3.3 Contact Resistance at a CVD-SiC/Ni Interface — G. E. Youngblood and E. Thomsen (Pacific Northwest National Laboratory)

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. In support of the U.S. dual-coolant lead-lithium (DCLL) fusion reactor blanket concept, recent efforts have focused on examining the electrical conductivity properties of SiC_f/SiC composites considered for application in FCI-structures.

SUMMARY

In a previous report, a fairly substantial correction due to contact resistance at a silicon carbide composite-metal (either gold or porous nickel) electrode interface was required to arrive at reliable transverse electrical conductivity values for the composite. A semi-logarithmic plot of the inverse specific contact resistance vs. 1000/K was nearly linear over a temperature range ~100-700°C, with an effective thermal activation energy of ~0.3 eV, which suggested that the contact resistance was due to electron tunneling through a Schottky-type barrier at the composite SiC seal coat/metallic interface. For the FCI-application, additional contact resistance at SiC composite wall/liquid Pb-Li interfaces could potentially and beneficially reduce the transverse electrical conductivity.

In this report, we further examine the behavior of the contact resistance; in particular, by examining contact resistance for a single pure, monolithic but polycrystalline CVD-SiC disc sample with nickel electrodes applied by physical vapor deposition (PVD). After making contact resistance measurements with the as-applied Ni electrodes, a heat treatment at 900°C was performed to lower the contact resistance, presumably by the formation of nickel silicide (NiSi) at the SiC-electrode interface. Using a 2/4-probe dc electric set up, we were able to simultaneously measure the total resistance across the sample disc with and without contact resistance from ambient up to 700ºC, with the difference representing the temperature dependent behavior of the contact resistance alone. Surprisingly, the specific contact resistance values for each electrode type at all temperatures were almost identical (~1000 Ω-cm^2 at RT decreasing continuously to <2 Ω-cm^2 at 700°C). The temperature dependence indicated a thermally activated interfacial conductance with effective activation energy of ~0.24 eV, a value slightly greater than that for ultra high-purity CVD-SiC (0.21eV). Apparently, the electrical conductance of the CVD-SiC/metal (Ni or NiSi) interface depends mostly on the near surface SiC electrical conductivity properties rather than the type of metallic conductor.

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PROGRESS AND STATUS

Introduction

In the U.S. dual-coolant fusion reactor blanket (DCLL) concept, flow channel inserts (FCIs) made with silicon carbide (SiC) materials to thermally and electrically decouple flowing Pb-Li coolant from a steel first wall are being examined [1-4]. In an FCI made with fiber reinforced SiC/SiC composite (or SiC_f/SiC), the molten Pb-Li metal would interface directly to dense, pure SiC applied by chemical vapor deposition (CVD) as a seal coat to composite wall surfaces. A contact-type electrical resistance in series with the resistance of the insert wall itself may develop at the liquid metal/CVD-SiC interfaces. Such additional resistance would be beneficial, as it would reduce any transverse electrical current induced by the MHD-effect in the DCLL flow channels. Therefore, it is important to examine the properties of this expected contact resistance as it might relate to the design and operation of an FCI.

Morley et al. first examined this possibility by measuring the contact resistance (R_c) across a CVD-SiC/Pb-17%Li (molten eutectic composition) interface from 300-550°C, somewhat simulating the materials interaction conditions expected in an operating FCI [5]. Initially on heat up, they found that R_c-values were significant, decreased continuously with increasing temperature, but were rather irreproducible during the cooling leg or for different trials with nominally the same materials. In general, after heat up over a period of a few hours, R_c changed with additional exposure time, which indicated that chemical reactions were taking place in their experimental set up. Indeed, visual inspection of the interface after daylong exposures revealed a scale formation had formed on their SiC disc sample. Likely, chemical reactions at the CVD-SiC/Pb-Li interfaces were responsible for the somewhat erratic R_c-behavior that they observed. However, such chemical reactions were not expected based on observations by Pint, et al., who reported little dissolution of similar CVD-SiC samples immersed in static Pb-Li capsule tests for 2000-hr. exposures at 800°C in vacuum [6]. If SiC actually is chemically stable in liquid Pb-Li for T<800°C, then R_c for a SiC/Pb-Li interface should be reproducible with temperature cycling; and it must have a physical, not chemical explanation. With this apparent contradiction, we decided to examine the behavior of a SiC/metal interface further.

At this point, it is noted that the electronics industry has expended great effort over the last two decades to reduce contact resistance for metal electrodes attached to single-crystal SiC, a wide band-gap semiconductor (~2.3 eV for beta-SiC) of current interest for high power and high temperature electronic device applications [7]. In particular, nickel or nickel-chrome electrodes on semiconductor SiC appear to be preferred for these applications as they form a stable "ohmic" contact with very low resistance under suitable conditions [8]. One of the conditions needed to attain low R_c-values is a highly doped (~10^{19}/cm^3) SiC surface layer, i.e., for example with nitrogen for n-doping [9]. Another condition, besides extremely careful SiC surface preparation, is to give nickel electrodes (applied by sputtering or e-beam methods) a high temperature anneal to induce nickel-silicide formation [10]. With proper processing, ohmic contacts with specific R_c-values as low as 10^{-2} to even 10^{-6} Ω-cm^2 have been achieved [8].

However, during our measurements of the electrical conductivity (EC) of SiC_f/SiC composite disc samples with polycrystalline CVD-SiC seal coats we found that R_c was rather large for sputtered gold electrodes, as well as for porous nickel electrodes [11-14]. Furthermore, we found that the R_c-values as a function of temperature were similar for monolithic CVD-SiC and seal coat CVD-SiC, both in contact with metal electrodes [15]. Moreover, these R_c-values

appeared to mimic somewhat the R_c-values reported by Morley for their CVD-SiC/metallic liquid lead-lithium interface [5, 14]. However, in our case R_c-values were not erratic, but were reproducible for three heating and cooling cycles up to 700°C. They also seemed to be rather independent of the type of metal electrode. This electrical behavior suggested to us that R_c at a polycrystalline CVD-SiC/metallic interface depends primarily on the near surface electrical properties of the SiC and not the type of solid metal interfaced to the SiC. Perhaps this could be the case when polycrystalline SiC is interfaced with molten Pb-Li, as in the FCI-application. It is the purpose of this work to examine this possibility further.

Experimental Procedure

The furnace and a progressive development of our EC measurement system as well as previous experimental results for 2D-SiC/CVI-SiC composite and for dense, monolithic CVD-SiC materials have been described in Fusion Material Semiannual Progress Reports [4, 11-14]. We found that two-probe (2-pt.) resistance measurements across SiC or SiC_f/SiC composite disc samples contained a significant contribution from R_c at the SiC/metallic electrode interface and must be corrected to obtain reliable EC-values [12]. However, four-probe (4-pt.) measurements eliminated R_c contributions during standard potentiometric measurements on polycrystalline CVD-SiC disc samples [13]. Thus, comparison of 2/4-probe potentiometric resistance measurements yield values of R_c itself, i.e., R_c = R(2-pt.) – R(4-pt.) [14]. Initially, we switched from 2-pt. to 4-pt. measurements by manually reconnecting external leads [13]. Therefore, we replaced this cumbersome measurement method by adding an electromechanical relay (National Instruments™ NI USB-9481) to our system that automatically makes almost simultaneous 2/4-pt. resistance measurements possible [16].

A 5-mm thick plate of high-purity, monolithic polycrystalline CVD-SiC, obtained from Rohm and Haas (Woburn, MA), was cut into a single sample disc (1-cm. dia. x 5-mm. thick). Then two centrally located holes (1-mm. dia. x 1-mm. deep) were bored into opposite faces in which to seat potential probes for 4-pt. measurements. The disc faces were diamond polished down to 0.5-μm grit, degreased, and carefully cleaned in a mild HF solution. In previous work, we applied nickel electrodes by applying a NiO paste to the sample disc faces and reducing the NiO to porous Ni, a convenient first-try method. In this new work, solid nickel film electrodes were applied to the disc faces by PVD at ~40°C. The CVD-SiC disc was placed in a vacuum chamber ~5” directly above a 3.0” nickel target. A small amount of argon was bled in and ionized by an applied voltage (~315V). It required ~20 minutes to deposit a 0.25-μm thick nickel coating to each surface. A removable wax plug prevented any nickel deposition in the central potential probe holes. The disc sample was then mounted in an enclosed alumina tube in which a low-flow, reducing atmosphere (3% H_2 in argon) was maintained (Figure 1).

Figure 1. Alumina tube and sample mounting fixture with the CVD-SiC disc sample shown removed below.

For both 2/4-pt. measurements, gold current foils were pressed onto disc faces by external spring-loaded alumina pushrods that securely held the sample in place. An additional gold wire was soldered to the gold foil on each face to act as the 2-pt potential leads. For the 4-probe potential measurements, platinum wires with beaded ends were threaded inside alumina thermocouple tubes that were independently spring-loaded and pressed into the centrally located holes in the disc faces. With this setup, cyclic I-V voltammograms (DC current vs. applied voltage swept between ±0.1 volts) were performed at each temperature step. All resistance or EC determinations reported here and in [16] were made on the same CVD-SiC disc sample using our automated 2/4-probe system.

Electrical resistance values were calculated from the slopes of the cyclic voltammograms. EC-values were calculated from the appropriate sample geometry assuming linear current patterns. Over the tested ±0.1 voltage range and for all temperatures the I-V data were linear and passed through the origin, which indicates “Ohmic-type” conduction (see Figure 2).

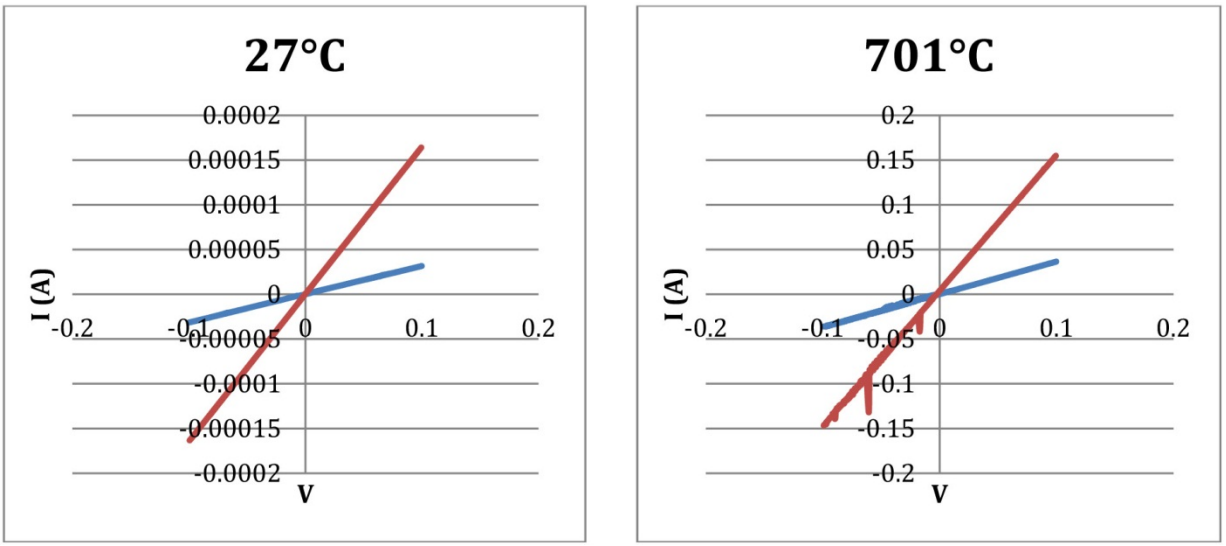

Figure 2. Typical examples showing linear behavior of I(V) potentiometric data for a low (27°C) and a high (701ºC) temperature. For each temperature, the applied voltage was swept in 0.001V steps through a range of ±0.1 volts. The slopes of the blue (red) lines represent the 2-pt. (4-pt.) resistance values at each temperature.

Resistance measurements were made in 40°C steps during three different temperature cycles, each cycle attaining a successively higher maximum temperature: RT to 400°C then back to RT, then RT to 550°C and back to RT, and finally RT to 700°C and back to RT. At each step the temperature was measured and measured again ten minutes later. If the two temperature measurements were within 2°C it was assumed that temperature equilibrium had been attained and I-V cycle proceeded. After completing the 2/4-pt. measurements at each temperature step, the temperature was changed to the next step at a rate of ~5°C per minute. Each temperature cycle required 20±5 hours.

For this same CVD-SiC sample, 2/4-pt. measurements were made for four different metallic electrodes: in order, evaporated Au, porous Ni, PVD-Ni, and heat-treated PVD-Ni. The heat treatment was performed in situ on the sample with the PVD-Ni electrode after completion of the 700°C cycle run. We heated and cooled the sample to 900°C (hold time 20 min.) in the reducing argon-3% hydrogen gas environment. This treatment should have been sufficient to completely convert the PVD-Ni to NiSi. In this reaction, Ni diffuses into and reacts with the SiC to give NiSi (or Ni_2Si), and leaves some small deposits of carbon at an interfacial region that no longer is abrupt [10].

Results for the first two types of electrodes were presented at ICFRM15 and will be published in JNM [16]. The results for the latter two types of electrodes are presented here.

Results

In Figure 3, the almost simultaneously measured 2/4-probe transverse resistance values (upper and lower curves, respectively) as a function of temperature for the polycrystalline CVD-SiC disc sample with the as-applied PVD-nickel electrodes are presented. For clarity, only the data for Run 3, the RT to 700°C cycle, is given. The data-curves for the just previously measured 400ºC

and 550°C cycles were exactly coincident with the 700°C cycle over their comparable temperature ranges. These 2/4-pt. transverse resistance values decrease continuously from ~3000/700 ohms at RT to ~2/0.7 ohms at 700°C, respectively. The difference between the two curves represents the contact resistance for the SiC/PVD nickel interface as a function of temperature.

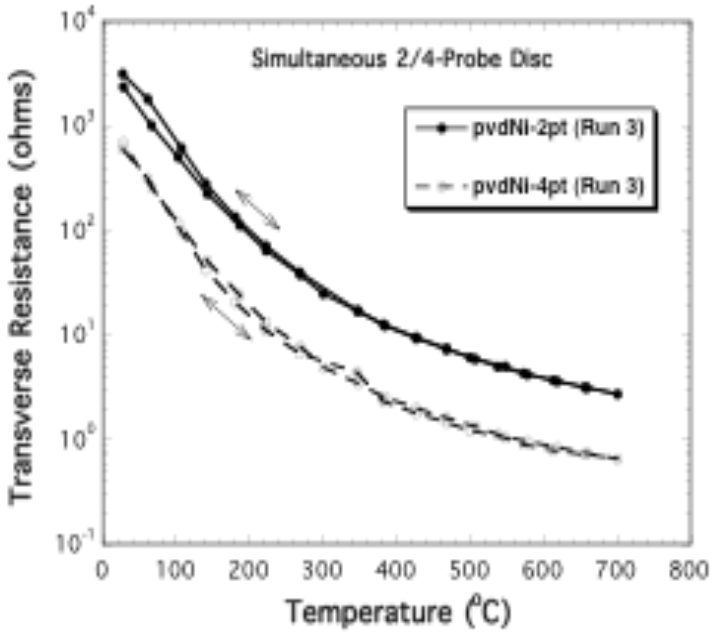

Figure 3. Transverse resistance measurements as a function of temperature for monolithic CVD-SiC disc sample with PVD-Nickel electrodes. The sample temperature was cycled in 40°C steps from RT -> 700°C -> RT. The upper (lower) curves indicate 2-pt. (4-pt.) probe data.

In Figure 4, the EC-values determined from the 4-pt. resistance measurements for our disc sample of CVD-SiC with the PVD-nickel electrodes (before and after the 900°C heat treatment) as a function of inverse temperature are presented. The curves are coincident, as expected for 4-pt. potentiometric measurements that are independent of contact resistance. The EC-values increase from ~0.05 S/m at RT up to ~50 S/m at 700°C, in line with values expected for ultra high-purity CVD-SiC [17]. In this semi-logarithmic plot, the EC-values decrease almost linearly with increasing inverse temperature. For the 300-700°C range, the apparent activation energy is ~0.21 eV, but is slightly larger for T<300°C.

Accurate 4-probe EC-values normally are obtained for bar samples where uniform one-dimensional current patterns are expected for homogenous materials. In our case, the two centrally placed holes in the disc faces for the potential probes, which are only ~2.6 mm. apart, certainly disrupt the assumption of uniform 1D-current distribution. Nevertheless, the reasonable agreement of the magnitudes and temperature dependence of our EC-values with reference values for CVD-SiC suggest consistency of our results.

In Figure 5, specific R_c-values as a function of temperature (the difference between the 2/4 pt. resistance values shown in Figure 3 after adjusting to specific values by multiplying R_c by the geometric disc face areas less the areas of the potential probe holes) for our CVD-SiC sample interfaced with either as-applied PVD-nickel or heat-treated PVD-nickel are given. The R_c-

values decreased continuously with increasing temperature from ~1000 Ω-cm^2 at RT down to <2 Ω-cm^2 at 700°C for each type of metallic interface.

In Figure 6, inverse specific R_c-values are shown plotted against reciprocal temperature in a semi-log form. The almost coincident data exhibit perfect linear dependence with an effective thermal activation energy of 0.24 eV over the ~200-700°C temperature range.

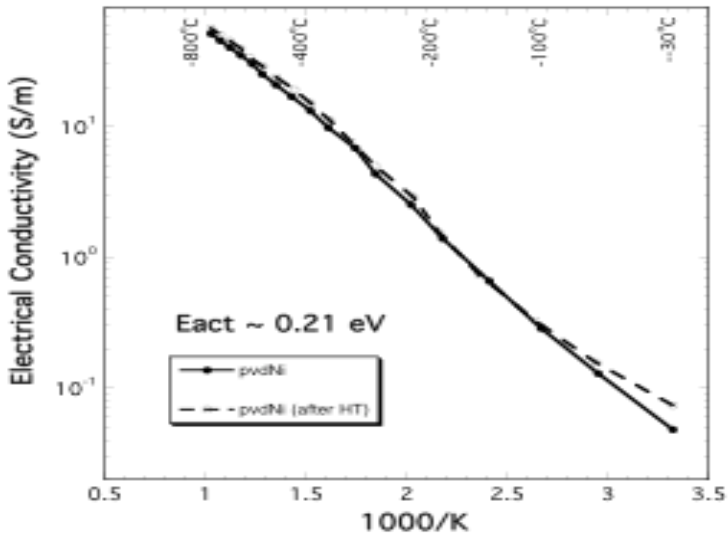

Figure 4. Electrical conductivity as a function of inverse temperature for a monolithic CVD-SiC disc sample with PVD-Nickel electrodes, as applied or heat-treated when using 4-probe measurements. The apparent activation energy determined from the best-fit straight line through the 300-700°C data is ~0.21 eV.

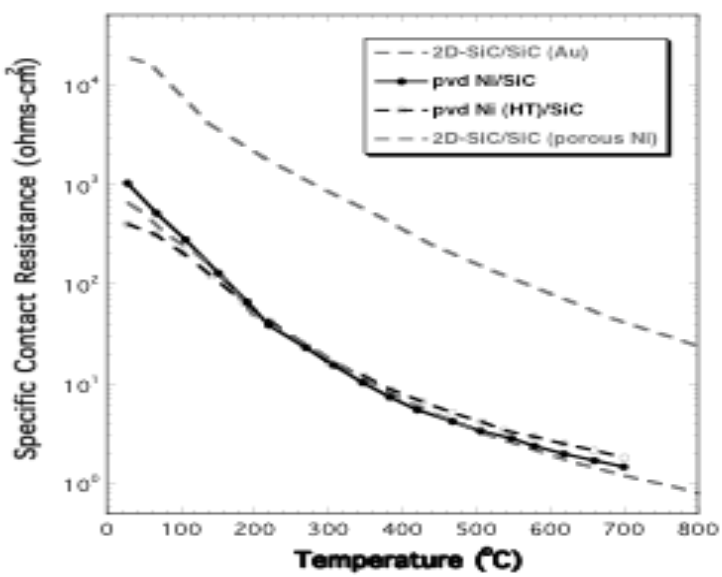

Figure 5. Specific contact resistance as a function of temperature for a monolithic CVD-SiC disc sample with as-applied or heat-treated PVD-Nickel electrodes. The grey dashed lines mark the range of R_c-values determined for various different SiC/SiC composites, but all with thin CVD-SiC seal coats upon which similar metallic electrodes were applied [15].

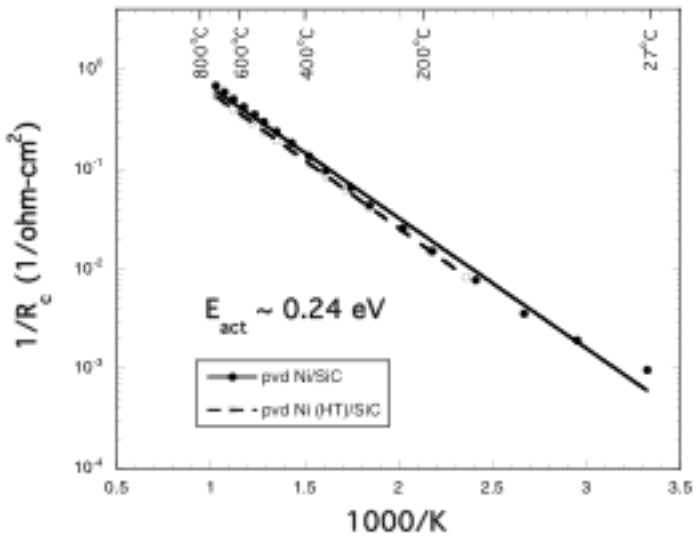

Figure 6. Inverse specific contact resistance of a CVD-SiC/Ni interface as a function of inverse temperature. The nickel electrodes were applied by PVD and also were heat-treated. The effective activation energy for both cases is 0.24 eV.

ANALYSIS AND DISCUSSION

As noted, relatively flaw free single crystal SiC is a useful high temperature, wide band-gap semiconductor. As such, its electrical conductivity is sensitively controlled by impurity doping; for example, nitrogen for n-type, boron or aluminum for p-type. Polycrystalline CVD-SiC generally is high-purity (Rohm and Haas quoted <5 ppm impurity content for our material). The CVD-SiC seal coats on SiC_f/SiC composite also should be high-purity. However, the grain-boundaries and stacking faults in polycrystalline CVD-SiC provide numerous surface energy states that prevent its use in semiconductor devices. Nevertheless, high-purity CVD-SiC exhibits some attributes of single crystal SiC semiconductor material; namely, the EC is thermally activated and it exhibits extrinsic-type conduction over a wide temperature range. For nominally high-purity CVD-SiC materials from various sources, we have measured EC-activation energies from 0.11 up to 0.25 eV in the temperature range 300-800°C [11]. For these various CVD-SiC materials, EC-values ranged from ~0.1 to 20 S/m at RT up to a range of 40 to 200 S/m at 800°C. Curves for samples with higher (lower) EC-values as a function of temperature always had lower (higher) activation energies and lower (higher) purity content, respectively. The point is, it is very difficult to get reproducible EC-values for CVD-SiC even when using 4-probe measurements on bars because the values depend so sensitively on even minor differences in impurity content and type. Getting reproducible EC-values for disc samples is even more difficult because of their unfavorable geometry factor. For this reason, in this work we chose to use only a single disc sample throughout; repolishing and reapplying different electrode types to the same CVD-SiC sample to at least have the same bulk EC and same geometry factor. As expected, we were successful in getting reproducible 4-pt. EC-values for three types of metallic electrodes: porous Ni [16], PVD-Ni, and heat-treated PVD-Ni (Figure 4). However, we had to give up microstructural examinations of any particular metal interface to preserve the disc sample.

In Figure 5, the calculated specific R_c-values for the CVD-SiC interfaced with PVD-Ni or heat-treated PVD-Ni were large, and they were almost coincident. The coincidence was a surprise. We assumed that a Schottky-type barrier (normally formed at a semiconductor/metal interface) was responsible for the relatively large values of specific R_c (~2 Ω-cm^2 at 700°C, for instance) that we have routinely observed. In fact, over the ~RT to 700ºC temperature range R_c was responsible for ~75% of the total resistance across our CVD-SiC/PVD-Ni disc sample (see Figure 3). Our intention was to reduce R_c by converting the pure PVD-Ni to NiSi with the 900ºC heat treatment and achieve an "ohmic" interface with specific R_c-values of <0.01 Ω-cm^2, as accomplished in the electronics industry. It just didn't work out that way!

At least, the specific R_c-values were reproducible over the three successive temperature cycles to 400, 550 and 700°C. This observation indicated that no chemical interactions occurred at the interface during the measurements. Even the chemical reaction converting PVD-Ni to NiSi during the heat-treatment didn't change R_c..

Our specific R_c-values matched previously obtained values for porous Ni electrodes on SiC_f/SiC composite with CVD-SiC seal coat (lower grey dashed line in Figure 5). Also, these new R_c-values are only slightly less than the R_c-values we reported for CVD-SiC interfaced with either porous nickel or sputtered gold electrodes (see Figure 1 in [16]). These relatively large values of R_c stayed the same and were stable, regardless of the type metal electrode or application method used. Apparently, our method of preparing the polycrystalline CVD-SiC surface, or the conductive properties of the CVD-SiC surface itself, was mostly responsible for the large values of R_c encountered.

It should be mentioned that we have made low R_c-interfaces with SiC_f/SiC composite by grinding off the surface layer of CVD-SiC seal coat down into the carbon-coated fiber layers [18]. In this case, the numerous direct contacts of the highly conductive carbon network to the metal electrode provided very low R_c. Similarly, Katoh et al. have quoted specific R_c-values <0.01 Ω-cm^2 for Ni electrodes applied to SiC_f/SiC (with seal coat removed) after heat treatment at >550°C [17]. Thus, 2-pt. resistance measurements are entirely appropriate for determining the transverse EC of SiC_f/SiC with carbon coated SiC fabric layers once the seal coat is removed. Minor corrections for the resistive contribution of the thin CVD-SiC seal coat are easily made [13].

In Figure 6, we examine the conductive property of the CVD-SiC/PVD-Ni interface (as applied or heat-treated) by plotting the inverse specific R_c vs. 1000/K. We assume that this inverse value is proportional to an interfacial conductance. Interestingly, the data lie on a nearly straight line from 200-700°C. For both metallic interfaces, the line slopes yield an effective activation energy of 0.24 eV, a value very close to the EC activation energy (0.21 eV) determined for our CVD-SiC sample (Figure 4). The closeness of these two conduction activation energy values suggests that the interfacial conductance truly is controlled by conduction in the near surface CVD-SiC, and not in the metallic electrode or at a Schottky-type semiconductor/metal barrier as we propose in reference [16]. This observation may be very important for the operation of an FCI made with SiC_f/SiC composite and containing the metallic liquid Pb-17Li alloy if the fairly large R_c-contribution is stable over long exposures.
A future test will examine this last point further. A new CVD-SiC/PVD-Ni disc sample will be held at first 550°C, then 700°C for a number of days to test the chemical stability of the interface using our 2/4-probe method. If that checks out, the sample will be removed from the sample

holder and resurfaced. Then a SiO_2 layer will be applied by a brief oxidation treatment of the sample in air prior to reapplying PVD-Ni electrodes and performing R_c measurements again.

CONCLUSIONS

(1) PVD-Ni metallic electrodes form an "ohmic" type interface with polycrystalline CVD-SiC with fairly high specific R_c-values. The R_c-values appear to be reproducible up to 700°C.
(2) The R_c-values do not appear to be due to a Schottky-type semiconductor/metal interfacial barrier, but do appear to be directly dependent on the near surface EC-properties of the SiC, and independent of the type of metallic nickel.

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