

TENSILE PROPERTIES OF STOICHIOMETRIC SILICON CARBIDE FIBER REINFORCED FCVI DERIVED SILICON CARBIDE MATRIX COMPOSITES

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OBJECTIVE

The objective of this study is to investigate mechanical performance of recently developed stoichiometric SiC fiber reinforced FCVI SiC matrix composites and also to identify the key implementation for the improvement of FCVI technique. High-temperature tensile properties and the effects of fabric configurations and interfacial conditions on them were investigated using small specimen test technique for tensile testing.

SUMMARY

Recently developed SiC/SiC composites with high-crystalline, near stoichiometric SiC fiber are one of the promising materials for fusion and other high-temperature materials, because of the excellent physical and mechanical stability at high-temperature. Therefore material development has been enthusiastically carried out at ORNL as a part of US-Japan collaboration. The objective of this study is to clarify good performance of these composites at severe environment and also to identify the key issues for material development; effects of the interphase thickness, fabric orientation, and porosity on tensile properties, by using small specimen tensile test technique. It was shown that the maximum stress of TyrannoTM-SA/FCVI-SiC composites was stable under high-temperature exposure up to 1300°C in mild oxidizing environment. In addition, it was revealed that TyrannoTM-SA/FCVI-SiC with single PyC interphase had its maximum strength, when the thickness of PyC was around 150~200 nm.

PROGRESS AND STATUS

1. INTRODUCTION

SiC/SiC composites are considered one of the promising materials for fusion and other applications in advanced energy industries, because silicon carbide (SiC) has inherently superior stability of mechanical properties at high-temperature, low-induced activation and after heat, and excellent corrosion resistance [1, 2]. High-crystalline and stoichiometric SiC fibers like Hi-NicalonTM Type-S and TyrannoTM-SA are, in particular, stable to oxidation at high-temperature and severe neutron exposure because of less impurities like oxygen and good structural order [3, 4]. Similarly, b-SiC matrix derived by forced-flow/thermal-gradient chemical vapor infiltration (F-CVI) process, which has also high-crystalline structure, would show good stability of strength against neutron [5-7]. From these reasons, SiC/SiC composites with high-crystalline and stoichiometric SiC fiber and matrix are considered to have excellent physical and mechanical properties under these severe conditions. Therefore many researches on F-CVI process have long been enthusiastically carried out at Oak Ridge National Laboratory (ORNL), as a part of Japan-US collaborations. This study focused on tensile properties of SiC/SiC composites with recently developed new SiC fibers, for the optimization of F-CVI process.

Several advantages are focused on to discuss CVI process; less residual stress due to the fabrication at relatively low temperature (<1200°C), good infiltration of high-purity and stoichiometric b-SiC within extremely small spaces among fiber bundles [3, 8]. In addition, high-accuracy of controlling fiber/matrix (F/M) interface is characteristic in CVI method. On the contrary, CVI method has several disadvantages; gradients of gas concentration, temperature, and gas pressure due to the

presence of thermal-gradient. These gradients make an effect on uniformity of formed SiC matrix. Most composites fabricated by CVI method, in spite of high-crystalline SiC matrix, have relatively large gradients of density and porosity in bulk materials. This has been pointed out and need to be improved.

For the evaluation of these composites, conventionally flexural test was often used because of its simplicity to conduct. However, contrary to this simplicity, two opposite fracture modes such as compression and tension made it very difficult to do analysis. In some cases, inter-laminar shear fracture also made it more difficult. Therefore effect of each fracture mode on composite strength is required to evaluate separately for further discussion. On the while, tensile test is possibly useful to meet these demands because of its simplicity of fracture mode. This helps us to analyze composite strength easier and to identify fracture behavior more clearly. Tensile test also gives us the most fundamental information for practical applications.

Small specimen test technique (SSTT) for ceramic matrix composites (CMCs) has been developed as one of the effective means for the evaluation of mechanical properties for neutron irradiation [9, 10]. Miniaturization of test specimen has also been considered to be very effective in economical use and statistical analysis. Moreover, this technique, which is based on specimen size effects, will be very useful for the estimation of the mechanical properties of both large-sized materials and extremely small specimens used in practical applications. In this study, possibility and usefulness of this technique were also evaluated.

2. EXPERIMENTAL

Materials

All the composite disks with 3-inch diameter and half-inch thickness were fabricated by FCVI method at ORNL. Plane-woven (P/W) sheets of Tyranno™-SA fiber (Ube Industries), which were stacked in $[-30^\circ/0^\circ/30^\circ]$ or $[0^\circ/90^\circ]$ directions, were used as reinforcements (Table 1). In order to reduce porosity and to obtain high density, fiber volume fraction of all the $[0^\circ/90^\circ]$ composites (ID: 1264, 1265 and 1266) was designed to be higher than that of previous series; $[-30^\circ/0^\circ/30^\circ]$ composites (ID: 1256, 1260 and 1261). This is because it was revealed that composite porosity decreased proportionally as fiber volume fraction increasing. Fiber volume fraction plays an important role in decreasing open porosities, most of which are distributed among lay-up fabric sheets, although closed pores might be still remained. Less than 20 % of porosity was attained in each composite fabricated in recent activities after complete infiltration, by using methyltrichlorosilane (MTS) carried by hydrogen. These porosities were uniformly distributed especially in inner parts of composites.

Pyrolytic carbon (PyC) interphase was deposited on the surface of each fiber before FCVI densification. Three kinds of thickness of PyC interphase; 75, 150 and 300 nm, were chosen for the evaluation of influences of their thickness on tensile properties. In order to fabricate the uniform

Table 1 Materials

Sample ID	Fabric Information			Fabrication of Interphase			Material Properties		
	Fiber	Weave	Orientation	Material	Thickness of Interphase [nm]		Estimated Fiber Volume Fraction [vol%]	Estimated Density [Mg/m ³]	Estimated Porosity [%]
					Aimed	Measured Average			
1256	Tyranno SA	P/W	$[-30^\circ/0^\circ/30^\circ]$	PyC	150	107.1	37	2.76	10.8
1260	Tyranno SA	P/W	$[-30^\circ/0^\circ/30^\circ]$	PyC	300	168.5	30.2	2.28	28
1261	Tyranno SA	P/W	$[-30^\circ/0^\circ/30^\circ]$	PyC	75	70.5	33.3	2.54	19.7
1264	Tyranno SA	P/W	$[0^\circ/90^\circ]$	PyC	150	116.4	35.4	2.61	17.7
1265	Tyranno SA	P/W	$[0^\circ/90^\circ]$	PyC	300	225.5	35.3	2.72	14.2
1266	Tyranno SA	P/W	$[0^\circ/90^\circ]$	PyC	75	42.3	35.2	2.62	17.4

interphase in F/M interface, deposition of PyC was carried out at two times separately with gas either flowing first from top and then the bottom. All the composites had a small gradient in interfacial thickness and it had a maximum at the center of upstream side. Unfortunately, these interphases were formed 20~30 % thinner than desired. More details were discussed elsewhere [11, 12].

Small Specimen Test Technique for Tensile Testing

Several miniature specimens were designed from our ongoing research on specimen size effects on tensile properties of SiC/SiC composites (Fig. 1, 2) [10]. In particular, for the high-temperature tensile test, edge-loaded miniature specimen were selected for this study. The main features of this specimen are described as follows.

Total specimen length was determined by the dimensional constraints of the irradiation capsule, about 50 mm or less. The gage length was 15-20 mm in order to leave enough gripping area and for easy comparison with previous results [9, 10]. Gage width was designed to have more than one tow (1.5 mm) in width within the specimen total width to reduce influences of the presences surface flaws induced by machining. Especially for the case of shorter gage widths, stress concentration at the root became the most critical factor for failure and in such a case composites fail at lower stress. Gage thickness was taken as 2.3 mm. Moreover, the reduced thickness made it easy to decrease composite strength due to the local load sharing theory [13, 14]. Transition between gage section and edge section was curved in order to reduce stress concentration and this radius was determined by finite element method analysis.

Measurements

Tensile tests were conducted by electromechanical testing machine (Instron Japan Co. Ltd.) on the basis of ASTM C1275 and C1359. All tests were conducted at a rate of 0.5 mm/min crosshead speed. The step-loading tests were performed for room-temperature tension in air for the precise evaluation of damage accumulation near proportional limit [15]. Monotonic tests were conducted for high-temperature tension at 1300°C in a flow of commercial argon with about 0.1 Pa of oxygen in partial pressure. High temperature tests were carried out following a 20 min ramp to the test temperature and a subsequent equilibration time of about 10 min. More details are provided elsewhere [16].

After the tensile tests, fracture behaviors of all the specimens were examined by using scanning electron microscopy (SEM). Besides, porosity, fiber volume fraction and thickness of PyC interphase near fracture plane were also measured.

Analysis

Mechanical properties were analyzed using normalized stress as below, on considering large scatter in porosity among the materials. In this equation, stress was calculated as applied force divided by real area of cross-section excluding the area of pores.

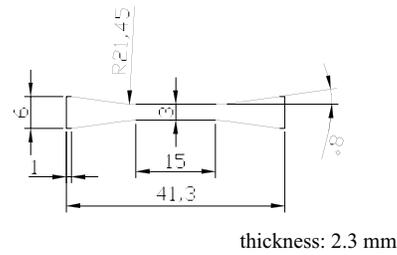


Fig. 1 Schematic illustration of miniature tensile specimen

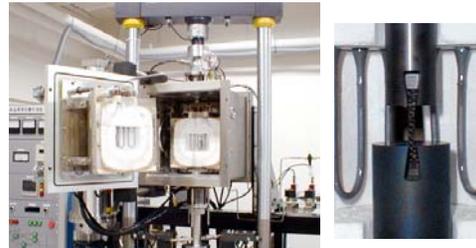


Fig. 2 High-temperature tensile testing machine

$$\text{Normalized Stress} = \frac{\text{Applied Force}}{\text{Cross Sectional Area} \times (1 - \text{Porosity})}$$

It is noted that, in this analysis, it was assumed that porosity was distributed equally in any cross-section.

3. RESULTS

It was revealed that maximum strength had no clear relationships in porosity, although elastic modulus was proportional to porosity. Elastic modulus increased as the porosity decreased (Fig. 3).

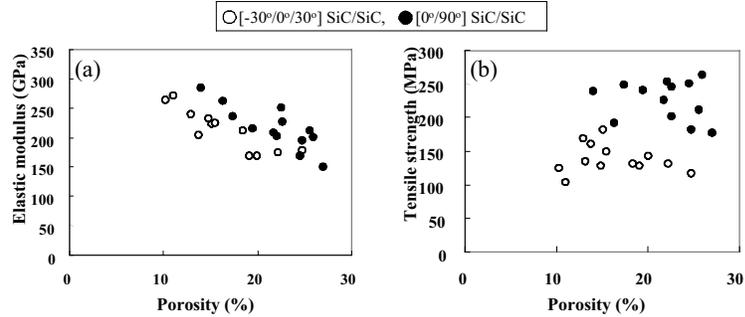


Fig. 3 Porosity dependencies on tensile properties; (a) tensile modulus and (b) maximum stress

Fig. 4 shows the stress-strain behaviors of [0°/90°] and [-30°/0°/30°] SiC/SiC composites at room temperature. Before the proportional limit, both curves were quite similar and slope of initial proportional region and this limit was almost the same. However, tensile behaviors in non-linear region were different. [-30°/0°/30°] SiC/SiC had larger accumulation of strain. The large reduction of slope of hysteresis in [-30°/0°/30°] SiC/SiC also explained this. Due to the accumulation of damage at lower stress, tensile strength of [-30°/0°/30°] SiC/SiC was reduced into about 60 % for [0°/90°] SiC/SiC (Fig. 5).

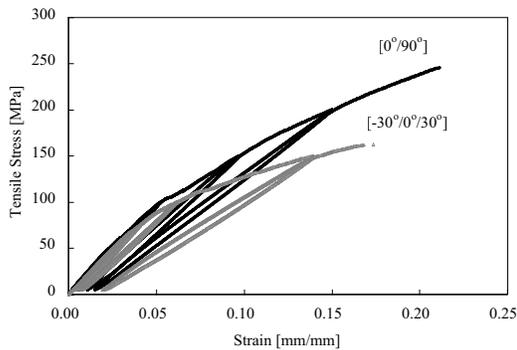


Fig. 4 Typical tensile behaviors of [-30°/0°/30°] and [0°/90°] SiC/SiC composites

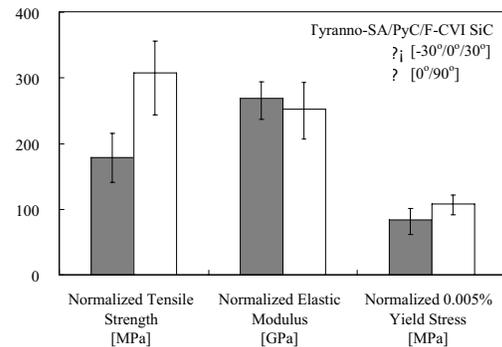
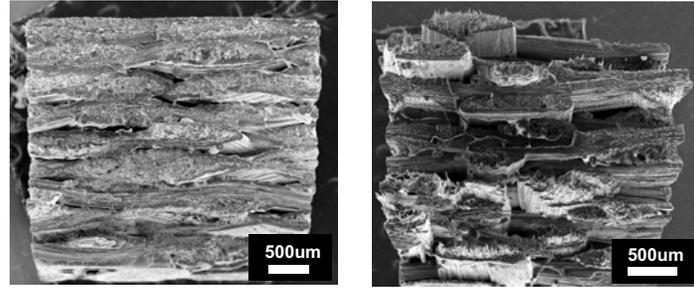


Fig. 5 Tensile properties of [-30°/0°/30°] and [0°/90°] SiC/SiC composites

According to fracture images (Fig. 6), fracture surface was nearly flat. However, there were a lot of pullouts of fibers, although they were relatively short.

Tensile strength of SiC/SiC with single PyC interface showed its maximum stress when the thickness of interphase was 150~200 nm (Fig. 7). However in this range, composite strength tended to maintain some constant value. This result was a little different from that of flexural strength. In flexure, Tyranno™-SA fiber reinforced composites with 200 nm thick PyC showed apparent its maximum strength [17].

Tyranno™-SA/PyC/FCVI-SiC had a good stability in mechanical properties under high-temperature exposure (Fig. 8). There was no significant degradation of tensile strength at 1300°C in mild oxidizing environment.



(a)

(b)

Fig. 6 Typical fracture surfaces of (a) [-30°/0°/30°] and (b) [0°/90°] SiC/SiC composites

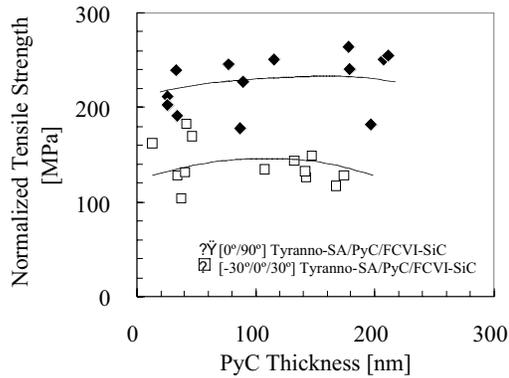


Fig. 7 Carbon interphase effect on tensile strength at room temperature

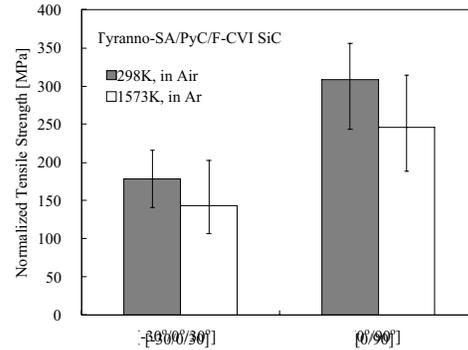


Fig. 8 High-temperature tensile properties of [-30°/0°/30°] and [0°/90°] SiC/SiC composites

4. DISCUSSION

Effect of Porosity on Tensile Properties

The SiC matrix fabricated by FCVI method grows radially from the fiber surface and traps tiny spaces in the developed matrix. Most pores were formed by the presence of the one-way flow of resource gas. Hence this made porosity (density) gradient in composites. Stress calculated as applied force divided by gauge area including pores, was usually used for the analysis, but this is not realistic for such high-porosity composites. This is one reason to apply normalized stress in this study.

It is well known that maximum stress significantly depends on axial fiber volume fraction [9, 18]. So tensile strength may not change if the quantity of fibers is constant in each specimen. In this case, most pores were induced by less matrix densification, with not relation to fibers. Hence, composite strength, which was governed by fiber strength, did not have any relation to porosity. In flexure, there was a clear relationship between maximum strength and porosity, and flexural strength was nearly proportional to density. This is due to the difference of key fracture mode that works on composite fracture. In tension, delamination, characteristic in flexure, did not make a significant effect on fracture behavior at maximum stress. In general, tensile strength was almostly determined by the fiber strength itself.

The mixture of the modulus of each component determines tensile modulus, and therefore tensile modulus is strongly affected by the occupation of all the components, i.e. porosity. PLS is often considered to be equivalent to matrix cracking stress. On considering most cracks emerged at the pores and sharp edges of the specimen, PLS might change by the presence of randomly distributed pores.

Effect of Fabric Orientation on Tensile Properties at Room Temperature

Maximum strength was dependent on fabric orientation due to the change of key fracture mode. Supposing that fiber strength aligned in the tensile axis made most significant effect on composite strength, then $[0^\circ/90^\circ]$ SiC/SiC, with higher volume fraction of fibers in tensile axis, showed higher tensile strength than $[-30^\circ/0^\circ/30^\circ]$ SiC/SiC. Of course, there were some other contributions to maximum strength such as off-axis tension, macroscopic in-plane shear between fiber bundles and microscopic interfacial shear between fiber and matrix. However, it seems very difficult to identify them only by tensile test.

Effect of Interlayer Thickness on Tensile Properties at Room Temperature

TyrannoTM-SA/SiC composite had maximum tensile and flexural strength at the 200 nm in thickness of PyC. However, in tension, there was not clear difference in PyC thickness. In particular in flexure, it was sited 50 nm thicker than that of Hi-NicalonTM/SiC [17]. One of the reasons is the difference of surface roughness of fibers. TyrannoTM-SA is composed of high-crystalline, large (>20 nm) grains and hence the fiber surface is so rough. Rough surface needs much interfacial material to obtain good bonding condition. From this reason, high-efficiency interfacial function was performed, even if the relatively thick PyC interphase was formed. Additionally, there was an advantage that friction along the F/M interface after debonding was higher. It is noted that smooth surface like Hi-NicalonTM made bonding strength and also friction after debonding lower, and most cracks easily propagated at the F/M interface. However, what was the most important was that almost of all the cracks developed between fiber and interfacial material, even if the bonding strength improved like Tyranno-SA/SiC [19]. Therefore there are still some issues to be improved and now many researches on multi-layer SiC/PyC interface are going on.

Tensile Behavior at High Temperature

SiC formed easily into SiO₂ in air by oxidation and, even if in inert environment, SiC is oxidized due to the reaction with oxygen included in as impurity [20, 21]. The former is well known as passive oxidation and also the latter is referred as active oxidation. SiC fiber and matrix used in this study were near-stoichiometric composition and hence there were few impurities. Indeed, it is reported that there was no significant degradation of tensile strength in TyrannoTM-SA fiber itself below 1300°C in inert environment [3, 22]. On the while, it was afraid that PyC might be easily burned out by oxidation. However, in the non-oxidized environment like this study, this seemed quite small, not zero. These good stabilities of each component made tensile strength of composites much stable to the oxidizing attack. Hence, $[-30^\circ/0^\circ/30^\circ]$ SiC/SiC showed no degradation in oxidizing environments. While, $[0^\circ/90^\circ]$ SiC/SiC slightly degraded at high-temperature but hopefully there seems little degradation in tensile properties. Otherwise, active oxidation to fiber and/or PyC might be performed in significant order. Anyway, further investigations are necessary to conclude this because of the shortage of test results.

5. CONCLUSIONS

In order to identify mechanical performance of recently developed SiC/SiC composites with high-crystalline, stoichiometric SiC fiber (Tyranno™-SA), several composites were fabricated by FCVI method at ORNL and ambient/high-temperature tensile tests were performed by small specimen test technique. Key conclusions were summarized as follows.

1. Maximum tensile stress of Tyranno™-SA/FCVI-SiC composites was significantly stable to high-temperature exposure up to 1300°C in mild oxidizing environment.
2. Tyranno™-SA/FCVI-SiC composite with single PyC interphase had its maximum strength when the thickness of PyC was about 200 nm.
3. Tensile strength was nearly no dependent on porosity. On the contrary, elastic modulus increases proportionally by improving composite density.

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