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The effects of neutron irradiation on shear properties of monolayered PyC and multilayered PyC/SiC interfaces of SiC/SiC composites

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Abstract

The effect of neutron irradiation on mechanical properties at the fiber/matrix interface of SiC/SiC composites was evaluated. The materials investigated were Hi-Nicalon™ Type-S fiber reinforced chemically vapor infiltrated SiC matrix composites with varied interphases: monolayered pyrolytic carbon (PyC) or multilayered PyC/SiC. The neutron fluence was 7.7×10^{25} n/m^2 ($E > 0.1$ MeV), and the irradiation temperature was 800 °C. Interfacial shear properties were evaluated by the fiber push-out test method. A modified shear-lag model was applied to analyze the interfacial shear parameters. Test results indicate that the interfacial debond shear strength and the interfacial friction stress for the multilayer composites were significantly degraded by irradiation. Nevertheless, the multilayer composites retained sufficient interfacial shear properties so that overall composite strength after neutron irradiation was unaffected. The actual mechanism of interphase property decrease for the multilayer composites is unknown. The interfacial shear properties of the irradiated monolayer composites appear unaffected.

1. Introduction

Silicon carbide (SiC) matrix composites are being developed for structural applications in fusion and nuclear fission power systems for their promising high-temperature performance and low induced activation. In recent years, the stability of highly crystalline and near-stoichiometric SiC fibers [1] has led to composites with very good irradiation stability [2,3]. However, the effect of neutron irradiation on the fiber/matrix interphase, typically pyrolytic carbon (PyC), remains as a critical issue due to the well-known instability of carbon. A recent study on SiC/SiC composites with >500 nm-thick PyC interphase implied probable degradation of interfacial shear properties even for low-dose neutron irradiation [4].

In non-nuclear applications, a multilayered interphase composed of a sequence of very thin (~50 nm) PyC and SiC has several advantages. First, the very thin PyC layer enhances fiber/matrix interfacial shear strength, resulting in improved debond strength [5]. Second, multilayered interfacial structures promote multiple crack deflections between layers [6] and the resulting tortuous crack path contributes effectively as a toughening mechanism [7].

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Additionally, the thin layered structures are more resistant to oxidation [8]. However, a fundamental question is whether the irradiation-induced swelling of carbon layers, albeit very thin layers in multilayered interphase, will impact composite performance. Presently, no quantitative data are available to evaluate irradiation effects on interfacial shear properties. The primary goal of this work is to provide a basis for evaluating the resistance of SiC/SiC composites with a monolayered PyC or a multilayered PyC/SiC interphase under irradiation.

2. Experimental

Unidirectional SiC/SiC composites reinforced with the irradiation-stable Hi-Nicalon™ Type-S fiber (Nippon Carbon Co., Ltd.) were prepared. The matrix was chemically vapor infiltrated (CVI) SiC. Both fiber and matrix possess high-crystallinity and are stoichiometric (Si/C $\sim$1). Either a PyC monolayer (720 nm-thick PyC) or a PyC/SiC multilayer ($\sim$20 nm-thick PyC $\times$ 5 layers and $\sim$100 nm-thick SiC sub-layers between PyC layers) interphase was chemically deposited on the fibers (Fig. 1). The mean measured densities for monolayer and multilayer composites were $\sim$2.6 and $\sim$2.7 g/cm^3, respectively. Fiber volume fraction and porosity were $\sim$30% and $\sim$16%, respectively, for both interphase types.

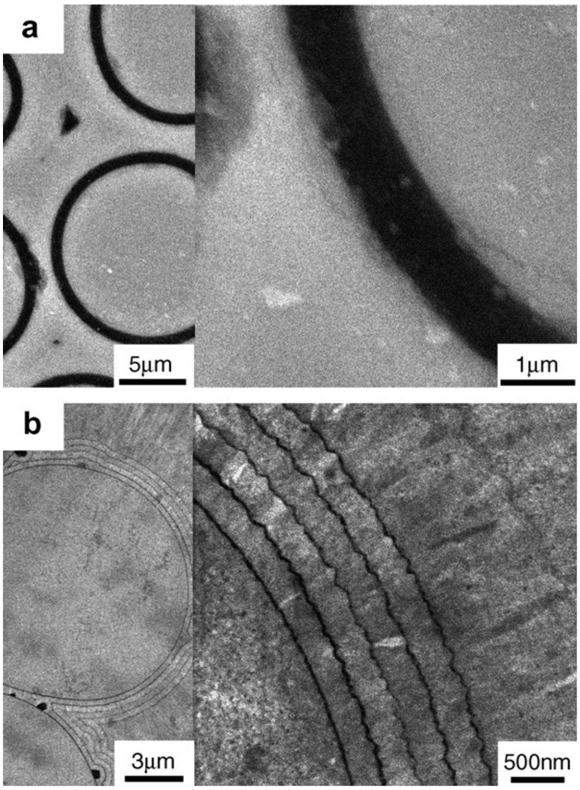

Fig. 1. Typical cross-sectional micrographs of (a) monolayered PyC and (b) multilayered interphase composites.

Neutron irradiation was performed in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The neutron dose was 7.7 dpa (assuming 1.0×10^{25} n/m^2 ($E > 0.1$ MeV) corresponds to one displacement per atom (dpa)), and the irradiation temperature was 800 °C. The temperature was measured and controlled in situ by thermocouples and capsule sweep–gas mixtures.

Fiber push-out tests were performed at room-temperature using a nano-indentation machine with a Berkovich indenter tip. Specimens were sliced and their cross-sections polished to 30–220 μm thickness with a surface finish of $\sim$0.5 μm using standard metallographic techniques. Fibers were randomly selected in a cross-section of the specimens and were monotonically loaded up to the system maximum load capacity (650 mN). The applied loading rate was a constant fraction of the applied load, 0.05 N/N s. For statistical analysis, more than 20 push-out tests were conducted for each test condition. Microstructural observations of pushed-out fiber surfaces were conducted by scanning electron microscopy. Details of the push-out test method have been described elsewhere [9].

3. Results

Fig. 2 shows typical push-out load vs. fiber end displacement curves for monolayer and multilayer composites. For both interphase types, push-out behavior before and after neutron irradiation were very similar, consisting of an initial parabolic segment due to penetration of the sharp indenter tip into the fiber and a second non-linear segment due to progressive fiber debonding, followed by complete debonding and sliding. A concave shape of the second non-linear segment for the multilayer composites indicates an occurrence of unstable debonding. Such a curve is characteristic of composites with overly-strong interfaces [9]. For the thick (>100 μm) specimens of the multilayer composites, complete debonding did not occur due to the very limited load range of the indentation equipment. In contrast, debonding occurred in 100% of the tests for the monolayer composites, indicating a relatively weak interfacial strength.

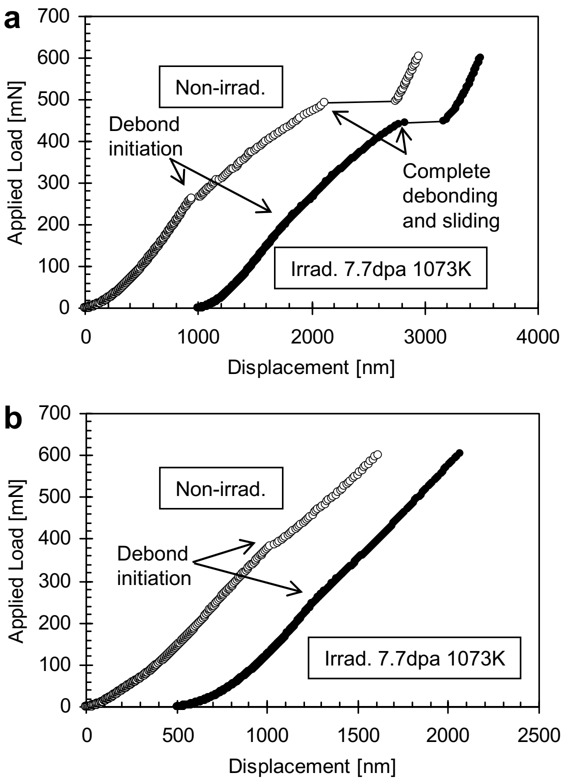

Fig. 2. Effects of neutron irradiation on push-out load vs. fiber end displacement curves of (a) monolayered PyC and (b) multilayered interphase composites.

Fig. 3 exhibits typical surface images of pushed-out fibers. In general, a primary crack was initiated at the fiber/carbon interface for monolayer composites before and after irradiation (Fig. 3(a) and (b)). The crack plane was typically very smooth. For multilayer composites, the very rough surface of the crack plane (Fig. 3(c)) suggests that the primary crack penetrated within the PyC interphase adjacent to the fiber before irradiation. However, following irradiation, it is speculated that the primary crack may propagate along the fiber/carbon interface rather than within the carbon layer due to the very smooth fiber surface (Fig. 3(d)).

Fig. 4 shows plots illustrating the effects of neutron irradiation on debond initiation stress, σ_d, and complete debonding stress, σ_{max}, with respect to the specimen thickness, t. These stress parameters are defined as the compressive load applied on the fiber end divided by the fiber cross-sectional area at each event. Error bars correspond to ± one standard deviation. The debond initiation stresses were nearly constant for specimens in the thickness range of 50–220 μm. The highest σ_d was obtained for the non-irradiated multilayer composites. Neutron irradiation slightly (~20%) decreased σ_d of the multilayer composites. In contrast, the reduction of σ_d by irradiation was less than 10% for the monolayer composites. On the other hand, σ_{max} is proportional to t and the non-irradiated multilayer composites show the highest σ_{max}/t ratio. Neutron irradiation caused a large (>50%) reduction of σ_{max}/t for the multilayer composites, while σ_{max}/t was nearly unchanged for the monolayer composites by irradiation. It is worth noting that, even with the large decreases of interfacial shear properties for the irradiated multilayer composites, they were still superior to those of the monolayer composites.

4. Discussion

4.1. Interfacial debond shear strength

The shear stress at debond initiation of the bonded interface, i.e., interfacial debond shear strength, τ_d, can be determined from σ_d using a non-linear shear-lag model [10,11]. This model assumes that a single fiber with a radius of r_f is embedded in a semi-infinite matrix with a constant shear stress distributed along the bonded interface. In this paper, a modified form of the shear-lag model was developed considering the effect of thermally-induced residual stress [10] and the precise stress interactions between the fiber and the matrix [11]. In this new model, a single fiber surrounded by the composite phase is considered due to high volume fraction of fibers. For simplicity, the effect of interlayer thickness is not considered. In this analysis, the effects of swelling and irradiation creep were ignored because of uncertainity of irradiation effects on the constituents. Then τ_d can be obtained by

$$\tau_d = -\frac{r_f\alpha}{2}\left\{\frac{\sigma_d[\exp(\alpha t)+\exp(-\alpha t)]-\beta(\sigma_d+\sigma_{th})[\exp(\alpha t)+\exp(-\alpha t)-2]}{\exp(\alpha t)-\exp(-\alpha t)}\right\}. \quad (1)$$

The constants α and β are determined by dimensions and elastic constants of the constituents, and σ_{th} is as a function of thermally-induced residual stresses. Assuming no contribution from thermal residual stresses, σ_{th} becomes zero. Post-irradiation material parameters estimated from irradiation data of CVD-SiC [12], PyC [13] and the composites [14] are listed in Table 1. For simplicity, high-density

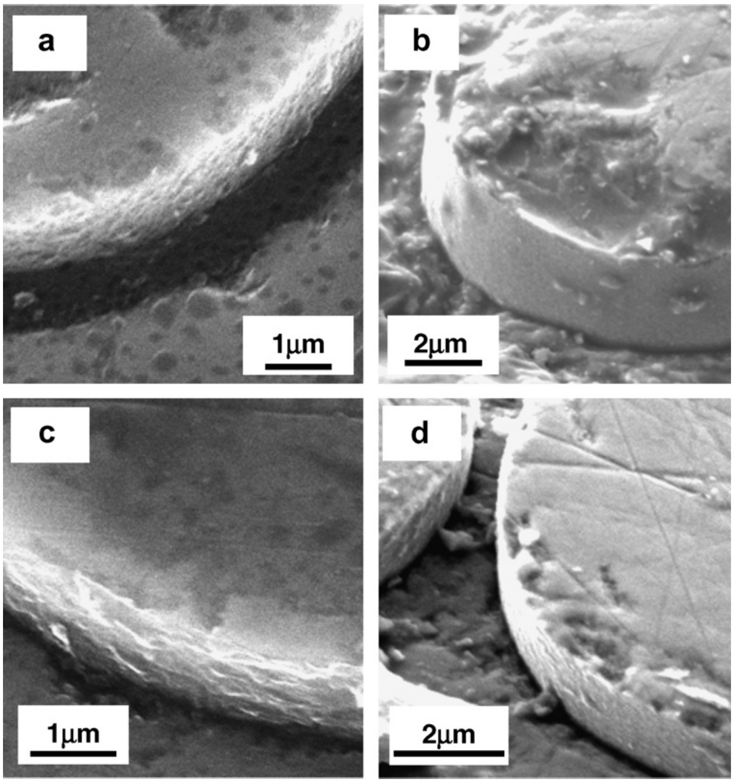

Fig. 3. Typical pushed-out fiber surfaces of the composites: (a) non-irradiated PyC monolayer, (b) irradiated PyC monolayer, (c) non-irradiated PyC/SiC multilayer and (d) irradiated PyC/SiC multilayer interphase composites. Neutron irradiation was performed up to 7.7 dpa at 800 °C.

and isotropic PyC with Bacon anisotropy factor of ~1 is assumed, though the structure near the fiber appears much more graphitic [15]. Thermal expansion coefficients are considered invariant with irradiation. Poisson's ratio and thermal expansion coefficients of the composites are estimated by the rule of mixtures.

In Fig. 4(a), the model predictions appear to fit the experimental debond initiation stresses. The calculated values of τ_d are ~280 MPa (non-irradiated) and ~250 MPa (irradiated) for monolayer composites, and ~650 MPa (non-irradiated) and ~510 MPa (irradiated) for multilayer composites. By neutron irradiation, τ_d was reduced 20% for the multilayer composites and ~10% for the monolayer composites.

4.2. Interfacial friction stress

Shetty's model [16] can provide the interfacial friction stress regardless of the shape of push-out curves. In this model, the complete debonding stress, $\sigma_{\max}$, is closely related to the compressive residual radial-stresses induced by thermal expansion mismatch, σ_r^{th}, by cracked plane surface roughness, σ_r^{rough}, and by differential swelling induced by neutron irradiation, σ_r^{swell}

$$\sigma_{\max} = \frac{E_f(1+\nu_m)}{E_m \nu_f}(\sigma_r^{th} + \sigma_r^{rough} + \sigma_r^{swell}) \times \left[\exp\left(\frac{2\mu E_m \nu_f t}{r_f E_f (1+\nu_m)}\right) - 1\right], \tag{2}$$

where μ is a friction coefficient, and E and ν are Young's modulus and Poisson's ratio. Subscripts f and m denote the fiber and the matrix, respectively. Intrinsic interfacial friction stress, τ_f^{int}, is then defined by

$$\tau_f^{int} = \mu(\sigma_r^{th} + \sigma_r^{rough} + \sigma_r^{swell}). \tag{3}$$

Specifically, τ_f^{int} is proportional to $\sigma_{\max}/t$ when the specimens are sufficiently thin

$$\tau_f^{int} \cong \frac{r_f}{2} \cdot \frac{\sigma_{\max}}{t}. \tag{4}$$

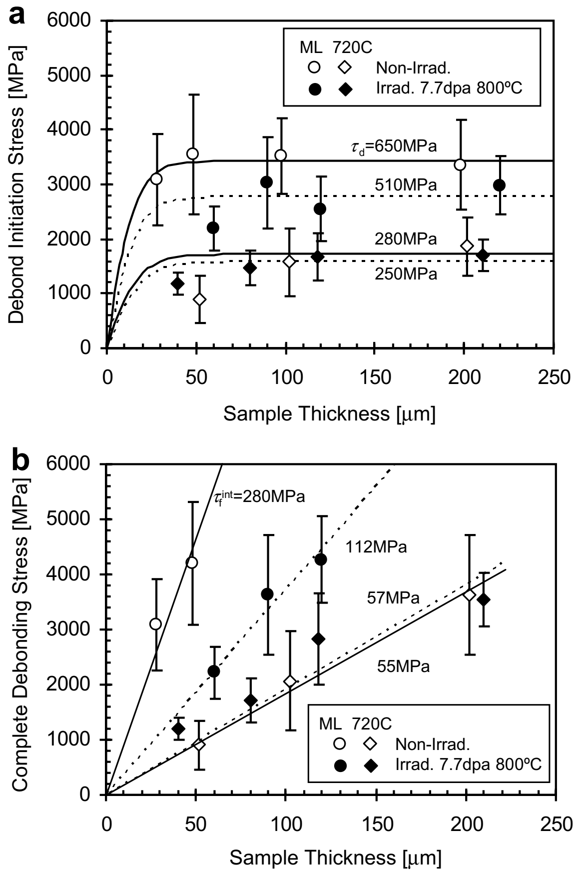

Fig. 4. Effects of neutron irradiation on (a) interfacial debond initiation stress and (b) complete debonding stress for monolayered PyC and multilayered PyC/SiC interphase composites.

In Fig. 4(b), the steep slope for the non-irradiated multilayer composites exhibits the highest τ_f^{int}. The least square fitting gives rough estimates of τ_f^{int}: ~55 MPa (non-irradiated) vs. ~57 MPa (irradiated) for monolayer composites and ~280 MPa (non-irradiated) vs. ~112 MPa (irradiated) for multilayer composites. No significant degradation of τ_f^{int} was obvious for the monolayer composites, while approximately 60% decrease was apparent for the multilayer composites. Of particular emphasis is that τ_f^{int} of the irradiated multilayer composites was still double that of the irradiated monolayer composites.

4.3. Effect of differential swelling on interfacial shear properties

Silicon carbide swells upon neutron irradiation due primarily to point defect and small defect cluster accumulation in the intermediate temperature range (150–1000 °C) [17–19], although the volumetric swelling of SiC is very small (<0.8%) at 800 °C [12]. The magnitudes of swelling for the Hi-Nicalon™ Type-S fiber and the CVI-SiC matrix are thought to be of the same order due to similar microstructure and stoichiometry. In contrast, irradiation-induced volume change of PyC depends significantly on the irradiation temperature and fluence [20]. Generally, PyC shrinks in the direction perpendicular to the deposition plane for the low neutron dose (~2 dpa) and then swells with increasing neutron dose, while it shrinks monotonically in the direction parallel to the deposition plane. The differential swelling between PyC and SiC consequently induces residual stresses at the fiber/carbon interface. However, the simple model prediction by the authors [21] implies that the irradiation-induced residual stresses are negligibly small for the irradia-

Table 1
List of material parameters used in analysis

Material	Neutron irradiation	Young's modulus (GPa)	Poisson's ratio	Thermal expansion coefficient (10^{-6}/°C)
Constituents				
Hi-Nicalon™ Type-S	Non-irradiation	420[a]	0.2[a]	5.1[a]
	7.7 dpa, 800 °C	400[b]	0.2[c]	5.1[c]
Isotropic PyC	Non-irradiation	20[d]	0.23[d]	5.5[d]
	7.7 dpa, 800 °C	60[d]	0.23[c]	5.5[c]
CVD-SiC	Non-irradiation	460[e]	0.21[e]	4.4[e]
	7.7 dpa, 800 °C	437[f]	0.21[c]	4.4[c]
Composites				
PyC interphase	Non-irrad	360[g]	0.21[h]	4.6[h]
	7.7 dpa, 800 °C	320[g]	0.21[c]	4.6[c]
Multilayered interphase	Non-irradiation	375[g]	0.21[g]	4.6[h]
	7.7 dpa, 800 °C	356[g]	0.21[c]	4.6[c]

[a] Material property data sheet from Nippon Carbon Co., Ltd.
[b] Estimated by the correlation with swelling data [12].
[c] Assumed to be unchanged by irradiation.
[d] CEGA-002820 [13].
[e] Material property data sheet from Romhm & Haas, Co.
[f] Experimental values by nano-indentation tests [12].
[g] Experimental values by tensile test [14].
[h] Calculation by the rule of mixtures.

tion condition up to 7.7 dpa at 800 °C. A very limited influence of swelling is therefore anticipated.

The most likely explanation for the reduction of interfacial shear properties for the multilayer composites is a changing crack propagation path resulting from irradiation. Originally primary interfacial cracks for the multilayer composites initiate within the PyC interphase due to strong bonding at the fiber/carbon interface. However, the irradiation changes the crack path: the crack path 'within' interphase before irradiation vs. the crack path 'along' the fiber/carbon interface by irradiation resulted in the decrease of surface roughness at the cracked plane, consequently causing a significant reduction of interfacial shear properties. The actual mechanism of the changing crack path for the multilayer composites is unknown.

4.4. Correlation between interfacial shear properties and tensile properties

Neutron irradiation can reduce τ_d regardless of the interphase type. However, the magnitude of interfacial shear degradation for the multilayer composites appears to be much more severe than for the monolayer composites. Significant reduction of τ_f^{int} was only obtained for the irradiated multilayer composites. However, the reduction of the interfacial shear properties of the multilayer composites does not necessarily produce degradation in overall composite performance under neutron irradiation. Indeed, no serious degradation of tensile fracture strength of the irradiated multilayer specimens was reported in companion work [4,14].

In contrast, a slight reduction of the proportional limit tensile stress (PLS) was reported for both types of composites [4,14]. In previous work [4], reduction of interfacial shear strength upon neutron irradiation was believed to be the primary cause to reduce the PLS. Large reduction of the interfacial shear properties for the multilayer composites is responsible for the reduction of the PLS. Also in contrast this study showed that the interfacial shear properties of the monolayer composites were insensitive to neutron irradiation. In a recent study by Katoh, et al. [14], the irradiation-induced creep of SiC constituents was suggested as another possible mechanism.

5. Conclusions

The effect of neutron irradiation on interfacial shear properties of Hi-Nicalon™ Type-S/CVI-SiC composites with different interphases, single-layered PyC or multilayered PyC/SiC, was studied by the single fiber push-out test. A non-linear shear-lag model was developed to determine interfacial shear parameters. Preliminary test results indicate that the multilayer composites had relatively large reduction of both interfacial debond shear strength and interfacial friction stress upon neutron irradiation, while only minor reduction was observed for the monolayer composites. However, the post-irradiation interfacial shear properties of the multilayer composites remain significantly higher than for the monolayer composites. The physical mechanism responsible for the irradiation-induced reduction of interfacial shear properties for the multilayered composites requires additional investigation.

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