MODELING THE ELECTRICAL CONDUCTIVITY OF SiC_F/SiC FOR FCI-APPLICATION –
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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 and thermal conductivity properties of SiC_f/SiC composites considered for application in FCI-structures in support of the U.S. dual-coolant, helium lead-lithium fusion reactor blanket concept.

SUMMARY

Using a combination 2/4-probe method to measure the electrical resistance across a disc-shaped CVD-SiC sample with evaporated gold electrodes, the average specific contact resistances at 200ºC and 500ºC were determined to be 12±2 and 7±1 Ωcm^2, respectively. The measured transverse electrical conductivity values for a high quality 2D-SiC/CVI-SiC composite made with Nicalon™ type S fabric were much lower than similar values measured for the same material with its SiC seal coat removed. This observation suggests that the pyrocarbon fiber coatings form an interconnected, highly conductive carbon network within the interior regions of the composite, and are largely responsible for the overall transverse electrical conductivity of the composite. At lower temperatures, the composite SiC seal coat should be an effective electrical insulator in the transverse direction across such 2D-SiC/SiC composites. However, the effectiveness becomes less as the temperature increases due to the rapidly increasing conductivity of SiC with increasing temperature. Nevertheless, the seal coat thickness (and type) can easily be adjusted during the composite fabrication to control the overall transverse electrical conductivity, an important parameter in the design of a FCI-structure. A simple three-layer series electrical conduction model fails to explain the unexpected low electrical conductivity values observed for the 2D-Nic S/CVI-SiC composite with a CVD-SiC seal coat. Importantly, up to 700ºC the transverse EC-values for a Nic S/CVI composite (with or without seal coat) appear to meet the desired criteria for FCI-application of < 20 S/m.

PROGRESS AND STATUS

Introduction

In the dual-coolant helium lead-lithium (DCLL) fusion reactor blanket concept considered for DEMO, an important component called a Flow Channel Insert (FCI) 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/CVI-SiC) is being investigated [1-3]. The SiC/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.

For modeling the performance of various DCLL designs, among other things, the thermal and electrical conduction behavior of the materials used in the FCI-structure are important input parameters. This paper examines the electrical conduction (EC) behavior of high purity SiC made by the chemical vapor deposition process (CVD-SiC) and a high quality, two dimensional (2D)-SiC/CVI-SiC composite made with Nicalon™ type S fiber. Initial results on the effects of contact resistance between SiC and various metallic materials also are reported.

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A 2D-SiC/CVI-SiC composite is very inhomogeneous. Normally, the SiC fibers are coated with pyrocarbon to provide fiber protection during composite fabrication as well as composite mechanical toughness. Furthermore, a significant amount of porosity (~10-15%) exists within the composite. Small diameter, needle-shaped pores are aligned parallel to the woven fiber tows, which contain 500 individual filaments; and larger, roughly lamellar-shaped pores are aligned with their flat planes parallel and between the woven fabric layers. The geometry of this porosity is a result of the woven fabric stacking and the SiC-matrix fill-in process by vapor infiltration that requires interconnected porosity. Detailed effects of this 2D-SiC/CVI-SiC layered structure on the transverse thermal conductivity have been described in reference [4].

In 2D-composites, the directional anisotropy of the EC is even more dramatic than observed for thermal conduction. Typically, the ratio of the in-plane to the transverse EC in 2D-SiC/CVI-SiC is >1000 near room temperature. It steadily decreases for increasing temperatures, but still is >50 at 600ºC. This condition is primarily due to the preferred in-plane alignment of the continuous and highly electrically conductive pyrocarbon fiber coatings, even though the volume of the carbon phase normally is only 1-2%. Furthermore, the carbon fiber coatings form a conductive interconnected network within the close-packed fiber tows, and to some degree they also interconnect the fiber fabric layers. In fact, the degree of interconnectivity of the carbon network forms the dominant electrical conduction path in both the in-plane and the transverse directions in 2D-SiC composites. However, in the transverse direction, the somewhat continuous SiC fill-in matrix, as well as the large interlaminar-shaped pores, may interrupt the carbon network in many places. Normally, the composite outer surfaces are coated with a dense, relatively thin SiC seal coat applied by CVD during the CVI-fabrication process. The seal coat also shields the carbon-networked interior region of the composite.

Thus, a reasonable electrical conduction model across a 2D-SiC/CVI-SiC plate is an interior, carbon net-worked SiC fabric-layered region in series with two outer layers of the densely adherent, single phase CVD-SiC seal coat. The transverse EC(T) for such a three-layered composite can be expressed by:

$$EC(T) = EC_c[1 - f(1 - R)]^{-1} \qquad [1].$$

In Eq. [1], T is temperature, f is the seal coat fractional volume, and EC_c is the transverse EC across only the net-worked interior region of a 2D-SiC/CVI-SiC. Roughly f = t/L and is a small quantitiy, where t is the average total thickness of the seal coats and L is the overall thickness of the composite. Also, R is the ratio EC_c/EC_{CVD}, where EC_{CVD} is the electrical conductivity of the seal coat.

The EC of carbon (~10^4–10^6 S/m) is much higher than that of SiC, and exhibits only slightly increasing EC-values with increasing temperature. As a result, electrical conduction in the interior region of the composite is controlled by the amount of carbon, and especially the amount or lack of interconnectivity of the carbon network. The EC of SiC, a semi-conductor, increases rapidly with increasing temperature. Because the volume of the SiC matrix phase is much larger than that of the carbon interface material, at higher temperatures EC of SiC becomes increasingly important. At sufficiently high temperatures, R≈1, and EC(T) ~ EC_c in Eq. [1]. Likewise, at lower temperatures, R<1, and EC(T) < EC_c, more so for larger values of f. Obviously, f, an easily controllable fabrication design parameter, is especially important at lower temperatures.

Experimental Procedure

Electrical conductivity measurements as a function temperature for monolithic SiC and various SiC/SiC composites have routinely been made in this laboratory over the last four years and have been described in previous reports [5-6]. Briefly, we make dc electrical resistance measurements (assuming ohmic conduction for a uniform, constant applied current) using a 4-probe method for slender bar samples (~15 x 6 x 2 mm^3) and a 2-probe method for relatively thin, disc-shaped samples (~10 mm dia x 2 mm tk). The EC is calculated from the measured potential drop and the appropriate sample geometry factor. The samples are heated in a tube furnace under various flowing inert or reducing gas atmospheres. The

temperature control and measurement system is totally automated. In a typical EC-run, the system is programmed to increase or decrease the sample temperature in steps between room temperature and ~800°C at a rate of ±1ºC/min, with a 15 min hold time at every 40°C step. For such a run, the complete 800ºC temperature cycle requires about 12 hours and conveniently can be carried out overnight with little attention.

A combination 2/4-probe method was developed whereby the electrical contact resistance at the interface between an applied metal electrode and a sample surface (a single phase material, usually CVD-SiC) can be estimated [5]. The contact resistance is simply the difference between the simultaneous 2- and 4-probe resistance measurements with a slight correction due to differences in the voltage probe separations for the two types of probe connections. However, only the 2-probe method has been used so far for our composite disc samples, although future measurements will examine various SiC/SiC composite/electrode combinations using the 2/4-probe method.

The EC of a high quality, 8-ply 2D-Nic S/CVI-SiC (made by GE Power Systems Composites using Hi-Nicalon™ type S fabric) was examined. Hereafter, this material will be referred to as simply "Nic S/CVI." Full characterization of this material was reported previously [7]. For this Nic S/CVI material, the thickness of each SiC seal coat surface layer was ~0.05 mm, as estimated from numerous SEM views of sample cross-sections. The electrical resistance was measured on disc samples of this material after the seal coat had been ground off to expose numerous underlying carbon coated fibers now intersecting the sample surface. Three different types of electrodes were applied to samples after removing the seal coat: (1) evaporated gold (our normally used electrode), (2) evaporated carbon and (3) porous nickel. The gold and carbon electrodes were applied in a similar manner using a SEM coater and were expected to make excellent electrical contact with the exposed carbon network at the sample surfaces. The porous nickel electrodes were formed by first applying a NiO paste to the disc surfaces, and then reducing the NiO in an argon + 3% H_2 atmosphere at 800°C (a method developed in our solid oxide fuel cell program). Measurements were made in a dry, hi-purity argon atmosphere on samples with gold or carbon electrodes. Measurements for samples with the Ni electrodes were made in the argon + 3% H_2 atmosphere after the NiO had been reduced in place at 800ºC. The preferred electrode-SiC connection used in the semi-conductor industry is nickel [8].

Results and Discussion

When combination 2/4-probe EC-measurements were made on two different CVD-SiC disc samples with evaporated gold electrodes, average specific contact resistances at 200ºC and 500ºC were estimated to be 12±2 and 7±1 Ωcm^2, respectively. The uncertainties represent just the differences in measurements between the two samples. A value of ~10 Ωcm^2 is in line with values obtained by Morley for CVD-SiC in contact with liquid Pb-Li at T < 400ºC or so, although Morley observed considerable variation between setups [9]. Morley also observed a rapidly continuous decrease in the specific contact resistance as temperatures increased for T > 400ºC, which agrees with the trend that we observed. For our case, the contact resistance at the interface between CVD-SiC and evaporated gold electrodes was a significant portion of the overall CVD-SiC sample resistance, and led to considerable uncertainty in the calculated EC for CVD-SiC disc samples when using a 2-probe method.

The 2/4 probe method of estimating the specific contact resistance has not been carried out on SiC/SiC composites because the two small diameter holes required to seat the potential probes for the 4-probe measurement would penetrate through the single phase SiC seal coat and into the carbon networked interior region. Therefore, the observed difference in resistance values for the two 2/4-probe connection cases would not represent the true contact resistance at the metal electrode-SiC interface. For this reason, only 2-probe measurements were made for the following composite disc sample cases.

In Figure 1, the calculated specific resistance (= resistance x surface area) as a function of temperature for two different disc samples, GE3 and GE4, are compared. Both samples were cut from the same plate of Nic S/CVI material after grinding off the SiC seal coat. Initially, measurements were made on GE3 with

gold electrodes, then, after grinding the gold off and applying Ni electrodes, a second set of measurements was made on the same sample. At this time, only measurements with carbon electrodes on the GE4 sample have been made.

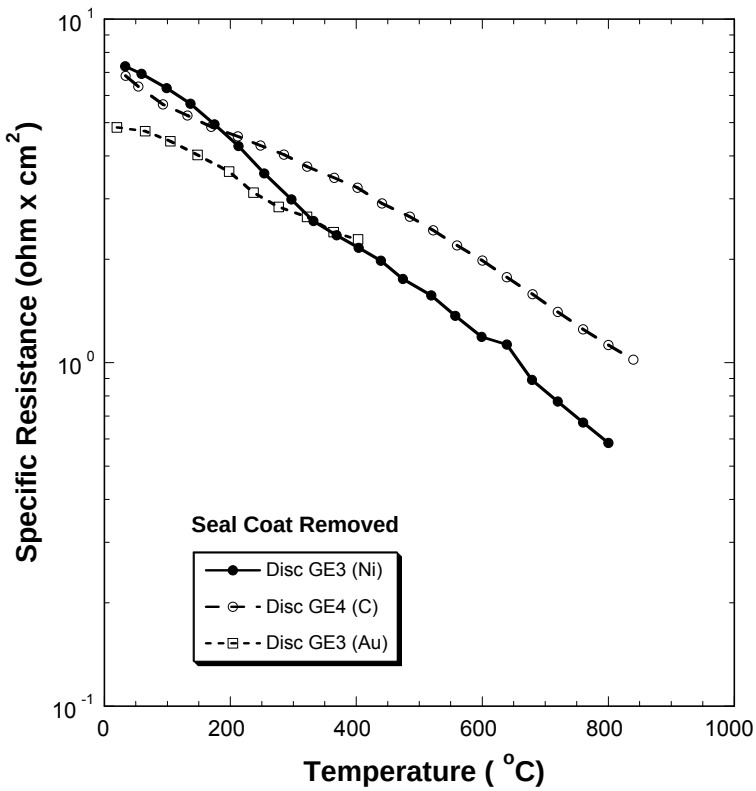

Figure 1. The specific resistance as a function of temperature for disc samples of GE "Nic S/CVI" composite after removing the SiC seal coat. The electrical resistance measurements were made using the 2-probe method on samples with three different electrodes (porous Ni, evaporated C and Au). For clarity, only the data obtained for decreasing temperatures are shown.

The specific resistance of these ~1-cm. diameter disc samples continuously decreased from ~6 to 0.8 Ωcm^2 as the temperature increased from RT to ~800ºC, respectively. As discussed, the contact resistance for these cases is expected to be minimal. Katoh [10] estimated the specific contact resistance for a similar setup to be <0.01 Ωcm^2. The ±10% variation between EC-values for different samples of the same material, and even between different runs on the same sample, appears to reflect the inhomogeneous nature of these composites or perhaps even small differences in sample surface preparation.

In Figure 2, the EC-values as a function of reciprocal temperature for various SiC-based materials are compared. In this figure, new data obtained for disc samples of "Nic S/CVI" (with and without SiC seal coat) and of R&H CVD-SiC are indicated with symbols. Previously reported EC-data for bar samples of CVD-SiC (Weber, Morton, and Hi-Purity) are indicated with bold solid lines. The literature EC-values for very high purity CVD-SiC (R&H Hi-Resistance CVD-SiC) also are indicated with bold solid lines [11]. Previously reported data for a Nicalon™ type S fiber bundle also are shown [5].

As discussed previously [5], the wide variation of EC-values for monolithic CVD-SiC reflects the influence of type and even small differences in the amounts of impurity between nominally the same materials. The negative slopes of the 1000/T dependence increase going from the upper to the lower set of bold-faced

curves. The 1000/T slopes generally increase as the expected level of impurity in the tested CVD-SiC materials decreases. The activation energies (Eact), estimated from an Arrhenius best-fit straight line to the higher temperature data for these CVD-SiC materials, decrease from ~0.12 eV to ~0.28 eV from top to bottom, in line with the decrease in the impurity levels, also top to bottom.

The EC(T)-values of our Nic S/CVI composite (no S.C.) very closely match similar values reported by Katoh for a similar composite made with Nicalon™ type S or with Tyranno™ SA fabric, except for Katoh's cases the carbon existed as multilayer coatings [10]. From the relatively high values of EC(T) for T<400ºC, Katoh, et al., concluded that transverse conduction was primarily through the carbon interphase network in the low temperature regime. In the high temperature regime, the steeper 1000/T temperature dependence suggested ever-increasing contributions from the SiC fibers and matrix. In fact, in this temperature regime, the 1000/T slopes for the composite SiC/SiC materials without seal coats approach that of the R&H and "Hi-Purity" CVD-SiC materials.

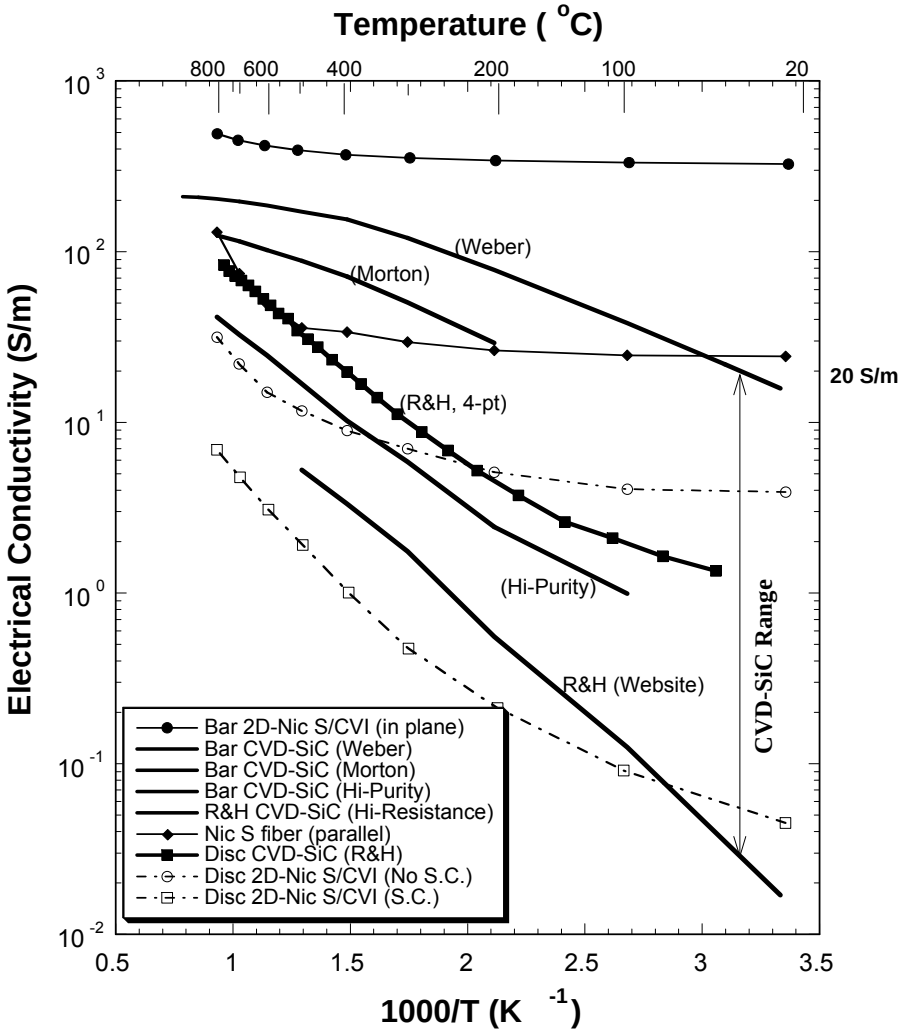

Figure 2. Electrical Conductivity as a function of reciprocal temperature for SiC-based materials. The EC measurements were performed using a 4-probe method for the bar samples and the Nic S fiber bundle, and a 2-probe method for the disc samples. The conduction was normal to the plane for the 2D-Nic S/CVI disc samples, where the SiC seal coat was either removed (no S.C.) or left intact (S.C.).

Interestingly, in Fig. 2 the shape of the curve representing the EC-values measured along the length of a bare Nicalon™ type S tow segment is very similar to the curve shape for Nic S/CVI (no S.C.), except that the Nic S EC-values are about x10 higher. Tanaka, et al. [12], reported a room temperature EC-value of 34 S/m for an early version of Hi-Nicalon™ type S fiber, which is in approximate agreement with our measurement at room temperature. However, Tanaka observed that when a thin (~56 nm), carbon rich surface layer (the carbon-rich layer naturally occurs during type S fiber fabrication) was removed by oxidation, the EC-value decreased to 0.5 S/m, which is in line with the room temperature EC-value of "Hi-Purity" CVD-SiC shown in Fig. 2. Here again the dominant influence of electrical conduction through very thin, carbon-rich layers in the type S fibers or through thin, fiber-coating carbon networks in SiC/CVI-SiC composites, especially in the lower temperature regime, is evident.

Somewhat surprisingly, the observed magnitudes of the transverse EC-values for the Nic S/CVI composite were even lower than the EC-values for the extremely high resistance CVD-SiC material fabricated by Rohm and Haas. Furthermore, the EC temperature dependence of this CVI-SiC composite with its seal coat intact more closely matches that of the high purity CVD-SiC than of Nic S/CVI (no S.C.).

Importantly, up to 700ºC the transverse EC-values for Nic S/CVI composite (with or without seal coat) appear to meet the desired criteria for FCI-application of < 20 S/m.

To examine these unexpected results further, it is instructive to use our series model (Eq. [1]) to predict the overall EC-values for transverse conduction to see if different thicknesses of SiC seal coat play a role. The seal coat thickness (or even type of material) is easily controlled during fabrication, so such a model would be a valuable tool for FCI-structural design. For instance, Henager, et al., have described different types of thermal barrier coatings potentially attractive for use in a nuclear environment, and which potentially could have application in forming FCI-structures [13].

Predictions of the EC-values for two cases were modeled, each for a seal coat of total thickness 0.001, 0.005 and 0.01 mm (f = 0.005, 0.025 and 0.05, respectively). The 0.01-mm thickness conforms to the actual seal coat thickness measured for our Nic S/CVI material. For the two cases, to calculate the input R-value we used the measured EC(T)-values for the Nic S/CVI material together with either the measured values of EC(T) for Hi-Purity CVD-SiC or a set of EC(T)-values derived for a hypothetical CVD-SiC with extremely low EC-values (i.e., a highly insulating seal coat case). To generate the EC(Hypo) values, the formula:

$$EC(Hypo) = (1.80 \times 10^{6}/K)\exp(-4094/K) \qquad [2]$$

was used. In Eq. [2], K is the temperature in Kelvin and the exponential numerical term is equivalent to a thermal activation energy Eact = 0.35 eV. Some representative predictions are shown in Fig. 3.

In Figure 3, only the predicted EC(T)-values for a single f-value of 0.05 are shown. The predicted curve barely deviates from the ECc curve, and then only for T<100ºC. Obviously, according to our simple series model, a seal coat of nominal high purity SiC and of a typical 0.05-mm thickness makes little difference in the overall EC compared to that of the interior region.

The lower set of dashed lines shown in Fig. 3 was calculated for a range of f-values (0.05, 0.025 and 0.005) to emphasize the relative effects of a thinner and thinner seal coat. As expected, for all f-values, the predicted EC(T) values approximate the ECc-values for T > 400ºC, and start to dramatically deviate below ECc-values for T < 400ºC or so, with the thickest seal coat deviating the most. Again, the model predicted EC-values are much greater than the measured values. Furthermore, the 1000/T temperature dependence of the model predictions is entirely different than observed, especially at lower temperatures where the contributions of the ever-decreasing EC-values of the seal coat SiC should become more important.

At this time a logical explanation for the discrepancy of the measured from the modeling results is not apparent. Perhaps the lack of continuous interconnectivity through the carbon network becomes more important, or is more complex at lower temperatures. Or perhaps the contact resistance between composite surfaces and applied electrodes plays a more important role than considered. Further work must be done before deciding on a preferred electrode material for different experimental setups.

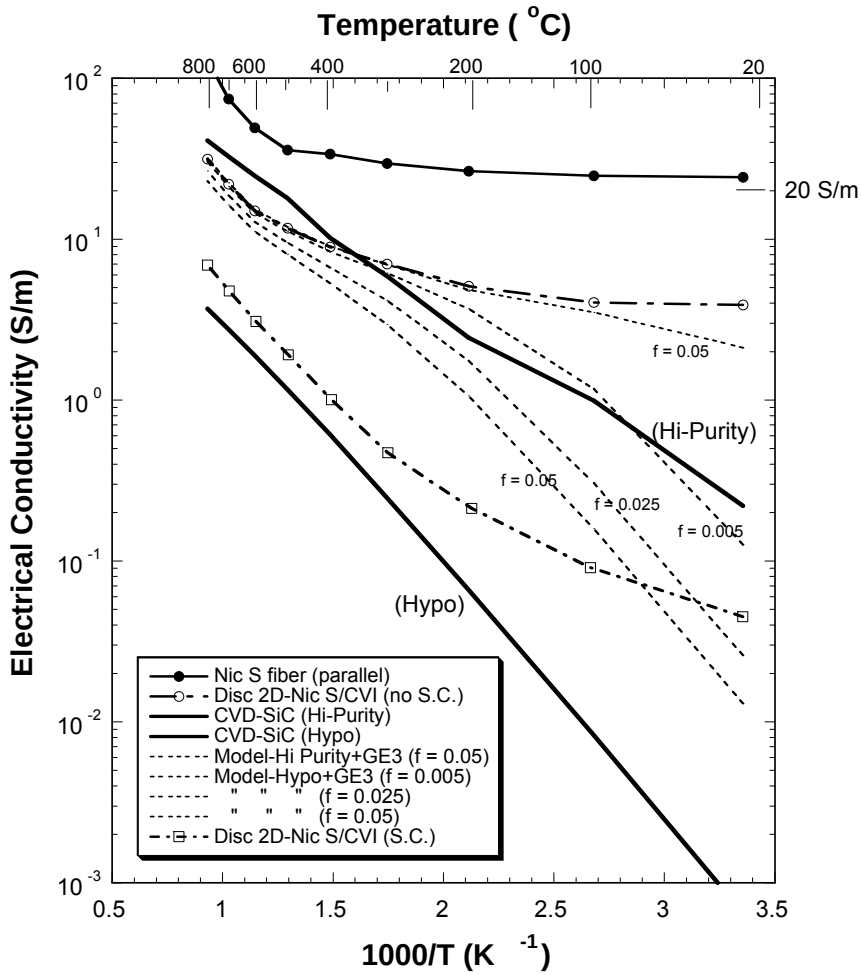

Figure 3. Model predictions of EC(T) for a Nic S/CVI composite with different thicknesses (or f-values) of SiC seal coat. The various EC prediction curves (shown as short dashed lines) are compared to measured EC-values for this Nic S/CVI material and the input EC-values for the interior Nic S/CVI (no S.C.) and either Hi-Purity or the hypothetical CVD-SiC.

CONCLUSIONS

1. Using a combination 2/4-probe method to measure the electrical resistance across a disc-shaped CVD-SiC sample with evaporated gold electrodes, the average specific contact resistances at 200ºC and 500ºC were determined to be 12±2 and 7±1 Ωcm^2, respectively.
2. The measured transverse electrical conductivity values for a high quality 2D-SiC/CVI-SiC composite made with Nicalon™ type S fabric were much lower than similar values measured for the same material with its SiC seal coat removed. This observation suggests that the pyrocarbon fiber coatings form an interconnected, highly conductive carbon network within the interior regions of the composite, and are largely responsible for the overall transverse as well as the in-plane electrical conductivity.

3. At lower temperatures, the SiC seal coat should be an effective electrical insulator in the transverse direction across such 2D-SiC/SiC composites. However, the effectiveness becomes less as the temperature increases due to the rapidly increasing conductivity of SiC with increasing temperature. Nevertheless, the seal coat thickness (and type) can easily be adjusted during the composite fabrication to control the overall transverse electrical conductivity, an important parameter in the design of a FCI-structure.
4. A simple three-layer, series electrical conduction model fails to explain the unexpected low electrical conductivity values observed for the 2D-Nic S/CVI-SiC composite with a CVD-SiC seal coat.
5. Importantly, up to 700ºC the transverse EC-values for a Nic S/CVI composite (with or without seal coat) appear to meet the desired criteria for FCI-application of < 20 S/m.

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