MICROSTRUCTURAL EXAMINATION OF SiC_F/SiC WOVEN FIBER COMPOSITES – D. S. Gelles and G. E. Youngblood (Pacific Northwest National Laboratory)*

OBJECTIVE

The primary objectives of this task are to: (1) 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) 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 and thermal conductivity properties of SiC_f/SiC composites considered for application in flow channel insert-structures in support of the U.S. dual-coolant lead-lithium fusion reactor blanket concept.

SUMMARY

Electrical and thermal conduction in 2D-SiC_f/SiC composites exhibit lower than expected values in directions normal to the fiber weave plane. Transmission electron microscopy was used to carefully examine if micro-porosity possibly remaining at the impingement interface regions of the columnar SiC grains growing outwardly from adjacent SiC fiber surfaces could be partly responsible for the observed lower than expected transverse EC- and TC-values. Instead, in these regions no micro-porosity was observed; but rather a complete filling in of the vapor deposited SiC had occurred. The actual connectivity and amounts of the constituent phases (fibers, fiber coatings and CVI-SiC matrix) in each direction and the individual EC-values of the constituents govern the overall transverse and normal EC-values in 2D-SiC_f/SiC composite.

PROGRESS AND STATUS

Introduction

In the dual-coolant lead-lithium (DCLL) fusion reactor blanket concept, an important component called a flow channel insert provides electrical and thermal decoupling of the hot (~700°C) lead-lithium from the load-bearing, structural steel channel walls of the blanket. For application as an FCI component, a silicon carbide, fiber-reinforced composite material made by chemical vapor infiltration (SiC_f/CVI-SiC) is being investigated [1]. The SiC_f/CVI-SiC for this application should have low transverse electrical and thermal conductivity to reduce MHD-induced pressure drop in the flowing lead-lithium and to protect the steel channel walls from excessive temperature, respectively.

Electrical (and thermal) conductivity measurements on two dimensional or 2D-SiC_f/CVI-SiC composites made with stacked CVI fabric layers of woven SiC fibers exhibit significant anisotropy in directions normal and parallel to the fabric layers [2-3]. In Figure 1, typical electrical conductivity (EC) data in the in-plane and normal directions for three types of advanced 2D-SiC_f/SiC composites are shown as a function of temperature.

The in-plane EC-values, which lie above the typical range of EC-values for pure SiC, are governed by the amount (thickness) of the pyro-carbon (PyC) fiber coatings that provide continuous high conductivity pathways even though the amount of PyC is only ~1% overall. The normal EC-values, which lie below the range of values for pure monolithic CVD-SiC and also below the FCI-goal of <20 S/m, are greatly reduced by the limited electrical connectivity through the fiber PyC-coatings because most of the fibers are separated by CVI-SiC matrix in the transverse direction. Therefore, normal EC-values are governed primarily by conduction through the continuous portions of the SiC (a semi-conductor) matrix as suggested by a temperature dependence characteristic of thermal activation. However, these conduction pathways also are limited by the amount and orientation of the mostly in-plane, lamellar-shaped macro-

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porosity observed between fabric layers. It is also possible that some concentrations of micro-porosity may exist in the CVI-SiC matrix that might further contribute to the decrease in the transverse EC. Such micro-porosity could be formed during CVI-processing at the numerous impingement interfaces between intersecting SiC grain growth patterns surrounding adjacent SiC fibers. Many of these interfaces would lie normal to the conduction direction.

The purpose of this work then was to carefully examine and identify all possible micro-structural features peculiar to the CVI-SiC process that might reduce the transverse EC (and perhaps the transverse thermal conductivity) in 2D-SiC_f/SiC composites. Transmission electron microscopy (TEM) was used to carry out this examination.

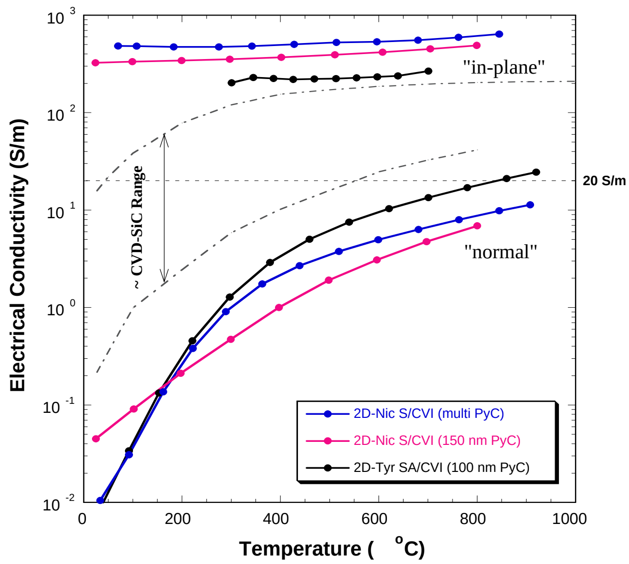

Figure 1. Electrical conductivity in two directions as a function of temperature for three types of advanced 2D-SiC_f/SiC composites. For comparison, an approximate range of EC-values for dense, high-purity monolithic CVD-SiC also is shown.

Experimental Procedure

The composite listed as 2D-Nic S/CVI (150 nm PyC) in Figure 1 was selected for detailed micro-structural examination by TEM. This commercially available composite was made by GE Power Systems using Hi Nicalon™ type S 5HS-0/90 woven fabric with relatively thin (nominally 150 nm) PyC fiber coatings. Results from previous testing of this material indicated that its quality was state of the art (e.g., 2.69 g/cc bulk density, 750 MPa and 284 GPa ultimate stress and elastic modulus at RT, respectively, and a transverse thermal conductivity of 27 W/mK at RT [4]). Little mechanical degradation occurred in this composite material after neutron irradiation for doses up to 10 dpa [5]. At 500°C, we measured transverse and in-plane EC-values of ~2 and 400 S/m, respectively for this material (see Figure 1). The transverse EC-value of 2 S/m is ~1/10th the goal for the FCI-application [6]. This composite exhibits about 10% open and connected porosity because of its layered woven fabric pattern and the required open pathways necessary for carrying out the matrix vapor infiltration process. However, the open porosity can be effectively sealed at plate surfaces by applying a thin, dense and adherent CVD-SiC "seal-coat" as a final step in the CVI-processing. This so-called advanced 2D-SiC_f/SiC best meets the requirements desired for application as a fusion reactor structural material, namely acceptable radiation resistance, mechanical strength and toughness as well as relatively high thermal conductivity, and is considered to be a reference SiC_f/SiC material. Except for its high values of transverse thermal conductivity (~20 W/mK unirradiated at 600°C), this material also meets the desired requirements for the FCI-application.

To examine porosity on a fine scale in such a material using transmission electron microscopy (TEM), two experimental requirements are needed. To view the pores, the specimen interfaces (perhaps containing pores) must be parallel to the electron beam and proper focusing conditions must be optimized. Therefore, several samples were prepared so that the cross-sectional view of at least one bundle of fibers in the 2D-weave pattern was parallel to the electron beam, and images were taken in an under-focused condition (~1000 nm under focused) so that porosity appears in strong white contrast. Two 3-mm diameter disks with the proper orientation were cut and thinned for electron microscopy by ion milling in a Precision Ion Polishing System (PIPS) from Gatan, Inc. using 5 KeV argon ions. Microstructure examinations by TEM were performed on a JEM 2010F analytical microscope operating at 200 KeV and equipped with an Oxford Instruments, Inc. X-ray spectrometer with INCA composition mapping software.

Results

In Figure 2, an optical microscopy view of a thinned sample illustrates the typical fiber arrangement in a 0/90 2D-SiC_f/SiC composite. In Figure 3, a TEM view at x18,000 illustrates the typical columnar grains growing outwardly from the fiber surfaces that were formed during CVI-SiC processing. The central triangular region is the cross-section of a needle-like cavity through which the deposition vapors flowed during processing. These needle-like pores run parallel between many of the fibers within a fiber bundle (500 filaments per yarn), but do not provide significant resistive barriers to EC in the in-plane direction. The curved light grey region surrounding each fiber is the pyro-carbon coating. Although nominally 150 nm thick, there appears to be significant variation in the coating thickness. Compositional mapping demonstrated that the carbon coating was securely attached to the fiber with no apparent separations between the fiber and its coating. However, some circumferential separations were observed within the pyro-carbon coatings themselves.

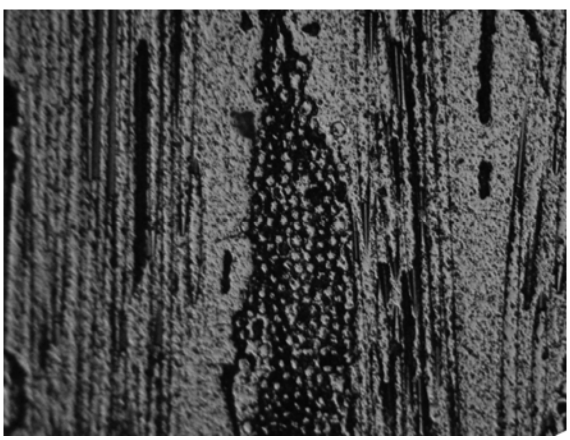

Figure 2. Optical micrograph showing the fiber bundle arrangement and microstructure of a typical 0/90 2D-SiC_f/CVI-SiC composite. The horizontal direction in the view plane is the transverse conduction direction.

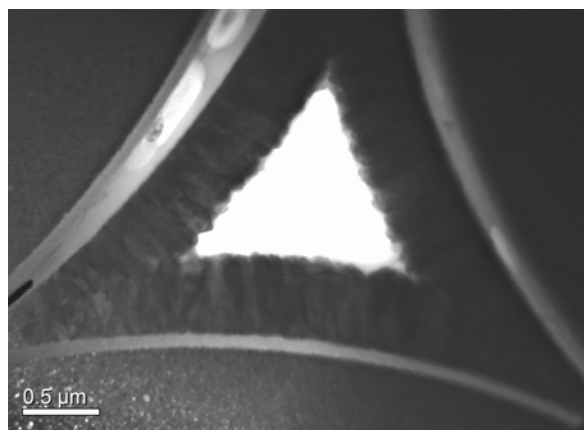

Figure 3. TEM micrograph showing typical columnar grains growing radially outward from the fiber surfaces that were formed during CVI-SiC processing. Also shown are the interface regions of interest between the intersecting growth patterns formed along three touching parallel fibers. The central triangular-shaped region is a cross-sectional view of a needle-like cavity through which the infiltration vapors flowed.

In Figure 4, a higher magnification view of the impingement region between the intersecting growth patterns shown on the lower left in Figure 3 is given. The columnar SiC grains are highly faulted, and their grain size is much larger than the grains in the Hi Nicalon™ type S fibers. Noticeably, the interface created between impinging columnar grain growth structures appears to be densely filled and cavity free.

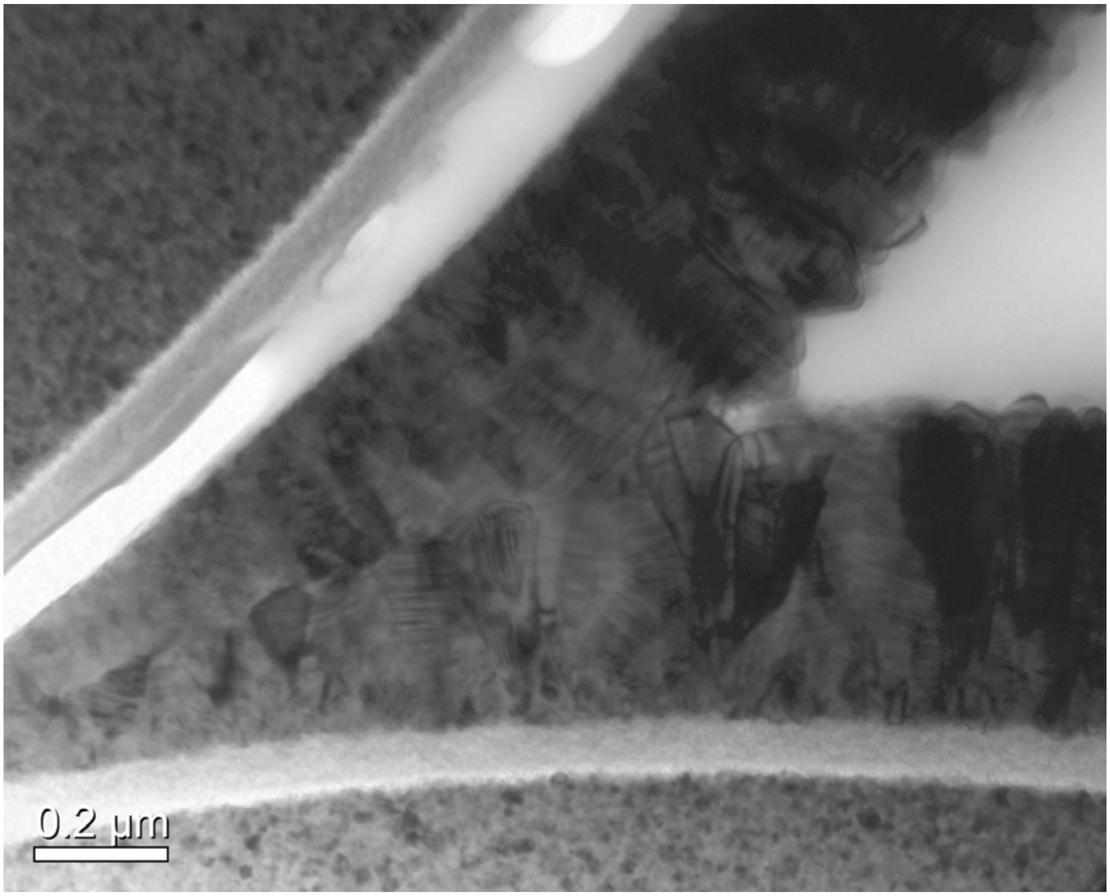

Figure 4. High magnification (x80,000) TEM edge-on view of the intersection interface region between impinging columnar grains growing outwardly from neighboring fiber surfaces as shown on the left side of Figure 3.

In order to make small pores or cavities visible, TEM images were under-focused (~1000nm) so that cavities, if they are present, should appear in stronger contrast. First, the region in the far left of Figure 4 is shown in Figure 5 at x100,000 magnification. The narrow white band shown in the upper-middle portion of Figure 5 is a separation (or crack) formed between the PyC coating and the CVI-SiC matrix. Note that it extends further between the coating and CVI-SiC matrix in Figure 4. Similar coating/matrix separations were observed in TEM views of other regions. In contrast, no separations were ever observed between the type S fiber/fiber coating interface. In a fiber-reinforced composite, this is a requirement to provide maximum protection of the fiber surface and to enhance the load transfer capability between fiber and matrix in a fiber-reinforced composite, and therefore the composite toughness and strength.

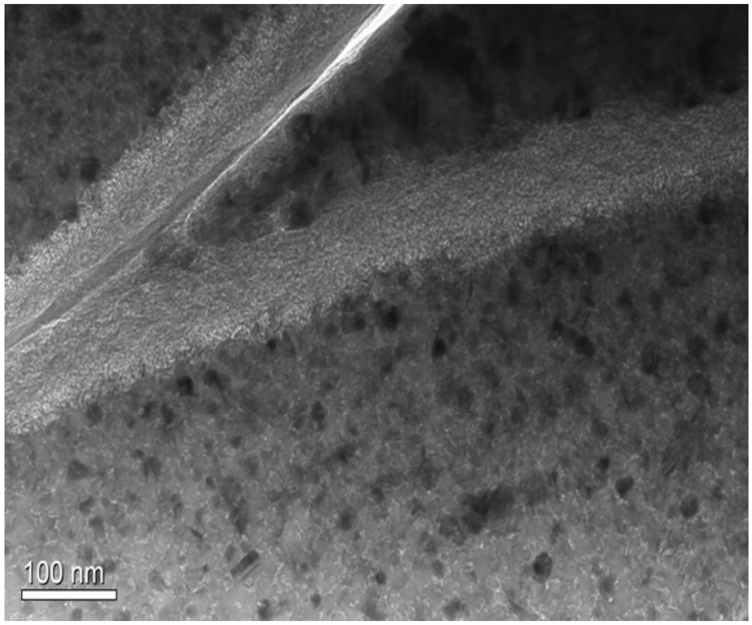

Figure 5. High magnification (x120,000) TEM micrograph of region near two touching fibers, under-focused. The two ~100-nm thick grey areas illustrate the turbostratic layered structure with <0001> texture of the PyC fiber coatings.

In Figure 6, another example of an under focused TEM view of the impingement interface at high magnification (x160,000) is shown. Again, no micro-porosity is revealed along the impingement interface.

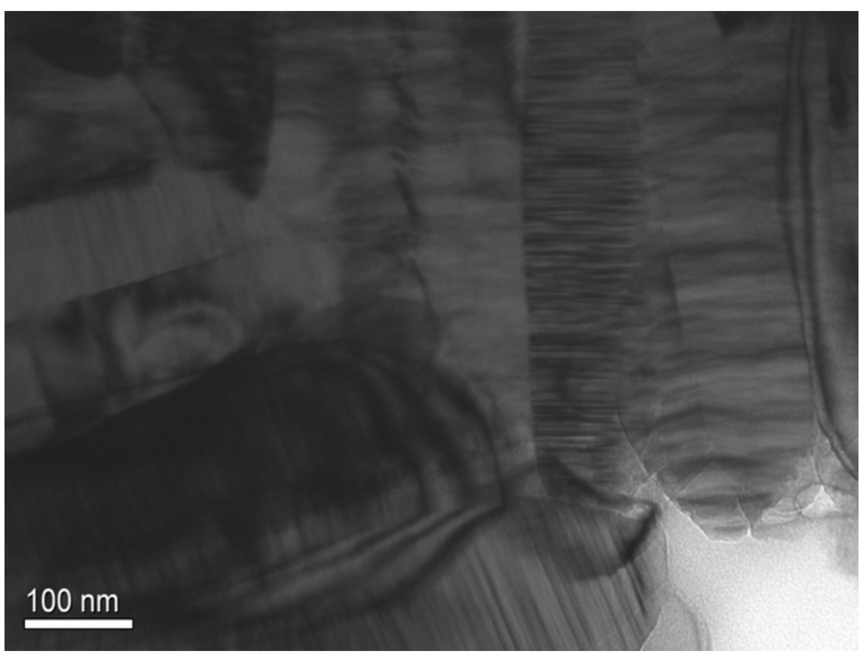

Figure 6. High magnification (x160,000) TEM view of another impingement interface region, under focused.

Discussion

In Reference [1], it was stated that simple parallel/series models based on constituent EC-values and geometry could not explain the observed highly anisotropic EC-values for the in-plane and normal directions in 2D-SiC_f/SiC (EC_x/EC_z > 100 where x and z are in the in-plane and transverse directions, respectively). It was conjectured that perhaps the many intersecting interfaces formed between the CVI-SiC columnar grains growing outwardly from neighboring fiber surfaces contained micro-porosity which could form barriers to conduction processes and could contribute to the lower than expected electrical conduction in the transverse direction. This region of the CVI-SiC pattern has received little attention until now. However, careful TEM examination of several interface regions did not reveal the presence of micro-porosity or cracking at these interfaces.

A search of the literature also did not identify such configurations. However, most micro structural examinations were primarily concerned with the fiber/coating and the coating/matrix interfaces as well as the nature of the PyC interphase itself [7-9]. In particular, most studies emphasized explaining the outstanding mechanical strength and toughness properties exhibited by SiC_f/SiC composites where the fibers were coated either with thin single layers of PyC or multiple C/SiC layers. Using SEM or TEM, the propagation of micro-cracks formed initially in the SiC matrix due to applied tensile stresses was examined in detail. It was revealed that the micro-cracks were blunted by deflection within single PyC fiber coatings or by branching between the multiple C/SiC coatings. However, no views of cracking along the intra-grain growth interfaces were ever shown, so apparently never observed.

In some sense, the negative results of this investigation looking for micro-porosity at grain growth interfaces in the CVI-SiC matrix explain why the thermal conduction in 2D-SiC_f/CVI-SiC is so high. The conduction path through the semi-continuous CVI-SiC matrix as well as across or through the nearly stoichiometric SiC fibers used in advanced SiC_f/SiC supports effective phonon conduction. Only the ~10% macro-porosity in the as-fabricated composites provides significant barriers to phonon conduction. Because of the shape and orientation of the macro-pores located primarily between the fiber bundles or fabric layers, these barriers have more than a linear influence on the transverse TC [10]. Likewise, the observed anisotropy of the thermal conduction (TC_x/TC_z ~ 2) for as-fabricated composite also is primarily due to the shape and orientation of the macro-porosity.

However, the electrical conduction for such composites is primarily due to electron conduction and the observed anisotropy is much larger (EC_x/EC_y ~100). Due to the much greater disparity between electronic conduction in SiC (a semi-conductor with EC-values in the 1-10^2 S/m range and exhibiting a thermal activation temperature dependence) and the PyC coatings (a metallic conductor with EC-values in the 10^4-10^6 S/m range and relatively independent of temperature), the overall transverse or in-plane EC-values of 2D-SiC_f/SiC depend on the actual connectivity and amounts of the constituent phases in each direction in these composites.

Finally, some evidence for separations within the PyC coating or at coating/CVI-SiC interfaces was observed by TEM. At this time, it is not known whether these observations are characteristic of the as-received GE composite, or were caused by the sample preparation. Further TEM examination of these regions in other samples of as-received composite must be carried out before any conclusions can be made concerning such separations.

Conclusions

No evidence for micro-porosity or cracking was observed by TEM in several views of the interface region formed between intersecting columnar SiC grains growing outwardly from neighboring fiber surfaces. In fact, rather complete fill-in of the CVI-SiC matrix occurred around the individual fibers except for the needle-like cavities (necessary for the flow of the CVI vapors) running parallel between many of the fibers in a bundle. The actual connectivity and amounts of the constituent phases (fibers, fiber coatings and

CVI-SiC matrix) in each direction and the individual EC-values of these phases determine the overall transverse and normal EC-values in 2D-SiC_f/SiC composite.

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