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PREPARATION OF SiC/C COMPOSITE SHEET FROM POLYCARBOSILANE/CARBON-BASED RESIN MIXTURE

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Abstract – SiC/C composites were prepared from a mixture of polycarbosilane and phenolic resin with weight ratio of 2/1 and 1/1 using PVB as a binder. The two types of green bodies which were formed by mould pressing method were treated in the temperature range from 1,000 °C to 1,500 °C under nitrogen. X-ray diffraction patterns, density, flexural strength and fracture surfaces of the composite were examined. The flexural strength of the composites at room temperature increased with heat-treatment temperature and showed a maximum value of 175 MPa at 1,300 °C. When the composite was heat treated at 1,400 °C, the flexural strength decreased rapidly due to the crystallization of SiC. The SiC/C composites showed good oxidation resistance up to 830 °C. The effective mixing ratio of PCS/phenolic resin to obtain improved mechanical property was 2/1.

Key words : Polycarbosilane, SiC, Crystallization

INTRODUCTION

Silicon carbide (SiC) is one of the promising candidate materials for high temperature structural components because of its many excellent properties, including strength retention, oxidation resistance at high temperature, and thermal shock resistance [Hasegawa et al., 1980]. SiC for industrial use has been produced by vapor phase reaction [Verbeek, 1974], condensation of evaporation [Hasegawa et al., 1983] carbothermal reduction of SiO_2 [Hasegawa et al., 1985], direct reaction of Si and C [Narita, 1988]; mainly as powder form the SiC powder should be fabricated by a complicated forming and sintering process to provide composites [Yosida, 1984]. In contrast to the SiC powder process, polymeric precursors allow processing at lower temperatures and pressures and use available polymers with well-defined flow characteristics. The major processing problems asssociated with polymeric precursors are their low yields and phase purity. These obstacles must be overcome to fully exploit the benefits of polymer pyrolysis over conventional processing techniques.

There have been many reports on the preparation of SiC composite. Okamura and co-workers [Yajima et al., 1990] reported the flexural strength of PCS/α-SiC mixture heat-treated at 1,000 °C was 57 MPa. Kawamura reported the flexural strength of the composite from PCS/Al_2O_3 powder mixture was 333 MPa [Kawamura, 1990]. Studies for improving the oxidation resistance of carbon composite were also developing. For example, Yoshida and co-workers reported [Yosida, 1984] preparation of SiC/C composite from SiC powder/cokes mixture. Okamura and co-workers [Okabe et al., 1979] reported preparation of SiC/C composite from PCS/cellulose mixture. In the present work, we investigated preparation of SiC/C composite from a PCS/Phenolic resin mixture, which has oxidation resistance and good mechanical properties.

EXPERIMENTAL

1. Materials

Extra pure GC analytical grade of dimethyldichlorosilane (DDS) from Fluka Chemica was used without further purification. Xylene (95 %), THF (95 %), methanol (99 %), ethanol (95 %) and n-hexane (95 %) (dried by refluxing 24 hr over sodium metal) were provided by Oriental Chem. Ind., and drying metal sodium (99.8 %) was supplied by BDH Chem. Co. Ltd. Phenolic resin (novlac type) as the mixture component was purchased from Kangnam Hwasung Co. Polyvinyl butyral resin (PVB) as organic binder BM-S grade from Sekish was used.

2. Preparation of Polycarbosilane (PCS)

Polycarbosilane as the precursor of SiC was synthesized by thermal decomposition of polydimethylsilane (PDS). To obtain PDS, into a 500 ml three-necked flask equipped with dropping funnel and reflux condenser were put 350 ml of xylene and 70 g (3 mol) of metallic sodium. The mixture was then heated at 100 °C under a nitrogen atmosphere, whereupon 182 ml (1.5 mol) of dimethyldichlorosilane (DDS) was added dropwise. The polymerization temperature was 100 °C for 15 h. After the termination of the reaction, xylene was removed by filtration. Residual sodium was removed by treatment with 500 ml methanol. By addition of 1 liter water, a white powder PDS was obtained. The amount obtained was 156 g (yield 88 %). To obtain PCS, in a 1 liter autocalve was put 100 g of the PDS, with filling by nitrogen at 1 atm. It was stirred while heating at a rate of about 400 °C/h. The polymerization temperature was 450 °C for 15 hr. At this decomposition temperature, the final pressure was 70 kg/cm^2. The product was a yellowish viscous substance. It was dissolved in n-hexane

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and the solution filtered. The solvent was removed with a rotary evaporator. By vacuum distillation, the fraction up to 280 °C under 1 torr was removed, resulting in the final product of a yellowish glassy polycarbosilane. After concentration the amount of PCS obtained was 45 g (yield 45 %).

3. Fabrication of Composites

Fabrication conditions of SiC/C composites are shown in Table 1. As shown in Table 1, a PCS/phenolic resin/binder mixture was made from PCS and phenolic resin by adding PVB as organic binder with the weight ratio of PCS to phenolic resin equal to 2/1 or 1/1. The mixture was mixed well by adding ethanol, xylene in a ball mill. A well-mixed PCS/phenol resin/binder mixture was put in the desicator to evacuate by rotary pump so that ethanol, xylene were removed and dried by for standing overnight. The dried mixture was put in the mold with the dimensions 40×150 mm. Curing of the mixture is a process of crosslinking of the PCS and phenolic resin by oxygen to make the mixture infusible during heat treatment. The first curing step was done under the curing temperature of phenolic resin and then the second curing step was followed under the curing temperature of PCS. PCS/Phenolic resin/binder mixture was cured at first by mould pressing of 50 kg/cm^2 at 120 °C and 160 °C, respectively, for 1 hr in air. The second curing of the mixture was done by mould pressing of 50 kg/cm^2 at 190 °C for 1 hr in air. The cured composites were placed in an alumina tube furnace and heat treated in the range of 1,000 °C to 1,500 °C for 1 hr under nitrogen atmosphere.

4. Measurements

Fourier transform infrared spectra were obtained with a Perkin Elmer 1750 spectrometer by the KBr pellet method. The spectrometer was used at a resolution 4 between 4,000 cm^{-1} and 600 cm^{-1}. X-ray diffraction patterns were obtained with a Rigaku D-Max IIIB instrument using nickel-filtered CuKα radiation (λ=1.52 Å). The density of SiC/C composite was measured with Gay-Lussac vessel with butanol at 20 °C. Three point bending tests were made in accordance with ASTM D-790 using an MTS testing machine at room temperature and a cross-head speed of 1 mm/min. This test was measured by three-point bending with 40 mm lower span for the pieces 60 mm long and 10 mm wide which were cut by diamond saw cut, and the measurement was done for at least five pieces of each sample. Scanning electron microscopy (SEM) was used to examine the fracture surface of the samples. Oxidation resistance of the samples was measured with TGA by raising temperature at 20 °C/min up to 1,300 °C in air atmosphere. The electric resistance was measured for the sheets at a fixed voltage by using a dc power supply at room temperature. An In-Ga alloy was used as an electrode. The resistivity ρ=RA/t, where R is the resistance, A the electrode area, and t specimen thickness.

Table 1. Fabrication conditions of SiC/C composites

Parameters	
Weight ratio	1/1/1
PCS/phenolic resin/binder	2/1/1
Mould press [kg/cm^2]	50
Curing temp. [°C]	
1st	120-160
2nd	190
Heat treatment temp. [°C]	1000, 1200, 1300, 1400, 1500

RESULTS AND DISCUSSION

1. Characterization of the Mixture Component

The changes in structures in converting the PDS to PCS can be discussed qualitatively by using FT-IR spectra. Fig. 1 shows the infrared transmission spectra of a representative selection of the PDS and PCS. Absorptions at 2,950 and 2,900 cm^{-1} C-H streching in methyl), 1,400 cm^{-1} (C-H deformation in Si-CH$_3$), 1,260 cm^{-1} Si-Me deformation) and in the vicinity of 800 cm^{-1} (Si-Me deformation and Si-C stretching) were seen. From these absorptions, the presence of PDS was confirmed. In the conversion process from PDS to PCS, which is available for producing SiC, the cleavage of the framework of Si-Si bonds occurred. Si-CH$_2$-Si and Si-H bonds were subsequently formed by the rearrangement reaction between radicals formed and Si-CH$_3$ bonds. The structure of PCS was confirmed at 600 to 920 cm^{-1} (Si-Me), 1,020 and 1,355 cm^{-1} (Si-CH$_2$-Si), 2,100 cm^{-1} (Si-H), and 1,260, 1,400, 2,900 and 2,950 cm^{-1}, which were observed also in PDS. In Table 2 are shown the properties of PCS and phenolic resin. The temperature of curing and the ceramic yield is somewhat dependent on the molecular weight of the oligomeric precursor. The conversion of PCS used in this study into SiCs was done by heating at 1,300 °C for 1 hr under nitrogen atmosphere. The SiC yields from PCS were 76 %. The residual weight of carbon from phenolic resin by heating was about 57 %.

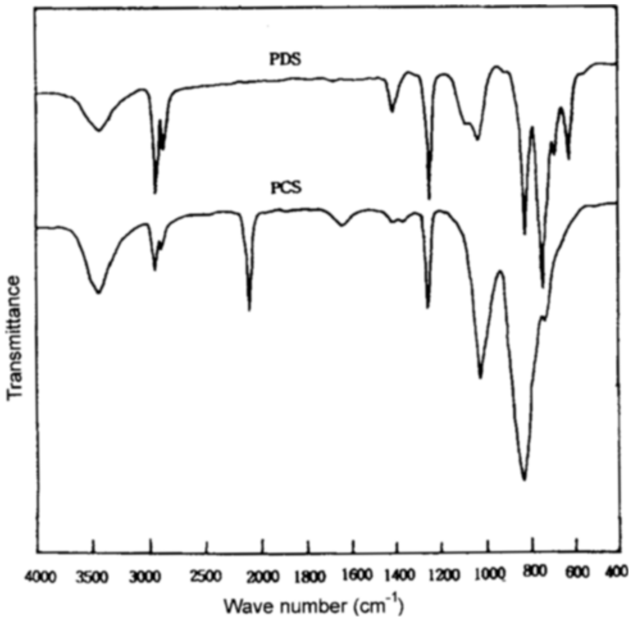

Fig. 1. FT-IR spectra of PDS and PCS.

Table 2. Properties of PCS and phenolic resin

	Melting point (°C)	Curing temp. (°C)	Yield (%)
PCS	280-300	190	SiC : 76
Phenolic resin	76-86	120-160	C : 57

2. Fabrication of SiC/C Composites

Important aspects of the preparation of SiC/C composites from PCS/phenolic resin/binder mixture are the use of an oligomeric PCS that has the proper molecular weight and curing process of the composites. After the curing steps the absorption bands due to Si-CH_3 and Si-H of the composite decreased and those due to free O-H stretching and C=O stretching newly appeared. These results indicate that the curing oxidized Si-H and Si-CH_3 groups and formed Si-O-Si and Si-O-C groups [Hasegawa, 1980].

3. X-ray Diffraction

The X-ray diffraction patterns of SiC/C composites heat treated at 1,000, 1,200, 1,300, 1,400, 1,500 °C are shown in Fig. 2. Fig. 2 shows the separation of the diffraction peak (002), (10), (004) and (110) of C, including the separation of the diffraction peak (111), (220) and (311) of β-SiC. The diffraction peaks become sharper as heat treatment temperature increases, suggesting a progressive crystallization process. Better crystallinity of β-SiC was observed at a higher temperature.

4. Density and Flexural Strength

The density of SiC/C composites is shown in Fig. 3. The density of SiC/C composite produced by 1/1 of mixing ratio was 1.70-1.80 g/cm^3 and that of 2/1 of mixing ratio was 1.77-1.85 g/cm^3. From the density measurement, it was observed that the increase in density of the SiC/C composite with variations on the mixing ratio and the heat treatment temperature was caused by difference in crystallinity of SiC.

In Fig. 4. are shown the flexural strength of the SiC/C composites heat treated at 1,000 to 1,500 °C. In the SiC/C composites made from 1/1, 2/1 of mixing ratio, maximum strength of 155 MPa, 175 MPa at 1,300 °C was observed, respectively. The flexural strength of 2/1 of mixing ratio was higher than that of 1/1. The strength at room temperature increased up to 1,300 °C with heat treat temperature; however, the flexural strength dropped rapidly over 1,300 °C. This result was similar to PCS derived SiC fiber [Yajima, 1977]. Kawamura reported that the decrease of flexural strength of SiC/ceramic mixture over 1,300 °C was caused by crystillization of SiC [Dutta, 1987]. From the flexural strength mesurement, this result shows that the increase of flexural strength up to 1,300 °C depends on the increase of PCS-derived SiC content. Furthermore, the strength of SiC/C composite fabricated in this study was larger than that of SiC/SiC composite produced from using Nicalon fiber and modified PCS [Hirai et al., 1988].

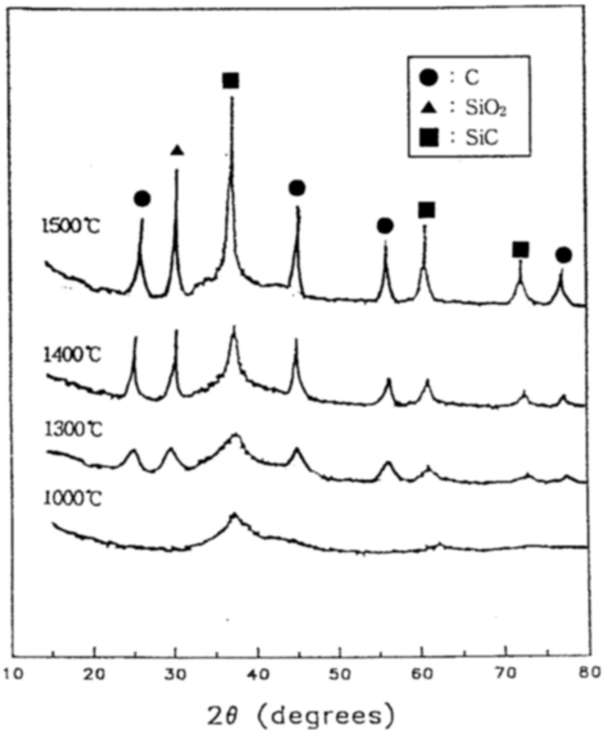

Fig. 2. X-ray powder diffraction patterns of SiC/C composite (PCS/phenolic resin=2/1) by heating at various temperature.

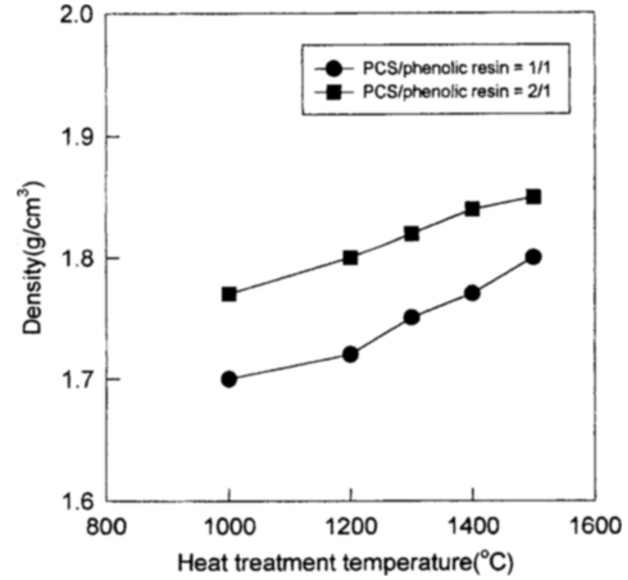

Fig. 3. Changes of density with flexural temperature for SiC/C composite.

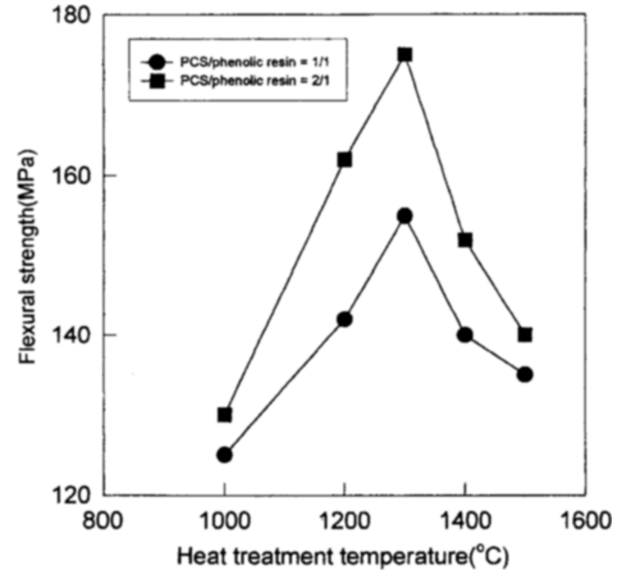

Fig. 4. Changes of flexural strength with heating temperature for SiC/C composite

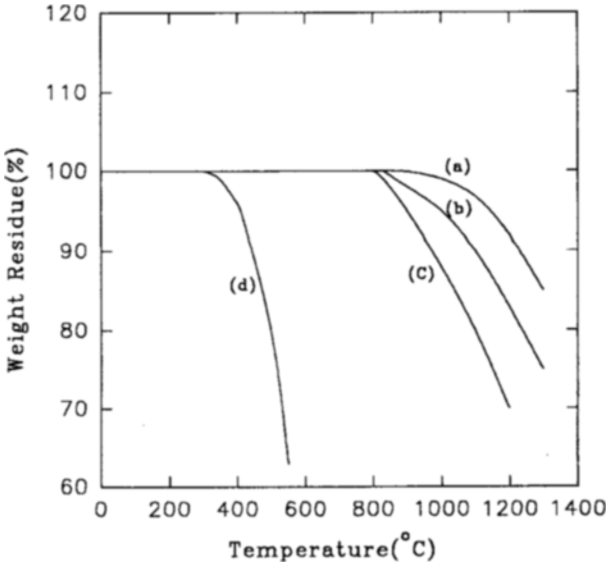

Fig. 5. Oxidation behavior of various composites which were left at 1,300 °C in air.
(a) SiC from PCS, (b) SiC/C composite (PCS/Phenolic resin=2/1), (c) SiC/C composite (PCS/Phenolic resin=1/1), (d) C/C composite

5. Oxidation Resistance and Electric Resistance

The oxidation resistance of SiC/C composite was measured with TGA by raising temperature at 20 °C/min to 1,300 °C in air atmosphere. These SiC/C composites display excellent oxidation resistance up to 830 °C, which is one of the most exciting aspects of this study. As shown in Fig. 5, C/C composites begin to oxidize at 400 °C while the SiC from PCS and SiC/C composite begin to degrade at 900, 830 °C, respectively. In the SiC/C composite case the oxidation kinetics above 830 °C depend on the mixing ratio of PCS/phenolic resin, that is, composites with 2/1 of mixing ratio show slightly different rate of weight loss. The resistivity of SiC/C composite sheets prepared in these experimental conditions was an order of 10^{-1} $\Omega\cdot$cm.

6. Microstructure of SiC/C

Figs. 6 and 7 show the SEM photographs of the fracture surface of SiC/C composite prepared by heating of PCS/phenolic resin mixture (1/1) and PCS/phenolic resin mixture (2/1), respectively. From the observations of the fracture surfaces, microstructures of SiC/C composite according to the fabrication conditions were well correlated with the behavior observed in the mechanical data. It was shown that the microstructures of SiC/C composites were dense as the heating temperature increased. As shown in Figs. 6-7, the adhesive effect between SiC component and carbon from phenolic resin looked good. It is thought that the increase of the bending strength of the composites depends on the adhesive effect of SiC and carbon in the composites.

CONCLUSION

Preparation of SiC/C composites from PCS/phenolic resin/

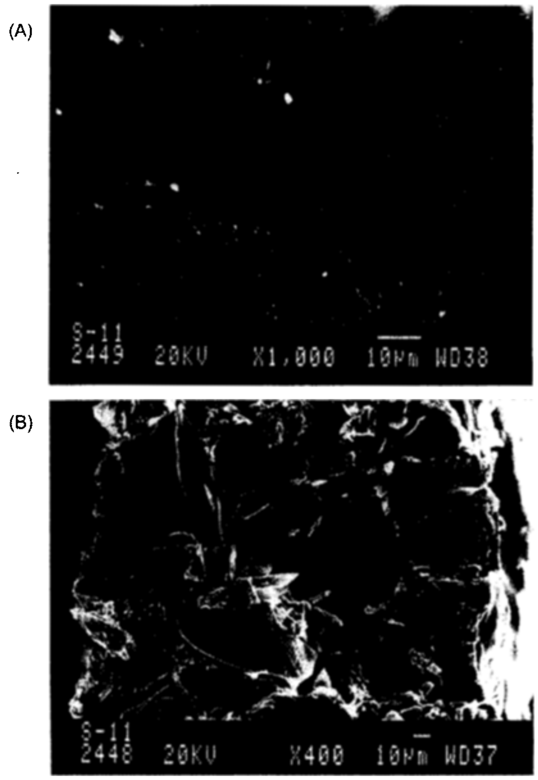

Fig. 6. SEM photographs of surface (A) and fracture section (B) of SiC/C composite sheet (PCS/phenolic resin=1/1) by heating at 1,300 °C.

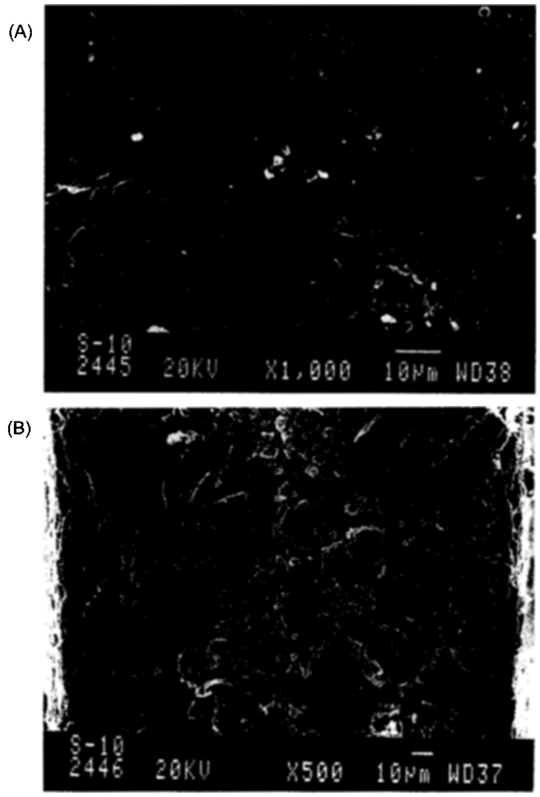

Fig. 7. SEM photographs of surface (A) and fracture section (B) of SiC/C composite sheet (PCS/phenolic resin=2/1) by heating at 1,300 °C.

binder mixture was successful. The flexural strength of the composites at room temperature increased with heating temperature and showed a maximum value of 175 MPa at 1,300 °C. When the composite was heat treated at 1,400 °C, the flexural strength decreased rapidly due to the process of crystallinity of SiC. The SiC/C composites showed good oxidation resistance up to 830 °C. The effective mixing ratio of PCS/phenolic resin to prepare improved mechanical property was 2/1.

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