OPTIMIZATION AND CHARACTERIZATION OF CHEMICAL VAPOR INFILTRATED SiC/SiC COMPOSITES

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ABSTRACT

SiC/SiC composites were fabricated by the forced-flow, thermal gradient chemical vapor infiltration (FCVI) method at the Oak Ridge National Laboratory (ORNL) and by the iso-thermal chemical vapor infiltration (ICVI) method at the National Institute for Materials Science (NIMS). The FCVI approach can fabricate relatively large composites in relatively short time, while the ICVI has significant controllability of fiber/matrix interphase formation. Fiber types included the near stoichiometric Tyranno SA and Hi-Nicalon Type-S. SiC/SiC composites with 75 mm in diameter and 12.5 mm in thickness and those with 300 mm in diameter and 12.5 mm in thickness were fabricated at ORNL. SiC/SiC composites with 40 mm in diameter and 1.5~3.0 mm in thickness were fabricated at NIMS. Microstructure was studied using SEM with EDS and TEM. Mechanical properties were evaluated by tensile test, flexural test and single fiber push-out test.

Density, the uniformity of fiber/matrix interphase and mechanical properties improved by increasing fiber volume fraction, optimizing processing conditions for both the FCVI and the ICVI processes. Porosity was decreased to approximately 15%. The effects of the interphase on mechanical properties and fracture behavior were studied. Tensile strength of 2D composites reinforced with Tyranno SA fibers and with optimized multilayer SiC/C interphase was approximately 300 MPa.

INTRODUCTION

CVI produces a stoichiometric, crystalline β-SiC. The major advantage of CVI over other processing routes is the low thermal and mechanical stress of the densification process owing in large part to the lower deposition temperature. In addition, the process imparts little mechanical stress to the preform. The excellent controllability of formation of fiber/matrix interphase, which affects mechanical properties significantly, is also advantage of the method. However it takes long time for CVI processing and the size was limited to relatively small fabric.

The forced-flow thermal-gradient chemical vapor infiltration (FCVI) developed at ORNL overcomes the problems of slow diffusion and restricted permeability [1,2] even in the large component with 300 mm in diameter and 15 mm in thickness. Composites have been fabricated using Nicalon™ fibers. However the optimum conditions using recent near stoichiometric high purity fibers such as Tyranno™ SA and Hi-Nicalon™ Type-S were not obtained. The iso-thermal chemical vapor infiltration (ICVI) method at NIMS [3] can form precise uniform fiber/matrix interphase within a composite. The interphase is one of keys to improve mechanical properties of composites [4,5]. The optimization of the interphase for composites reinforced with high-purity fibers is required.

SiC-sintered fibers, which are near stoichiometric and highly crystalline SiC fibers such as Sylramic™ [6] of Dow Corning, Hi-Nicalon™ Type-S [7] of Nippon Carbon and Tyranno™ SA [8,9] of UBE industries, were developed. These SiC fibers have been reported to show superior thermal stability than low-oxygen fibers, since the oxidation of excess C in air into CO at high temperatures resulted in the formation of pores in the latter [9]. These fibers are also expected to be stable under neutron irradiation. Therefore development and evaluation of the SiC/SiC composites reinforced with the highly crystalline fibers is desired.

One of the objectives of this study is to optimize processing conditions of both ICVI and FCVI using high purity SiC fibers focusing to increase density and to obtain uniform fiber/matrix interphase through thickness. Another objective is to characterize fiber/matrix interphase and improve mechanical properties of the composites. The effect of the interphase on mechanical properties was evaluated.

EXPERIMENTAL

SiC/SiC composites with 40 mm in diameter and 1.5~3.0 mm in thickness were fabricated using plain woven Hi-Nicalon and Tyranno SA fibers by ICVI at NIMS. The fibers were stacked in [0°/90°] direction. C and multilayer of C and SiC were applied as interphase between fiber and matrix. The precursors were methane (CH_4) for C deposition and methyltrichlorosilane (MTS, CH_3SiCl_3) or ethyltrichlorosilane (ETS, $C_2H_5SiCl_3$) for SiC deposition. Hydrogen was used as carrier gas for MTS and ETS. The temperature (900~1100 °C) of the furnace and flow rate of gas is controlled. Each gas flows into the bottom of the furnace. Thickness control of interphase in this system is difficult due to changing the conditions through the thickness of the preform. Temperature must be as same as possible within the fabric. Slower deposition rate is better to control the thickness of interphase. In order to obtain uniform thickness of interphase within a composite, effects of the temperature, gas flow rate and the position of a preform on microstructure were evaluated and those experimental conditions were optimized.

At ORNL, SiC/SiC composites were fabricated by FCVI using plain-woven high-purity SiC fibers, Tyranno SA and Hi-Nicalon Type-S. The fibers were stacked in [-30°/0°/30°] or [0°/90°] directions in the graphite holder. The fabric size for small furnace is 75 mm in diameter and 12.5 mm in thickness and that for large furnace is 300 mm in diameter and 12.5 mm in thickness. C, SiC/C or multilayer $(SiC/C)^6$ was applied to fiber/matrix interphase followed by matrix SiC deposition. C was deposited by decomposition of propylene (C_3H_6) at 1100 °C. SiC was deposited by decomposition of MTS at 1000~1200 °C. A graphite coating chamber radiatively heats the fibrous preform exterior and its interior is cooled with a water-cooled line following deposition of the fiber/matrix interphase. The MTS carried in hydrogen is injected inside the preform. The gas infiltrates through the preform thickness and exhausts at atmospheric pressure. The properties of the composites fabricated in this study are summarized in table I. The fiber volume fraction (V_f) and the porosity on the tables were estimated from cross-sectional scanning electron microscopy (SEM) images. The thickness of interphase on the

Table I. Properties of SiC/SiC composites with 75 mm in diameter fabricated by FCVI

ID	Fiber	Orientation	F/M Interphase	Nominal thickness of Interphase [nm]	V_f [%]	Density [Mg/m^3]	Porosity [%]
1256	Tyranno SA	[-30/0/30]	PyC	150	37	2.76	15.1
1257	Hi-Nicalon Type-S	[-30/0/30]	PyC	150	33	2.39	23.5
1258	Hi-Nicalon Type-S	[-30/0/30]	PyC	75	36.1	2.7	-
1259	Hi-Nicalon Type-S	[-30/0/30]	PyC	300	35	2.58	13.9
1260	Tyranno SA	[-30/0/30]	PyC	300	30.2	2.28	24.2
1261	Tyranno SA	[-30/0/30]	PyC	75	33.3	2.54	20.4
1264	Tyranno SA	[0/90]	PyC	150	35.4	2.61	23.3
1265	Tyranno SA	[0/90]	PyC	300	35.3	2.72	18
1266	Tyranno SA	[0/90]	PyC	75	35.2	2.62	18.1
1267	Tyranno SA	[0/90]	SiC/C	100/150	38.8	2.74	15.7
1268	Tyranno SA	[0/90]	SiC/C	100/150	38.8	2.69	18
1269	Tyranno SA	[0/90]	SiC/C	100/300	38.8	2.71	17.2
1270	Tyranno SA	[0/90]	$(SiC/C)^6$	$50/50/(200/50)^3/(500/50)^3$	39.8	2.52	26.88
1271	Hi-Nicalon Type-S	[0/90]	PyC	150		Not evaluated	
1272	Tyranno SA	[0/90]	$(SiC/C)^6$	$50/20/(200/20)^3/(500/20)^3$			

tables is nominal value.

Mechanical properties of composites were evaluated by three-point flexural tests and tensile tests. The specimens with dimensions 30 mm (long) × 4 mm (wide) × 1.5 mm (thick) were used for the flexural tests. The test span of the flexural tests was 18 mm. The flexural tests were conducted at a cross-head speed of 1.8 mm/min at ambient temperature. Tensile tests were conducted on the basis of ASTM C1275. The test specimens were Edge-loaded with dimensions 41.3 mm (long) × 6.0 mm (wide) × 2.3 mm (thick). The dimension of the gauge section was 15.0 mm (long) × 3.0 mm (wide) × 2.3 mm (thick). Details of the specimen and the tensile test are described elsewhere [10]. All tests were conducted at a cross-head speed of 0.5 mm/min at ambient temperature. The step-loading tests were performed for the precise evaluation of damage accumulation near proportional limit [11]. The mechanical properties of fiber/matrix interphase were evaluated by single-fiber push-out tests [12]. Specimens were sliced from composites normal to the fiber direction, which were mechanically polished to a final thickness of approximately 50 μm. For the tests the specimens were mounted on top of a holder containing a groove of 50 μm wide. Isolated fibers with the fiber direction perpendicular to the holder surface on the groove were selected with a video microscope and were pushed out using a Berkovich-type pyramidal diamond indenter tip with maximum load capability of 1 N. Microstructure was observed by optical microscopy and field emission SEM (FE-SEM). The thickness of interphase was measured by FE-SEM at several regions in a specimen. Fracture surface after tensile tests was examined by SEM with EDS.

RESULTS

<u>Optimization of ICVI</u>

Previously deposition rate of C was so high that most of the C precursor was deposited at the upstream side. Thickness of C interphase was quite different between upstream side and downstream side. For example, the thickness of C interphase at upstream was more than 1 μm, while C interphase was not identified at downstream side. However uniformity of interphase thickness was significantly improved by optimum experimental conditions, temperature, gas flow rate and position of the sample in the furnace. The optimized deposition rates of C and SiC are approximately 2 μm/min and 20 μm/min respectively. The scatter of temperature within composites improved to less than 1 % of controlled temperature. Apparent difference of interfacial thickness between upstream side and downstream side was not identified in the optimized composites.

Density of SiC/SiC composites was also increased with optimization of CVI conditions, while CVI processing time was significantly shorten from 40~50 hour to 15~20 hour. In the case of previous composites, upstream side was deposited easily and sealed prior to infiltration within the sample. Then the composites were removed and reversed to infiltrate another side. In contrast to previous composites, the deposition began within composites in the optimum conditions. Another key to increase the density was increasing fiber volume fraction. Fiber fabrics were well-aligned stacked and thickness of the preform was reduced. The density of the optimized composites reinforced with Hi-Nicalon was approximately 2.5~2.6 Mg/m^3, which corresponds to approximately 85% of the theoretical density, while 2.0~2.2 Mg/m^3 in the previous composites, which corresponds to approximately 70 % of the theoretical density.

Characterization of fiber/matrix interphase

To understand interfacial mechanical properties, single fiber push-out tests were carried out. The interfacial shear strength (ISS) (τ_{is}) was obtained from the 'push-out' load (P) in single fiber push-out testing and calculated from Eq. 1.

$$\tau_{is} = \frac{P}{\pi D t} \qquad (1)$$

where D is fiber diameter and t is specimen thickness. The resultant effect of thickness of C interphase on the interfacial shear strength of composites reinforced with Hi-Nicalon (a) and composites reinforced with Tyranno SA (b) is shown in Fig. 1. The Interfacial shear strength drastically decreased with increasing C interphase thickness. It was found that the interfacial shear strength of composites reinforced with Tyranno SA fibers was larger than that of composites reinforced with Hi-Nicalon if the thickness of C interphase is same.

The effect of thickness of C interphase on the proportional limit stress (PLS) and flexural strength of composites reinforced with Hi-Nicalon (a) and composites

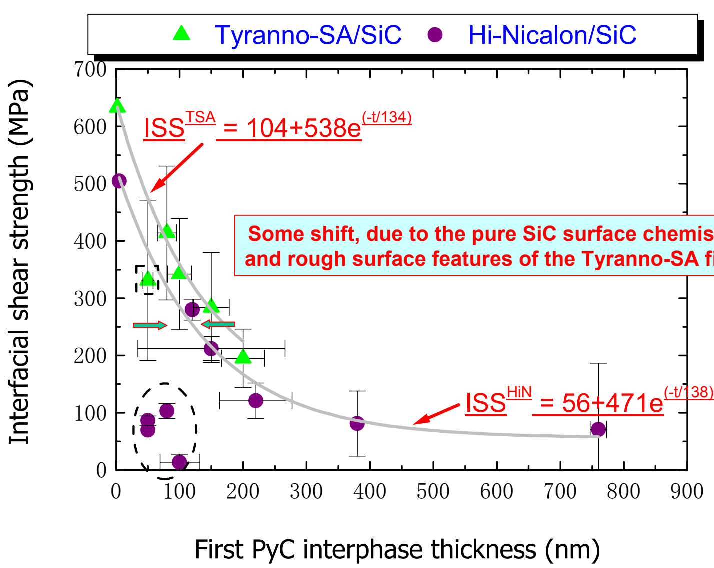

Fig. 1. Effects of thickness of PyC interphase on interfacial shear strength

reinforced with Tyranno SA (b) is shown in Fig. 2. The composites reinforced with Hi-Nicalon fibers showed the peak PLS and the flexural strength at about 150 nm in thickness of C interphase, while the composites reinforced with Tyranno SA showed the peak at about 100 nm. It was found that the mechanical properties of composites reinforced with Tyranno SA fibers are more insensitive than that of composites reinforced with Hi-Nicalon fibers.

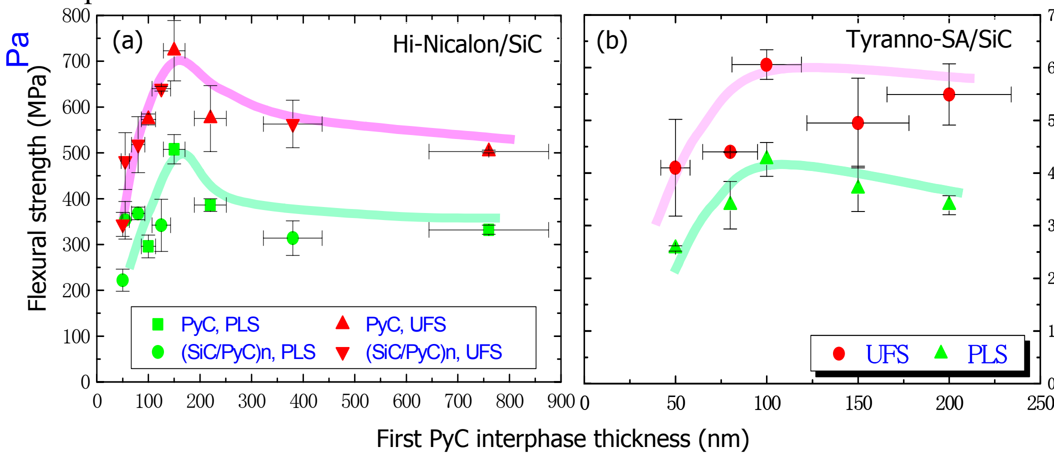

Fig. 2. Effect of C interphase thickness on the Flexural Strength

SEM and TEM observation showed that the interfacial crack almost always propagated along the interface between fiber and interphase [12]. This behavior was not limited only to C interphase. Multilayer C/SiC and "porous" SiC interphase showed the same behavior. Fracture surface of fibers was smooth. This led to low frictional stress of the debonded interface allowing easy crack propagation. This fracture behavior is attributed to a smooth fiber surface and weaker bond between the interphase and fiber than between the interphase and matrix SiC. In particular, the bond between fiber and C layer is weaker than the bond between C layer and SiC matrix. In order to improve interfacial fracture behavior and mechanical properties, the SiC layer was formed on fibers. Fiber and fiber bundle pull-out of composites with the SiC/C interphase reinforced with Hi-Nicalon fibers were shorter than those of composites without the first SiC layer. Both C and Si were detected from pull-out fiber surfaces of the composites without the SiC layer by EDS, and the atomic ratio of C to Si corresponded to that of Hi-Nicalon fiber [6]. In the case of composites with the first SiC layer, almost all species detected on pull-out fiber surface were C. The first SiC layer on Hi-Nicalon fiber induced strong bond between fiber and interphase and turned the crack path from between the fiber and the interphase to the inside of C interphase. Rough fracture fiber surface was seen, interfacial frictional stress was increased and mechanical properties of tensile tests were improved [13].

Optimization of FCVI

To understand the distribution of thickness of interphase and porosity within a composite, thickness of interphase and porosity were measured at nine regions in a composite. The porosity of previous composites was high and mostly more than 20% as shown in Table I. The bottom region, which is upstream side of precursor gas, and the outer region tended to have higher porosity in the previous composites. It was found that porosity was significantly affected by fiber volume fraction. As the fiber volume fraction increased, the porosity decreased as shown in Table I. Fig. 3 compares the distribution of porosity of improved composites with that of previous composite. In the improved composites porosity is independent of position, and the tendency seen in the previous composites was not confirmed.

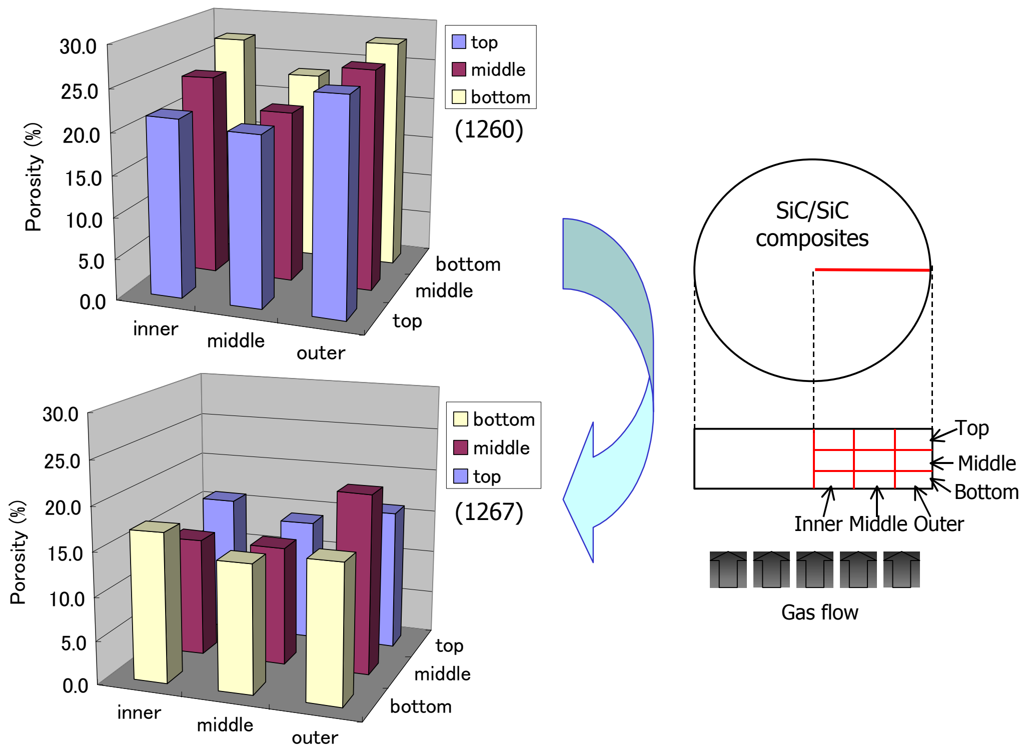

Fig. 3. Distribution of Porosity in Composites

The thickness of interphase was different thorough thickness. The interphase of bottom region was thicker than that of top region. One of the solutions to decrease the scatter of the thickness was to change the upstream side and the downstream side of the preform in the middle of interphase deposition process. Fig. 4 shows the distribution of the thickness of interphase. The scatter of the thickness was significantly improved by changing the upstream side and the downstream side.

Typical tensile properties of composites fabricated in this study are shown in Fig 5. The elastic modulus of composites fabricated in this work is almost twice as large as the reported elastic modulus of the composites reinforced with Nicalon fibers fabricated by CVI [14]. The fracture strain of composites fabricated in this work is less than half of that of the composites reinforced with Nicalon fibers.

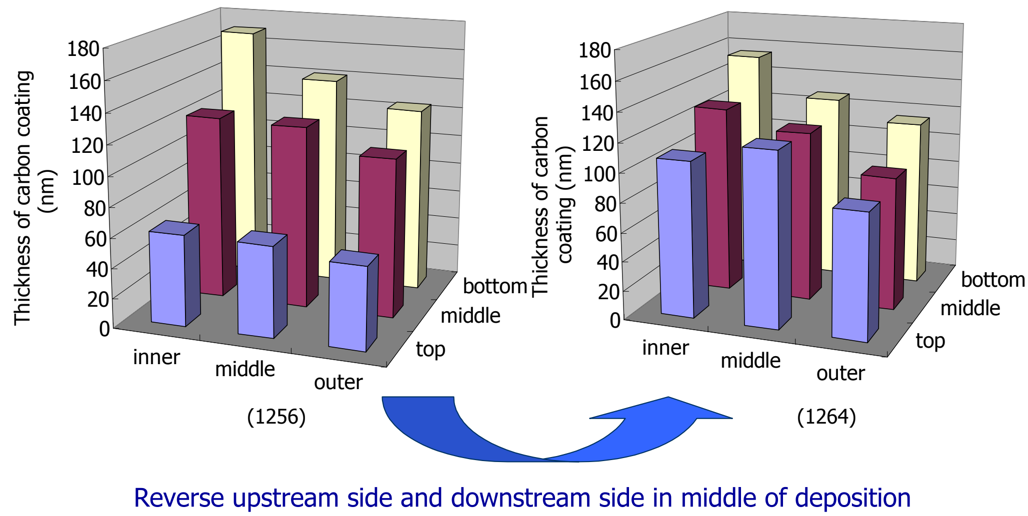

Fig. 4. Improvement of Scatter of F/M Interphase Thickness

These properties are attributed to the intrinsic fiber properties. Both tensile strength and proportional limit stress of composites fabricated in this work are superior to those of composites reinforced with Nicalon fibers.

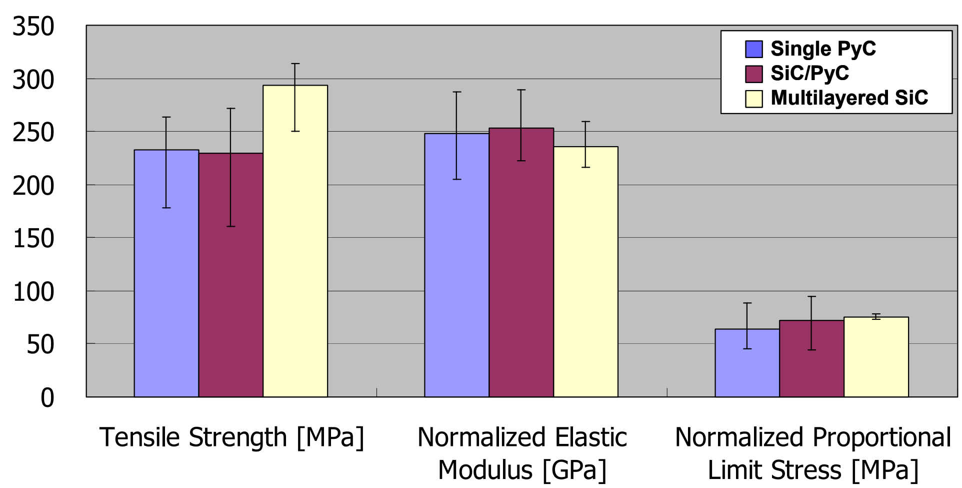

Fig. 5. The effect of fiber/matrix interphase on tensile properties

The thickness range of C interphase applied was about 20~300 nm. The average thickness of SiC layer of the SiC/C interphase was approximately 60 nm. Apparent effects of C interphase thickness and the first SiC layer on tensile properties were not seen. The multilayer interphase with new concept was developed in this study. Fig. 6 shows SiC/C multilayer interphase. The first thin SiC layer (50 nm) is to strengthen bond between fiber and interphase. The next three SiC layers (200 nm) are for multiple interfacial fractures of fibers. The next two thick SiC layers (500

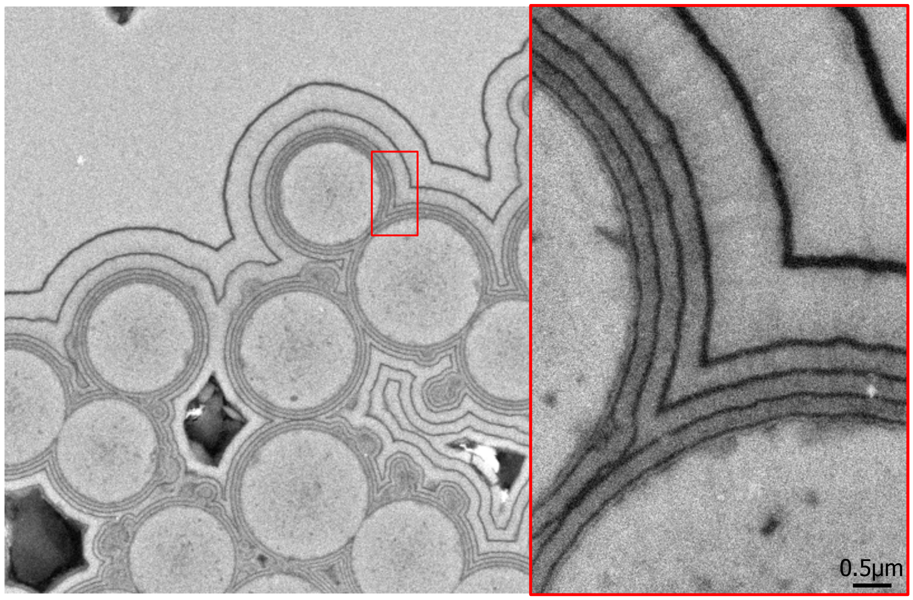

Fig. 6. SEM Images of Composites with SiC/C Multilayer Interphase

nm) are for multiple fractures of bundles. Thin C layers (50 nm) are used just to separate SiC layers. The composites with the multilayer SiC/C interphase showed the multiple fracture of interphase. The tensile strength of the composites with the multilayer was nearly 30 % larger than the composites with C interphase and with SiC/C interphase as shown in Fig. 5.

The large composites with 300 mm in diameter are supposed to be fabricated using Tyranno SA fibers for irradiation experiments and round robin tests. Prior to using Tyranno SA fibers, the large composites were fabricated using Nicalon fibers to understand distribution of porosity and uniformity of interphase. Dense composites were fabricated in the first trial. Although the porosity of outermost regions was higher than that of the other, the average porosity was 14.4 %. The interphase was not formed uniformly. There was a gradient of the thickness, i.e. the interphase at the top side and the center was thicker.

DISCUSSIONS

Pores existing within fiber bundle are limited and they don't affect porosity significantly in case of CVI composites. It is difficult to fill large space at inter-bundle of fibers by CVI processing. The large pores existing at inter-bundle of fibers significantly affect the porosity. In this study, increasing fiber volume fraction decreased porosity. Increasing the fiber volume fraction induced the reducing the space at inter-bundle of fibers and the total amount of large pores existing inter-bundle of fibers decreased.

The composites reinforced with Hi-Nicalon fibers showed the peak PLS and the flexural strength at about 150 nm in thickness of C interphase. The ISS of composites reinforced with Hi-Nicalon fibers was about 200 MPa at about 150 nm in thickness of C interphase. The composites reinforced with Tyranno SA showed the peak at about 100 nm. The ISS of composites reinforced with Tyranno SA fibers was about 350 MPa at about 100 nm in thickness of C interphase. The optimum ISS for the composites reinforced with Hi-Nicalon fibers is less than that for composites reinforced with Tyranno SA. The modulus of Hi-Nicalon is much smaller than CVD SiC, while the modulus of Tyranno SA is similar to CVD SiC. It means that the stress of matrix is larger than that of Hi-Nicalon fiber before crack initiation, while similar in composites reinforced with Tyranno SA fibers. Matrix cracking stress (σ_m) depends on fiber modulus (E_f) as shown in Eq. 2 [15].

$$\sigma_m = \left(\frac{6\tau G_m V_f^{\,2} E_f E_{cl}^{\,2}}{\left(1 - V_f\right) E_m^{\,2} r} \right)^{1/3} - \sigma_r$$

where σ_r is the residual stress, τ is the interfacial frictional stress, G_m is the critical mode I energy release rate, V_f is the volume fraction of fibers, E is the elastic modulus of the matrix ($_m$) or composite ($_{cl}$) and r is fiber radius. One of the roles of the interphase is to arrest matrix crack by interfacial debonding. It is assumed that the optimum ISS of the composites reinforced with Tyranno SA fibers is larger than that of composites reinforced with Hi-Nicalon fibers since the matrix cracking stress of the composites reinforced with Tyranno SA fibers is larger than that of the composites reinforced with Hi-Nicalon fibers. The gap between matrix cracking stress and maximum strength is relatively small in composites reinforced with Tyranno SA fibers. The effect of interphase on mechanical properties of composites reinforced with Tyranno SA fibers is smaller than that of composites reinforced with Hi-Nicalon.

The first SiC layer in fiber/matrix interphase was very effective for composites reinforced with Hi-Nicalon fibers. The crack path in the interphase was turned from fiber/interphase interface to within the interphase. The interfacial frictional strength was increased. The interfacial fracture behavior and mechanical properties were improved. However the apparent effect of the first SiC layer was not seen in the composites reinforced with Tyranno SA fibers. The one of the reasons is due to fiber modulus as discussed in the previous paragraph. The matrix cracking stress of composites reinforced with Tyranno SA should be larger than that of composites reinforced with Hi-Nicalon. The effect of interfacial shear strength on mechanical properties of composites reinforced with Tyranno SA fibers is smaller than that of composites reinforced with Hi-Nicalon. Another reason is rough feature of Tyranno SA fiber surface compared with that of Hi-Nicalon fiber. It is considered the interfacial frictional stress is enough large without the first SiC layer. The first SiC layer is expected to be effective under severe environment in which the interfacial shear strength is reduced by oxidation or neutron irradiation. The experiment under the severe environment is required to understand the necessity of the SiC layer.

The multilayer interphase with new concept was developed in this study. It is considered that not only fiber pull-out but also fiber bundle pull-out plays important role, so the concept of the bundle interphase was applied to the multilayer. Most of composites with C/SiC multilayer interphase without the first SiC layer on fibers did not have multiple fracture of the interphase and showed very brittlr fracture behavior due to large interfacial shear strength. However both the multiple fracture of fibers and fiber bundles were attained in the composites with the multilayer SiC/C interphase. It is condidered that the first SiC layer is the key of multiple fracture.

CONCLUSIONS

(1) The SiC/SiC composites fabricated by the ICVI system at NIMS were significantly improved by optimization of gas flow rate, temperature, the position in the furnace, increasing fiber volume fraction and the precursor gas. The uniformity of the fiber/matrix interphase, the density and mechanical properties were significantly improved while the time for fabrication became less than half of that for a previous sample.

(2) The Interfacial shear strength drastically decreased with increasing of C interphase thickness. It was found that the interfacial shear strength of composites reinforced with Tyranno SA fibers was larger than that of composites reinforced with Hi-Nicalon if the thickness of C interphase is same.

(3) The composites reinforced with Hi-Nicalon fibers showed the peak PLS and the flexural strength at about 150 nm in thickness of C interphase, while the composites reinforced with Tyranno SA showed the peak at about 100 nm. It was found that the mechanical properties of composites reinforced with Tyranno SA fibers are more insensitive than that of composites reinforced with Hi-Nicalon fibers.

(4) The first SiC layer in the fiber/matrix interphase improved interfacial fracture behavior and mechanical properties significantly in composites reinforced with Hi-Nicalon fibers, while apparent effect of the first SiC layer was not seen in composites reinforced with Tyranno SA fibers due to large modulus and rough feature of fiber surface.

(5) The density and the scattering on interphase of composites fabricated by FCVI was significantly improved by optimization of temperature and gas flow, increasing fiber volume fraction and reversing the up-stream side and down-stream side of the gas in the middle of deposition.

(6) Although thickness of C interphase and the first SiC layer didn’t affect tensile properties of composites reinforced with Tyranno SA, the tensile strength of the composites with the multilayer SiC/C interphase improved.

(7) Large composites with 300 mm in diameter was successfully fabricated by FCVI with the porosity of 14.4 %, although the interphase was not formed uniformly.

ACKNOWLEDGEMENT
Authors would like to thank T. Noda and H. Araki of NIMS and J.C. McLaughlin for the assistance of the fabrication of SiC/SiC composites. This work was supported by Core Research for Evolutional Science and Technology operated by the Japan Science and Technology Corporation, by Japan-USA Program of Irradiation Test for Fusion Research II and by the office of Fusion Energy Science, US DOE under contract DE-AC-05-00OR22725 with UT-Battelle, LLC.

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