2.3 CHARACTERIZATION BY SEM OF THE PYROCARBON FIBER COATING IN 2D-SiC/CVI-SiC -

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OBJECTIVE

The primary objectives of this task are: (1) to assess the properties and behavior of SiC_f/SiC composites made from SiC fibers (with various SiC-type matrices, fiber coatings and architectures) before and after irradiation, and (2) to develop analytic models that describe these properties as a function of temperature and dose as well as composite architecture. Recent efforts have focused on examining the electrical conductivity properties of SiC_f/SiC composites considered for application in flow channel insert (FCI) structures in support of the U.S. dual-coolant lead-lithium (DCLL) fusion reactor blanket concept.

SUMMARY

The previous report examined electrical conductivity (EC) data from RT to 800°C for several forms of two-dimensional silicon carbide composite made with a chemical vapor infiltration (CVI) matrix (2D-SiC/CVI-SiC), an important quantity needed for the design of an FCI. We found that both in-plane and transverse EC-values for 2D-SiC/CVI-SiC strongly depended on the total thickness of the highly conductive pyrocarbon (PyC) fiber coating and the alignment of the carbon coating network. Furthermore, the transverse EC depended on the degree of interconnectivity of this network. For our EC-modeling efforts we used either "nominal" coating thickness values provided by the composite fabricator or we made thickness estimates based on a limited number of fiber cross-section examinations using SEM. Because of the importance of using a truly representative coating thickness value in our analysis, we examined numerous new SEM cross-sectional views to reassess the reliability of our limited number of original coating thickness measurements as well as to obtain an estimate of the variation in thickness values for different composite configurations.

PROGRESS AND STATUS

Introduction

A clear demonstration of how important the total PyC coating thickness is in determining the EC of a 2D-SiC/CVI-SiC is illustrated in Figure 1 (Fig. 1 is Fig. 2 from the previous FMSPR report [1]).

The in-plane EC(T)-curves in Fig. 1 appear to separate into four groupings with parallel curves, in which each group exhibits similar temperature dependence. The major observation is the marked decrease in EC-values as the total "nominal" PyC fiber coating thickness of each group decreases from 310 nm down to 50 nm. In fact, the relative decrease in magnitude of the EC-values is almost linearly proportional to the decrease in the coating thickness values. This behavior of the in-plane EC is due to its dependence primarily on conduction through the thin PyC fiber coatings with little dependence on the conductivity of the majority SiC matrix or fiber components. A somewhat similar dependence on coating thickness was observed for the transverse EC(T)-curves (see Fig. 5 in [1]). However, for 2D-SiC/CVI-SiC the transverse EC exhibits some dependence on conductivity through the SiC matrix and fiber components as well as through the PyC fiber-coating network, as indicated by the generally lower magnitude of the EC and its overall temperature dependence. Most importantly, the transverse EC also depends on the degree of interconnectivity of the fiber coating network within the fiber bundles as well as between the fabric layers.

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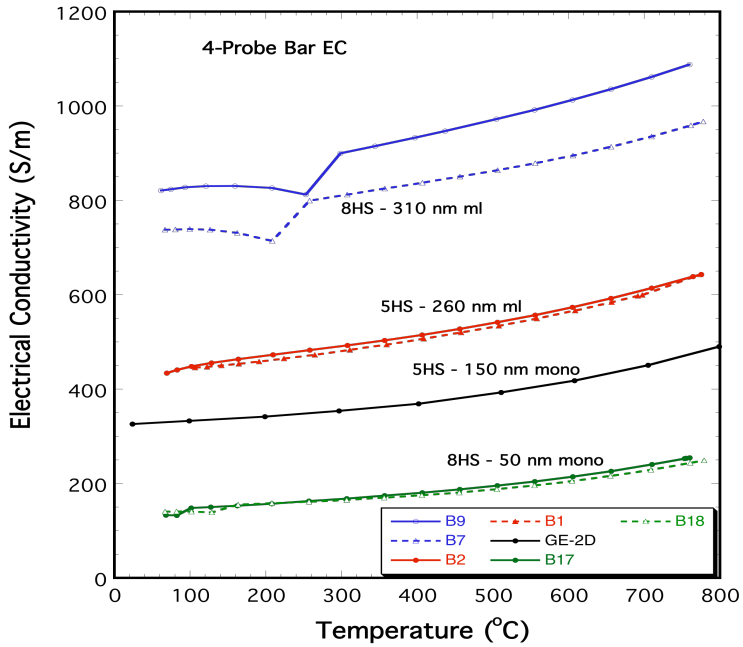


Figure 1. In-plane EC(T)-values for representative 2D-SiC/CVI-SiC bar samples with 0/90 weave and different total "nominal" PyC fiber coating thickness. The four groupings (two samples each) are labeled according to their total PyC coating thickness in descending order: 310 nm (multilayer), 260 nm (multilayer), 150 nm (monolayer), and 50 nm (monolayer).

In Ref. [1], a simple "series layer" model was introduced that described the transverse EC(T) of a 2D-SiC/CVI-SiC plate in terms of the interior carbon-networked, fabric-layered region EC (EC_{int}) in series with outer "seal coat" layers of densely adherent, single phase CVD-SiC of EC (EC_{sc}):

$$EC(T) = EC_{int}[1 - 2f(1 - R)]^{-1} \qquad [1]$$

In Eq. [1], T is temperature, f = t/L where t is the average thickness of a seal coat layer, L is the composite plate thickness (including the seal coat layers). Values of EC_{int} are determined by making EC measurements on a disc sample with the seal coat layers removed by grinding each surface down well into the fabric-layered interior region. Also, R is the ratio EC_{int}/EC_{sc}, where in our case EC_{sc} was calculated for a CVD-SiC seal coat using values of EC measured for representative samples of pure, monolithic CVD-SiC. Because f in Eq. [1] is relatively small, the magnitude of the overall transverse EC(T)-values, especially in the moderate 200-700°C temperature range, depends primarily on the electrical conduction of the carbon-networked interior region of a 2D-SiC/CVI-SiC composite through EC_{int}. In turn, EC_{int} depends on the amount of relatively high conductivity carbon (even though it is only a few per cent of the total volume) and on the interconnectivity of the carbon network within this interior region.

In reference [2], Katoh, et al, presented a method to quantify the degree of interconnectivity in the interior region of a 2D-SiC/CVI-SiC composite. The authors defined a "through-thickness interphase bypass efficiency" $\eta = 2\sigma_t/f_i\sigma_i \approx \sigma_t/\sigma_{ip}$, where they considered that ~1/2 of the interphase film contributes to in-plane conduction in one of the 0/90 fiber directions. In this expression, σ and f are electrical conductivity and volume fraction; and the subscripts t, ip and i denote through-thickness (transverse), in-plane and interphase, respectively. They stated that η-values should be dependent on interphase thickness and packing density of the SiC fabrics. For two types of monolayer interphase composites and a multilayered

composite, they measured η-values of 1.2–1.7%, and ~2.8%, respectively. They stated that the η-values of multilayered composites should exceed that of monolayer composites because in a multilayered composite the different layers have a higher chance of transverse bridging over multiple fibers since the outer PyC layers tend to envelope multiple fibers.

This report will examine in more detail how to determine the actual amount and thickness of the PyC fiber coating and will determine the degree of the PyC network interconnectivity calculated according to the "Katoh" method for four types of 2D-SiC/CVI-SiC, two with multilayered and two with monolayer PyC fiber coatings.

Materials and Procedures

Four of the 2D-SiC/CVI-SiC samples examined in the previous report were selected for reexamination here. They contained either multilayer (nominally a relatively thick ~200 nm PyC layer covered by four alternating 100-nm SiC layers/20-nm PyC layers) or a single ~150 nm or ~50 nm monolayer PyC coating. The samples were fabricated by CVI in a similar manner by Hyper-Therm, HTC or GE Power Systems Composites using Hi-Nicalon™ type S fabrics [1]. The "50-nm" PyC monolayer composite was made by Hyper-Therm specifically to satisfy the desired FCI-application goal of having a total transverse EC <20 S/m for all temperatures up to 800°C.

Sample cross-sections were cut and mounted in resin plugs, and polished smooth to 1-µm diamond followed by a final colloidal silica polish. Each sample plug was examined in a field emission SEM (FEI Helios Nanolab FIB, Hillsborough, OR). For each sample, the fiber-coating interphase configuration and dimensions were examined in views of ~30 different surface locations at low (~x5000) and high (x80,000 to x250,000) magnifications. To statistically determine a representative fiber PyC coating thickness and its variation, ~10 thickness measurements were made at different locations on each view for ~300 or more total measurements for each sample. To reduce electron beam spreading and improve resolution a low energy electron beam (5 KeV) was used. A backscatter electron detector at 3.2-mm working distance produced sufficient atomic number contrast to clearly define the SiC matrix or fiber components and PyC fiber coatings at the cross-section surfaces.

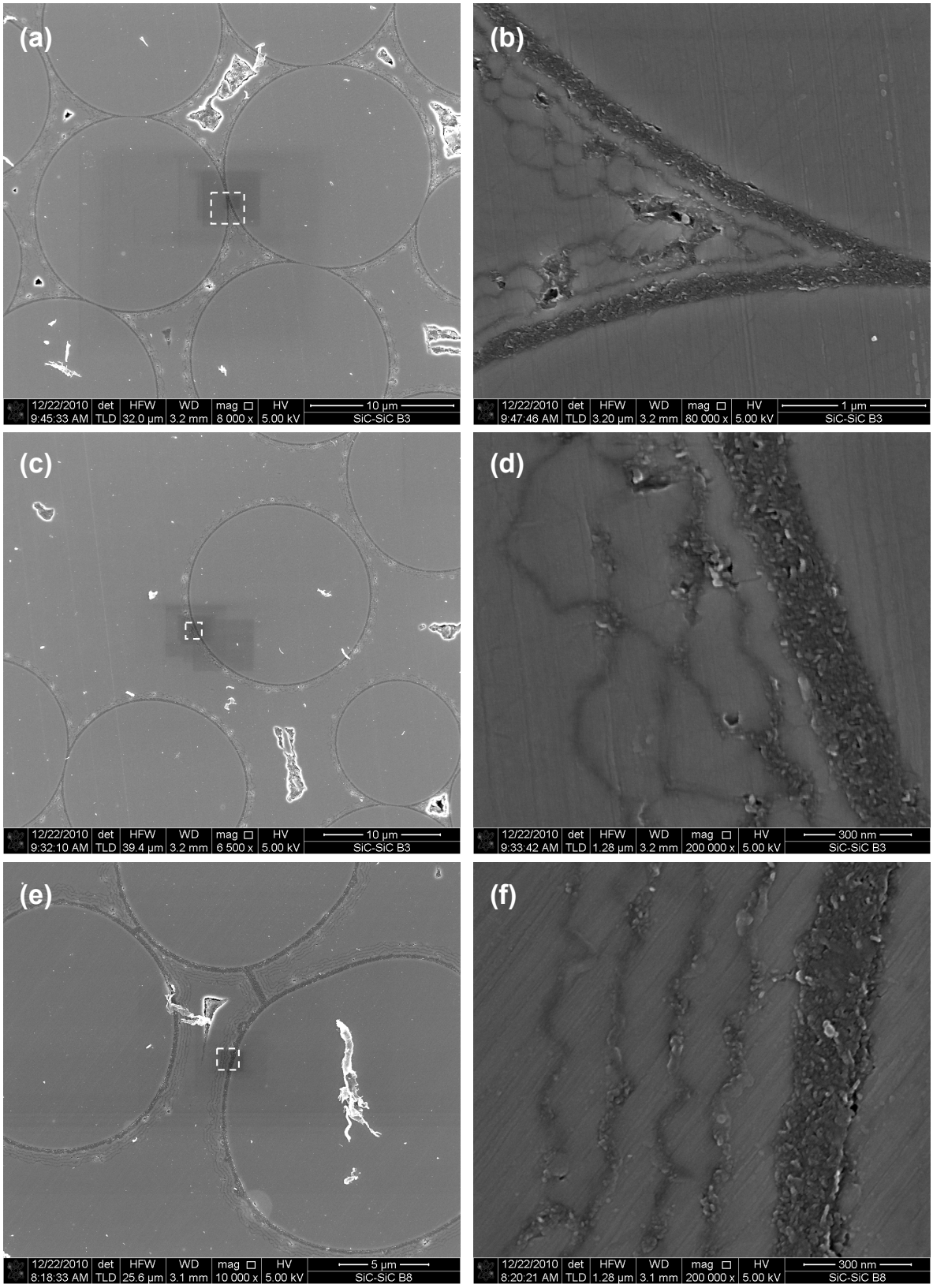
Results

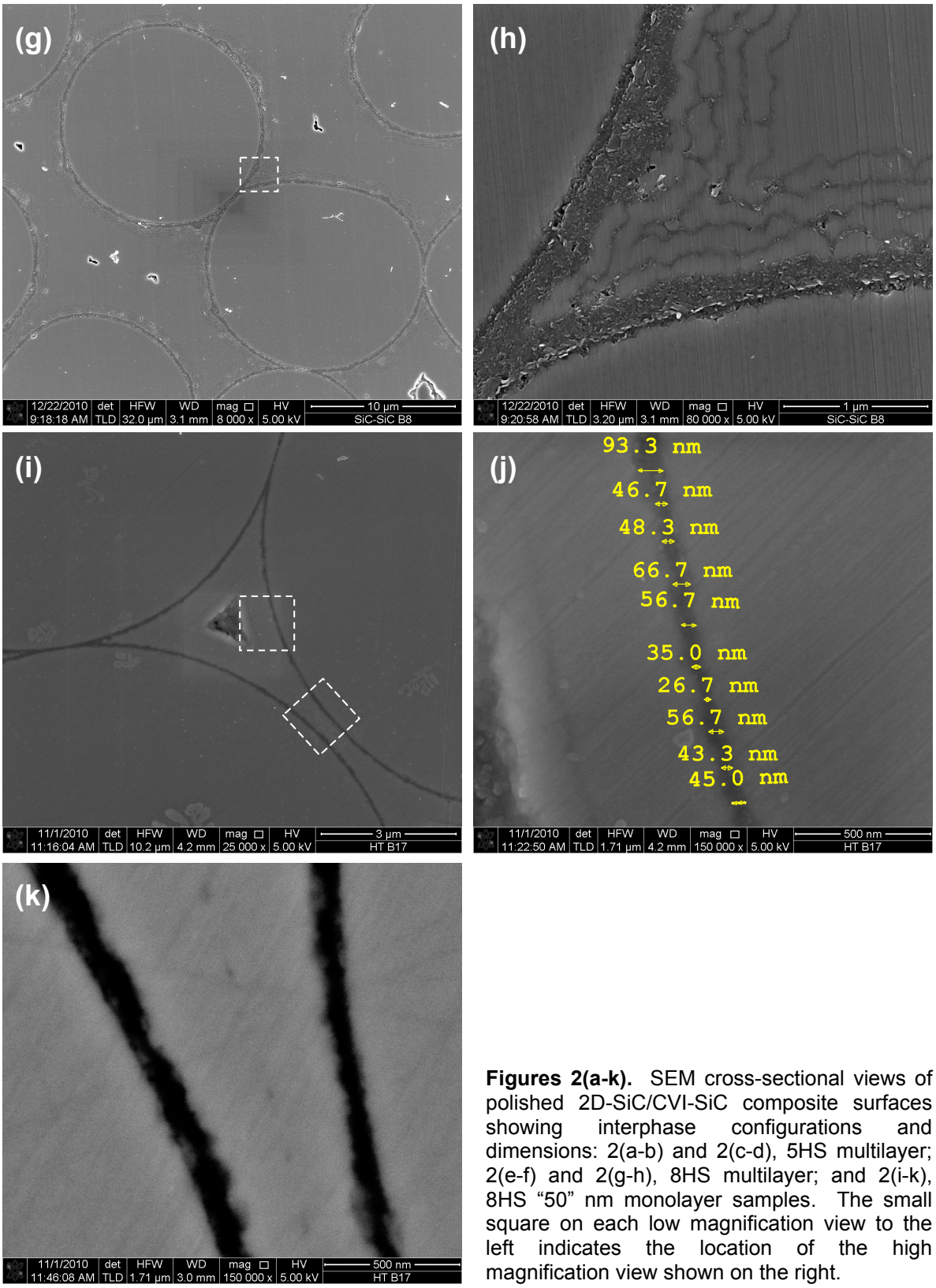
In Table 1, the measured in-plane and transverse EC-values and the estimated transverse bypass efficiencies (using Katoh's method) for the four examined samples are given along with their weave types (either five or eight harness satin, 5HS or 8HS, respectively) and nominal multilayer (ml) or monolayer (mono) PyC coating thickness(es).

Table 1. Bypass efficiency estimates for four 2D-SiC/CVI-SiC sample types

Weave – PyC thickness (nm)	σ_{ip} @ 30°C (S/m)	σ_t @ 30°C (S/m)	$\eta \approx \sigma_t/\sigma_{ip}$ (%)
5HS -180 + 4(20), ml	440 ± 10 (2 samples)	10.0	2.3
8HS -230 + 4(20), ml	770 ± 40 (" ")	12.5	1.6
5HS -150 mono	325 ± 10 (" ")	2.6	0.8
8HS -50 mono	150 ± 10 (" ")	1.2	0.8

At this point, general agreement with Katoh's findings was found. That is, the by-pass efficiency η for the composites with multilayer coatings was approximately twice the values for the composites with a monolayer coating. Also, the η–magnitudes were in reasonable agreement (1.6 – 2.3 compared to 2.8 ml, and 0.8 compared to 1.2 – 1.7 for mono, respectively).
In Figures 2(a-k), representative SEM views of the PyC fiber coatings for three of the four sample types are given. The views for the 5HS-150 nm monolayer sample were not ready in time for this report.


(a)
12/22/2010 9:45:33 AM | det TLD | HFW 32.0 µm | WD 3.2 mm | mag 8 000 x | HV 5.00 kV | 10 µm | SiC-SiC B3
(b)
12/22/2010 9:47:46 AM | det TLD | HFW 3.20 µm | WD 3.2 mm | mag 80 000 x | HV 5.00 kV | 1 µm | SiC-SiC B3
(c)
12/22/2010 9:32:10 AM | det TLD | HFW 39.4 µm | WD 3.2 mm | mag 6 500 x | HV 5.00 kV | 10 µm | SiC-SiC B3
(d)
12/22/2010 9:33:42 AM | det TLD | HFW 1.28 µm | WD 3.2 mm | mag 200 000 x | HV 5.00 kV | 300 nm | SiC-SiC B3
(e)
12/22/2010 8:18:33 AM | det TLD | HFW 25.6 µm | WD 3.1 mm | mag 10 000 x | HV 5.00 kV | 5 µm | SiC-SiC B8
(f)
12/22/2010 8:20:21 AM | det TLD | HFW 1.28 µm | WD 3.1 mm | mag 200 000 x | HV 5.00 kV | 300 nm | SiC-SiC B8



Figures 2(a-k). SEM cross-sectional views of polished 2D-SiC/CVI-SiC composite surfaces showing interphase configurations and dimensions: 2(a-b) and 2(c-d), 5HS multilayer; 2(e-f) and 2(g-h), 8HS multilayer; and 2(i-k), 8HS "50" nm monolayer samples. The small square on each low magnification view to the left indicates the location of the high magnification view shown on the right.

In these views the SiC matrix or fiber components appear light grey, and the PyC coatings appear dark grey by atomic number contrast. Several cross-sections of needle-shaped pores lying parallel and between individual fiber filaments also are observed. In Table 2, a summary of the fiber coating thickness measurements is compared to their nominal values given by the fabricator. When possible, the standard deviations were calculated for ~60 different coating thickness measurements and are included in the table in parenthesis. The typical scatter in coating thickness measurements is illustrated in Fig. 2(j) for ten measurements made on one a representative of the 8HS-"50-nm" PyC monolayer sample surface.

Table 2. Summary of PyC/SiC fiber coating thickness measurements

Weave type	Nominal dimensions (nm)	Measured dimensions (nm)
5HS, ml	180 PyC + 4[100 SiC/20 PyC]	183 (±15) PyC + 60 (±8) SiC/22 (±18) PyC +3[?/?]
8HS, ml	230 PyC + 4[100 SiC/20 PyC]	226 (±40) PyC + 4[118 (±9) SiC/32 (±6) PyC]
8HS, mono	50 PyC	61 (±10) PyC

Analysis and discussion

Fortuitously, the newly determined thickness values of the inner PyC fiber coating for each multilayer sample agree very well with the previous "nominal" thickness values, values that had been based on only a few random thickness measurements. However, the thickness of the so-called nominal "50-nm" PyC monolayer actually is 61±10 nm. Based on these newly determined PyC coating thickness values, for these high quality 2D-SiC/CVI-SiC composites all the conclusions previously reached concerning the dependence of the in-plane and the transverse EC-values on the total PyC fiber coating thickness are still valid [1].

The largest uncertainty in the coating thickness values appears to be in the values determined for the alternating SiC/PyC multilayers that cover the relatively thick initial PyC layer, especially for the 5HS sample. For this material the initial PyC layer is well defined as is the initial SiC layer (Figs. 2(a-d)), although the initial SiC layer is somewhat thinner (60±8 nm) than the designed 100-nm layer. However, the three following PyC/SiC layers appear to intersect numerous times so that a consistently separated layer pattern did not result from the processing conditions. From previous detailed TEM examinations of a CVI-SiC fiber/matrix interface [3], columnar SiC growth texture may lead to rough, nodular surfaces; thus an inconsistent SiC/PyC layer pattern may result, as observed in Figs. 2(b) and 2(d). Obviously, the PyC network for the 5HS material is well interconnected, at least within a fiber bundle. However, the rough, inconsistent texture of the PyC/SiC multilayers is not so evident for the 8HS multilayer sample. For this material, consistent thickness measurements were possible for the alternating SiC/PyC multilayers, and they agreed fairly well with the nominal design dimensions. This observable microstructural difference between the 5HS and 8HS multilayer composites likely led to the calculated differences in their η-values, 2.3 versus 1.6, respectively.

Even though a low 5 KeV energy electron beam was used to reduce beam spreading, there was sufficient scattering at the PyC/SiC interfaces to make distinct thickness measurements difficult. Therefore, for our modeling efforts we continue to use the nominal value of 20 nm provided by the fabricator for the thin PyC layer thicknesses.

An effort was made to discern any preferred deposition rates in regions of tight or open fiber packing. However no trends were observed, so we assume that the deposition rates were similar throughout during the CVI processing of these relatively thin (~3 mm) plate composites. However, the degree of infiltration and the deposition rates definitely depend on thickness for thicker plates, as observed in a microstructural study performed on a 12.0-mm thick plate made by forced chemical vapor infiltration (FCVI) [4].

CONCLUSIONS

A detailed examination by high magnification, field emission SEM of the PyC coating configurations for several 2D-SiC/CVI-SiC composites with either PyC/SiC multilayer or PyC monolayer fiber coatings was performed. Previous coating thickness values generally were confirmed, and all the conclusions based on these measurements concerning the dependence of the in-plane and the transverse EC-values on the total PyC fiber coating thickness still apply [1]. However, it is wise to perform a quality control examination of composite structures rather than accepting nominal design parameters for use in performing further analysis.

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