**FAST FRACTURE STRENGTH OF THIN PYROLYTIC CARBON INTERPHASE SILICON CARBIDE COMPOSITES**—Y. Katoh, T. Nozawa, and L. L. Snead (Oak Ridge National Laboratory), T. Hinoki and A. Kohyama (Kyoto University, Japan), and W. Yang (National Institute for Materials Science, Japan)

## OBJECTIVE

The objective of present work is to determine factors responsible for the reported deteriorative effects of thin pyrolytic carbon interphase on mechanical properties of chemically vapor-infiltrated silicon carbide matrix composites with conventional silicon carbide-based ceramic fibers and to evaluate the applicability of very thin pyrolytic carbon interphase to near-stoichiometric silicon carbide fiber composites for use in nuclear environments.

## SUMMARY

The applicability of very thin pyrolytic carbon (PyC) interphase between fibers and matrices in silicon carbide (SiC) fiber-reinforced, chemically vapor-infiltrated SiC matrix composites was studied based on investigations on the effect of interphase thickness on fast fracture properties. It appears that the mechanical properties of near-stoichiometric high-crystallinity SiC fiber composites are not subject to strong interphase thickness effect, which has been reported for non-stoichiometric SiC fiber composites. This difference was discussed from the viewpoints of thermal residual stress, process-induced damages, fiber surface features, and interfacial bonding and friction. A preliminary conclusion is drawn that a thin PyC interphase, as low as ~25nm, will be generally beneficial for both fast fracture and lifetime limiting properties in stoichiometric SiC-based composites.

## PROGRESS AND STATUS

### Introduction

Continuous silicon carbide (SiC) fiber-reinforced SiC matrix composites (SiC/SiC composites) are considered as favorable options for structural materials in nuclear fusion and fission reactors, as well as in other advanced energy systems [1,2]. This is primarily due to the fact that the combination of inherent heat resistance, neutron tolerance, and low induced activation / low decay heat properties unique to SiC is of great benefit for core structure applications in nuclear systems. However, although stoichiometric crystalline SiC has demonstrated outstanding neutron tolerance [3], non-stoichiometric SiC-based ceramics, such as ceramic grade (CG-) Nicalon™ and Hi-Nicalon™ fibers, reaction-bonded or polymer-derived SiC-based matrices, and pyrolytic carbon (PyC) interphase are substantially susceptible to neutron-induced degradation [4-6]. Therefore, among presently available SiC/SiC composites, chemically vapor-infiltrated (CVI) near-stoichiometric SiC fiber-reinforced composites with minimal usage of PyC in their interphase appear to be the most appropriate for nuclear applications, and the thinner PyC interphase is likely to provide extended service life [7].

On the other hand, for SiC/SiC composites with PyC interphase between fiber and matrix, optimum flexural strength has reportedly been obtained for an intermediate interphase thickness [8]. It has also been reported that flexural strength decreases drastically when the interphase decreases in thickness with respect to this optimum value. Very limited neutron irradiation data show that, near-stoichiometry SiC

fiber-reinforced CVI-SiC composites with 150~200nm-thick PyC interphase do not undergo detectible degradation to a dose of ~$8x10^{25}$ $n/m^2$ (E > 0.1MeV), while a sign of degradation was noted for similar composite with >500nm PyC interphase at the same dose [9]. This dose level corresponds to less than 10% of the desired lifetime in fusion power reactor applications [10]. Therefore, applicability of even thinner PyC interphase might be crucial for this material system. The present work is intended to determine the factors responsible for reported strength degradation in conventional thin-PyC interphase SiC/SiC composites and to evaluate the applicability of thinner PyC interphase to advanced SiC/SiC composites for nuclear applications.

**Materials and Method of Evaluation**

The materials evaluated were CVI-SiC matrix PyC interphase composites reinforced by two-dimensional (2D) plain-woven fabrics of various SiC-based fibers, namely, CG-Nicalon™, Hi-Nicalon™, Hi-Nicalon™ Type-S (Nippon Carbon Co., Tokyo, Japan) and 7.5-micron-diameter Tyranno™-SA Grade-3 (Ube Industries, Ltd., Ube, Japan). Details of the fibers are compiled elsewhere [11]. All the composites were matrix-densified by forced-flow CVI following PyC interphase deposition by isothermal CVD on fabrics stacked in 0°/90° or 0°/30°/60° sequences and tightly constrained in refractory fixtures [12,13]. The interphase thickness was tailored in a range of 0 to 760nm by varying deposition time. The interphase precursor was methane or propane and the optimum deposition temperature and pressure were selected for respective precursors, but the deposition rate of PyC was similar in a range of 30 to 100 nm/hr and the resultant microstructures were turbostratic carbon with very similar lattice images in all cases. The matrix precursor was methyltrichlorosilane (MTS) carried by hydrogen in all cases. Fiber volume fractions and the final porosity were 30 - 43% and 11 – 28%, respectively.

The mechanical property evaluation was performed at ambient temperature by either four-point flexure, three-point flexure, or tensile testing, following general guidelines of ASTM Standards D790, C1341 and C1275, respectively. Miniature specimens were used due to the limited availability of materials [14]. Fracture surfaces were examined for selected specimens by scanning electron microscopy (SEM). Fiber-matrix interfacial shear properties were evaluated by single fiber push-out / push-back method using a load / displacement-sensing nano-indentation device [15].

**Results and Discussion**

It was very clearly demonstrated that the ultimate tensile / flexural strength of the near-stoichiometry SiC fiber composites are much less sensitive to PyC interphase thickness than that of more conventional SiC-based fiber composites. As shown in Fig. 1, while CG-Nicalon™ and Hi-Nicalon™ composites exhibit their peak strength at an interphase thickness of 100 – 200nm, the strength of Tyranno™-SA and Hi-Nicalon™ Type-S composites is nearly independent of interphase thickness in the range of 25 – 250nm.

The ultimate strength of composites is determined by the strength and number of 'working' fibers and thus governed by the mean strength and Weibull modulus for strength of fibers and frictional stress at fiber-matrix interface in an ideal system [16]. Such a simple theory gives a reasonable explanation for the decrease in ultimate strength with increasing interphase thickness regardless of fiber type, as a result of decreasing frictional stress, beyond the strength peak. For near-stoichiometric SiC fiber composites, the Hi-Nicalon Type-S composites shows a slightly negative correlation between interphase thickness and UTS, while UTS of the Tyranno-SA composites is nearly constant over 25-250nm of interphase thickness. This difference could be attributed to the more pronounced dependence of interfacial frictional stress on interphase thickness in this range in the Hi-Nicalon Type-S composites arising from the significantly smoother fiber surface.

The situation on the thin side of the peak strength is more complex. For the case of CG-Nicalon composites, the interphase thickness effect has been discussed from viewpoints of interfacial bonding, friction, moderation of thermal residual stress [8], composites' macroscopic fracture toughness, interlaminar shear strength [17], and the influence of elastic properties of interphase on crack propagation criteria [18]. These discussions apply to Hi-Nicalon composites, since both fibers have similar surface chemistry and morphology, coefficient of thermal expansion (CTE), and elastic moduli. The result of interfacial shear strength evaluation on Hi-Nicalon composites by single fiber push-out testing is presented in Fig. 2. In this test, the calculated stress reflects contributions from bonding and sliding stresses [13]. As shown by the results of Fig. 2, the interfacial bond readily fails in Hi-Nicalon composites when the interphase thickness is < ~100nm, except for the no-interphase case. Therefore, interfacial damage or substantial energy release due to CTE mismatch, which occurs either during

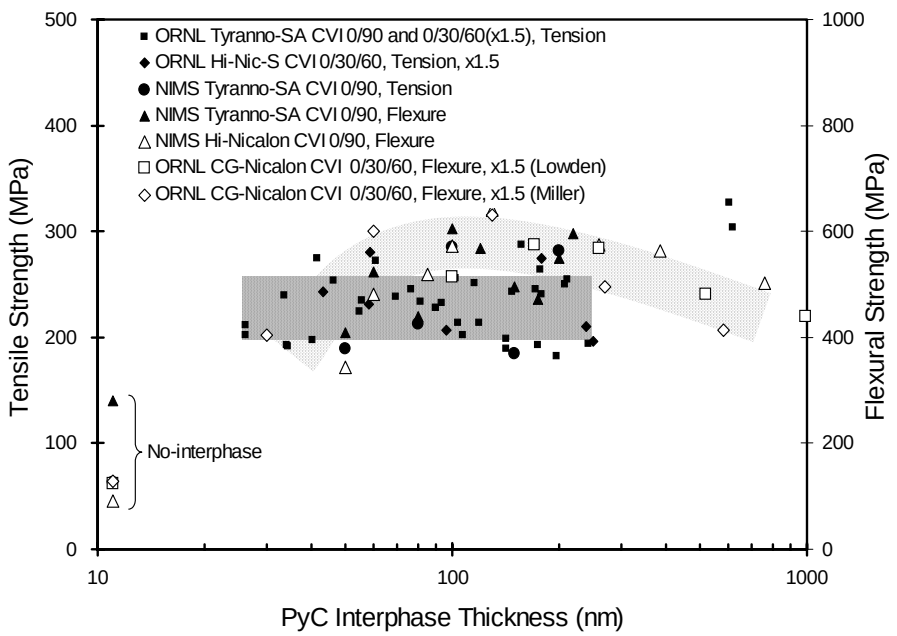


Fig. 1. The influence of PyC interphase thickness on ultimate tensile and flexural strength of CVI-SiC matrix composites reinforced with various SiC-based fibers. The strength of composites with a 0°/30°/60° architecture is plotted after multiplying a factor of 1.5 in order to compensate the smaller fraction of longitudinal fibers than in 0°/90° composites.

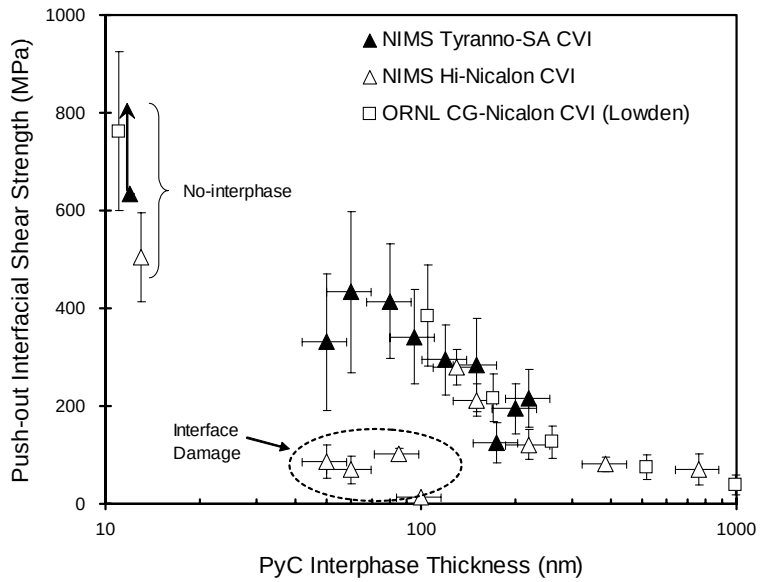


Fig. 2. The influence of PyC interphase thickness on interfacial shear strength as measured by single fiber push-out test. Vertical error bar corresponds to standard deviation. The minimum shear strength is shown for no-interphase Tyranno-SA composites since the interface did not debond in the test. Note the very small interfacial shear strength for Hi-Nicalon composites with PyC interphase thinner than ~100nm.

processing or during testing, is likely to be contributing to the observed interphase thickness effect. Another function of the PyC interphase is to protect the fibers against potential chemical attack by the matrix precursor. Excess carbon in non-stoichiometric SiC fiber reacts with the precursor gas to form SiC [19]. SEM examination of fiber fracture surfaces confirmed that uncoated Hi-Nicalon fibers clearly degrade during matrix processing, while a PyC coating of more than 50nm is sufficient to protect the fibers.

The greatly reduced sensitivity of fast fracture strength of near-stoichiometric SiC fiber composites to PyC interphase thickness may be primarily attributed to smaller CTE mismatch. This means that there exists less significant thermal residual stress in the matrix. Both types of the near-stoichiometric SiC fibers comprise primarily of cubic SiC and the C/SiC atomic ratios are 1.05~1.07. The excess carbon exists in a form of graphitic pockets at multi-grain junctions of cubic SiC grains of typically 20~200nm. A minor CTE mismatch between these fibers and cubic SiC matrix occurs due to the presence of graphitic phase, however, the extent of that is believed to be significantly smaller than for (Hi-) Nicalon composites. Detailed temperature dependent CTE data have not been published for near-stoichiometric SiC fibers. The proportional limit tensile stress (PLS) of Tyranno-SA composites exhibited slightly negative correlation with interphase thickness. Due to the radially graded concentration of excess carbon in Tyranno-SA, which results in better stoichiometry in near surface, the shear component of thermal residual stress at the fiber-matrix interface near matrix cracks should be even smaller than estimated from macroscopic CTE of the fiber.

In Fig. 3, fracture surfaces of Tyranno-SA composites are compared for uncoated and 120nm-thick PyC-coated fibers. Although practically no pullout is observed for the uncoated fibers reflecting strong

interfacial shear strength, the fiber fracture surface appears typical of undamaged fibers. Therefore, matrix processing presumably does not impose significant chemical damage to the near-stoichiometric SiC fibers.

Representative tensile stress-strain curves including intermediate unloading / reloading sequences are compared in Fig. 4 for Tyranno-SA composites with average interphase thickness of 25nm and 250nm, where little difference in fast fracture behavior is observed. This suggests that the interphase thickness effect, through energy release upon crack extension, was not active in this system, probably due to strong interfacial friction. The UTS difference noticed in Fig. 4 was not statistically significant. However, statistically significant interphase thickness dependence is found for tensile modulus and PLS, both of which negatively correlate with the interphase thickness [20]. The composites' elastic modulus moderation by the presence of interphase can reasonably be explained by relatively very small elastic

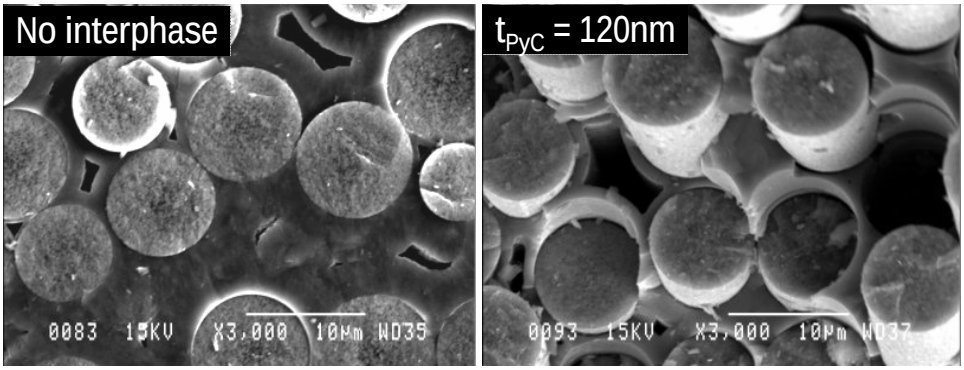


Fig. 3. SEM fracture surfaces of Tyranno™-SA composites without and with PyC interphase.

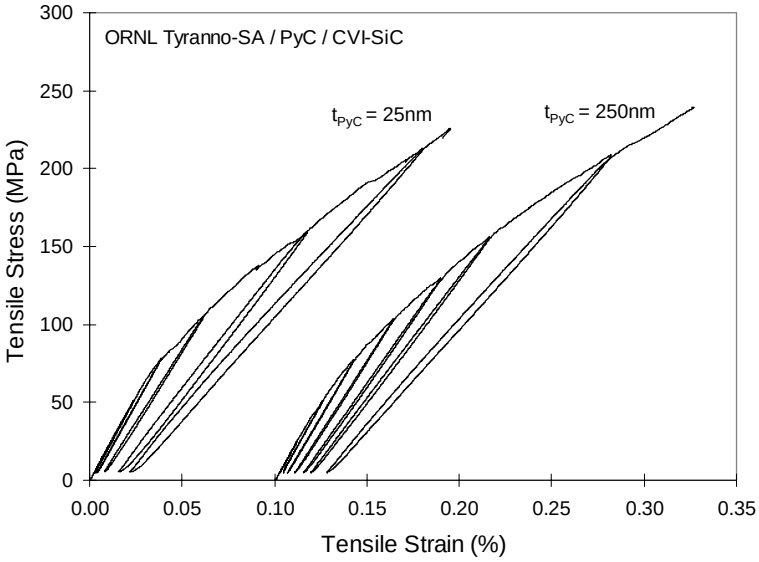


Fig. 4. Tensile behavior of Tyranno™-SA composites with PyC interphase thickness of 25nm and 250nm.

modulus of PyC. Proportional limit tensile strain was not affected by the interphase thickness, probably because the responsible matrix cracking initiates due to stress concentration at the surface of large inter-fiber-tow pores. Therefore, higher PLS in thinner interphase composite comes from the higher composite modulus.

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