Hi-NicalonTM Fiber-Reinforced CVI-SiC Matrix Composites: II Interfacial Shear Strength and Its Effects on the Flexural Properties

Wen Yang¹, Hiroshi Araki¹, Akira Kohyama², Yutai Katoh², Quanli Hu¹,
Hiroshi Suzuki¹ and Tetsuji Noda¹

¹National Institute for Materials Science, Tsukuba 305-0047, Japan

²Institute of Advanced Energy, Kyoto University, CREST-ACE, Uji 611-0011, Japan

The interfacial shear strengths (ISSs) of a series of 2D Hi-Nicalon/SiC composites with various pyrolytic carbon (PyC) or PyC-SiC multiple fiber/matrix interlayers were investigated using the single fiber pushout tests. The influence of the obtained ISS on the proportional limit stress (PLS) of the materials upon bending was discussed based on the experimental results and a theoretical model calculation. The ISS showed close PyC layer thickness dependence. The ISS decreased quickly from 505 MPa to ~100 MPa with increasing the PyC layer thickness up to ~200 nm, beyond which slight decrease of the ISS occurred till 760 nm of the PyC layer. The ISS showed significant influence on the PLS. Good agreement between the model calculations and the experimental results was obtained, when correlating the PLS to the ISS. The comparison between the model calculation and the experimental results may be indicative on further efforts on further improvement of the mechanical performance of SiC/SiC composites.

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1. Introduction

The main attractions of continuous fiber reinforced ceramic matrix (CFCC) composites is that by the incorporation of high strength reinforcement fibers, the low fracture toughness of ceramics can be readily improved. In a CFCC composite, a transverse matrix crack can be deflected with energy dissipating occurring via several mechanisms:¹⁾ debonding at the fiber/matrix interface, crack deflection, crack bridging by the fibers, fiber sliding, and eventual fiber fracture. These energy-dissipating mechanisms provide for improved apparent fracture toughness and result in a non-catastrophic mode of failure. Obviously, the performances of these crack deflection and fiber sliding, and thus the performance of the materials, are closely dependent on the fiber/matrix bonding strength. A weaker fiber/matrix bonding is prone to crack deflection at interface while in order to take advantage of the high strength of the composite fiber reinforcement, the interface must be strong enough for effective load transfer between the fiber and the matrix.

The interfacial bonding strength can be controlled through the deposition of a coating or multiple coatings on the fibers.²⁾ Carbon remains the most effective interphase materials due mainly to its compliant nature of the carbonaceous fiber coating.³⁾ In a companion study,⁴⁾ the flexural properties and fracture behaviors of a series of Hi-Nicalon fiber reinforced CVI-SiC/SiC composites with various PyC or PyC-SiC multilayers were investigated. The results showed significant effects of the various interlayers on the strength and interfacial crack behaviors of the materials. The optimum PyC layer thickness, in terms of the flexural properties, was defined to be ~150 nm. The effects of the interlayers on the flexural properties are due to their modification of the interfacial bonding in these composites. To get clear understanding on the effects of the interlayers on the interfacial properties, and therefore, on the mechanical performance of SiC/SiC composites, it is

necessary to study the interfacial properties of above composites, and to correlate them to the interlayers and the flexural properties.

Interfacial shear strength (ISS) and frictional stress (IFS) are the two important properties that characterize the behavior of fiber/matrix interface. The ISS is more important on determining the composites proportional limit stress (PLS), while the IFS is generally important on determining the curved regions in the load/displacement curves from both bending and tensile tests.⁵⁾

In this study, the ISS of above composites were investigated using single fiber pushout tests. The main interest is the relationship of the interlayers, the ISS and the PLS upon bending.

2. Experimental

2.1 Composites

The composites are those materials reported in the companion paper.⁴⁾ The interlayer structures, porosities, PLS of the composites are given in Table 1. The PLSs were derived from the companion study.⁴⁾

2.2 Single fiber pushout tests

Single fiber pushout tests were carried out to extract the ISS using a load controlled micro-indentation testing system with a Berkovich type diamond pyramidal indenter. Figure 1 shows the schematic of the test. The maximum load of the indenter is 0.88N. Detailed experimental procedure can be found elsewhere.⁶⁾ The ISS was defined by^{6,7)}

$$ISS = P/\pi Dt \quad (1)$$

where P is the onset load for fiber pushout to occur. D and t are the fiber diameter and specimen thickness.

The pushout specimens were cut from each composite and were carefully ground and polished at both surfaces with di-

Table 1 Interlayers, porosities, PLS and ISS of the composites.

Specimen I.D.	Interlayer structure and thickness (nm)	Porosity (%)	PLS (MPa)	Specimen thickness (μm)	ISS (MPa)
NL	F/M	15.8	91(18)	34.0	505(91)
SL-100	F/C100/M	16.3	296(25)	77.5	14(4.6)
SL-150	F/C150/M	15.3	508(32)	60.6	212(33)
SL-220	F/C220/M	17.4	386(14)	55.5	121(31)
SL-760	F/C760/M	17.9	332(1)	76.0	71(31)
2L-125	F/SiC250/C125/M	18.4	342(57)	60.0	280(37)
2L-380	F/SiC250/C380/M	18.4	294(28)	89.0	81(14)
3L-80	F/C80/SiC150/C70/M	15.3	368(14)	58.5	103(10)
3L-50	F/C50/SiC150/C50/M	15.6	353(41)	90.0	86(34)
4L-50	F/SiC50/C50/SiC100/C50/M	17.8	222(24)	83.0	70(28)

Fig. 1 Schematic drawing of the single fiber pushout test.

among paste to reduce the thickness to several tens of micrometers (see in Table 1). The final polish grain size was 1 μm . About 20 pushout tests were conducted for each specimen. The polished surface and pushed/popped fibers after pushout tests were examined with scanning electron microscope (SEM) using JEOL JIM-6700F.

3. Results and Discussion

3.1 ISS and the effects of the PyC layer

The ISS of the composites derived from the pushout tests are summarized in Table 1. Included in the parenthesis are the standard deviations. The ISS for composite with no intentional interlayer (NL) is as large as 505 MPa. When single PyC or PyC-SiC multilayers were employed, the ISS was drastically decreased. It was found in the flexural properties study of these composites⁴⁾ that the interfacial debonding/sliding took place mostly at the interface adjacent to the first PyC layer (most near to the fiber). Rebillet *et al.*⁸⁾ has also reported that the interfacial characteristics seemed to be related to the thickness of the first carbon layer on the fibers in as-received Nicalon fiber reinforced CVI SiC/SiC composites with $(\text{C-SiC})_n$ interlayers. Therefore, it is assumed that the first PyC layer is the most important factor affecting the ISS. Figure 2 correlates the ISS to the first PyC layer thickness, which shows a strong PyC layer thickness dependence of the ISS. The ISS decreased quickly from 505 MPa to ~ 100 MPa with increasing the PyC layer thickness up to ~ 200 nm, beyond which slight decrease of the ISS occurred till 760 nm of the PyC layer. This suggests that no significant influence on the ISS is provided by the carbon in the PyC layers beyond ~ 200 nm.

Fig. 2 The first PyC layer thickness dependence of the ISS.

Fig. 3 SEM image of as-polished specimen from composite SL-100, showing pre-debonding at the interface.

Table 1 shows rather small ISS, 14 MPa, for composite SL-100. This was attributed to the finding that large amount of fibers in the specimen from this composite were pre-debonded before the pushout test as shown in Fig. 3, likely due to some damages of the interface near the specimen polished surface during the cut and polishing procedure.

The ISSs for composites 3L-80, 3L-50 and 4L-50 seem also too low according the trend showing in Fig. 2. No clear evidence for pre-debonding or interfacial damage was found by SEM examination at the as-polished surfaces of the speci-

mens from these composites. Anyhow, interfacial and/or PyC layer damages due to either the mechanical force (from the cut and polishing procedure) or the thermal residual stress (from the CVI process) are the current consideration for the seemingly low ISS, considering the very thin PyC layer from 50 to 80 nm in the three composites. Further study is undergoing.

3.2 Effects of ISS on proportional limit stress

As mentioned before, the PLS of SiC/SiC composites is significantly affected by the ISS. Inghels *et al.*⁹⁾ developed a theoretical model to predict the strength of unidirectional SiC/SiC composites upon flexural loading from the properties of the constituents (the fiber, the matrix and the interface). The PLS was given by,

$$\text{PLS} = E_c \left(\frac{12\gamma_m E_f V_f^2 \tau_i}{E_c E_m^2 V_m r_f} \right)^{1/3} \left(\frac{E_c + E_f V_f}{2E_f V_f} \right) \left(\frac{4E_f V_f}{3E_c + E_f V_f} \right)^{1/3} \quad (2)$$

where γ_m is the surface energy of CVD-SiC, which was given as 25 Jm^{-2} .⁹⁾ τ_i is the interfacial shear strength, ISS. E_m and E_f are the Young's modulus of the matrix and the fiber, 400 and 270 GPa for typical CVI-SiC matrix and the Hi-Nicalon fiber, respectively. V_m and V_f are the volume fractions of the matrix and the fiber. E_c is the composite modulus determined from the law of mixture.⁹⁾

The model was developed for SiC/SiC composites with 1D reinforcement while the reinforcements in the present composites are 2D plain-woven fabrics. Here for simplicity, the 0° fiber bundles are regarded as the reinforcement while the 90° bundles are regarded as 'matrix'. Thus the total volume fraction of the matrix is the volume fractions of the real CVI-SiC matrix and the 90° direction fibers given by:

$$V'_m = 1 - V_p - V'_f \quad (3)$$

where V_p is the volume fraction of pores, as given in Table 1. V'_f is the volume fraction of the 0° fiber bundles (half of V_f).

Clearly, crack is easier to initiate and propagate in the 90° bundle 'matrix'. Therefore, the load-bearing ability of this 'matrix' under above simple treatment was over estimated, let along the possible pre-exist cracks in the real CVI-matrix due to the mechanical and thermal residual stresses resulting from the fabrication process. In addition, in practical composites, the reinforcement fibers are, more or less, curved. This phenomenon, which is not considered in the model, is enhanced in 2D plain-woven or more complex woven fabric preforms, resulting in a decrease of the load-sharing ability of the fibers. Assuming that the effects of above factors on the PLS can be expressed by simply applying a constant coefficient, K , in eq. (2), then, by applying eq. (3) into (2), a modified model to correlate the properties of the constituents to the PLS of the present 2D plain-woven fabric reinforced composites is obtained as:

$$\text{PLS} = K E_c \left(\frac{12\gamma_m E_f V_f^2 \text{ISS}}{E_c E_m^2 (1 - V_p - V'_f) r_f} \right)^{1/3} \times \left(\frac{E_c + E_f V'_f}{2E_f V'_f} \right) \left(\frac{4E_f V'_f}{3E_c + E_f V'_f} \right)^{1/3} \quad (4)$$

Figure 4 shows the calculated PLSs as well as the experi-

Fig. 4 Calculated and experimental PLS via ISS of the composites.

mental results via the ISS. Composites SL-100, 3L-80, 3L-50 and 4L-50 were not included in the calculation due to the reason described in Section 3.1. Initially, the coefficient K was assumed to be 1 and the PLS was far over estimated compared with the experimental results. As discussed before, assuming $K = 1$ means a simple theoretical prediction of the strength of a composite from the properties of the constituents, without considering the effects of the 90° direction fiber bundles, the preexist defects (crack) in the fibers and matrix, and the curvature of the fibers. Therefore, the over estimated values of the PLSs are, in fact, the theoretical goal by the model. As shown in Fig. 4, assuming $K = 0.66$, a much better agreement to the experimental results was obtained when the ISS is less than ~ 200 MPa, beyond which the model predicted a continuous increase of the PLS with the ISS while the experiment results showed a reversed trend.

One of the main assumptions of the model⁹⁾ is that multiple matrix cracking occurs with constant distance between two consecutive cracks when the matrix crack initiated, followed by interfacial debonding and fiber sliding without further damage of the matrix until the failure of the fibers. However, this is not always true in practical materials, especially for composites with strong interfacial bonding. When the interfacial bonding is strong, interfacial debonding or matrix crack being deflected at the interfaces or bridged by the fibers are difficult to occur. Instead, significant stress concentration will take place at the crack tip. Extremely, when the fiber/matrix bonding is so strong that before interfacial debonding and matrix crack deflections occur, a single main matrix crack(s) forms and propagates through the thickness of the composite, resulting in a brittle failure behavior (without fiber pullout) with low PLS, as exhibited by present composites NL. This is likely to be the reason that the model predicted a simple increase with the ISS while the experimental results displayed a contrary tendency when the ISS is over a certain value. This indicates that there is a threshold of ISS beyond which the model becomes invalid. For the present Hi-Nicalon/SiC composites, this threshold seems to be ~ 200 MPa at which the highest PLS was achieved among all the composites.

It is known from above discussion that although the total coefficient K in eq. (4) is from the consideration of the effects

of the woven type of the reinforcement fibers and the preexist defects in the fibers and the matrix, it is rather a coefficient describing the difference between the theoretical prediction and the practical measured results of the PLS. Therefore, it is more suitable to re-write eq. (4) as:

$$PLS = K \sigma_{PLS}^{Th} \quad (5)$$

where σ_{PLS}^{Th} is the theoretical prediction of PLS by the model given as:

$$\sigma_{PLS}^{Th} = E_c \left(\frac{12\gamma_m E_f V_f'^2 ISS}{E_c E_m^2 (1 - V_p - V_f') r_f} \right)^{1/3} \times \left(\frac{E_c + E_f V_f'}{2E_f V_f'} \right) \left(\frac{4E_f V_f'}{3E_c + E_f V_f'} \right)^{1/3} \quad (6)$$

It might provide better estimation of the above effects when modified moduli of the fiber ($K_f E_f$, due mainly to the fiber curvature and possible cracks in the fiber from the fabrication process), the matrix ($K_m E_m$, due mainly to the 90° fiber bundle ‘matrix’ and possible preexist cracks in the matrix), and the composite ($K_c E_c$, K_c can be derived from K_f and K_m through the law of mixture) are used in eq. (4) instead of the total coefficient K . However, to determine the expressions for K_f and K_m will be a big challenge and several difficulties are exist such as, it is hard to get sufficient information about the defects and preexist cracks in the as-fabricated composites. Anyhow, Fig. 4 shows that with an appropriate value of K , the simple treatment and modification of the model (eqs. (5) and (6)) can give a sufficient accurate estimation of the PLS and predicted an effect of the ISS on the PLS that is in good agreement with the experimental results. The value of K ($=0.66$) suggests that further improvement of the strength of the composites is possible through appropriate arrangements of the reinforcement (woven type) and the optimization of the fabrication process for high quality matrix densification.

This study showed that the ISSs of the composites decreased quickly with increasing the PyC layer thickness up to ~ 200 nm, beyond which slight decrease of the ISS occurred. The composite with 150 nm PyC layer yielded an ISS ~ 200 MPa, which seems to be the optimum value in term of the PLS for the 2D plain-woven Hi-Nicalon/SiC composites. These findings are in good agreement with the results in the study⁴⁾ on the flexural properties of these composites that the PLS showed sharp increase with the increase of the PyC layer thickness till ~ 150 nm, and then decreased gradually. When the PyC layer was thicker than ~ 200 nm, the PLS showed little change with the PyC layer thickness. The optimum PyC layer thickness has been defined to be ~ 150 nm, in terms of

the flexural properties.

4. Conclusion

The ISS of a series of Hi-Nicalon fiber reinforced CVI-SiC/SiC composites were investigated. The effects of the various interlayers on the ISS were discussed. The influence of the obtained ISS on the PLS of the materials upon bending was also discussed based on the experimental results and a theoretical model calculation. The conclusions are:

(1) The ISS showed close PyC layer thickness dependence. The ISS decreased quickly from 505 MPa to ~ 100 MPa with increasing the PyC layer thickness up to ~ 200 nm, beyond which slight decrease of the ISS occurred.

(2) The PLSs were correlated to the ISSs. The highest PLS was obtained by the composite with ~ 200 MPa of the ISS. Either lower or larger ISS would cause decrease of the PLS.

(3) By applying the compliant coefficient K ($=0.66$), good agreement between the model calculation and the experimental results was obtained when the ISS was lower than a critical value, which was defined to be ~ 200 MPa for the present 2D plain-woven Hi-Nicalon/SiC composites.

(4) The comparison between the model calculation and the experimental results may be indicative on further efforts on further improvement of the mechanical performance of SiC/SiC composites.

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