Journal of Nuclear Materials 386–388 (2009) 639–642

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

DC electrical conductivity of silicon carbide ceramics and composites for flow channel insert applications

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ABSTRACT

High purity chemically vapor-deposited silicon carbide (SiC) and 2D continuous SiC fiber, chemically vapor-infiltrated SiC matrix composites with pyrocarbon interphases were examined. Specifically, temperature dependent (RT to 800 °C) electrical conductivity and the influence of neutron irradiation were measured. The influence of neutron irradiation on electrical properties appeared very strong for the SiC of this study, typically resulting in orders lower ambient conductivity and steeper temperature dependency of this conductivity. For the 2D composites, through-thickness (normal to the fiber axis') electrical conductivity was dominated by bypass conduction via interphase network at relatively low temperatures, whereas conduction through SiC constituents dominated at higher temperatures. Through-thickness electrical conductivity of neutron-irradiated 2D SiC composites with thin PyC interphase, currently envisioned for flow channel insert application, will likely in the order of 10 S/m at the appropriate operating temperature. Mechanisms of electrical conduction in the composites and irradiation-induced modification of electrical conductivity of the composites and their constituents are discussed.

1. Introduction

There have been several fusion breeding blanket designs employing lead–lithium eutectic (LLE) liquid as both the breeding material and the primary or secondary coolant all assuming the use of flow channel inserts (FCI) as the insulating components in the coolant ducts. Such blanket designs were proposed in the EU advanced lead–lithium blanket concept [1], the US ARIES-ST [2], adopted in proposed US dual-cooled lead–lithium (DCLL) test blanket module (TBM) for ITER [3], the Chinese dual functional lithium–lead (DFLL) TBM [4], and the EU power plant conceptual study (PPCS) Model C [5]. The dual-coolant type blanket designs incorporating insulating FCI are attractive because they can rely on industrially more experienced steels as the structural materials while using the liquid coolant at the average temperature well beyond the operating limits for steels.

Key requirements for FCI have been identified as: (1) adequate thermal insulation, (2) adequate electrical insulation, (3) chemical compatibility with LLE, (4) leak-tightness against LLE, (5) mechanical integrity under rather severe secondary stresses, and (6) ability to maintain the above requirements throughout operation under the harsh fusion blankets conditions [6]. Such operating conditions include irradiation by fusion neutrons, developing flow conditions coupled with temperature and field gradients, and mechanical loadings such as those induced by plasma instability events. One study of magnetohydrodynamic (MHD) and thermal analysis suggests an optimum combination of thermal and electrical conductivities ~2 W/m-K and 5–100 S/m, respectively, for the US DCLL TBM [7]. The maximum operating temperatures are ~470 °C for ITER TBM and >700 °C envisioned for demonstration reactors. The insulating requirements, operating temperature, and the anticipated temperature drop across the FCI wall may significantly vary among specific blanket designs.

Silicon carbide (SiC)-based materials are presently the primary candidates as the materials for FCI, based on the proven neutron irradiation tolerance in terms of structural and mechanical integrity [8] and chemical stability in stagnant LLE at elevated temperatures [9]. Irradiation and chemical stabilities have been demonstrated for high purity, crystalline SiC in forms of monolith or continuous fiber-reinforced composites. Main technical issues remaining for SiC-based FCI are: (1) to address electrical conductivity issues, (2) to address secondary stress issues, and (3) to secure adequate thermal insulation. This work is intended to help addressing the first issue: to establish control schemes for electrical conductivity of SiC composites by identifying the conduction mechanism in composite structures and to address neutron irradiation effects on electrical conductivity in SiC composites and constituents.

2. Experimental

Materials used were chemically vapor-deposited (CVD) SiC with the manufacturer-claimed purity (except nitrogen) >99.9995%

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doi:10.1016/j.jnucmat.2008.12.237

(Rohm&Haas Advanced Materials, Woburn, MA) and continuous SiC fiber composites with two-dimensional (2D) woven-fabric architectures, chemically vapor-infiltrated (CVI) SiC matrices, and fiber-matrix interphases consisting of pyrocarbon (PyC) or PyC/SiC multilayers. SiC fibers used were Hi-Nicalon™ Type-S (Nippon Carbon Co., Tokyo) and Tyranno™-SA3 (Ube Industries, Ltd., Ube, Japan). Architectures of the composites used are summarized in Table 1. The interphase deposition and matrix infiltration were performed by Hypertherm High-Temperature Composites, Inc. (Huntington Beach, CA). The primary impurity in both CVD SiC and CVI SiC matrices are nitrogen.

Neutron irradiation was performed in flux trap positions of High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory. The neutron dose and irradiation temperature were in ranges 1.4–8.1 dpa and 400–1120 °C, respectively. An equivalence of one displacement per atom (dpa) = 1×10^{25} n/m^2 ($E > 0.1$ MeV) is assumed. The accuracy in temperature was typically ±5% of the absolute temperature in K.

Both faces of composite samples were ground flat into fabric layers prior to irradiation. Electrical resistivity measurement was performed in a high vacuum furnace in 4-probe configuration for monolithic specimens [10] or in 2-probe configuration for composite specimens in through-thickness orientation. For the 2-probe measurement, the specimen faces were metalized with nickel by heat treatment to make sufficiently low resistivity ohmic contacts [11]. The interface resistivity was confirmed to be $<1 \times 10^{-6}$ ohm-m^2 after heat treatment at >550 °C.

3. Results

Results of through-thickness electrical conductivity measurements on the non-irradiated composite materials are shown in Fig. 1. All three composites shown in Table 1 were tested in a non-irradiated condition. Total thickness of the multilayered interphase is ~500 nm and in total ~100 nm of that is occupied by PyC layers. All the materials exhibited ohmic conduction. In all three composites, with increasing temperature, electrical conductivity stays fairly constant until it starts to increase at ~400 °C. The through-thickness electrical conductivity at <~400 °C was several S/m with substantial variation by both materials and specimens, whereas it seems to converge to ~20 S/m at 1000 °C.

Fig. 2 summarizes the through-thickness electrical conductivity of irradiated composite materials and the bulk electrical conductivity of irradiated CVD SiC. The irradiated materials also exhibited ohmic conduction property. The composite specimens tested were HNLS/ML irradiated at 800 °C to 1.4 dpa and 1120 °C to 8.1 dpa. Electrical conductivity of the composite specimen irradiated at 800 °C exhibited temperature dependence similar to those for non-irradiated composites. The composite specimen irradiated at 1120 °C behaved rather anomalously, showing electrical conductivity continuously increasing from ambient to high temperatures.

The irradiated CVD SiC specimens exhibited steeply temperature-dependent electrical conductivity. Regardless of irradiation temperature in a range 400–1020 °C, all three specimens showed the same activation energy for the controlling process at >~200 °C, implying the energy level of ~375 meV for the common responsible defect. Higher irradiation temperatures resulted in lower electrical conductivity at all temperatures. The transition in slope in Fig. 2 indicates that different types of defects are governing the electrical conductivity in different temperature regimes. Ambient temperature electrical conductivity decreased from the typical non-irradiated value of 1–1000 S/m by a few to several orders as shown in Fig. 3, depending strongly on irradiation temperature. Comparison of temperature dependence at relatively high temperatures between the CVI composites and CVD SiC, controlling mechanism for electrical conductivity may be significantly different.

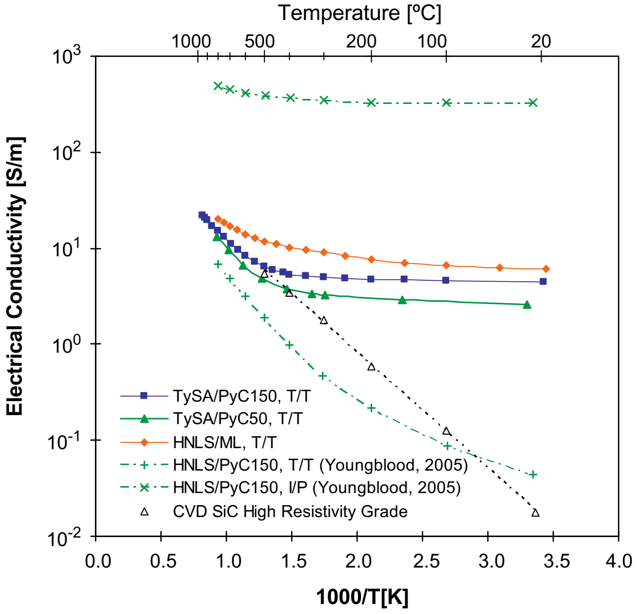

Fig. 1. Unirradiated electrical conductivity of various 2D continuous SiC fiber, chemically vapor-infiltrated SiC matrix composites. Data labels indicate fiber type (TySA for Tyranno-SA3 or HNLS for Hi-Nicalon Type-S) and interphase (PyC for pyrocarbon or ML for PyC/SiC multilayer, followed by thickness in nanometer). T/T and I/P stand for through-thickness and in-plane, respectively. Data by Youngblood were taken from Ref. [9].

4. Discussion

The temperature dependence of non-irradiated through-thickness electrical conductivity for composites qualitatively resembles that of in-plane conductivity of a very similar material as shown in Fig. 1 [12]. The in-plane conductivity is obviously dictated by bypass conduction through PyC interphase [10,12]. Moreover, the temperature dependence of through-thickness conductivity below

Table 1
Constitution and non-irradiated electrical conductivity for 2D composites.

Material designation	HNLS/ML	TySA/PyC150	TySA/PyC50
Reinforcement	SW Hi-Nicalon™ Type-S 0/90°	PW Tyranno™-SA3 0/90°	PW Tyranno™-SA3 0/90°
Interphase	$5 \times (\mathrm{PyC}_{20\mathrm{nm}}/\mathrm{SiC}_{100\mathrm{nm}})$ Multilayered	$\mathrm{PyC}_{150\mathrm{nm}}$	$\mathrm{PyC}_{50\mathrm{nm}}$
Matrix	CVI SiC	CVI SiC	CVI SiC
Electrical conductivity (20 °C) [S/m]			
In-plane, estimated interphase contribution	250	550	180
In-plane, experiment	200	360	150
Through-thickness, experiment	5.5 (±0.8 for 8 samples)	4.5	2.6
Efficiency of through-thickness bypass	2.8%	1.2%	1.7%

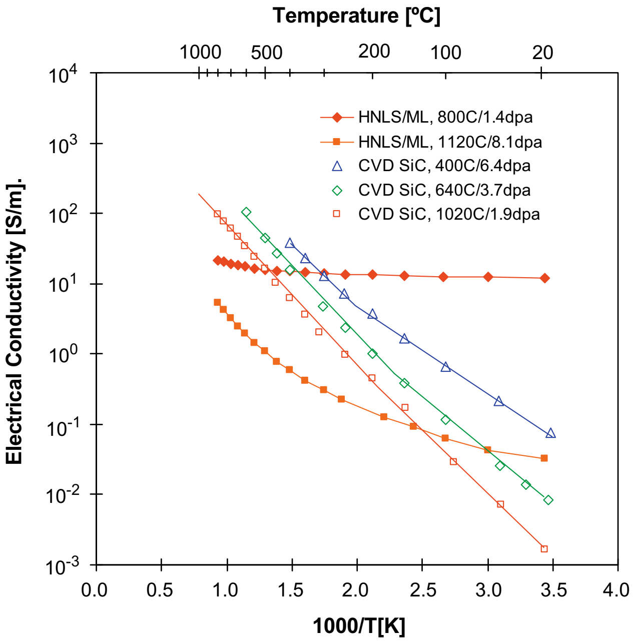

Fig. 2. Neutron-irradiated electrical conductivity of 2D Hi-Nicalon Type-S SiC fiber, chemically vapor-infiltrated SiC matrix, pyrocabon/SiC multilayered interphase composite and chemically vapor-deposited SiC. Data label indicates material, irradiation temperature and dose.

~400 °C is consistent with those for typical near-isotropic carbon materials [13], but is very different from those for typical CVD SiC. Therefore, one can conclude that the through-thickness conduction in the low temperature regime is primarily through the interphase.

In 2D composites, it can be assumed that ~1/2 of the interphase film is oriented in favor of through-thickness bypass conduction, but a small fraction is contributing to the macroscopic conduction due to the poor interconnection. Considering ~1/2 of the interphase film also contributes to in-plane conduction in one of the fiber directions, through-thickness interphase bypass efficiency may be defined as $\eta \equiv 2\sigma_t/f_i\sigma_i \approx \sigma_t/\sigma_{ip}$, where σ and f are electrical conductivity and volume fraction, the subscripts, t, ip, and i, denote through-thickness, in-plane, and interphase, respectively. The η values should be dependent on interphase thickness and packing density of fabrics, and were estimated to be 1–2% for the present monolayered interphase and ~3% for the multilayered interphase (Table 1). The difference in η values between the two monolayered interphase composites is considered within a reasonable range of scatter, considering the general sensitivity of interconnecting probability to the packing density of conducting media in the vicinity of the critical packing density [14]. Obviously, the multilayered interphase gives a higher chance to interphase for transverse bridging over multiple fibers, because the outer PyC layers tend to envelope multiple fibers.

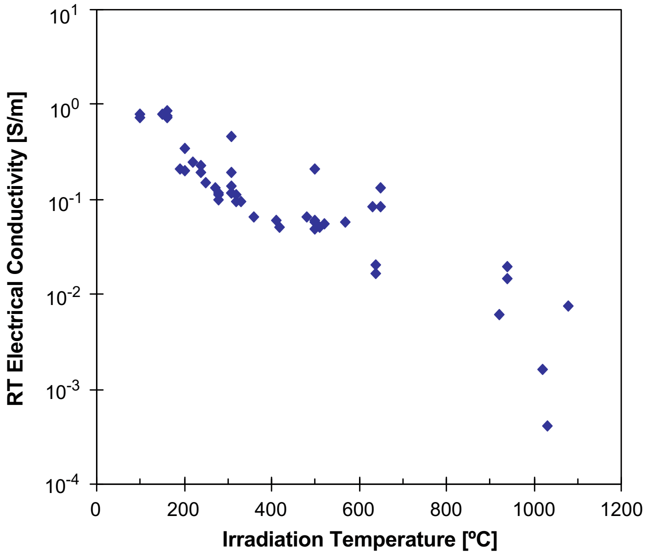

Fig. 3. Effect of neutron irradiation temperature on ambient temperature electrical conductivity of high purity, chemically vapor-deposited SiC.

In the high temperature regime, steeper temperature dependence obviously indicates the dominance of contributions from SiC constituents. Thus, these composites can be considered a parallel circuit of imperfect interphase network and SiC. A transition to the SiC-dominated conduction occurs when the apparent conductivity through SiC becomes comparable with that of the interphase bypass. The transition temperature obviously depends not only on the interphase bypass efficiency but also on electronic properties of SiC, which vary by many orders with impurity elements and concentrations.

Meanwhile, the composite makes a serial circuit of 'fabric layer composite' discussed above and SiC when: (1) the composite faces are not ground into fabric layers, (2) any two fabric layers are electrically separated with SiC matrix, or (3) composite is over-coated with SiC. In such cases, SiC constituents dictate electrical conduction at all temperatures. A typical example is through-thickness conduction of the HNLS/PyC composite in Fig. 1 [12].

Conduction in non-irradiated CVD SiC at ambient or higher temperatures is governed by non-primary impurities. Neutron irradiation lowered electrical conductivity very significantly, Fig. 2. This is consistent with the observation by Kanazawa et al. [15] who reported reduction in both carrier density and mobility after low dose neutron irradiation to N-doped 6H and 4H SiC, and may be reasonable considering the ionic properties of Frenkel defects in SiC [16]. However, the roles of radiation defects are not limited to carrier trapping, because irradiation at lower temperatures with higher defect concentration resulted in higher ambient electrical conductivity. The electrical conduction at elevated temperatures is likely to be governed by defects of single type, with an electronic level ~375 meV, regardless of irradiation temperature. Considering the irradiation temperature range, the responsible defect must be readily produced at 400 °C, stable at 1020 °C, and stable in configuration between the two temperatures. These conditions eliminate from possibility either interstitial type, the Si vacancy, and perhaps interstitial clusters. The electronic level coincides with the defect level of V_{Si}–V_C in 3C–SiC, 0.38 eV above E_v, obtained by Li and Lin-Chung [17]. Importantly, non-irradiated and irradiated SiC are very different electronic materials because all of carrier density, carrier mobility, and electronic level of controlling feature are different.

Neutron irradiation in HFIR produces small concentration of transmutation products in SiC such as P from ^{30}Si. The effect of transmutation doping on as-irradiated electronic properties is considered negligible, because the concentrations of transmutation dopants are very small compared to the those of self defects [18]. However, this may not be the case for fusion neutron spectrums, by which much greater amount impurities such as Al, Mg, and Be will be produced [19].

The two irradiated composite specimens exhibited dissimilar temperature dependence of through-thickness electrical conductivity. The electrical conduction in the specimen irradiated at 800 °C is obviously dominated by the interphase bypass at most temperatures, whereas the one irradiated at 1120 °C likely involves the interphase network which is electrically detached in the through-thickness direction. The conduction mechanism of the 1120 °C-irradiated specimen is also dissimilar from the irradiated CVD SiC samples, suggesting influences of much higher impurity concentrations in the CVI SiC matrices or contributions from the interphase and/or fibers.

The 800 °C-irradiated composite specimen exhibited electrical conductivity slightly higher than that for non-irradiated composites. PyC interphases in CVI SiC/SiC are often microstructurally similar to glassy carbon rather than near-isotropic graphite. These results seem reasonable, considering the reported electrical conductivity increase by neutron irradiation for glassy carbon [20]. However, an electrical conductivity decrease is typically observed following neutron irradiation of graphitic carbon [21], being consistent with the observed decrease in in-plane electrical conductivity for irradiated uni-directional CVI SiC/SiC with PyC interphase [10]. The effect of neutron irradiation on electrical conductivity of PyC interphase in SiC/SiC remains unclear, however, it is not as dramatic as of SiC. Therefore, tailoring the through-thickness electrical conductivity of 2D composites by appropriately engineering the interphase structure and configuration is considered feasible.

5. Conclusions

The electrical conduction mechanism in 2D woven-fabric SiC/SiC composites with conductive PyC interphase was identified; (1) through-thickness conduction within the stacked fabric layers is typically accommodated by the interphase bypass network at relatively low temperatures, (2) over-coating and/or internal layers of semiconducting SiC, if present, add serial resisters to the through-thickness circuit, (3) in-plane conduction is governed by conduction through axial interphases at relatively low temperatures, and (4) conduction through SiC constituents dominates at high temperatures.

Neutron irradiation influences the composite electrical conductivity by modifying electrical properties of both PyC and SiC constituents. Electrical conductivity of PyC interphase is relatively insensitive to irradiation and may decrease or increase, depending on its starting microstructure. Irradiated SiC is electronically a different material from non-irradiated SiC. Semiconducting properties of SiC become governed by radiation defects after neutron irradiation, resulting in steeper temperature dependence of electrical conductivity in a temperature range of interest. The role of nuclear transmutation on electrical conductivity of irradiated high purity SiC is likely negligible in fission neutron irradiation. However, transmutation effects on electronic properties are potential critical issues for SiC-based FCI for DEMO, which will receive high dose irradiation of fusion neutrons.

Through-thickness electrical conductivity of neutron-irradiated 2D SiC/SiC with thin PyC interphase will likely be in the order of 10 S/m in the typical operating temperature range for FCI. Applying SiC over-coating will be beneficial in reducing electrical conductivity at relatively low temperatures at the expense of more significant irradiation effect and steeper temperature dependence. Electrical conductivity tailoring by engineering interphase structure and configuration in composite materials is considered feasible.

Acknowledgement

The authors are thankful to Dr R. Stoller for providing useful comments on the manuscript. This research was sponsored by the Office of Fusion Energy Sciences, US Department of Energy (DOE), under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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