ELECTRICAL CONDUCTIVITY OF SIC/SIC—G. E. Youngblood, E. Thomsen, and G. Coffey (Pacific Northwest National Laboratory)[*]

OBJECTIVE

The primary objective of this fusion materials research effort is to support component design and future testing for the International Tokamak Experimental Reactor (ITER).

SUMMARY

In this report, experimental measurements of the transverse electrical conductivity (EC) for a conventional 2D-SiC/CVI-SiC are presented that indicate that the desired EC-goals for operation of a Flow Channel Insert (FCI) made with this material can be achieved.

Several 2-probe DC and AC and 4-probe DC methods for measuring the electrical conductivity (EC) of various SiC forms as a function of temperature up to 800°C were examined. A 2D-SiC/SiC composite made by the isothermal chemical vapor infiltration (ICVI) process with Hi-Nicalon™ type S fabric and a thin pyrolytic-carbon (PyC) interphase was used as a reference material. To estimate the influence of the PyC interphase on the EC, conductivity measurements were made in the in-plane direction for as-received composite and for composite with the PyC removed by oxidation. Also, the EC was measured for monolithic CVD-SiC and for bare bundles and single filaments of SiC fiber types Nicalon™ S and Tyranno™ SA as well as for the transverse direction of our reference SiC/SiC.

For temperatures above 500°C, a temperature range relevant for operation of an FCI in an ITER blanket test module, EC-values for both bare SiC fiber and fiber bundles and monolithic CVD-SiC exceed the desired upper limit of 20 S/m for such an application. However, repeated measurements of the transverse EC for our reference 2D-SiC/ICVI-SiC composite exhibit EC-values less than ~ 1/10th the 20 S/m value. If true, this is an important, very surprising discovery. The EC for the in-plane direction is ~ 100 times that in the transverse direction; hence, the EC for our reference 2D-SiC/ICVI-SiC is very anisotropic, a condition that in general is characteristic of 2D-CVI-SiC composites.

PROGRESS AND STATUS

Introduction

The design of a Dual Coolant Blanket Module (DCBM) is being considered as one element of the U. S. "ITER Mission." Within the flow channels of a DCBM, a key component is a Flow Channel Insert (FCI) that provides electrical and thermal insulation between the flowing, hot liquid Pb-Li metal and the helium-cooled ferritic steel channel walls. FCIs basically are free-floating channels with walls of typical thickness ~ 5 mm, individual channel cross-sections of about 0.08 m^2 and with lengths in meters. Although structurally relatively simple, the total volume of FCI-material required could be large.

A ceramic, fiber-reinforced silicon carbide composite (SiC/SiC) has been proposed as a promising high temperature, radiation and corrosion resistant material for construction of FCIs [1]. To carry out the required FCI-functions, the SiC/SiC material should have relatively low and uniform transverse electrical (EC) and thermal conductivity (TC). According to preliminary models, in the envisioned 500–800°C temperature operating range for an FCI the desired values are ~ 20 S/m and 2 W/mK, respectively [2]. The low and uniform transverse EC-values are required to reduce the induced MHD pressure drop within the FCI channels and to maintain a flow balance among the neighboring channels. In our first report, analysis of EC and TC for various SiC and SiC/SiC forms suggested that an architectural or

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"engineering" composite design solution would be necessary to achieve the desired transverse EC and TC goals for 2D-SiC/SiC [3].

Experimental Procedure

Materials

Monolithic CVD-SiC (polycrystalline -SiC with density 3.21 g/cc and with impurity content < 5 wppm) was obtained from Morton Advanced Materials (now Rohm and Haas, Woburn, MA) [4]. A very high purity bar sample with reduced nitrogen impurity, obtained from Y. Katoh at Oak Ridge National Laboratory, also was examined. Beta-SiC is a wide band gap (~ 2.3 eV) semi-conducting material. By doping with n-type elements, its EC can be increased to ~ 10^4 S/m at room temperature [5].

Single filaments and as-received fiber bundles of two types of polycrystalline, near stoichiometric SiC fibers were examined: Hi-Nicalon™ type S and Tyranno™ SA. A 2D-SiC/SiC composite (made by GE Power Systems in 2002) with either six or eight plies of 2D-5HS weave type S fabric and an ICVI-SiC matrix was used as our reference material. The fabric lay-up was coated with a relatively thin (110 nm) pyrolytic-carbon (PyC) layer prior to matrix infiltration. The bulk density was 2.69 g/cc and the nominal overall fiber content was 40%. Further characterization of this composite material is given in Ref. [6].

4-Probe and 2-Probe DC Methods

Figure 1 shows a schematic diagram of our automated EC measurement system. A type S thermocouple placed within ~ 1 mm of the sample was used to monitor the sample temperature. A programmable computer (Labview™) controls the temperature (RT to 1000°C) in a closed end alumina tube furnace, the atmosphere mass flow (dry argon, argon plus 3% hydrogen or air), and the potentiometric measurements made with a Solartron™ 1480 Multistat. The 1480 was used to control and record cyclic voltamagrams (DC current vs. voltage), generally for a ±0.1volt range at 5 mV/sec. Over this range, the voltamagrams were always linear and the sample resistance could be calculated from the voltamagram slopes. The sample EC was then calculated from the measured resistance and the sample geometry factor when assuming uniform linear current flow.

A standard 4-probe method, as depicted in Fig. 1, was used for all bar samples (typically 15 x 1-4 x 2 mm^3). Gold lead wires were attached to various types of bar samples (CVD-SiC and in-plane SiC/SiC composite, as well as fiber bundles) by twisting a loop around the bar or fiber bundle. Gold paste was applied to make sample-to-wire contact. For the relatively thin disc-shaped samples (CVD-SiC or transverse SiC/SiC composite, typically 9 mm dia x 2 mm thick), a less reliable 2-probe method had to be used. Disc surfaces were carefully cleaned with dilute HF, rinsed with sonicated deionized water, and air-dried prior to applying

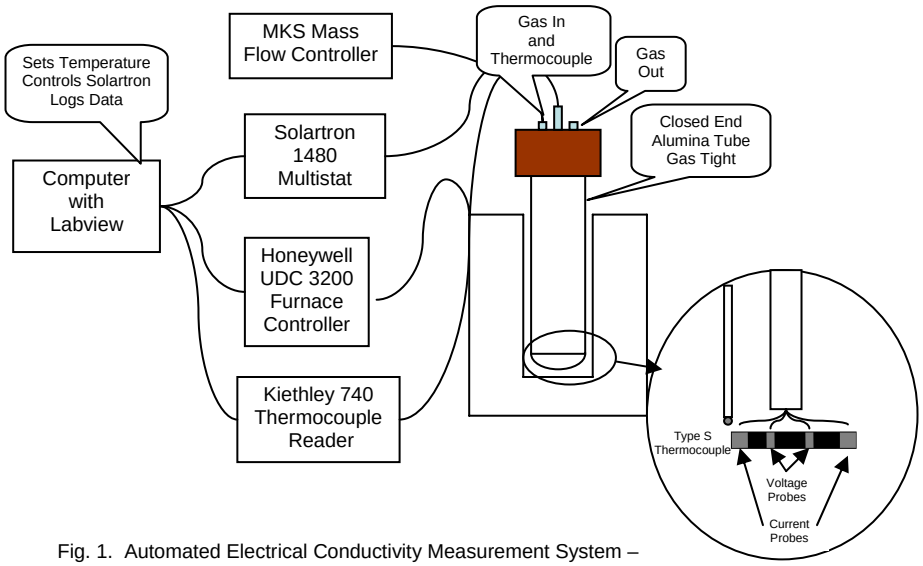

Fig. 1. Automated Electrical Conductivity Measurement System – RT to 1000°C, atmosphere controlled.

gold electrodes to both disc faces by vacuum evaporation using a conventional SEM sample coating system. Gold wire leads were spot-welded to gold foil on top of gold gauze contacts that were then pressed onto the gold-coated disc faces by an external spring-loaded push rod. The HF and water rinse was also given to the fiber bundles prior to mounting.

In the 4-probe potentiometric method, no current flows through the inner voltage contacts on a bar sample, so there is no contact resistance. In the 2-probe potentiometric method, the measured voltage drop includes contact resistances between each vacuum-coated gold electrode and the SiC disc sample face. For reliability, efforts were taken to reduce this contact resistance to well below the actual sample resistance. A typical resistance value for our 9-mm diameter reference SiC/SiC disc samples was 20Ω at 800°C. Therefore, the contact resistance should be maintained < 0.6 Ωcm^2 to reliably keep the error in the resistance measurements to < 5%.

Initially, a 2-probe AC impedance method was examined in an attempt to estimate the contact resistance. This method was not appropriate for these materials, so was abandoned.

Results

Monolithic CVD-SiC

In Fig. 2, temperature dependent EC(T)-values for three different CVD-SiC samples are compared with the EC-values ( ) for a commercially available sintered -SiC sample (Hexoloy™ SA) [7,8]. As expected, the EC(T)-values increase with increasing temperature. Apparent activation energies (E_a) were derived from a linear least squares data fit to = $_o$exp(-E_a/kT) in an Arrhenius plot for the low temperature 20–400°C range and are given in the legend.

Bare SiC fiber

In Fig. 3, 4-probe EC(T)-values (solid symbols) for bundles of Nicalon™ type S and Tyranno™ SA fibers are compared to data for these same fibers measured by Scholz (solid lines) [9]. Room temperature 2-probe EC-values for single filaments of these two fiber types are indicated with open symbols.

2D-SiC/SiC

In Fig. 4, 4-probe in-plane EC(T)-values for a bar are compared to 2-probe transverse EC(T)-values for a disc of our reference 2D-SiC/SiC. For the latter case, measurements were made on two different discs nominally fabricated in the same manner, one with six plies and the other with eight plies of Nicalon™ type S fabric. The transverse EC(T)-values had a similar temperature dependence, but were more than two orders of magnitude less than the in-plane EC(T)-values, which ranged from > 300 S/m at RT up to ~ 500 S/m at 800°C.

Discussion

In Fig. 2, order of magnitude variation of EC-levels for nominally similar high-purity, dense polycrystalline CVD-SiC reflects the dominant influence of type and even small levels of impurity in this wide band-gap semi-conducting material, at least in the RT-1000°C test range. The E_a-values (0.12 to 0.19 eV) are characteristic of n-type extrinsic conduction for the CVD-SiC. Note that the EC (logarithmic scale) at 500°C for the n-type extrinsic CVD-SiC samples is about X20 the EC at room temperature. The Hexoloy™ SA -SiC material contains boron (a p-type dopant in SiC) as a sintering aid. Its EC-values are less than 10^{-4} S/m up to 200°C, but increase rapidly with increasing temperature because of its high E_a (0.78 eV).

In Figs. 2–4, for reference the 500°C and 20 S/m dashed lines form a window (lower right-hand corner) that encloses the range of EC(T)-values desired for FCIs. All the EC-values for high-purity monolithic SiC lie above this window, although a few of the lower temperature EC-values are very near the upper limit. It appears that special processes will be necessary to attain the desired low EC-values for nominally pure and dense SiC in the FCI operating range.

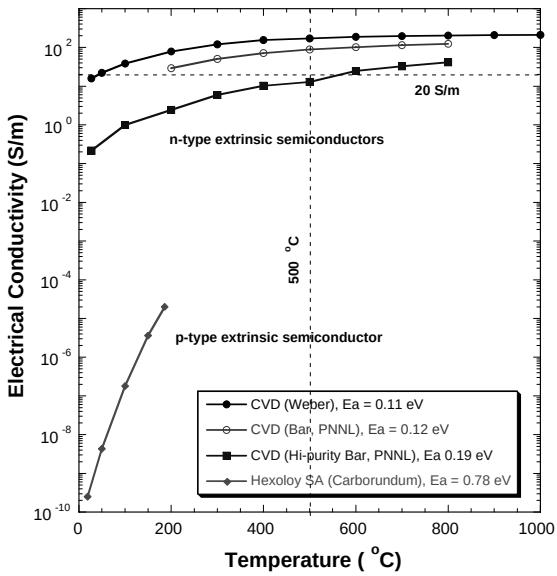

Fig. 2. Electrical conductivity of monolithic SiC.

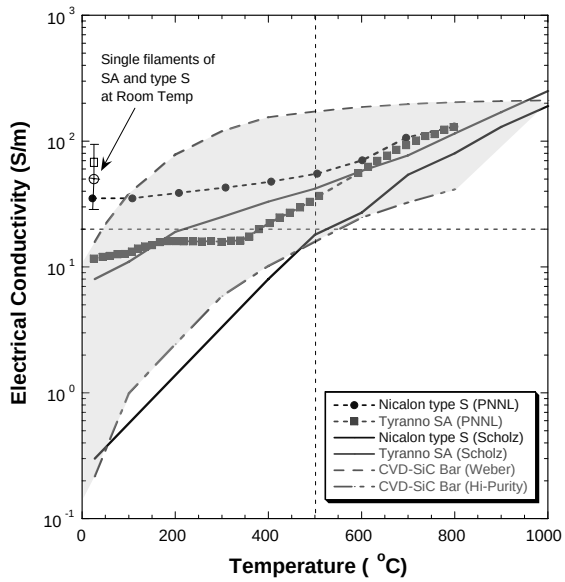

Fig. 3. Electrical conductivity of bare SiC fiber bundles and single filaments of Nicalon™ type S and Tyranno™ SA.

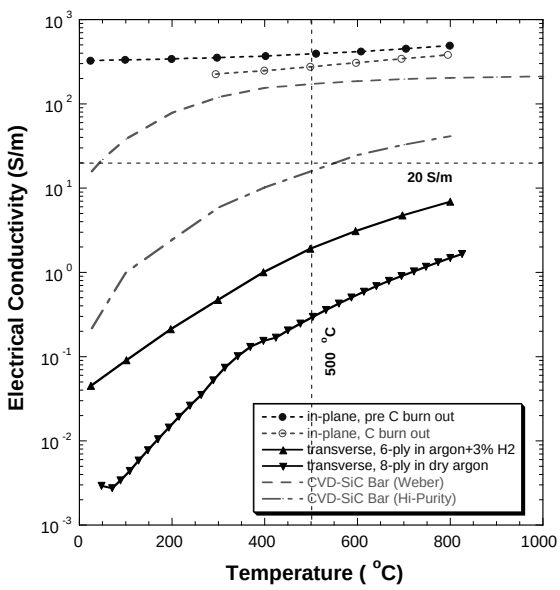

Fig. 4. Anisotropic electrical conductivity of 2D-Nic S/ICVI-SiC composite.

In Fig. 3, for reference the range of EC(T)-values from Fig. 2 for the high-purity CVD-SiC are shown in grey between dashed lines, and the FCI-window is again indicated. Although the EC-values for these two fiber types generally increase with increasing temperature, the temperature dependence did not fit an Arrhenius equation, so E_a-values were not estimated. The EC for a bare Nicalon™ type S bundle at 500 and 800°C was 50 and 130 S/m, respectively. Above 500°C, the EC-values for a Tyranno™ SA bundle were only slightly lower. Again, the EC(T)-values for polycrystalline SiC fiber appear to lie above the FCI-window.

For the Tyranno™ SA fiber, very close correspondence of EC(T)-values with Scholz data were obtained. However, for the type S fiber EC(T)-values were considerably greater than the Scholz data for this fiber. It is very easy for a thin layer of electrically insulating silicon dioxide to form on SiC, which may have been responsible for the much lower EC-values observed by Scholz. Our HF treatment should have removed any oxide layers if they were present, so we are confident that this new EC-data is more representative of the Nicalon™ type S fiber.

The ±40% error bars for the 2-probe data at room temperature represent the standard deviation for measurements on at least 20 different filaments for each fiber type. Apparently, the EC for polycrystalline SiC fibers is far from homogeneous between different filaments or along the lengths of the same filament. This again reflects the sensitive dependence of the EC on the type, amount and distribution of even small amounts of impurities in SiC.

Referring to Fig. 4, the EC-values for our reference 2D-SiC/SiC in the in-plane direction exceeded 300 S/m and were well above the FCI-window. To examine the influence of the thin, but highly conductive PyC interphase in our reference composite, the EC(T)-values were re-measured for the same in-plane bar sample after the PyC fiber coatings had been “burned out” by oxidation in air (1.5 hrs at 800°C in situ). For this condition, the EC decreased ~ 30%, which is reasonable for removal of the thin PyC layers along the fiber component lying parallel to the conductivity direction. The relatively high EC-values for the in-plane direction reflect the dominant contribution of the highly conductive PyC fiber coatings. The coatings are thin and represent only ~ 2% of the sample volume. Nevertheless, they are continuous and provide effective parallel electrically conductive pathways for 1/2 of the fiber component.

In contrast, measurements of the transverse EC for two different samples of our reference 2D-SiC/SiC composite exhibit EC-values less than ~ 1/10th the desired 20 S/m upper limit, so lie well within the FCI-window. The EC for this 2D-SiC/SiC made by a conventional ICVI-process electrically is highly anisotropic with ratio $_x/\ _z$ > 100. This condition likely is characteristic of CVI-processing of 2D-SiC/SiC.

Simple parallel/series models based on constituent EC-values and geometry cannot explain these results. One possible explanation for this seemingly fortuitous result is that during ICVI-infiltration of a SiC fabric layer preform many intersecting interfaces are formed by the SiC growth rings surrounding the individual SiC filaments as the rings coalesce. Observations of matrix growth interfaces have been made with polarized light for thin sections of similar material [10]. Many of these interfaces lie perpendicular to the transverse conduction direction, and may act as numerous thin electrically insulating layers in series with the SiC fiber and matrix components. The individual SiC fibers and their PyC coatings are separated one from another by the interfaces, which then very effectively reduce the overall transverse EC. The number of these growth ring interfaces is reduced by a factor of ~ 1/2 for the in-plane direction of a 2D-SiC/SiC, in which case the highly conductive PyC coatings as well as 1/2 of the SiC fiber filaments provide many continuous parallel conductive pathways.

Conclusion

For temperatures above 500°C, EC-values for both bare SiC fiber and monolithic CVD-SiC exceed 20 S/m, the desired upper limit for EC in the transverse direction for an FCI. Nevertheless, repeated measurements for a 2D-Nic S/CVI-SiC composite with a thin PyC interface made by a conventional

ICVI-process exhibit transverse EC-values less than 1/10th the 20 S/m value. If true, this is an important, very surprising discovery. The desired EC-goals required to reduce MHD pressure drop likely can be achieved for an FCI constructed with 2D-SiC/CVI-SiC.

Future Work

To examine the reliability of our 2-probe transverse EC method, 2- and 4-probe measurements will be made on a unidirectional SiC/SiC and compared for both transverse and in-plane directions.

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