ELECTRICAL CONDUCTIVITY MEASUREMENTS OF SIC-BASED MATERIALS—G. E. Youngblood, E. Thomsen, and G. Coffey (Pacific Northwest National Laboratory)[1]

OBJECTIVE

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

SUMMARY

We have made electrical conductivity (EC) measurements of several types of 2-dimensional (2D) silicon carbide (SiC) composites using either 2- or 4-probe potentiometric methods. To assess the uncertainty in our transverse EC-measurements for thin disc-shaped composite samples when using a 2-probe method, we have developed a more reliable 4-probe method. At the same time, by comparing 2- and 4-probe measurements, we were able to estimate the error due to contact resistance and assess its effect on previous 2-probe EC measurements. From this analysis, it appears prudent to routinely use the new 4-probe set-up for all transverse EC-measurements of thin SiC-based samples.

PROGRESS AND STATUS

Introduction

SiC/SiC has been proposed as a structural material for the flow channel insert (FCI) component in a U.S. designed test blanket module for ITER. To carry out the required FCI-functions, among other things the SiC/SiC material should exhibit relatively low and uniform transverse electrical conductivity (EC). According to preliminary models, in the envisioned 500-800°C temperature operating range for an FCI these desired EC-values are <20 S/m [1].

In our first report in 2005 [2], for the FCI-application we projected that an architectural or "engineering" design solution would be necessary to achieve the desired low transverse EC (as well as low thermal conductivity) values in conventional 2D-SiC/SiC composite. However, in our next report in 2006 [3], we reported measuring transverse EC-values much lower than expected for such a composite, a so-called "reference" 2D-SiC/SiC made by isothermal chemical vapor infiltration (ICVI). This commercially available composite was made by GE Power Systems using Type S Nicalon™ 5HS woven fabric coated with a relatively thin (110 nm) pyrocarbon (PyC) interphase. Results from previous testing of this SiC/SiC 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 27 W/mK TC at RT) [4]. Furthermore, little degradation occurred in this composite 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. The transverse EC-value of 2 S/m was ~1/10th the FCI-goal. However, this 2D-SiC/SiC is highly anisotropic with in-plane EC-values of ~x200 the transverse EC-values. Such anisotropy in the EC could potentially lead to a MHD pressure drop increase of ~20% along the Pb-Li liquid coolant in an FCI-channel, and is undesirable [6]. Also, this material exhibits about 10% open porosity because of its layered woven fabric pattern and the required open pathways necessary for carrying out the matrix vapor infiltration fill-in process. Nevertheless, if the open porosity could be sealed at the outer surfaces of such a SiC/SiC composite made by conventional ICVI, its properties could meet the requirements desired for the FCI-application.

In general, EC measurements are made using a reliable 4-probe potentiometric method or a less reliable 2-probe method [3]. The 2-probe method is less reliable because EC-values measured by this method include a resistance contribution from the material/electrode contact surfaces in series with the

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material resistance that lies between the coincident potential-current probes. If this contact resistance is of the same magnitude or larger than the material resistance, a distinct possibility for thin SiC-based samples, serious errors could occur. Before this study, because of geometric constraints and for convenience, we used a 2-probe method to determine the transverse EC for thin (~2 mm), disc-shaped samples. However, the more reliable 4-probe method was always used to measure the in-plane EC for relatively long bar samples.

At this point, before accepting lower than expected transverse EC-values measured by the 2-probe method for our reference 2D-SiC/SiC, the most important direction for the FCI-application, we sought to carefully reexamine these measurements. To do this we replaced our 2-probe method with a more reliable 4-probe method that would be amenable to measuring the EC across thin disc or plate-shaped SiC materials. At the same time we sought to estimate the level of uncertainty in our previous 2-probe measurements as well as the conditions under which the 2-probe method could still be used with confidence. For instance, a typical minimum resistance value for our reference 2D-SiC/SiC disc samples (2 mm x 7.1 mm dia.) was 20Ω at 800°C. Thus, to reliably keep the error in the 2-probe EC-values <5%, the total contact resistance for both sample-voltage probe interfaces should be <1Ω or <0.8 Ωcm^2 for this composite.

The subject of this report then is the development of a 4-probe potentiometric method for measuring the transverse EC across relatively thin plates of SiC-based or SiC/SiC composite materials, thus eliminating any contact resistance contribution. Also, the efficacy of using either the 2- or 4-probe methods when making these measurements will be assessed.

Experimental Procedure

Materials

We selected two types of SiC-based materials to use during this assessment: a dense high-purity monolithic CVD/b-SiC as a trial material and a relatively dense SiC/SiC composite with uniaxial fiber alignment made by the NITE™ process. Details on the material characteristics as well as results of 4-probe EC measurements made on standard bar-shaped samples of this CVD-SiC material obtained from Rohm and Haas were reported previously [3]. The uniaxial 2D-NITE™ composite was obtained from the Institute of Advanced Energy at Kyoto University [7]. This SiC composite had a density of ~3.0 g/cc and was received in the form of six bars (35.6 x 4.00 x 2.54 mm), three each cut with fibers oriented parallel or perpendicular to the bar lengths, and five discs (10.0 mm dia x 2.0 mm thick) with fibers parallel to the disc surfaces. All surfaces had been machined smooth. This composite contained ~30% Tyranno™-SA fibers coated with a ~500-nm thick PyC interphase. Properties of various forms of monolithic or composite NITE™-SiC are presented elsewhere [8,9]. Note though that the Tyranno-SA™ fiber component contains ~1 wt% alumina, while the NITE-SiC matrix contains ~10 wt% additions of alumina and yttria in mostly crystalline form due to the ~1800ºC sintering temperature. Also note that the PyC interphase makes up ~ 4 vol% overall in these NITE™ samples.

4-Probe and 2-probe EC methods

Our automated EC-measurement system and sample preparation procedures were discussed previously [3]. The new 4-probe configuration for thin disc-shaped SiC samples is depicted in Fig. 1. This configuration has been successfully used in our fuel cell program to determine EC(T) in various atmospheres for several types of ceramic electrode materials [10].

In this new configuration, a small hole (1.5 mm dia x 0.5 mm deep) was bored at the center of each disc face into which potential probes were placed. The potential probes consisted of a gold wire threaded through an electrically insulating alumina thermocouple tube. The thermocouple tube in turn was placed inside a hollow, flat-bottomed alumina push rod, one pair of which was independently spring loaded outside the hot zone. The sample disc faces were prepared in the same manner as for previous 2-probe set-ups, i.e., a mild HF solution was used to remove any oxide surface layer, and then a Au-film was applied to each face using a SEM vacuum coater. As before, the two current electrodes consisted of gold gauze backed by a gold foil disc that were pressed against the disc faces by the alumina push rods. With this configuration 2-probe or 4-probe resistance measurements (R2 and R4, respectively) could be carried out on the same disc sample by reconnecting the i-v probes externally. The contact resistance Rc was then estimated from Rc = R2 - R4. To do this, R4 must first be prorated for the difference in the disc thicknesses for the 2- and 4-probe configurations. This simple estimate procedure assumes that the resistances are ohmic and that the sample is isotropic in the transverse direction.

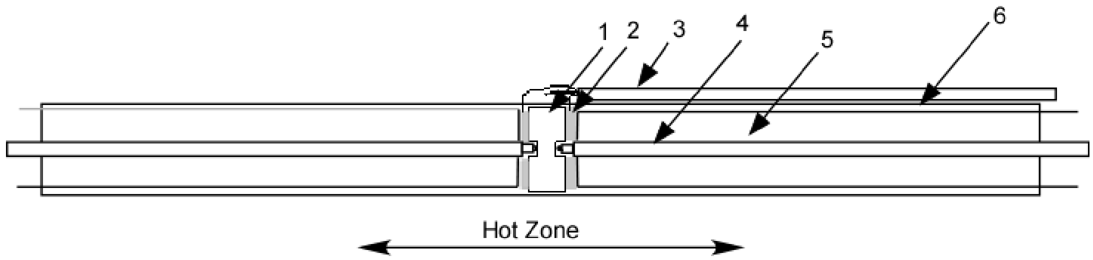

Fig. 1. Sample holder and configuration for 4-probe EC measurements of thin, disc-shaped SiC-type materials. Key: 1. SiC disc-shaped sample (~2 mm x 10 mm dia). 2. Vacuum-evaporated Au film + Au gauze current electrode. 3. Alumina thermocouple tube. 4. Spring loaded thermocouple tube containing independent Au wire voltage and current probes probe. 5. Alumina push rod (10 mm od with 1.6 mm id). 6. Alumina alignment sleeve.

Results and Discussion

<u>Monolithic CVD-SiC</u>

In Fig. 2, the temperature dependent EC(T)-values determined by our new 4-probe set-up for a thin disc sample of CVD-SiC are compared to previously measured values determined using the standard 4-probe method for bar-shaped samples of similar CVD-SiC materials.

The new EC(T)-data shown in Fig. 2 were measured while first increasing temperature to ~800°C, then decreasing temperature to RT and then repeating measurements for a second temperature cycle. The data were reproducible for both cycles, so only the increasing temperature data for the first cycle are plotted. The new data fall within a rather wide range of EC(T)-values measured previously in this laboratory for bar samples of nominally high-purity CVD-SiC from different sources. Apparent activation energies (E_a) were derived from a linear least squares data fit to $EC(T) = ec_0 exp(-E_a/kT)$ in an Arrhenius plot and are given in the legend.

The spread in EC-values for the different, but all nominally high-purity CVD-SiC materials reflects the influence of type and even small amounts of impurity in a temperature range where the electrical conduction is extrinsic for this wide band-gap semi-conducting material. At least the modest agreement of our new 4-probe disc data with previous 4-probe bar data indicated that the new configuration was satisfactory and should provide reliable EC(T)-values.

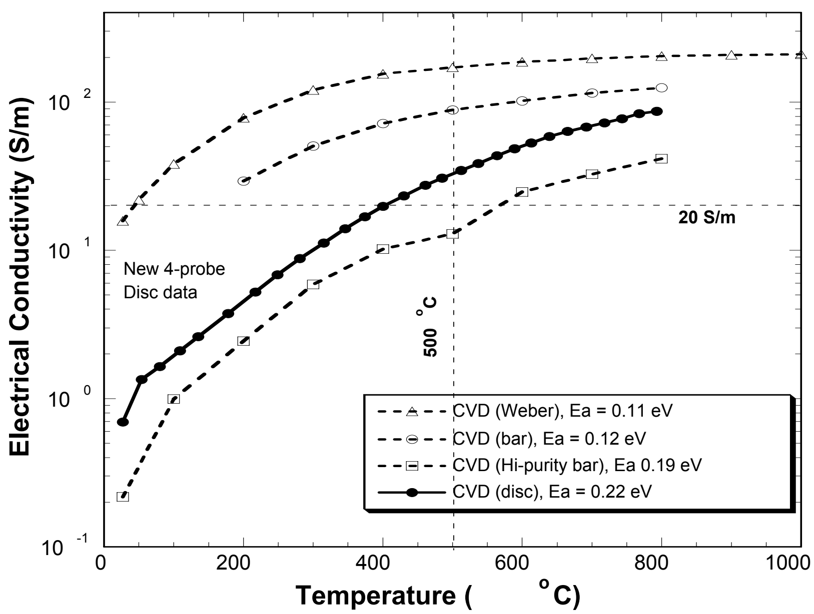

Fig. 2. Electrical conductivity of monolithic CVD-SiC determined by our new 4-probe method for a thin disc-shaped sample (solid symbols) compared to EC(T)-values measured previously on other CVD-SiC bar-shaped samples (open symbols).

Uniaxial 2D-NITE™ SiC/SiC composite

In Fig. 3, measured 4-probe EC(T)-values (solid symbols) for a bar sample of 2D-NITE™ SiC composite with 0º fiber alignment and for a disc sample with 90º fiber alignment are compared to the typical range of EC(T)-values determined for monolithic CVD-SiC (open symbols).

The EC of this 2D-NITE™ SiC/SiC composite is anisotropic with EC-values of ~10^4 or ~300 S/m (a ratio EC(0)/EC(90) of ~30) when the uniaxial fiber alignment is either parallel (0º) or perpendicular (90º) to the current direction, respectively. These EC-values exhibit little temperature dependence and are much greater than the EC-values for high-purity monolithic CVD-SiC.

Similar to the anisotropic reference 2D-SiC/ICVI-SiC, the primary reason that EC(0) >> EC(90) for this uniaxial 2D-NITE™ composite is the dominate contribution of the highly conductive PyC fiber coatings. For the EC(0) case, all the PyC coatings (which make up ~4 % of the total sample volume) are aligned parallel to the current direction. EC-values for PyC coatings have not been explicitly measured, but are expected to lie between 10^4 to 10^6 S/m, the range reported for “soft” amorphous carbon or “hard” crystallized graphite, respectively. A simple parallel conduction model suggests that the coating EC should be ~2 x 10^5 S/m, which appears feasible. Furthermore, the observed temperature independence of EC(0) is characteristic of electronic conduction in graphite. However, the fact that EC-values for the NITE (90) sample are > 4-6 times the EC-values for CVD-SiC suggests that the NITE™ matrix SiC itself has higher EC-values than nominally pure CVD-SiC. We plan to test this possibility by measuring EC on a monolithic NITE™-SiC sample.

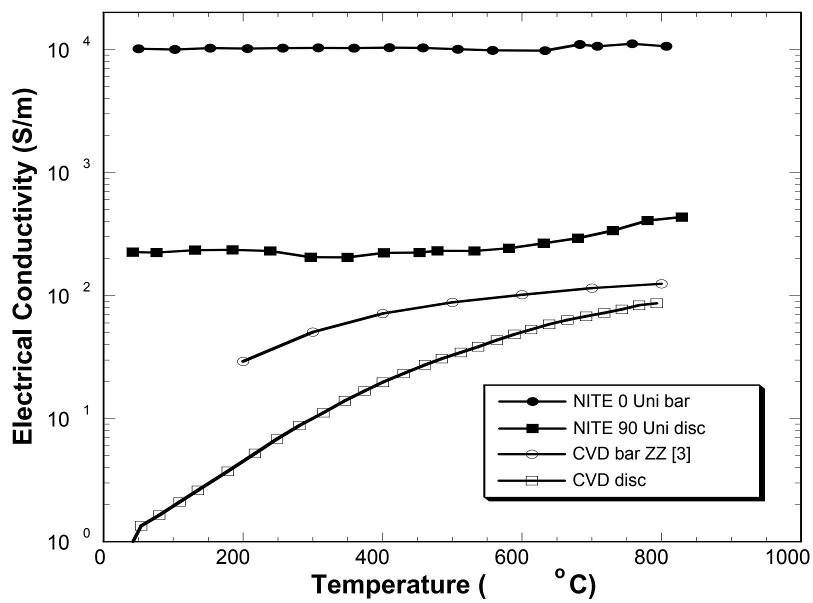

Fig. 3. Electrical conductivity of a uniaxial 2D-NITE™ SiC/SiC composite with either 0º or 90º fiber alignment compared to typical EC(T)-values for monolithic CVD-SiC all measured using 4-probe methods.

Contact resistance estimates

Qualitative estimates of the contact resistances were made for the 4-probe NITE™ 90 and CVD disc configurations at 200 and 500ºC and are given in Table 1.

From Table 1, a qualitative estimate of Rc for the 2-probe configuration with a smooth, pure CVD-SiC surface in contact with a thin gold metal film is ~10Ω or ~9.2 Ωcm^2. In contrast, Rc for a smooth NITE-SiC/SiC surface in contact with gold metal is only ~1.2Ω or ~0.95 Ωcm^2. Such relatively high Rc-values in comparison to the measured 4-probe R4-values result in large error factors for the corresponding 2-probe configurations.

Table 1. Qualitative estimates of the contact resistance for different types of disc-shaped SiC samples

Material	**Disc thick**	**Temp (ºC)**	**R2 (Ω)**	**R4 (Ω)**	**Rc (Ω)***	**Error Factor***
CVD	2.49 mm	200	20.1	6.2	13.9	x2.2
“	“	500	9.41	1.07	8.3	x7.8
NITE-90 uni	2.00	200	1.20	0.11	1.09	x10
“	“	500	1.38	0.12	1.26	x11
2D-SiC/SiC ref	2.20	200	1378	nm	est 10	~0.007
“ “	“	500	107	nm	est 10	0.10
“ “	“	800	16.3	nm	est 10	x1.6

*Rc = R2 – R4 and Error Factor = Rc/R4.

The magnitude of the contact resistance, in general, is quite variable since it depends upon so many factors, primarily the mating surface roughness (the actual contact area between flat surfaces of dissimilar materials) as well as contact pressure, temperature, mode of electrical conduction between dissimilar materials, etc. [11]. Therefore, the following analysis is qualitative.

The difference between the Rc-values for the CVD and NITE-90 2-probe set-ups can be explained by considering the types of mating dissimilar materials for each of these cases. Apparently, for the interface between a highly conductive metal and only a moderately conductive semi-conductor, as we prepared them, Rc was rather high. For the NITE-90 configuration, the SiC surface is interspersed with numerous highly conductive PyC coating intersections, which dramatically reduces the Rc magnitude. Nevertheless, the error factor is still quite large for this set-up. Because of the apparently large error factors and the uncertainty connected with making Rc corrections, 2-probe measurements are deemed unacceptable for determining EC for the CVD-SiC and 2D-NITE SiC/SiC materials. Only 4-probe EC-measurements should be used for disc samples of SiC-based materials with relatively high EC.

At the bottom of Table 1, error factor estimates expected at three temperatures (200, 500 and 800ºC) for the case of measuring the transverse EC for our reference 2D-SiC/ICVI-SiC using a 2-probe set-up are added. This SiC/SiC composite had a dense CVD-SiC seal coat (~0.1 mm thick); so the actual contact surfaces for our reference 2D-SiC/SiC set-up likely were similar to those encountered in our 2-probe CVD-SiC set-up. Therefore, Rc was estimated to be ~10Ω for all temperatures. For this after the fact case, the error factor exceeds 10% only when the temperature exceeds 500ºC. Thus, only for a limited low temperature range where the EC-values are fairly low would the 2-probe method yield acceptable EC-values. In fact, the influence of contact resistance may explain why an analysis of the transverse EC(T)-values for the reference 2D-SiC/SiC did not yield a typical Arrhenius temperature dependence.

From this analysis of measured and expected relatively large contact resistances for various 2-probe configurations, it appears prudent to routinely use the new 4-probe set-up when determining the transverse EC of thin disc-shaped samples of SiC-type materials from now on. As a final note, contact resistance itself may not be bad. In the FCI-application, a contact resistance between the Pb-Li coolant and the extensive surface of a SiC/SiC insert may be beneficial in reducing the MHD-induced electrical currents.

Conclusion

Making EC(T)-measurements of most thin samples of SiC-type materials using a 2-probe method is unreliable due to inherent relatively large and highly variable contact resistances. To overcome this problem, a more reliable 4-probe potentiometric method was designed and assessed. Previously reported transverse EC-values for 2D-SiC/SiC need to be corrected.

Future Work

Our previous transverse EC(T) measurements for several types of 2D-SiC/SiC composites will be redone using the more reliable 4-probe method.

References

[1] N. B. Morley et al., Current understanding of feasibility of SiC/SiC composites for flow channel inserts in Dual Coolant Pb-17Li blankets, presented at TBM meeting, June 4, 2004, UCLA.
[2] G. E. Youngblood, R. J. Kurtz, and R. H. Jones, Development of SiC/SiC for Application as a Flow Channel Insert, Fusion Materials Semiannual Progress Report for period ending December 31, 2004, DOE-ER-0313/37, 3–8.
[3] G. E. Youngblood, E. Thomsen, and G. Coffey, Electrical Conductivity of SiC/SiC, Fusion Materials Semiannual Progress Report for period ending December 31, 2005, DOE-ER-0313/39, 46–51.
[4] G. E. Youngblood and R.H. Jones, Characterization of a 2D-SiC/SiC composite made by ICVI with Hi-Nicalon™ Type S fabric, Fusion Materials Semiannual Progress Report for period ending June 30, 2003, DOE-ER-0313/34, 34–40.
[5] T. Hinoki et al., The effect of high dose/high temperature irradiation on high purity fibers and their silicon carbide composites, J. Nucl. Mater. 307–311 (2002) 1157–1162.
[6] S. Smollentsev, UCLA, Los Angeles, private communication.
[7] J-S. Park, Kyoto University, Kyoto, Japan, private communication.

[8] J. S. Park et al., Tailoring the microstructure of hot-pressed SiC by heat treatment, J. Nucl. Mater. 329–333 (2004) 558.
[9] Y. Katoh, A. Kohyama, T. Nozawa, and M. Sato, SiC/SiC composites through transient eutectic-phase route for fusion applications, ibid. 587.
[10] G. Hsieh, T. O. Mason, and L. R. Pederson, Experimental limitations in impedance spectrometry, effect of reference electrode geometry/position, Solid State Ionics 96(3–4) (1990) 153.
[11] N. Ben Jemaa, J. L. Quffelec, and D. Travers, Electrical contact resistance study of cleaned and corroded materials, Meas. Sci. Technol. 1 (1990) 282.