In addition, the PCOCF coating remarkably improves the powder fluidity and packing, and its high ceramic yield is also desirable. Thus green compacts with high quality can be prepared by the PCOCF coating.

### 3.3 Properties of sintered SiC compacts

Density and four-point bending strength of the hot press sintered samples are shown in Fig. 8. Density and bending strength of the phenol coated SiC are plotted in the left part of the figure. Small amount of PCOCF coating is effective for increase in density, which reflects the high green density of SiC powders. Coating of 10 mass% of PCOCF, however, decreases in density even if the relative density of the green compact is the highest. It may be due to trapping gases from PCOCF during sintering.

Pore concentration variation in the sintered body possibly results from green density variations caused by

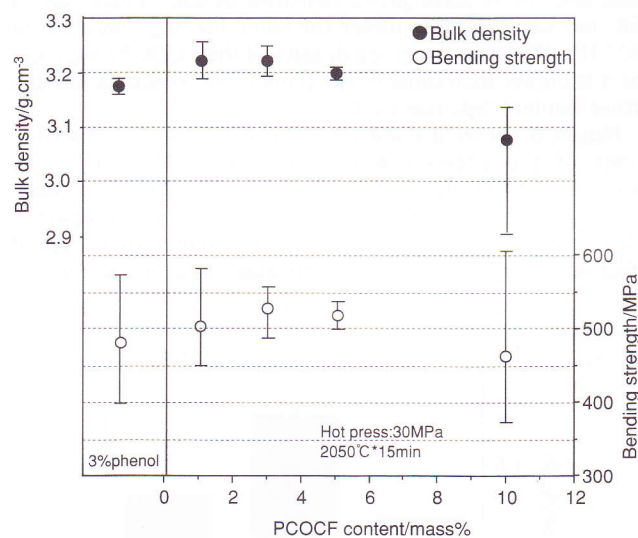


Fig. 8. Bulk density and four-point bending strength of hot press sintered SiC compacts as a function of PCOCF content.

particle-particle friction during forming, as well as from particle size variations in the starting material. Green density of the PCOCF/SiC powder compact is higher than that of the phenol/SiC because of its excellent powder fluidity as shown in Figs. 3 and 4, so the density of the sintered PCOCF/SiC is high.

The bending strength slightly increases by PCOCF coating ( $<10 \text{ mass}\%$ ), and it takes the maximum (550 MPa) at 3 mass% PCOCF coating. The scatter in strength values of the phenol/SiC is relatively large. However, the scatter was significantly decreased by PCOCF coating (3 to 5 mass%) and the mean value of the bending strength increased. Bending strength of the sintered compact with 5 mass% PCOCF is slightly lower than that of the sintered compact with 3 mass% PCOCF.

The polished and etched surfaces of the sintered compacts with different amount of PCOCF coating were observed by SEM as shown in Fig. 9. The PCOCF (3 mass%)/SiC sintered body consists mainly of uniform fine grains (3 to  $10 \mu\text{m}$ ) containing a small amount of elongated grains. Constituent grains in the sintered compact coated with 5 mass% PCOCF are larger than those of the sintered compact coated with 3 mass% PCOCF, and the microstructure is very similar to that of the phenol/SiC compact. Lots of elongated grains can be seen in the sintered PCOCF (10 mass%)/SiC.

The fracture surface of each test piece was observed by SEM. Numbers of fracture surfaces were observed and the typical fracture surfaces are shown in Fig. 10. Both samples show the intra-grain fracture behavior. Some pores less than  $1 \mu\text{m}$  can be seen at the fracture surface of the

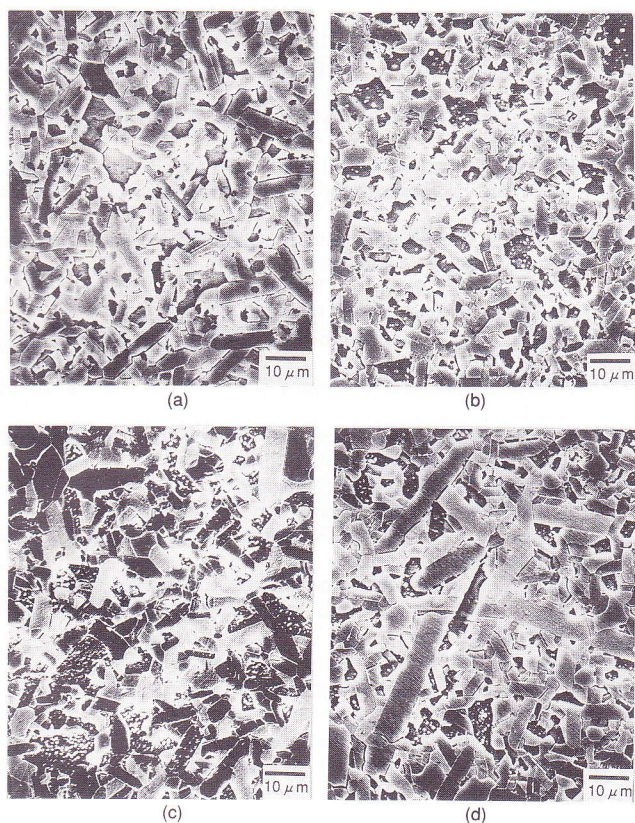


Fig. 9. SEM photographs of the polished and etched surfaces of SiC+0.5%B+ (a) 3% phenol, (b) 3% PCOCF, (c) 5% PCOCF and (d) 10% PCOCF.

phenol/SiC, while no large pore can be seen at the fracture surface of the PCOCF/SiC.

Boron and carbon are used as the sintering aids in this experiment, and sintering of both samples occurs by the solid state process. In such case, the interface between two solid grains reaches equilibrium by the surface diffusion process and the large pores remain in the sintered body. The critical radius,  $R$ , of the pore which is not eliminated during sintering is  $R=1.4 r_0$  in the first approximation, where  $r_0$  is the average particle diameter of the starting powder.<sup>21)</sup> The phenol/SiC powder compact contains pores larger than  $1.4 r_0$  ( $0.7 \mu\text{m}$ ) as shown in Fig. 6, thus the sintered phenol/SiC body contains pores as shown in Fig. 10 and its bending strength varies in wide range. The ceramic yield of the PCOCF is as high as 75%, and it converts to SiC phase<sup>19)</sup> which fills up the gaps among the matrix grains. Therefore, comparing with the phenol/SiC powder compact, pore size distribution of the PCOCF/SiC powder compact is sharp and the average pore diameter is small, thus the sintered body may contain less amount of pores, which results in the decrease in scatter of the strength value.

Fracture toughness of all the sintered compacts is almost constant at about  $3.0 \text{ MPa}\sqrt{\text{m}}$ . Thus the bending strength increases and the scatter in strength values decreases by PCOCF coating ( $<10 \text{ mass}\%$ ) without decreasing the fracture toughness.

It can be concluded that the PCOCF coating is very effective to improve in powder fluidity, powder packing property and ceramic conversion in high yield, which results in high reliability of the sintered body in terms of the less scatter of the fracture strength. However, too much PCOCF addition (10 mass% or more) enhances the grain growth of SiC, which possibly results in the decrease in the bending strength. Thus, small amount of PCOCF coating (3 to 5

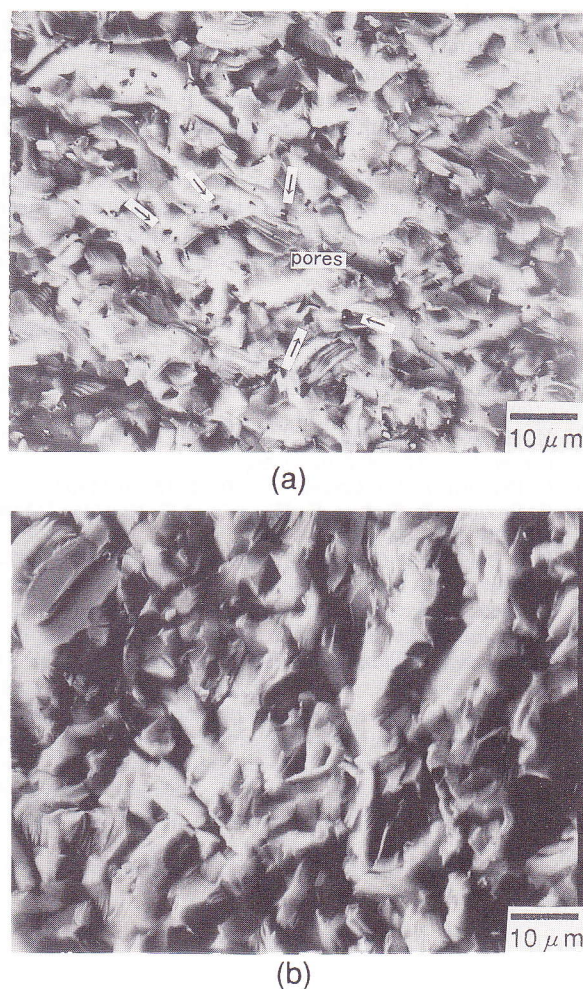


Fig. 10. SEM photographs of the fracture surfaces of SiC+0.5%B+ (a) 3% phenol and (b) 5% PCOCF.

mass%) is effective for increase in the density, increase in the bending strength and decrease in the scatter in strength values of the SiC sintered body.

#### 4. Conclusion

In this work, the chemically modified polycarbosilane containing organofluorine groups, PCOCF, was synthesized and applied as the compaction binder for SiC powders. PCOCF coated SiC powder shows improved packing properties, owing to the organofluorine side chains of PCOCF as follows.

- (1) Angle of repose of the PCOCF coated SiC powder is lower than that of the phenol coated SiC powder.
- (2) Tap density of the PCOCF coated SiC powder is higher than that of the phenol coated SiC powder.
- (3) Green densities of the PCOCF coated SiC powders are higher than those of the phenol and the other binder coated powders at the content between 1 and 10 mass%.
- (4) Average pore diameter of the PCOCF/SiC compact is smaller than that of the phenol/SiC compact.
- (5) Pore size distribution of the PCOCF/SiC compact is sharper and its peak pore diameter is smaller than those of the phenol/SiC compact.

The conclusions (1) to (5) indicate that the PCOCF coating does lubricate the SiC particles better than phenol, which results in higher compaction for the same loading conditions. So the PCOCF/SiC compact contains less large pores, and therefore, mechanical strength of the PCOCF/SiC sintered body is improved as follows.

(6) Four-point bending strength is increased by PCOCF coating, and it takes the maximum (550 MPa) at 3 mass% PCOCF coating.

(7) The scatter in bending strength values of hot press sintered SiC significantly decreases by PCOCF coating.

**Acknowledgment** This work has been entrusted by NEDO as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program promoted by AIST, MITI, Japan. The authors are members of the Joint Research Consortium of Synergy Ceramics.

#### References

- 1) K. Niihara, *J. Ceram. Soc. Japan*, **99**, 974-82 (1991).
- 2) T. Yanai and K. Ishizaki, *J. Ceram. Soc. Japan*, **101**, 764-68 (1993).
- 3) K. Hirao, T. Nagaoka, M. E. Brito and S. Kanzaki, *J. Am. Ceram. Soc.*, **77**, 1857-62 (1994).
- 4) G. Pezzotti, *J. Am. Ceram. Soc.*, **76**, 1313-20 (1993).
- 5) G. Pezzotti, B. T. Lee, K. Hiraga and T. Nishida, *J. Mater. Sci.*, **29**, 1786-94 (1994).
- 6) P. F. Becher and G. C. Wei, *J. Am. Ceram. Soc.*, **67**, C267-69 (1984).
- 7) G. Pezzotti, I. Tanaka, T. Okamoto, M. Koizumi and Y. Miyamoto, *J. Am. Ceram. Soc.*, **72**, 1461-64 (1989).
- 8) T. Hansson, R. Warren and J. Wasn, *J. Am. Ceram. Soc.*, **76**, 840-48 (1993).
- 9) M. W. Lindly and D. J. Godfrey, *Nature*, **229**, 192-93 (1971).
- 10) P. J. Lamicq, G. A. Bernhart, M. M. Dauchier and J. G. Mace, *Am. Ceram. Soc. Bull.*, **65**, 336-38 (1986).
- 11) A. G. Evans and D. B. Marshall, *Acta Met.*, **37**, 2567-83 (1989).
- 12) K. Ueno, *Ceramics Japan*, **18**, 1040-46 (1983) [in Japanese].
- 13) S. Yajima, J. Hayashi and M. Omori, *Chem. Lett.*, 931-34 (1975).
- 14) S. Yajima, T. Shishido and K. Okamura, *Am. Ceram. Soc. Bull.*, **56**, 1060-63 (1977).
- 15) S. Yajima, T. Iwai, T. Yamanaka, K. Okamura and Y. Hasegawa, *J. Mater. Sci.*, **16**, 1349-55 (1981).
- 16) T. Ishikawa, T. Yamamura and K. Okamura, *J. Mater. Sci.*, **27**, 6627-34 (1992).
- 17) F. Babonneau and G. D. Soraru, *J. Eur. Ceram. Soc.*, **8**, 29-34 (1991).
- 18) F. Babonneau, G. D. Soraru, K. J. Thorne and J. D. Mackenzie, *J. Am. Ceram. Soc.*, **74**, 1725-28 (1991).
- 19) Y. Sawai, Y. Iwamoto, S. Okuzaki, Y. Yasutomi, K. Kikuta and S. Hirano, *J. Am. Ceram. Soc.*, to be published.
- 20) Y. Iwamoto, S. Okuzaki, K. Kikuta and S. Hirano, *Ceramic Transactions* (submitted).
- 21) W. D. Kingery, H. K. Bowen and D. R. Uhlmann, "Introduction to Ceramics," 2nd ed., John Wiley & Sons, Inc., USA (1976) Chapter 10.