EFECT OF FIBER PROPERTIES ON MECHANICAL PROPERTIES OF CRYSTALLINE SILICON CARBIDE COMPOSITES

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ABSTRACT

Unidirectional SiC/SiC composites with three kinds of stoichiometric SiC fibers (Hi-Nicalon™ Type-S, Tyranno™ SA and SCS-9A™) and three kinds of fiber/matrix interphases (C, Multilayer C/SiC and 'porous' SiC), were prepared by isothermal chemical vapor infiltration. Tensile testing, double-notched specimen shear testing, single fiber push-out testing and transthickness tensile testing were carried out at ambient temperature to evaluate the mechanical properties of these materials. The microstructure and fracture surfaces of the test specimens evaluated were studied by scanning electron microscopy. Composites reinforced with SCS-9A fibers showed the highest ultimate tensile strength, more than 1 GPa, while the proportional limit stress of composites reinforced with Hi-Nicalon Type-S fibers was larger than that of the other composites. The composites reinforced with Tyranno SA fibers showed larger modulus of elasticity, although its fracture behavior was brittle due to the large interfacial shear strength and low fiber volume fraction. Among composites reinforced with the same fiber, those with multilayer C/SiC interphase showed brittle fracture behavior compared with the other composites due to large interfacial shear strength. The transthickness tensile strength of composites reinforced with Hi-Nicalon Type-S was larger than that of composites reinforced with Tyranno SA fibers, although the interlaminar shear strength of both materials determined by the compression of double-notched specimens was similar.

INTRODUCTION

Silicon carbide has excellent high temperature mechanical properties, chemical stability and low activation properties and therefore SiC/SiC composites are expected to be used as structural materials for high temperature industrial and nuclear application [1,2]. The physical and mechanical properties of ceramic matrix composites depend on the properties of their various constituents, their geometry and concentration (e.g., volume fraction of fibers, fiber/matrix interphase structure, fiber weave architecture and matrix properties). In particular the reinforcing fibers and the fiber-matrix interface control the in-plane tensile strength and the fracture behavior of the composite [3].

The first generations of small-diameter SiC fibers (e.g.- Nicalon™ (Si-C-O) and Tyranno™ Lox M (Si-Ti-C-O) fibers) were found to contain too much oxygen, 11.7 % in a Nicalon [4] and 10.2 % in a Lox M [5]. As a result of carbothermal reduction reactions at temperatures above 1200 °C these fibers degrade resulting in a loss of tensile strength and creep resistance [6,7]. These characteristics will limit their use as reinforcements for CMCs. It was reported that SiC fibers with reduced oxygen content and improved thermal stability could be obtained by using an irradiation-curing method. These low oxygen fibers, Hi-Nicalon™ [4], Tyranno TE™ and ZE™ [5], have been successfully

industrialized. The thermal decomposition rate of these fibers is found to be determined by the diffusion-controlled nucleation and growth of SiC grains involving the diffusion of C in the fiber. By applying this mechanism, new SiC-sintered fibers, which are near stoichiometric and highly crystalline SiC fibers such as Sylramic™ [8] of Dow Corning, Hi-Nicalon™ Type-S [4] of Nippon Carbon and Tyranno™ SA [9,10] 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 [4]. These new fibers are also expected to be stable under neutron irradiation and therefore the evaluation of the SiC/SiC composites with the highly crystalline fibers is desired.

The objective of this work is to understand the effect of highly crystalline fiber properties on the mechanical properties (tensile strength, interlaminar shear strength, transthickness tensile strength and fiber/matrix interfacial shear strength) of SiC/SiC composites before and after neutron-irradiation. In this paper, the properties of SiC/SiC composites with highly-crystalline fibers are reported, and the effect of neutron irradiation on their mechanical properties will be reported in the near future.

EXPERIMENTAL

The materials used in this study were unidirectional SiC fiber-reinforced SiC matrix composites fabricated by isothermal chemical vapor infiltration (I-CVI) at Hyper-Therm High-Temperature Composites, Inc. for the ORNL/Kyoto University round robin irradiation program. All fibers used were low-oxygen containing, near stoichiometric SiC fibers: Hi-Nicalon™ Type-S (HNL-S), Tyranno™ SA (Ty-SA) and SCS-9A™. SCS-9A fibers have a carbon core, 33 μm in diameter, and outer silicon-rich carbon layers [11]. The Ty-SA fiber used in this work has been identified as "grade 1". It is a research grade fiber, and its properties are slightly different from Ty-SA "grade 3" fiber, which currently is commercially available. The tensile strength of grade 1 fibers is 2.0 GPa, while that of grade 3 fibers is larger than 2.5 GPa. Prior to matrix infiltration the fibers were coated with either carbon, multilayer C/SiC or 'porous' SiC by CVI. Mixtures of methyltrichlorosilane, argon, methane and hydrogen gases were used to deposit the 'porous' SiC interphase onto the fibers. In the multilayer C/SiC interphase, the first SiC layer was deposited following the deposition of a thin, interrupted layer of pyrolytic C. Four SiC layers were deposited with interrupted pyrolytic C [12]. The properties and characteristics of the SiC/SiC composites used in this work are presented in Table I. The thickness of the interphase and fiber volume fraction were estimated from cross sectional SEM images. One of the reasons for the low fiber volume fraction obtained was the extra SiC seal coating applied to the composites, which was 50 μm thick on average.

Table I. Properties of unidirectional composites

ID	TST1	TST2	TSM	TSP	SAC	SAM	S9C	S9M	S9P
Fiber	Hi-Nicalon™ Type-S				Tyranno™ SA		SCS-9A™		
Fiber Diameter (μm)	12				10		79		
Fiber Strength (GPa)	2.6				2.0		3.5		
Fiber Coating	C		Multilayer C/SiC	Porous' SiC	C	Multilayer C/SiC	C	Multilayer C/SiC	Porous' SiC
Coating Thickness (nm)	520	720	580	380	560	880	330	580	240
Density (g/cm^3)	2.58	2.58	2.65	2.56	2.55	2.53	2.64	2.6	2.56
V_f (%)	29	29	38	26	21	24	32	33	38
Porosity (%)	19	19	16	19	19	20	14	15	15

Tensile tests were carried out on test specimens with fibers aligned in the loading direction according to ASTM test method C1275. The test specimens were straight-sided with dimensions 50

mm (long) × 4.0 mm (wide) × 1.5 mm (thick) for HNL-S and Ty-SA specimens and 50 mm (long) × 4.0 mm (wide) × 1.0 mm (thick) for SCS-9A specimens. The gauge section was 18 mm-long in the middle of the specimen. The specimens were gripped using a pair of wedge-type grips and aluminum end tabs, which were adhesively bonded to the specimen to promote uniform stress in the gripping area. The magnitude of the clamping pressure was sufficiently large to prevent slippage between the grips and a specimen. The grips were connected to the load train using universal joints to promote self-alignment of the load train during the movement of crosshead and to reduce unwanted bending strains in the specimen. The strain was measured by means of a low-contact force capacitive extensometer which consists of two balanced arms, pivoted in the center, that transmit the displacement of the specimen to an outboard capacitive transducer to measure the specimen strain. Because the distance between these two arms in the original design is 25 mm, two supplementary arms were fixed to the original in order to measure the deformation of the specimen over a shorter gauge length of 18 mm. All tests were conducted at a cross-head speed of 10 μm/sec at ambient temperature.

The double-notched specimens (DNS) for interlaminar shear strength tests [13,14] were machined to dimensions 25 mm (long) × 4.0 mm (wide) × 1.5 mm (thick) and contained two centrally-located notches, 6 mm apart, that were machined halfway through the thickness using a dicing saw. The shear tests by compression of DNSs were carried out at ambient temperature at a constant cross head displacement rate of 10 μm/sec. The specimens were end-loaded using a fixture to provide lateral support to prevent specimen buckling. Fracture surfaces following the tensile tests and the shear tests of DNSs were studied by scanning electron microscopy (SEM).

Interfacial shear properties were obtained by single-fiber push-out tests [15]. Samples were sliced from composite specimens normal to the fiber direction into 500 μm-thick sections, which were mechanically polished to a final thickness of approximately 50 μm. In a thicker specimen, the debond crack typically initiates near the top surface when the fiber is pushed in. Eventually when the debond crack propagates in a stable manner through the entire thickness of the specimen the fiber is pushed out. However when a specimen is sufficiently thin (the thickness depends on interfacial shear strength), the push-in load corresponds to push-out load, i.e.- the debond crack propagates through the thickness of the specimen in an unstable manner. 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.

Transthickness tensile tests were also carried out [16]. The samples were machined to dimensions, 5.0 mm (long) × 5.0 mm (wide) × 1.5 mm (thick). The test specimens were adhesively-bonded with epoxy to a pair of holders, with 5 mm square faces The holders were connected to the load train using a pair of universal joints to promote self-alignment of the load train during the movement of crosshead to minimize sample bending. All tests were conducted with the cross-head speed of 10 μm/sec at ambient temperature.

RESULTS

Representative stress-strain curves of composites with C interphases reinforced with HNL-S (TST1), Ty-SA (SAC) and SCS-9A (S9C) fibers are shown in Fig. 1. The figure on the right is a magnified view of the inset in the figure on the left. These curves illustrate the typical effect of fiber type on the tensile properties and the trend observed in the results. Composites reinforced with SCS-9A fibers exhibited the larger average ultimate tensile strength (UTS) and strain, while the proportional limit stress (PLS) of composites reinforced with HNL-S fibers was the largest. The PLS was obtained from using the 0.01 % strain offset criterion. The average modulus of elasticity, obtained from the linear region of the stress-strain curve, was found to be largest for composites reinforced with Ty-SA fibers. The fracture surfaces of the tested composites are shown in Fig. 2. It

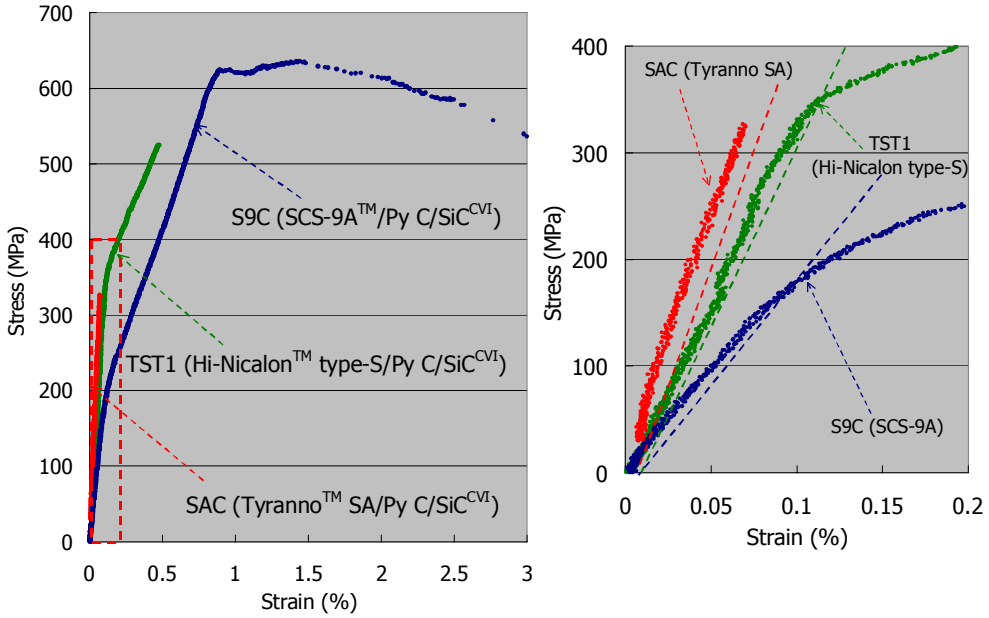
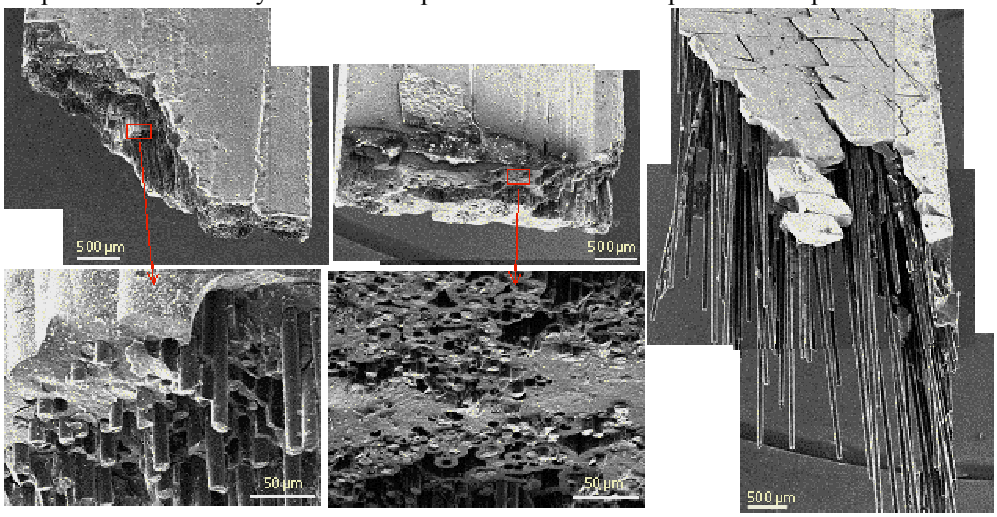


Fig. 1. Effect of fiber properties on strain-stress curve of tensile tests

was found that composites reinforced with SCS-9A fibers had fiber pullouts of the order of a few millimeters. In contrast, composites reinforced with HNL-S fibers showed relatively short fiber pullouts, while composites reinforced with Ty-SA fibers showed brittle fracture behavior.

It was also found that the tensile properties and fracture behavior of these composites were affected by the fiber/matrix interphase. The magnitude of the UTS for composites containing multilayer C/SiC interphase was smaller than that of the other composites. For composites reinforced with HNL-S and Ty-SA fibers the PLS and modulus of elasticity were smaller for composites with multilayer C/SiC interphase than for composites with carbon interphases. Composites with multilayer C/SiC interphase were brittle compared to composites with the other



Hi-Nicalon type-S/C/SiC Tyranno SA/C/SiC SCS-9A/C/SiC

Fig. 2. Effect of fiber properties on fracture surface

interphase. Composites with 'porous' SiC interphase and SCS-9A fibers had larger UTS than composites with C interphase, although the magnitude of UTS of composites with C interphase were larger in composites reinforced with HNL-S fibers. The tensile results are presented in Table II.

Table II. Summary of mechanical properties

ID	TST1	TST2	TSM	TSP	SAC	SAM	S9C	S9M	S9P
Tensile modulus (GPa)	336	306	256	307	417	350	203	294	373
Tensile PLS (MPa)	339	268	229	276	220	148	166	246	227
UTS (MPa)	442	319	229	282	220	148	622	562	860
Shear strength (MPa)	62.8	64.1	60.7	85.8	65.8	56.7	-	-	-
Interfacial shear stress (MPa)	163	149	180	212	211	341	-	-	-
Transthickness tensile stress (MPa)	26.9	-	-	-	20.2	-	-	-	-

The shear stress versus cross head displacement curves obtained from the compression of DNS specimens were slightly parabolic up to the peak load which was followed by a sudden load drop when the specimens failed. The apparent shear strength (τ) was determined from Eq. 1, as the ratio of the peak load, P_{max}, divided by the surface area of the imaginary plane between the notches.

$$\tau = \frac{P_{\max}}{wL} \tag{1}$$

where w is the specimen width and L is the notch separation. It was found that there were no significant differences among the shear strength values obtained for the composites evaluated except for composites reinforced with HNL-S and with 'porous' SiC interphase (Fig. 3). The shear strength of composites with multilayer C/SiC interphases was slightly smaller than those of composites with other interphases.

The interfacial shear strength (ISS) (τ_{is}) of these materials was approximated from the 'push-out' load (P) in single fiber push-out testing and calculated from Eq. 2.

$$\tau_{is} = \frac{P}{\pi D t} \tag{2}$$

where D is fiber diameter and t is specimen thickness. Although this is only an approximation, the objective of these tests was establishing a simple procedure for evaluating the effect of neutron irradiation on the interfacial properties of SiC/SiC composites. The results from ISS are compared with those from shear strength testing of DNS in Fig. 3. Error bars of the ISS represent one standard deviation about the mean value whereas the error bars in the DNS shear strength data represent

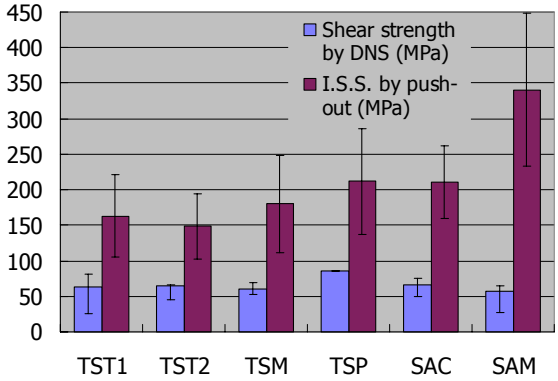


Fig. 3. Effect of fiber and fiber coating properties on shear strength and interfacial shear strength

maximum and minimum values. Although the state of stress in these two test configurations are very different, and therefore a direct comparison may not be appropriate, the results obtained from these tests will provide the means for identifying changes in the interfacial properties of these materials that may be induced by neutron irradiation. For composites with the same interphase, the ISS of composites reinforced with Ty-SA fibers was slightly larger than that of composites reinforced with HNL-S fibers. In composites reinforced with same fiber, the ISS of composites with multilayer C/SiC interphase and 'porous' SiC interphase was slightly larger than that of composites with C interphase.

The cross head displacement vs. stress curves obtained from transthickness tensile testing were slightly parabolic up to the peak load which was followed by a sudden load drop when the specimens failed. The average transthickness tensile strength of SAC (Ty-SA/C/SiC) and TST1 (HNL-S /C/SiC) composites was 20.2 MPa and 26.9 MPa, respectively. It was found that in this test the crack propagated interlaminarly between large pores in the matrix. Mechanical properties are summarized in Table II.

DISCUSSION

The higher proportional limit stress of composites reinforced with HNL-S fibers is attributed to higher fiber volume fraction than that of composites reinforced with Ty-SA fibers and smaller fiber diameter than that of composites reinforced with SCS-9Afibers. High fiber volume fraction increases the matrix cracking stress, which is directly related to proportional limit stress [3].

The ISS of composites reinforced with Ty-SA fibers obtained from single fiber push-out tests was larger than that of composites reinforced with HNL-S fibers and similar interphase. These differences can be explained from the differences in the surface topography of these fibers as a result of the differences in grain sizes. These results are consistent with the difference in tensile behavior that was observed between composites reinforced with these two fibers, particularly the differences in the magnitude of fiber pullouts observed during fractographic examination which is related to the magnitude of the interfacial shear stress according to:

$$h = \frac{\sigma_m{}^2 r}{2\tau} \tag{3}$$

where h is pullout length, σ_m is matrix cracking stress, r is fiber radius and τ is interfacial shear strength. The matrix cracking stress of composites reinforced with Ty-SA fibers, which has the smallest diameter among the fibers investigated, is smaller and the interfacial shear strength of the composites is larger than that of the other composites. So pullout length of composites reinforced with Ty-SA fibers should be shorter than that of the other composites. In contrast to composites reinforced with Ty-SA fiber, composites reinforced with SCS-9A fiber, which has the larges diameter among the fibers investigated, and pullout length of the composites should be long.

The theoretical modulus of composites (E_c) is calculated from Eq. 4.

$$E_c = V_f E_f + V_m E_m \tag{4}$$

where $E_f$and E_m are moduli of fiber and matrix, V_f and V_m are volume fractions of fiber and matrix. From this calculation, the moduli of the composites used in this study must be comparable and in the case of composites reinforced with HNL-S and Ty-SA fibers containing C interphase should be 363 GPa. However the modulus of the composites reinforced with Ty-SA fibers is larger than that of the composites reinforced with HNL-S. The modulus of composites reinforced with Ty-SA fibers is larger than the modulus obtained from Eq. 4 and therefore, it is likely that the actual modulus of Ty-SA fiber is larger than the value reported by the manufacturer.

The UTS of unidirectional composites is influenced primarily by the fiber properties, fiber volume fraction and the interfacial properties [17]. If we define the "relative UTS" as:

$$V_f\left(\frac{\sigma_0{}^m}{r}\right)^{1/(m+1)} \tag{5}$$

where V_f is the fiber volume fraction, σ_0 is the fiber characteristic strength, and m is the Weibull modulus of the fiber, and compare the "relative UTS" with the experimental values obtained, we find a good correlation if we assume that $m = 6$. These results are presented in Fig. 4 and the error bars correspond to the minimum and maximum values, respectively. Composites with C interphase showed superior UTS to that of composites with multilayer C/SiC interphase, although it is expected that composites with multiplayer C/SiC interphase will show better resistance to neutron irradiation than composites containing carbon interphases.

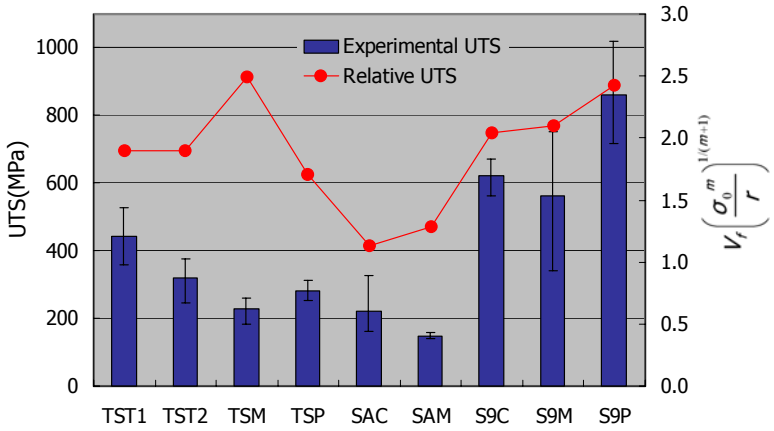


Fig. 4. Comparison of the experimental and the estimated relative UTS

In composites with the same fiber, the magnitude of the ISS for composites containing multilayer C/SiC interphase and 'porous' SiC interphase was larger than that of composites containing C interphase. In the particular case of composites reinforced with Ty-SA and multilayer C/SiC interphases, the magnitude of the ISS was much larger than of composites containing C interphases. In composites with multilayer C/SiC interphase, the fiber surface roughness is reflected in the rough features of the fracture surface with large interfacial frictional strength, since the first C layer is very thin. The results of ISS do not correlate with the results of DNS shear strength. Shear strength by DNS is affected by porosity, fiber volume fraction and pore size. To understand the different trends between ISS and DNS shear strength, further investigations are required.

There was no significant effect of fiber type on the magnitude of the interlaminar shear strength determined by the compression of double-notched specimens. However, the transthickness tensile strength of composites reinforced with HNL-S fibers was much larger than that of composites reinforced with Ty-SA fibers. DNS shear strength is affected by the roughness of fracture surface, while transthickness tensile strength is not affected significantly. Porosity of composites reinforced with HNL-S fibers was lower than that of composites reinforced with Ty-SA fibers. The average pore size of composites reinforced with Ty-SA fibers seemed larger than that of composites reinforced with HNL-S fibers. These results induce that the large interfacial strength of composites reinforces with Ty-SA fibers is attributed to large interfacial frictional strength.

CONCLUSIONS

(1) Composites reinforced with SCS-9A fibers showed superior UTS (> 1 GPa) than composites reinforced with either HNL-S, or Ty-SA fibers, while the proportional limit (0.01%) stress of composites reinforced with HNL-S fibers was larger than that of composites reinforced with

SCS-9A fibers. It was found that differences in UTS can be attributed to fiber strength and fiber volume fraction.

(2) The proportional limit stress of composites reinforced with HNL-S fibers was larger than that of composites reinforced with SCS-9A and Ty-SA fibers. This is due to the higher fiber volume fraction in composites reinforced with these fibers than that of composites reinforced with Ty-SA fibers and smaller fiber diameter than SCS-9A fibers.

(3) The interfacial frictional stresses were larger in composites reinforced with Ty-SA fibers than in composites reinforced with HNL-S fibers, and this difference was explained based on the difference in surface topography between these fibers. It was also found that the magnitude of interfacial bonding in composites with HNL-S was larger than that of Ty-SA.

(4) Composite materials containing multilayer C/SiC interphases exhibited less and shorter fiber pullout and brittler behavior than composites containing other interphases, since the average interfacial shear strength in composites with multilayer C/SiC interphases is larger than that of composites containing C interphases. It was found that the magnitude of the difference of interfacial shear strength was the largest for composites reinforced with Ty-SA fibers.

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