EVALUATION OF BONDING STRENGTH BETWEEN SiC-COAITNG AND C/C COMPOSITE

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SUMMARY: Carbon fiber-reinforced carbon matrix composites (C/Cs) are usually used with anti-oxidation coating applied on their surface. The data of bonding strength between the coating and C/C substrate is indispensable for material design of C/C structures. Standardized measuring methods to evaluate the bonding strength, however, have not been established and the scratch method or the indentation method have attempted to be used. The results by these methods, however, do not give quantitative bonding strength and are useful only for relative comparison between specimens with the same geometry. In this paper, the bonding strength between SiC coating and the C/C substrate with various coating conditions was attempted to be measured by newly designed shear loading method. Experimental results were discussed in terms of thermal and mechanical loading conditions. Through these discussions, it was revealed that the energy release rate criterion could predict the bonding strength between the SiC coating and the C/C substrate.

KEYWORDS: C/C Composite, SiC Coating, Bonding Strength, Shear Load Method

INTRODUCTION

C/C composite is an unique material, which possess exceptional high heat resistance together with light weight, high stiffness and high strength. For this reason, the C/C composite has been expected to be applied to high temperature structures in such as aerospace and nuclear fusion industries [1-3]. However, the C/C composite is easily vaporized under oxidizing environment above 800K[4]. To overcome this difficulty, anti-oxidizing ceramic coatings on the surface of the C/C composites have been studied extensively. Requirements for the coating materials are strong bonding with the C/C substrates as well as thermo-mechanical compatibility and chemical stability in the oxidative environment at elevated temperature. In various candidate materials, silicon carbide (SiC) is one of the most successful coating, which has been used for heat shields of the Space Shuttle.

The SiC-coated C/C composite is expected as a material for the future high temperature system used under severe heating condition such as high performance turbine systems, reentry heat shields of space vehicles, etc. Due to extremely high thermal stresses between the coating and the C/C substrate, coating spallation would become a serious problem in their actual use. Because of this, failure criteria for the bonding between the SiC coating and the C/C substrate is indispensable to the material and structural design. However, conventional evaluation method such as the scratch test or the indentation test can only provide relative bonding strength when the specimens are in the same geometry.

In this paper, the bonding strength of the SiC coating are attempted to evaluate quantitatively by introducing newly designed loading system ("plunger method"), which can apply shear stress directly on the SiC coating by a plunger. First of all, interlaminar shear strength of C/C composite is evaluated to examine the validity of the testing method, and applicability of the fracture toughness criterion is also examined with these results. In the next step, the bonding strength of the SiC coating on the C/C composite was evaluated by taking processing temperature and the coating thickness as parameters. Finite element analyses were carried out to predict fracture loads of bonding in terms of fracture toughness criteria.

EXPERIMENTAL PROCEDURE

Materials

The C/C composite used in this experiments were produced by the Preformed Yarn Process (Across Co. Ltd.)[5]. In this process the preformed yarns, in which a carbon fiber bundle and row materials for the matrix (coke powder and bulk mesophase powder) were sheathed with nylon, were at first arranged unidirectionally in order to make preform sheets. They were then stacked in the preferred directions, and hot-pressed at 873 K for carbonization in an inert atmosphere. Heat treatment at 2273 K for graphitization was finally carried out in an inert atmosphere. In this study, high modulus type carbon fibers (M40, Toray) were used as the reinforcement, and orientations of the fibers in the C/C composites were set in the unidirectional (UD) and the cross-ply (0°/90°) stacking sequences with a total volume fraction of 50% (nominal).

The SiC coating on the C/C composite was processed by chemical vapor deposition. The SiC coating consists of two layers. One is conversion layer which was formed by direct reaction between Si gas and the C/C substrate. Thickness of the conversion layer is several _m and is expected to increase the bonding strength of the coating. The other is thick SiC layer with the thickness of 80 ~ 180 _m formed on the conversion layer by the CVD process.

Definition of Shear Testing Direction

Considering anisotropy in the C/C substrate, loading direction of shear tests can be classified into thee type. In this paper, they are defined as shown in ***Fig.1***, taking the hot-pressing direction during processing into account. One is the shear test for the SiC coating on a top surface perpendicular to the y-axis in the figure (the y-surface). In this test, the load is applied along the x-axis (perpendicular to the hot pressing direction and also to the fiber direction). This case is denoted by ***Top I***. In another case, the SiC coating on the x-surface was loaded in the y-direction. (denoted by ***Top II***). The third case is for the SiC coating on the side surface (the z-surface). The load was applied in the y-direction (denoted by ***Side***). In case

of 0°/90° C/C composite, only the two case, ***Top I*** and ***Side***, was tested, because ***Top II*** and ***Side*** are equivalent.

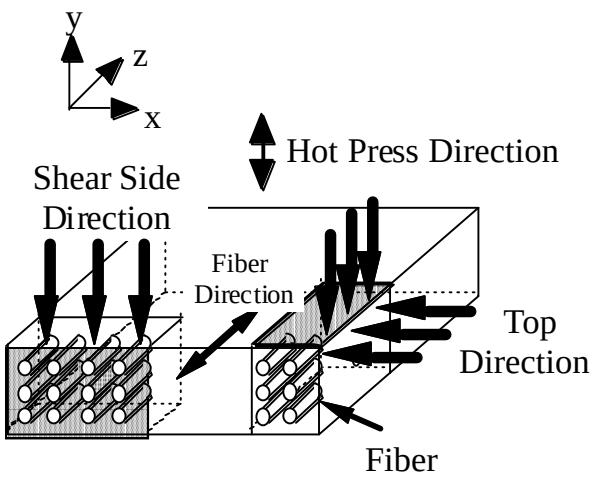

Fig.1 Definition of testing direction

Plunger Method

For quantitative evaluation of the bonding, newly designed loading system ("the plunger method") is prepared. As schematically shown in ***Fig.2***, the specimen is placed on the support stage and fixed by the plate. The specimen was adjusted to proper position using two micrometer dials and was checked by a reading microscope and a CCD camera. In the shear test, the SiC coating was directly loaded by the plunger using the Instron type testing machine with cross-head speed of 0.01 mm/min.

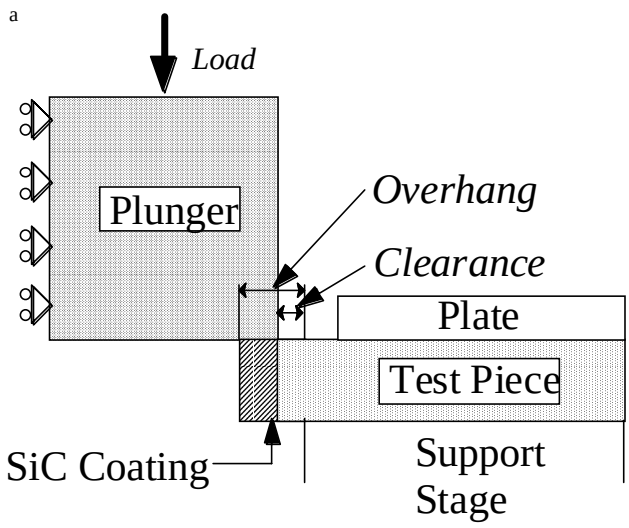

Fig.2 Schematic drawing of test fixture to measure shear strength of the coating

At first, interlaminar shear strength of the C/C composite is evaluated to examine the validity of the testing method. The tests were carried out on the UD and the 0°/90° specimens in ***Top I*** and ***Top II*** directions by taking thickness of the specimen as a parameter. Dimension of the specimen was set to 18mm x 3mm x ^{t}0.6~3.2mm.

In the next step, the bonding strength of the SiC coating was examined. Both UD and 0°/90° C/C composite were used as substrates. The shear tests were carried out in the ***Top I*** and ***Side*** directions for both specimens, and the dimensions of the each loading type specimen was set to 18mm x 3mm x ^{t}2mm and 18mm x 3mm x ^{t}3.2mm, respectively.

RESULTS

Interlaminar Shear Strength of Bare C/C composite

Figure3 represents average shear strength in ***Top I*** direction of the UD C/C composite obtained by the plunger method for various specimen thickness. The average shear strength is defined as the fracture load divided by the cross-sectional area of the shear loaded plane. As shown in the figure, the averaged fracture shear stresses are in the same level when the thickness is lower than 2 mm. In the specimens with thickness more than 2 mm, the averaged

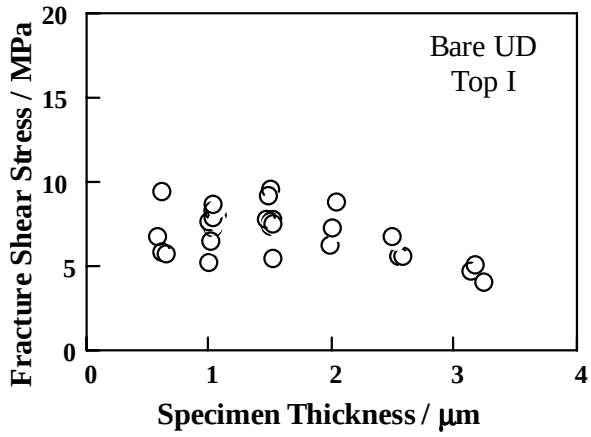

Fig.3 Averaged fracture shear stresses as a function of specimen thickness

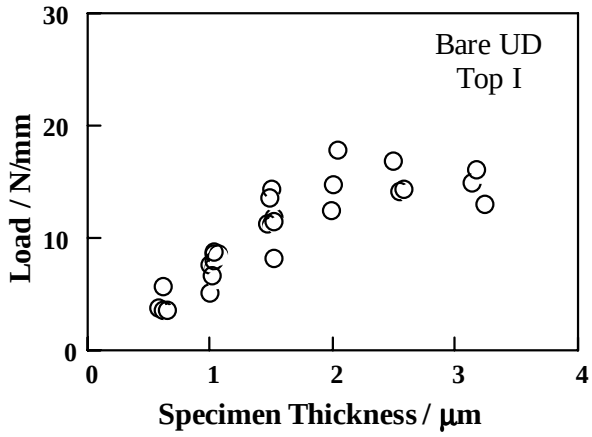

Fig.4 Fracture load as a function of specimen thickness

Table I Shear fracture stresses of bare C/C composites.

UD		0°/90° (MPa)	
Top I	**Top II**	**Top I**	**Top II**
6 ~ 9	**9 ~ 16**	**10 ~ 16**	——

fracture shear stresses decreased with increasing the thickness. When those results are re-plotted taking the fracture load as the y-axis, the fracture loads are constant when the thickness of the specimen is larger than 2mm as shown in ***Fig.4***. This results suggest that the shear fracture was affected by the stress concentration around the plunger tip, when the thickness of the specimen is larger than 2mm. In other words, the fracture of the specimen with thickness larger than 2mm is controlled by the fracture toughness criterion. On the other hand, the specimen less than 2mm thick might be controlled by the average shear strength criterion. All the tested results are summarized in ***Table I***.

For the specimen more than 2 mm thick, finite element analyses were carried out to obtain the critical energy release rate (G_C). The calculation model is shown in ***Fig.5***. In the analysis, the energy release rate (G) was obtained by the virtual crack extension method. The fracture loads of the experiments were used as applied loads in the analysis. Material properties of the C/C composite used in these analysis are listed in the ***Table II***.

Figure6 shows calculated results of G as a function of crack length for various specimen thickness. As shown in the figure, when the thickness is larger than 2 mm (solid mark), every G almost agree with each other at an early stage of the crack extension. With these results, G_C is expected to be applied as the shear fracture criterion in the plunger tests. On the other hand, each G showed different behavior when the thickness of the specimen is less than 1.5 mm. This is because the fracture in this region is

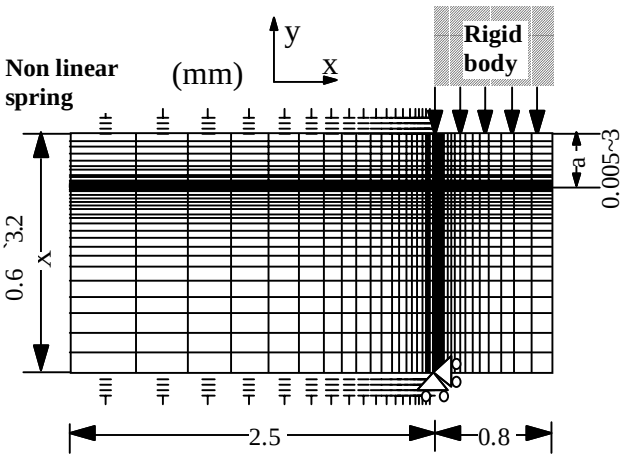

Fig.5 FEM model for bare C/C composite

Table II Materials Properties used in calculation

x,y=1,2

Material	Young's modulus (GPa)		Poisson's ratio	CTE x10^{-7} (1/°C)					
				1200°C		1600°C		1800°C	
	E1	E2	ν	$\alpha_{//}$	$\alpha_{\perp}$	$\alpha_{//}$	$\alpha_{\perp}$	$\alpha_{//}$	$\alpha_{\perp}$
C/C	200	15	0.3	1.5	89.8	4.6	91.0	6.1	91.3
SiC	490		0.25	48.91		49.23		49.51	

controlled by the average shear stress criterion

Because the SiC coated C/C composites examined in this paper were 2 mm or more thick, the fracture toughness criterion is expected to be applied for fracture prediction of the bonding.

Shear Test on Interface between SiC Coating and C/C Composite

Figure 7 summarize the shear fracture stress in various type of the specimen as a function of coating thickness and conversion time. All the coatings in the figure were processed at 1473 K, and the directions of the loading are ***Top I*** and ***Side***. In case of the SiC coating on the UD C/C substrate, ***Side*** specimens showed higher strength than ***Top I*** one. Contrary to this, ***Top I*** specimen of the SiC coating on the 0°/90° C/C composites showed lower strength than ***Side*** one.

Accordign to observation during experiments by the CCD camera, behavior of crack initiation and extension was different between ***Top I*** and ***Side*** specimen. In case of ***Side*** specimen, a crack initiated from the bottom of the bonding interface and extended along the interface. In contrast, a crack initiated and extended in the C/C composite in case of ***Top I*** specimens. These differences were observed in both laminate type of the C/C substrates. Actually, comparing the shear fracture stress in the figure with the shear strength in ***Table I***, they are well agree with

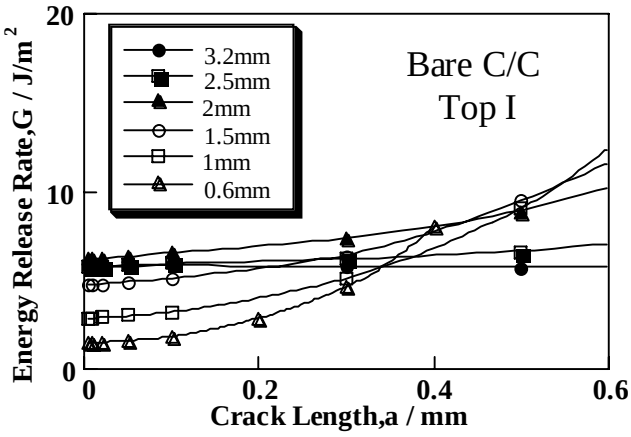

Fig.6 Energy release rate as a function of crack length for Bare UD C/C composites

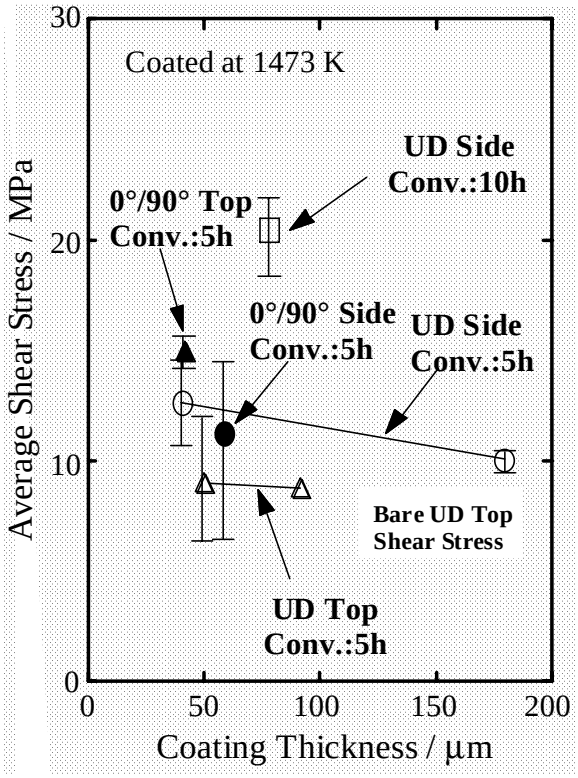

Fig.7 Averaged debonding shear stress as a function of coating thickness.

each other. This means that the bonding strength of ***Top I*** specimen is higher than the shear stress shown in the figure.

DISCUSSION

Factors Affecting Bonding Strength of Coating

The bonding strength of the SiC coating is expected to be affected by the following two factors. One is residual thermal stress in the SiC coating, which is induced during cooling process after the coating. The stresses will be positive in the fiber direction of *Top* specimen and negative in all directions of ***Side*** specimen. The residual stresses are expected to lower the apparent bonding strength of the SiC coating. In case of UD C/C composites, residual thermal stress in the fiber direction of ***Top*** specimen is much higher than that of ***Side*** specimen. Because of this, the bonding strength of ***Side*** specimens is believed to be higher than ***Top*** specimens in UD C/C composites, although shear fracture stresses of ***Top*** and ***Side*** specimen cannot be directly compared due to the difference in the fracture mode.

The other factor is existence of cracks on the surface of the C/C composites. In the 0°/90° C/C composites, many cracks along the fibers were originally introduced on the surface and inside of the composites due to thermal mismatch between the laminae ("transverse crack [5]). During the CVD process, SiC was formed partly in the transverse crack as well as on the surface of the C/C composites. The SiC in the transverse crack is expected to increase the shear fracture stress by acting like an "anchor" against shear deformation. In the 0°/90° C/C composites, the fraction of transverse crack is higher in the ***Top*** surface compared with the ***Side*** surface. This difference must be a major reason of the contrary results in the 0°/90° C/C specimens to the UD one.

Prediction of Fracture Load of Interface by FEM

Based on the experimental results, shear fracture load was predicted by FEM for various coating conditions. The ***Side*** specimen of the UD C/C composites was analyzed, because fracture occurred at the bonding interface. In the FEM model, shown in ***Fig.8***, eight node isoparametric elements were used assuming plain strain. Energy release rate was obtained at the bonding interface by introducing a crack in the model.

shows typical calculated results of energy release rate (*G*) as a function of crack length taking applied load as a parameter. Processing temperature and thickness of the SiC coating are assumed as 1200 °C and 173 _m. At the fracture load in experiments (35 N/m), *G* decrease with increasing crack length up to 2.7 mm. In this region, crack will extend stably. When the crack is longer than 2.7mm, G tend to increase rapidly, which means the crack will extend in an unstable

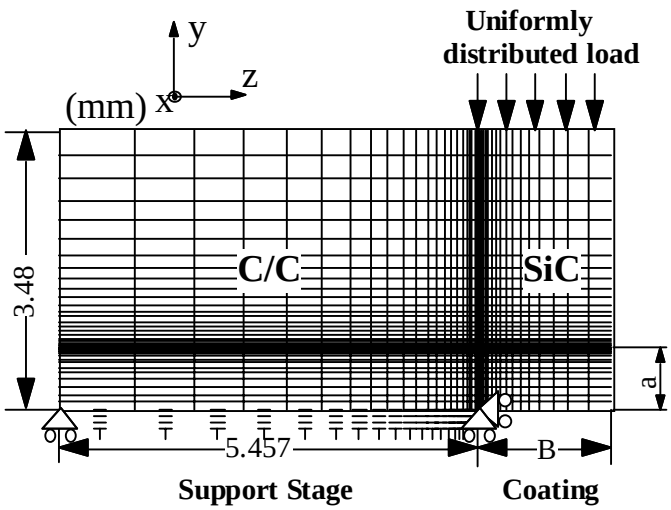

Fig.8 Finite element model for ***Side*** specimen of coated UD specimen

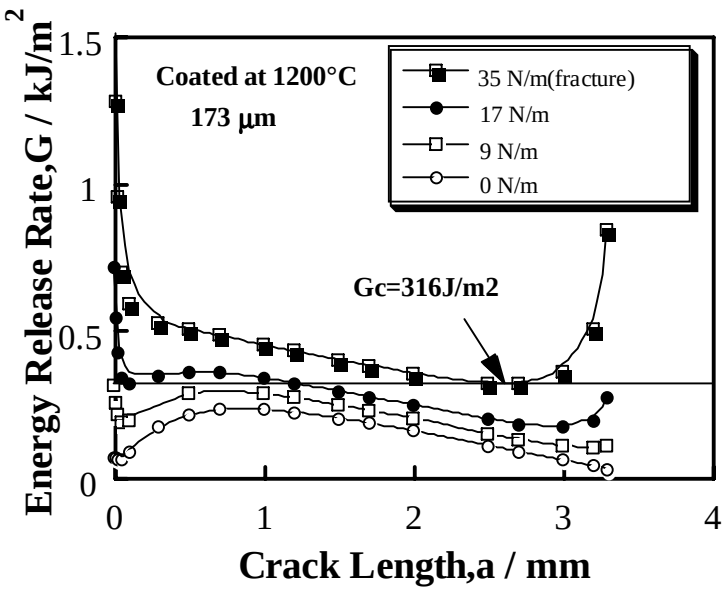

Fig.9 Energy release rate for different crack length and applied load.

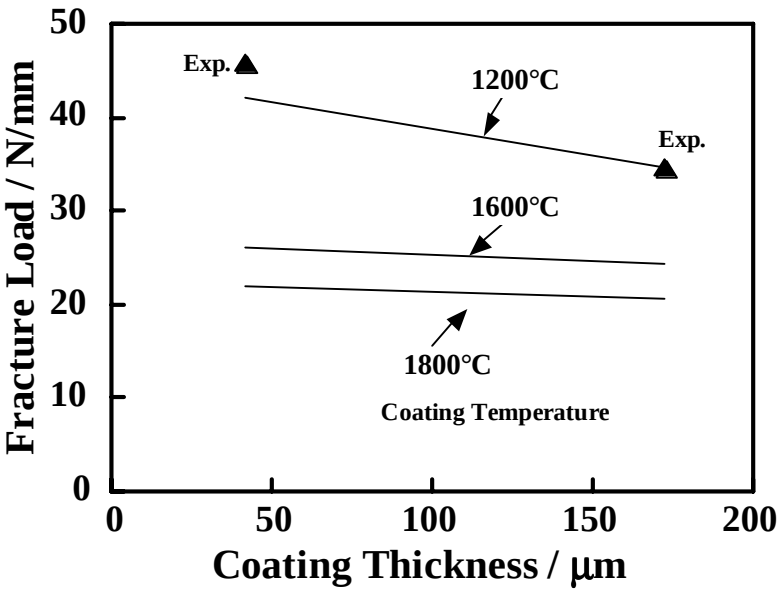

Fig.10 Predicted fracture loads for coated UD C/C specimens with various coating temperature and thickness.

manner. These results suggest that the minimum value of G at the fracture load is the critical condition of unstable crack extension at the interface, G_C (316 kJ/m^2). Assuming G_C = 316 kJ/m^2, fracture loads of various specimen were predicted as shown in ***Fig.10***. Results indicated that the lower coating temperature and thinner coating thickness will increase shear fracture load of the SiC coating. Actually, the other experimental results (coating temperature of 1200°C and thickness of 50 _m) is well predicted by the analysis.

From these experiments and analyses, it is concluded that the shear fracture load of the interface can predict by the energy release rate criterion.

CONCLUSION

Bonding strength of the SiC coating and C/C composites was evaluated quantitatively by introducing newly developed loading method (the plunger method). FEM analyses were also carried out based on the experimental results. Through the discussion, following conclusions were obtained.

(1) The bonding strength of SiC coating can be evaluated by the plunger method, when the SiC is coated on the ***Side*** surface of UD or 0°/90° C/C composites.

(2) Shear fracture of bare C/C composites are dominated by the fracture toughness criterion when the thickness of the specimen is more than 2 mm.

(3) According to FEM analyses assuming critical energy release rate, lower processing temperature and thinner coating thickness provide higher fracture load of the interface. This prediction was well agreed with the experimental results.

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