

Properties of Silicon Carbide-Carbon Fiber Composites Prepared by Infiltrating Porous Carbon Fiber Composites with Liquid Silicon

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Silicon carbide-carbon fiber composites have been prepared by partially infiltrating porous carbon fiber composites with liquid silicon at a reaction temperature of 1670°C. Reaction between molten silicon and the fiber preform yielded silicon carbide-carbon fiber composites composed of aggregates of loosely bonded SiC crystallites of about 10 μm in size and preserved the appearance of a fiber. In addition, the SiC/C fiber composites had carbon fibers coated with a dense layer consisted of SiC particles of sizes smaller than 1 μm. The physical and mechanical properties of SiC/C fiber composites were discussed in terms of infiltrated pore volume fraction of carbon preform occupied by liquid silicon at the beginning of reaction. Lower bending strength of the SiC/C fiber composites which had a heterogeneous structure in nature, was attributed to the disruption of geometric configuration of the original carbon fiber preform and the formation of the fibrous aggregates of the loosely bonded coarse SiC particles produced by solution-precipitation mechanism

Key words : Carbon fiber, Silicon carbide, Infiltration, Solution-precipitation, Liquid silicon, Fiber composites

I. Introduction

Since reaction-bonded silicon carbide (RBSC), in which liquid silicon reacts with solid carbon to form SiC, was developed by P. Popper in 1960,¹ a number of commercialized RBSC products such as K-T, NC-435, or REFEL are available and widely used for structural applications in high-temperature environments.² Most of studies on RBSC have been focused on fabrication techniques of carbonaceous porous preform containing SiC powders, and effect of composition variables on the properties of dense Si/SiC composite materials.^{3,4} The raw materials used for preparation of preform to produce Si/SiC composites generally consists of SiC powders and elemental carbon, which can be added as particles or produced in situ as carbonaceous powders by decomposition of polymers.

Another method of consolidating Si/SiC composites, so called SILCOMP process, utilizes carbon fiber rather than carbon powder as a source of elemental carbon.^{4,11} The SILCOMP process uses carbon fibers in the form of tow, cloth, felt or yarn to build up complex shapes of preform by any of the methods used to make fiber-reinforced polymer matrix composites. During infiltration with molten silicon, the capillary formed by carbon fiber allows rapid infiltration of liquid silicon into the interior of the preform and the individual carbon fibers convert to aggregates of SiC particles by dissolution precipitation mechanism. The resulting Si/SiC materials produced by SILCOMP process are fully dense materials with the SiC content varying 25~90%. It is claimed that

reaction between carbon fiber and liquid silicon forms SiC crystals, which maintain the original filament distribution of the carbon fibers. This suggests that melt infiltration process has a potential for producing complex shapes of SiC fiber composites directly from carbon fiber composites.

In this study based on infiltration techniques similar to SILCOMP process, porous SiC/C fiber composites were prepared by partial infiltration of liquid silicon into porous carbon fiber composite preform at 1670°C. The present work is aimed for development of a fabrication route by exploitation of porous carbon fiber composites to yield porous SiC fiber composites. The effects on the physical and mechanical properties of the resultant SiC/C fiber composite materials were investigated by varying molar ratios of infiltrating liquid silicon and carbon preform, which consequently determined a level of direct contact of the former with the latter. We focus our attentions on the morphology of converted SiC fiber and its effects on the strength of SiC/C fiber composites.

II. Experimental Procedure

1. Raw materials and preparation of carbon fiber composite preform

A carbon fiber composite preform of 20 mm in diameter and 10 mm thick was fabricated from a mixture of chopped carbon fibers and phenolic resin using a vacuum molding process.¹² The carbon fiber (TZ-307, Tae Kwang, Korea) has a nominal diameter of 6.8 μm and a density of 1.80 g/cm³. The average particle size of phenol-

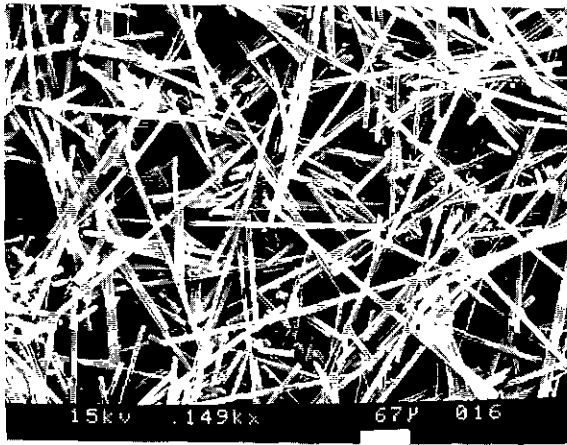


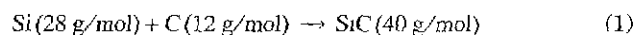
Fig. 1. Micrograph of carbon preform.

ic resin (KNG-119, Kolong, Korea) was $24\ \mu\text{m}$ and the carbon yield after pyrolysis was 55 wt%. The carbon fiber tows were chopped to pass through a sieve screen of 40 mesh with a rotary knife cutter. The chopped fibers were mechanically slurried in water and a phenolic resin was added to the water-fiber mixture. The weight ratio of phenolic resin to the carbon fiber was 4:6. The slurry was vacuum molded into a disc shape of 20 mm in diameter and 10 mm thick. After drying of the molded samples, carbonization of phenolic resin binder was achieved at 850°C for 30 minutes in flowing N_2 gas.

The measured porosity and bulk density of the resultant carbon fiber composites using Archimedes' principle were about 82% and $0.28\ \text{g/cm}^3$, respectively. Fig. 1 shows a microstructure of a porous carbon preform, in which carbon fibers are bonded with carbonized phenolic resin particulates. The medium pore diameter of the carbon preform measured by mercury porosimetry was about $43\ \mu\text{m}$, and pores were monodispersed.

2. Infiltration process and characterization

The porous carbon fiber composite preform was infiltrated with liquid silicon in a vacuum of 13.3 Pa at about 1670°C by induction heating and kept at that temperature for one hour. The reaction temperature was calibrated using Ti powder. The molar amount of the silicon powder used for a reaction was in the range of 1~2.6 times of that of the carbon preform. The amount of liquid silicon required for a complete infiltration into a porous carbon preform was estimated from Eqs. (1) and (2) with the measured physical properties of carbon preform.



$$V_p = (W/\rho) \times P \quad (2)$$

where V_p , W , ρ and P denote the pore volume, weight, bulk density and porosity of the carbon preform, respectively. According to the Eq. (1), the amount of silicon me-

tal required for a complete reaction with 1 g of carbon is about 2.34 g. For the complete infiltration of liquid silicon into a pore volume of one gram of carbon preform with a bulk density of $0.28\ \text{g/cm}^3$ and a porosity of 82%, 7.23 gram of silicon metal with a density of $2.47\ \text{g/cm}^3$ is required. Therefore, the molar ratio of infiltrating liquid silicon and carbon preform, i.e., Si/C molar ratio, is about 3:1 to saturate the pore volume of the carbon preform with a liquid silicon.

In this work the Si/C molar ratios of 1.0, 1.6, 2.2 and 2.6 were employed to react liquid silicon with carbon precursor at reaction temperature of 1670°C for one hour. The primary reason to choose such a reaction temperature much higher than the one used in a conventional silicon process, i.e., 1415°C , was to remove a part of unreacted silicon from a reaction product by high temperature evaporation in vacuum, and thereby, any risk of fiber fracture in the reacted sample due to a 95 vol% expansion of unreacted silicon on freezing⁹⁾ was reduced.

The required amount of silicon metal powders was packed on the top of the carbon preform contained in a graphite crucible. The diameter of the preform was just fit into the crucible so that all the liquid silicon in the crucible was infiltrated into the pore of carbon preform. The ratio of the calculated pore volume of carbon preform occupied by liquid silicon at the beginning of reaction and that of carbon preform before infiltration is defined as infiltrated pore volume fraction (IPVF) in this work. For the Si/C molar ratios of 1.0, 1.6, 2.2 and 2.6, calculated values of IPVFs are 32, 52, 71 and 84%, respectively. All the properties of the resultant SiC/C fiber composites reported in this work were measured after elimination of residual Si phase from the reacted sample by boiling in 10% NaOH. The strength of the SiC/C fiber composites was compared by the three-point bending test for the $6\ \text{mm} \times 6\ \text{mm} \times 17\ \text{mm}$ specimens with a span length of 11 mm. The reason chosen the IPVF as a major variable in this paper is that the value of IPVF directly shows a level of physical contact of liquid silicon with a carbon fiber preform, which is necessary for the description of properties of SiC/C fiber composites with a heterogeneous structure as described below.

III. Results and Discussion

1. Density and porosity

Fig. 2 shows the variations in apparent density (A) and bulk density (B) and porosity (C) of SiC/C fiber composites with infiltrated pore volume fraction. The apparent density and bulk density, and porosity of carbon preform before reaction, i.e., at 0% IPVF, were $1.56\ \text{g/cm}^3$, $0.28\ \text{g/cm}^3$ and 82%, respectively. At 71% IPVF, both of the apparent density and bulk density of SiC/C fiber composites increased to $2.86\ \text{g/cm}^3$ and $0.96\ \text{g/cm}^3$, respectively, while the porosity decreased to 66%. It can be not-

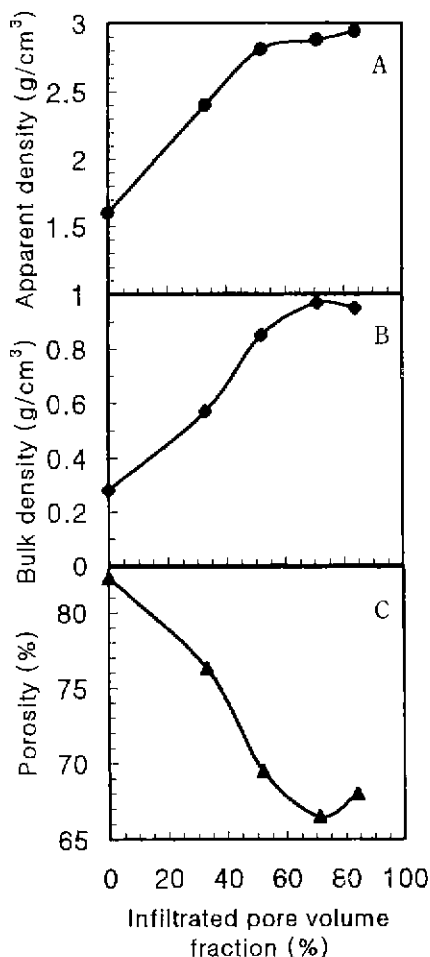


Fig. 2. Effect of infiltrated pore volume fraction on properties of SiC/C fiber composites. (A) apparent density, (B) bulk density and (C) porosity.

ed that the SiC/C fiber composites prepared with 84% IPVF show higher apparent density (2.93 g/cm^3) and porosity (68%), and a lower bulk density (0.94 g/cm^3) than those (2.86 g/cm^3 , 66%, 0.96 g/cm^3 , respectively) of the composites prepared with 71% IPVF. This results suggest that the structure of SiC/C composites prepared with 84% IPVF expands more than the one with 71% IPVF. The structural expansion of SiC/C fiber composites seems to occur because of either volume expansion caused by the freezing of unreacted silicon remained in the pore of the composites upon cooling to room temperature, or conversion of original carbon fiber to SiC/C fiber.

The weight fractions of SiC in the resultant SiC/C fiber composites are calculated and shown in Fig. 3(A), assuming that the apparent density shown in Fig. 2(A) is equal to the theoretical density. If the density of multiphase materials follows the rule of mixtures, density of the composites consisted of SiC and carbon fiber can be written as $\rho = \rho_{\text{SiC}} \cdot \rho_{\text{C}} / (X_{\text{SiC}} \cdot \rho_{\text{C}} + X_{\text{C}} \cdot \rho_{\text{SiC}})$ where X is the weight fraction of SiC or carbon fiber, SiC and C refer to the SiC reaction product and carbon fiber reactant, $X_{\text{SiC}} +$

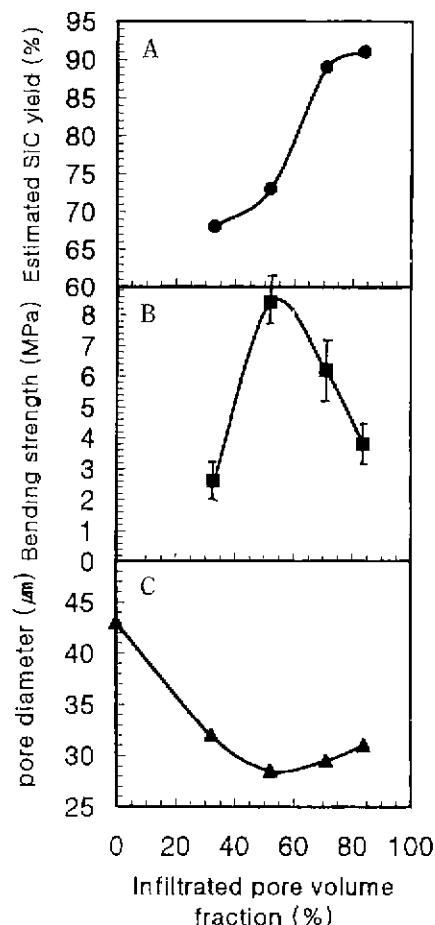


Fig. 3. Effect of infiltrated pore volume fraction on properties of SiC/C fiber composites. (A) SiC yield, (B) bending strength and (C) median pore diameter.

$X_{\text{C}}=1$, and ρ is the assumed theoretical density of SiC grain or carbon fiber, $\rho_{\text{SiC}}=3.20 \text{ g/cm}^3$ and $\rho_{\text{C}}=1.80 \text{ g/cm}^3$, respectively. As the infiltrated pore volume fraction increases from 32% to 84%, the measured weight fraction of SiC in SiC/C fiber composites increases from 68% to 91% as shown in Fig. 3(A). If the formation of SiC occurs only in the pore region of carbon preform occupied by liquid silicon, it can be shown that 61% and 94% are the weight fractions of SiC in SiC/C fiber composites produced with IPVFs of 32% and 84%, respectively.

2. Pore size distributions

Mercury porosimetry were performed on the carbon preform and SiC/C fiber composites to acquire microstructural information. Shown in Fig. 3(C) are the variations in median pore size of SiC/C fiber composites plotted as a function of weight fraction of SiC yielded in the reacted samples. As the weight fraction of SiC increases from 0% to 73%, the median pore diameter decreases from $43 \mu\text{m}$ to $29 \mu\text{m}$. The reduction of the median pore size with increasing SiC fraction can be explained in terms of the molar volume of reactants and products. The molar volumes of the carbon fiber, liquid

silicon and silicon carbide grain are 6.7 mL, 11.3 mL and 12.5 mL, respectively. The volume occupied by the carbon fibers becomes double as the carbon fiber is converted to SiC. The volume increase results in the reduction of the median pore size of SiC/C fiber composites as the weight fraction of SiC increases. However, the median pore size of the SiC/C fiber composite sample of 89 wt% SiC is larger than that of 73 wt% SiC. Therefore, it can be concluded that for the SiC/C fiber composite of 89 wt% SiC, an increase in the pore size caused by volume expansion of unreacted silicon remained in pores on freezing is larger than a reduction in the pore size caused by molar volume increase resulted from conversion of carbon to SiC.

3.3 Strength and morphology

Figure. 3(B) shows the bending strength of SiC/C fiber composite samples as a function of infiltrated pore volume fraction. The number of sample in each data was six. The strength of the samples varied from 2.6 MPa to 8.3 MPa. The highest strength was found for the sample prepared from a preform with 52% IPVF. Because of the scatter in the strength data, only a qualitative interpretation would be meaningful as described below. In literature on the mechanical behavior of porous fiber materials with homogeneous structure,^{12,13} the general trend of an increasing strength (i.e., from 0.52 MPa to 1.12 MPa) with increasing bulk density (i.e., from 0.19 g/cm³ to 0.25 g/cm³) is found, although strength data shown in the literature are much scattered. However, the strength of composite samples prepared in this study does not seem to depend on the bulk density of composite as shown in Figs. 2(A) and 3(B).

The strength results shown in Fig. 3(B) were evaluated by observation of SiC/C fiber composite with a scanning electron microscope (SEM). Microstructures of the samples with two different IPVFs, 71% and 52%, are shown in Figs. 4 and 5, respectively. SEM observation re-

vealed some differences in microstructure between these two samples. Though the sample shown in Fig. 4 retains a porous structure of the original carbon preform as determined by mercury porosimetry (Fig. 3(A)), much amount of its original fibrous structure shown in Fig. 1 seems to be lost due to the extensive clustering of coarsened and agglomerated SiC particles as shown in Fig. 4. On the other hand, the SiC/C fiber composite sample prepared with 52% IPVF (Figs. 5(A), (B) and (C)) shows a

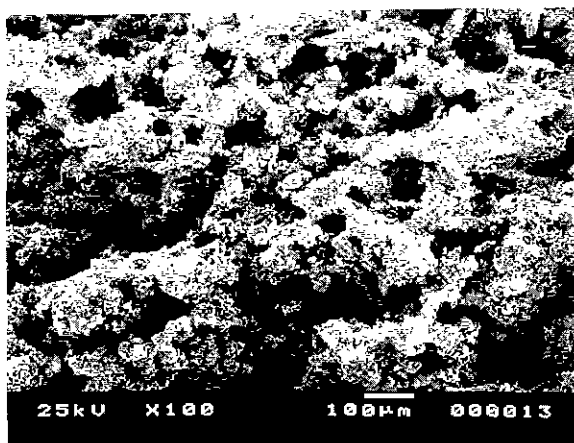


Fig. 4. Micrograph of SiC/C fiber composites obtained with 71% IPVF showing extensive clustering of SiC particles.

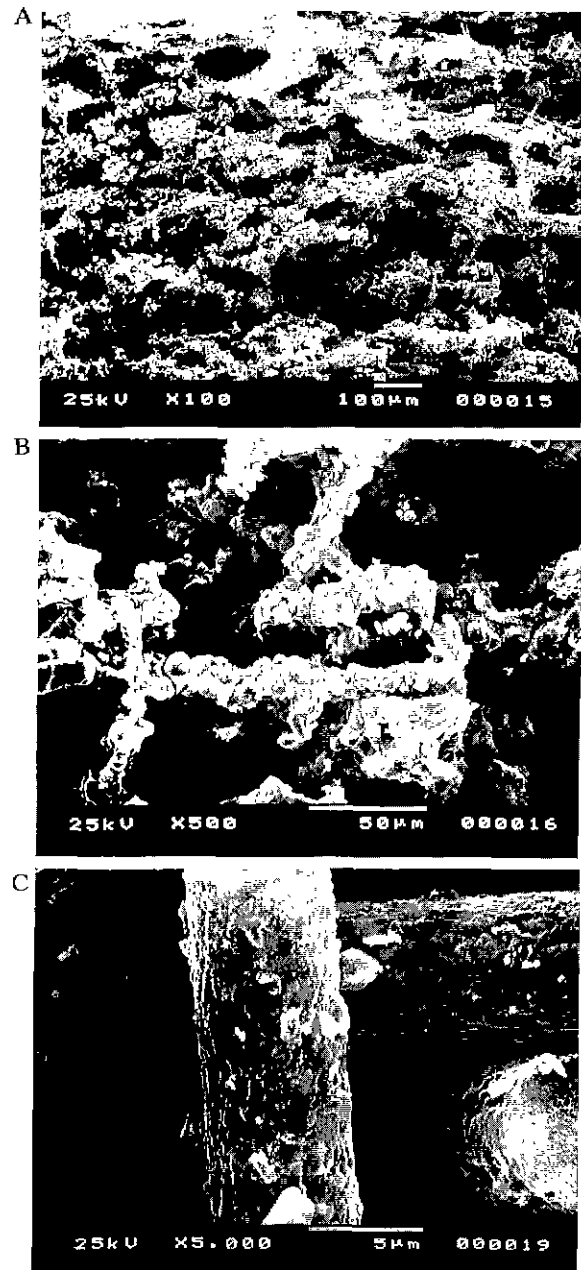


Fig. 5. Micrograph of SiC/C fiber composites obtained with 52% IPVF: (A) aggregated fibrous SiC/C composites, (B) chains of loosely bonded SiC particles of about 10 µm in size and (C) carbon fiber coated with fine SiC crystallites of sizes smaller than 1 µm.

structure of relatively less clustered SiC particles and retains more of its original fibrous structure of the carbon fiber preform than the one prepared with 71% IPVF (Fig. 4). The fibrous SiC fibers shown in Fig. 5(B), resemble the chains of SiC grains and consist of an aggregate of loosely bonded SiC crystallites as large as 10 μm . From the studies of the microstructure of SILCOMP, it has been deduced that the reaction between molten silicon and carbon fiber occurs at the fiber-liquid interface or the converted SiC solid-liquid interface, and dissolution or precipitation of the converted solid-liquid interface.^{11,14} Microstructures of the SiC particles similar to the one shown in Fig. 5(B) can be found in the work of Hillig *et al.*^{9,11} who had studied a fully dense Si/SiC ceramic composite using carbon tows. They showed carbon fibers directly contacted with molten silicon converted to coarsened SiC crystallites of sizes in the range of 1 to 50 μm .

Meanwhile, the SiC/C fiber composite sample prepared with 52% IPVF (Fig. 5(C)) reveals carbon fibers coated with a dense layer consisted of fine SiC crystallites of sizes smaller than 1 μm . These fine SiC layers must be formed by reaction of carbon fiber with silicon vapor, and responsible for an increase in the strength of SiC/C fiber composite made of partial infiltration of liquid silicon into carbon preform. Therefore, we may conclude that the structure of the SiC/C fiber composites has a heterogeneous nature due to the reaction condition in this study. It is also considered that formation of SiC crystallites grown by dissolution-precipitation mechanism may disrupt geometric configuration of the original carbon fiber preform, which may weaken the structure and led to a decrease in the strength of the SiC/C fiber composites.

IV. Summary and Conclusions

Silicon carbide-carbon fiber composites were prepared by partial infiltration of porous carbon fiber preforms with liquid silicon. Experiments were performed to characterize the role of SiC crystallites formed from the converted carbon fiber on the mechanical properties of SiC/C fiber composites. Experimental results were interpreted in terms of the infiltrated pore volume fraction of carbon preform by liquid silicon, which directly characterized the reaction condition between carbon preform and molten silicon. An increase in the pore size caused by volume expansion of unreacted silicon remained in pores on freezing and a reduction in the pore size caused by molar volume increase resulted from conversion of carbon to SiC occurred simultaneously in SiC/C fiber composite. The mechanical strength of SiC/C fiber composites was not simply depended on the SiC fraction or bulk density of reaction product. The Si/C molar ratio that was required to produce SiC/C fiber composites of the maximum strength and bulk density, and the minimum porosity was 1.6, which corresponded to the 52%

infiltrated pore volume fraction of carbon precursor. It was found that lower strength of SiC/C fiber composites resulted from disruption of geometric configuration of the original carbon fiber preform and formation of fibrous aggregates of loosely bonded coarse SiC particles as large as 10 μm grown by dissolution-precipitation mechanism. During reaction between carbon preform and liquid silicon, silicon vapor was produced and reacted with carbon fiber to produce fine crystallites of sizes smaller than 1 μm , which increased the strength of the SiC/C fiber composites. Therefore, the difficulty in obtaining 100% SiC fiber structure of fine SiC crystallites and geometric configuration of the original carbon fiber preform hinders application of melt infiltration process to carbon fiber preform to produce SiC fibrous material for a structural use.

Acknowledgments

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References

1. P. Popper, "The Preparation of Dense Self-Bonded Silicon Carbide," *Special Ceramics*, 209-219, Heywood, London, 1960.
2. C. W. Forrest, P. Kennedy and J. V. Shennan, "The Fabrication and Properties of Self-Bonded Silicon Carbide Bodies," *Special Ceramics*, Vol. 5, pp. 99-123, Brit. Ceram. Res. Ass. Stoke-on-Trent, U.K., 1972.
3. C. B. Lim and T. Iseki, "Strength Variation of Reaction-Sintered SiC Heterogeneously Containing Fine-Grained β -SiC," *J. Mat. Sci.*, **23**, 3248-3253 (1988).
4. O. P. Chalkrabarti, S. Ghosh and J. Mukerji, "Influence of Grain Size, Free Silicon Content and Temperature on the Strength and Toughness of Reaction-Bonded Silicon Carbide," *Ceram. Inter.*, **20**, 283-286 (1994).
5. Y. M. Chiang, R. P. Messner, C. D. Terwilliger and D. R. Behrendt, "Reaction-formed Silicon Carbide," *Mat. Sci. Eng.*, **A144**, 63-74 (1991).
6. I. S. Han, J. H. Yang and D. S. Suh, "Properties of Reaction-Bonded Silicon Carbide Depending on Graphite Additions," *J. Korean. Ceram. Soc.*, **30**[1], 69-77 (1993).
7. Y. W. Kim and J. G. Lee, "Reactive Sintering of SiC," *J. Korean Ceram. Soc.*, **20**[2], 115-122 (1983).
8. M. J. Lee, B. J. Kim, S. M. Kang, J. K. Choi, B. S. Jeon and K. H. Orr, "A Study on the Reaction Between Silicon in Melt and Carbon," *J. Korean. Asso. Cryst. Growth*, **4**[4], 336-346 (1994).
9. W. B. Hillig, "Making Ceramic Composites by Melt Infiltration," *Am. Ceram. Soc. Bull.*, **73**[4], 56-62 (1994).
10. K. L. Luthra, R. N. Singh and M. K. Brun, "Toughened Silicomp Composites-Process and Preliminary Properties," *Am. Ceram. Soc. Bull.*, **72**[7], 79-85 (1993).
11. W. B. Hillig, R. L. Mehan, C. R. Morelock, V. J. Decarlo and W. Laskow, "Silicon/Silicon Carbide Composites," *Am. Ceram. Bull.*, **54**[12], 1054-1056 (1975).

12. G. C. Wei and J. M. Robbins, "Carbon-Bonded Carbon Fiber Insulation for Radioisotope Space Power Systems," *Am. Ceram. Bull.*, **64**[5], 691-699 (1985).
13. Y. Ota, T. Kasuga and Y. Abe, "Preparation and Compressive Strength Behavior of Porous Ceramics with β -Ca(PO₃)₂ Fiber Skeletons." *J. Am. Ceram. Soc.*, **80**[1], 225-231 (1997).
14. R. Pampuch, E. Walasek and J. Bialoskorski, "Reaction Mechanism in Carbon-Liquid Silicon Systems at Elevated Temperature," *Ceram. Int.*, **12**, 99-106 (1986).