Report DE/FG02/07ER46364-5

1. DOE award number, name, and address of the recipient (Institution).

DE-FG02-07ER46364

Clemson University
Office of Sponsored Programs
300 Brackett Hall
Clemson, SC 29634

2. Project Title and name of the Principal Investigator and Project Director (if applicable).

Title: "Surface Anchoring of Nematic Phase on Carbon Nanotubes: Nanostructure of Ultra-High Temperature Materials"

PI: Prof. Amod A. Ogale

3. Date of the report and award period covered by the report with approved budget amount.

27 April 2012
1/2007 – 1/2012 (including 2-yr no-cost extension)
DOE budget: $ 450,000
(Clemson University cost-share required: $ 45,000)

4. Participating National Laboratory(s) if applicable.

Oak Ridge National Lab
(Carbon Materials Group)

5. A brief description (abstract) of project goal and objective. (Limit: 5,000 characters)

Nuclear energy is a dependable and economical source of electricity. Because fuel supply sources are available domestically, nuclear energy can be a strong domestic industry that can reduce dependence on foreign energy sources. Commercial nuclear power plants have extensive security measures to protect the facility from intruders [1]. However, additional research efforts are needed to increase the inherent process safety of nuclear energy plants to protect the public in the event of a reactor malfunction. The next generation nuclear plant (NGNP) is envisioned to utilize a very high temperature reactor (VHTR) design with an operating temperature of 650-1000°C [2]. One of the most important safety design requirements for this reactor is that it must be *inherently safe*, i.e., the reactor must shut down safely in the event that the coolant flow is interrupted [2]. This next-generation *Gen IV* reactor must operate in an inherently safe mode where the off-normal temperatures may reach 1500°C due to coolant-flow interruption. Metallic alloys used currently in reactor internals will melt at such temperatures. Structural materials that will not melt at such ultra-high temperatures are carbon/graphtic fibers and carbon-matrix composites. Graphite does not have a measurable melting point; it is known to sublime starting about 3300°C. However, neutron radiation-damage effects on carbon fibers are poorly understood. Therefore, the goal of this project is to obtain a fundamental understanding of the role of nanotexture on the properties of resulting carbon fibers and their neutron-damage characteristics.

Although polygranular graphite has been used in nuclear environment for almost fifty years, it is not suitable for structural applications because it do not possess adequate strength, stiffness, or toughness that is required of structural components such as reaction control-rods, upper plenum shroud, and lower core-support plate [2,3]. For structural purposes, composites consisting of strong carbon fibers embedded in a carbon matrix are needed. Such carbon/carbon (C/C) composites have been used in aerospace industry to produce missile nose cones, space shuttle leading edge, and aircraft brake-pads. However, radiation-tolerance of such materials is not adequately known because only limited radiation studies have been performed on C/C composites, which suggest that pitch-based carbon fibers have better dimensional stability than that of polyacrylonitrile (PAN) based fibers [4]. The thermodynamically-stable state of graphitic crystalline packing of carbon atoms derived from mesophase pitch leads to a greater stability during neutron irradiation [5]. The specific objectives of this project were: (i) to generating novel carbonaceous nanostructures, (ii) measure extent of graphitic crystallinity and the extent of anisotropy, and (iii) collaborate with the Carbon Materials group at Oak Ridge National Lab to have neutron irradiation studies and post-irradiation examinations conducted on the carbon fibers produced in this research project.

6. A description of accomplishments (no more than about 5 pages)

Experimental:

- Rheological experiments: Extensive rheostructural measurements were performed initially to understand the orientation of the discotic mesophase by shear-induced alignment.
- Dispersion and Fiber Spinning: CNTs were dispersed into mesophase pitch via melt mixing using a twin-screw extruder at 305°C under nitrogen atmosphere. Pure and CNT dispersed pitches were extruded through a 12-hole spinneret with a diameter of 150 μm into thin fibers by a uniaxial drawing process at 315°C.
- Heat Treatment: As-spun fibers were thermo-oxidatively stabilized in an air convection oven preheated at 205°C for 20~40 hours depending upon fiber diameter. At this step, fibers obtain about 8~10 % average weight gain sufficient to make thermoset fiber. Stabilized fibers then carbonized and graphitized in an *Astro 1100* furnace under a helium atmosphere up to a maximum temperature of 2400-2540°C.
- Morphological studies: Microstructure of fibers was extensively studied using a *Hitachi S-4800*, field-emission scanning electron microscope (FESEM). Nano-texture was examined using *Hitachi H-9500* transmission electron microscope (TEM). Anchoring behavior of graphene layer and development of orientation at the edge of CNTs was studied by using image analysis software, *Image-J* (shareware) and *Photoshop* (*Adobe*). Wide-Angle X-ray Diffraction (WAXD) was conducted to study crystalline structure such as d_{002} spacing and stack height (L_c), and stack width (L_a) of the carbon fibers, a X-ray (*Rigaku-MSC*, Houston, TX) diffraction.
- Extensive single-filament testing was conducted for electrical resistivity (ρ) using a four-point probe technique in conjunction with a *Keithley 580* micro-ohmmeter and tensile using MTI Phoenix machine.
- A series of carbon fibers were provided to Dr. T. D. Burchell (ORNL collaborator) to conduct irradiation studies to assess the effects of neutron damage on the fibers structure and dimensions. Four of the fibers where commercial products, namely, pitch based K1100, P100, and P25 fibers, along with one PAN (T300) fiber. The remaining six experimental fibers were spun from ARHP mesophase pitch. Four of the ARHP mesophase fibers additionally contained multi-walled carbon nanotube at 0.1 or 0.3 wt%. The experimental fibers were heat treated at two temperatures, 2000 or 2400°C.
- Neutron irradiation was successfully conducted in the target region of the HFIR (High Flux Isotope Reactor) by ORNL personnel under the direction of Dr. Burchell. The fibers were encapsulated in a graphite carrier with precisely machined hole to accommodate the fibers, and threaded and caps to retain the fibers during irradiation. The graphite holder was contained in a "rabbit" capsule. Two capsules were constructed and irradiated attaining neutron damage doses of ~6.6 and 10.2 displacements per atom at an irradiation temperature of 900 ± 25°C. Each capsule additionally contained two SiC temperature monitors which were read to ascertain the actual irradiation temperature.

Results and Discussion: ***Pre-irradiation Properties***

- A severe, line-origin radial orientation was observed at different shear rates, irrespective of the capillary size. Presence of vortices in the converging region of flow, such as that encountered during fiber spinning, was detected [6].
- The addition of 0.1~0.3wt% MWNTs to an ARHP mesophase pitch precursor further confirmed the disruption of the severe, radial microstructure of the resulting carbon fibers, and also showed a thermal conductivity enhancement effect.
- Tables 1-3 display the mechanical and electrical properties of pure and nanomodified carbon fibers at various carbonization temperatures. Lower heat treatment temperature help retain a high strain-to-failure of over 1% (in Table 1) that is important for safe handling of fibers during composite processing
- As expected, fibers carbonized at higher temperature (2400°C) are stronger, less flexible, but highly conductive.
- The reduced anisotropy, due to surface-anchoring of mesogens on MWNTs, is accomplished while still retaining a high graphitic content that can help toward neutron damage tolerance
- Figure 1 displays tensile properties for the pure and nanomodified carbon fibers at various carbonization temperatures, and SEM micrographs of the carbonized fibers are listed as insets. It is also showing that the strain to failure decreases as carbonization temperature increases. As displayed in the series of images, the radial graphitic structure was highly developed as carbonization temperature increased.
- Figure 2 showed SEM micrographs of 0.3wt% SPU_L modified carbon fibers HT at 600°C. In the first two cross-sectional SEM micrographs, bundle of CNTs was captured and magnified, and the last TEM micrograph is clearly showing multi-wall structure of SPU_L nanomodifier.

Table 1 Properties of pure, 0.3wt% SPU_L, and 0.3wt% SES_S modified carbon fibers HT at 1500 and 2600°C.

Temperature [°C]		Diameter [μm]	Tensile strength [Gpa]	Apparent Modulus [Gpa]	Strain-to-Failue [%]	Electrical resistivity [μΩ·m]	Thermal conductivity prediction* [W/mK]
1500 °C	0.0wt% AR CF	9.1 ± 0.5	2.3 ± 0.6	206 ± 30	1.1	9.6	66
	0.3wt% SPU_L CF	11.6 ± 0.3	0.4 ± 0.1	175 ± 48	0.2	–	–
	0.3wt% SES_S CF	8.7 ± 0.3	0.6 ± 0.2	254 ± 65	0.3	–	–
2400~2540 °C	0.0wt% AR CF	8.7 ± 0.5	2.5 ± 0.7	495 ± 75	0.4	3.0	494
	0.3wt% SPU_L CF	10.1 ± 0.4	0.9 ± 0.2	371 ± 68	0.2	2.4	585
	0.3wt% SES_S CF	7.0 ± 0.5	1.2 ± 0.5	512 ± 95	0.2	2.1	651

* Lavin-Issi correlation: thermal conductivity = 440,000/(ρ+258)-295 where ρ is electrical resistivity in [μΩ·cm]

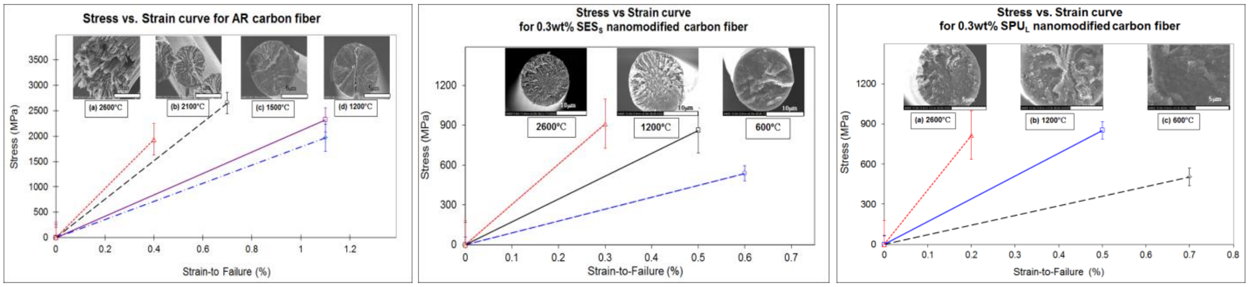

Figure 1 SEM (FESEM – Hitachi S4800) micrographs and Stress-strain curves for the pure AR and 0.3wt% SES$_S$ and SPU$_L$ CNTs modified carbon fibers heat treated at various temperatures.

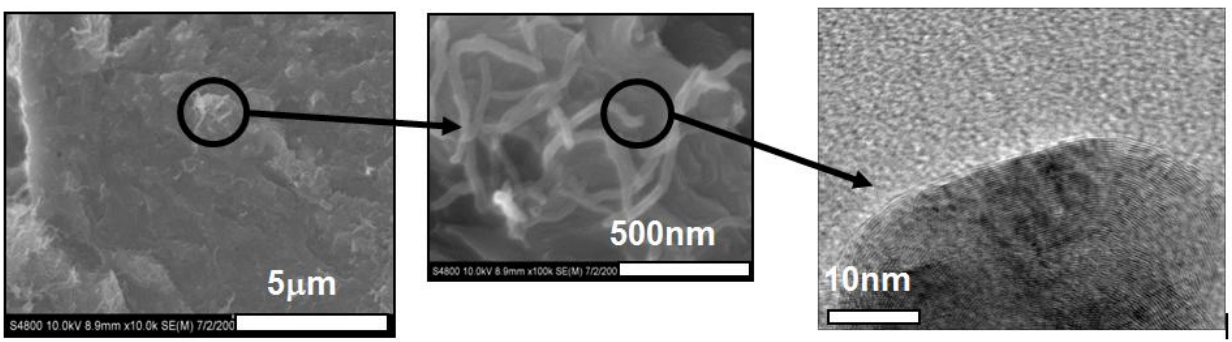

Figure 2. A sequence of SEM and TEM micrographs to systematically examine the texture of a 0.3wt% SPU$_L$ modified carbon fiber heat treated at 600°C.

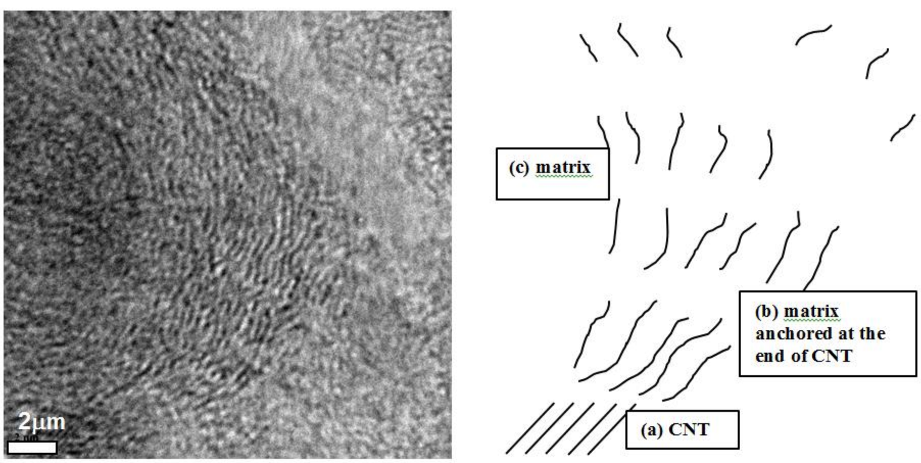

Figure 4. TEM micrographs of 600°C treated 0.3wt% SES$_S$ modified carbon fiber showing anchoring behavior at the end of CNTs

Post-Irradiation Analysis

The SiC monitor ER data indicate an irradiation temperature of 900 ± 10 °C [7]. After irradiation experiments, individual fiber bundles were examined for dimensional changes, and following conclusions drawn [7]:

- All fiber samples shrank during irradiation, confirming the crystal a-axis shrinkage.
- The greater shrinkage for larger neutron doses is consistent with literature studies on highly oriented pyrolytic graphite and nuclear graphite.
- For commercial K1100 fibers, reduced shrinkage correlated with increased modulus/conductivity, i.e., with improved crystallinity. Again the role of enhanced fiber crystallinity in increasing stiffness and conductivity, and minimizing irradiation induced axial shrinkage was confirmed. In contrast, T300 PAN fibers exhibited greater shrinkage than all of the pure pitch-based carbon fibers. This behavior may be explained by the fact PAN fibers cannot form a graphitic structure and possessed the least ordered crystallographic structure.
- For nanomodied carbon fibers, there is less shrinkage in the fibers heat treated at 2400°C compared with 2000°C. For such fibers, the novel observation is that the shrinkage does not always increase with dose when nanotubes are incorporated, suggesting a possible improvement in crystallinity or nanotexture derived from a sufficient fraction on nanotubes. Further studies of the structure of the carbon fibers by XRD and SANS will be conducted at ORNL to help elucidate the mechanisms associated with irradiation damage.

References

[1] www.nei.org website for Nuclear Energy Institute, 1776 I Street, NW, Suite 400, Washington, D.C. 20006-3708

[2] W. R. Corwin, *Advanced Reactor, Fuel Cycle, and Energy Products Workshop for Universities*, Workshop for Universities, Gaithersburg, MD, June 16-17, 2005

[3] R. L. Klueh, P. J. Maziasz, D. T. Hoelzer, N. Hashimoto, I. S. Kim, and K. Miyahara, "Tensile and creep properties of an oxide dispersion-strengthend ferritic steel", 10th International Conference of Fusion Reactor Materials, October 14-19, 2001, Baden-Baden, Germany, to be published in *Journal of Nuclear Materials*

[4] J. P. Schaffer, A. Saxena, S. Antolovich, T. H. Sanders, and S. B. Warner, *The Science and Design of Engineering Materials*, 2nd Ed., WCB-McGraw Hill, Boston, 1999

[5] T. D. Burchell, "Radiation effects in graphite and carbon based materials", MRS Bulletin, 22(4), 29-35 (1997)

[6] S. Kundu and A. A. Ogale, "Rheostructural Studies of a Discotic Mesophase Pitch at Processing Flow Conditions", Rheologica Acta, **49**(8), 845-854, 2010

[7] T. D. Burchell and A. Ogale, "Neutron Irradiation Induced Changes in the Microstructure of Carbon And Graphite Fibers", *submitted* Journal of Nuclear Materials, 2011

7. List of Publications (acknowledging support from DOE-EPSCoR grant):

1. Rebecca Alway-Cooper, Merlin Theodore, David P. Anderson, Amod A. Ogale*, “Thermal conductivity measurements for carbon fibers”, Proceedings of CARBON 2008, Nagano, Japan, P0466

2. S. Kundu, Dana Grecov, Amod A. Ogale*, and Alejandro D. Rey*, Shear flow induced microstructure of a synthetic mesophase pitch, Journal of Rheology, 53(10), 85-113, 2009

3. S. Kundu and A. A. Ogale, “Rheostructural Studies of a Discotic Mesophase Pitch at Processing Flow Conditions”, Rheologica Acta, **49**(8), 845-854, 2010

4. S. Lee and A. A. Ogale*, “Nanotextured Carbon Fibers For Next-Generation Nuclear Energy Production”, Proceedings of ISAF 2010, International Symposium on Advanced Fibers Fukui, Japan, 2010, pp. 15-17.

5. T. D. Burchell and A. A. Ogale, “Neutron irradiation induced changes in the microstructure of carbon and graphite fibers”, Proc. International Conference on Fusion Reactor Materials, *ICFRM-15*, Charleston, October 2011;

6. Y. P. Jeon, R, Alway-Cooper, M. Morales, and A. A. Ogale*, “Carbon Fibers”, Book Chapter for Handbook of Advanced Ceramics, 2nd Edition, Elsevier, Eds. S. Somiya and M. Kaneno, 2011

7. T. D. Burchell and A. Ogale, “Neutron Irradiation Induced Changes in the Microstructure of Carbon And Graphite Fibers”, *submitted* Journal of Nuclear Materials, 2011

8. Y. P. Jeon, T. D. Burchell, and A. A. Ogale*, “Anchoring of Discotic Mesophase on Carbon Nanotubes”, *to be submitted* Carbon

8. List of Personnel:

Post-Doctoral Associates: Dr. S. Lee (~90%); Dr. Y. P. Jeon (~25%)

PhD students: Rebecca Alway-Cooper (~40%); Santanu Kundu (0%); Daniel Sweeney (0%), Marlon Morales (~10%)

A number of undergraduate research assistants were provided training to do carbon testing and characterization (individuals spent variable time on the project depending upon course load, and devoted nominally 100 hours or higher): Matt Vyrostek, Michael Martin, Ben Donner, Peter

Beshay, Taylor Clasen, Melissa Clevenger, Njeri Gachago, Darius Hilliard, Azikewe Hooker, Shameka Murphy, Jaki Redden

Senior Honors Thesis students: Mitchell Huff (course credit; not funded); Jonathon Cribb (50%; honors course credit not funded)

Diversity

Personnel included 5 minority students (African-American) and three women.

Presentations and lab tours of Clemson Carbon Fiber Lab was conducted for minority graduated high school students doing summer workshop at Claflin College through South Carolina Alliance for Minority Participation, June 12, 2009

9. List of Other Support (Current and Pending, federal and non-federal):

Sponsor, Project Title; Funding; Project Duration; relationship of project to DOE-EPSCoR effort

- Army Research Lab through SERDP, "Carbon Fibers Derived From Sustainable Precursors"; $ $699,998; 4/2009 -3/2013; Relationship - no direct relationship with DOE-EPSCoR effort; project deals with carbon fibers derived from sustainable, bio-based precursors with low graphitic content
- Advanced Thermal Technolgies/NSF, "Rheological Characterization and Melt-Spinning of Industrial Mesophase Pitch Precursors, $ 82,870 (Ogale credit: $ 82,870), 7/2010 – 6/2012; Relationship: industrial collaboration on high thermal conductivity carbon fibers derived from liquid crystalline pitch for thermal management
- ERG s.p.A - *Carbonization/Graphitization and Characterization of Pitch-based Carbon Fibers;* $ 37,500; 04/01/08-05/25/12; Relationship – industrial grant; potential commercial source for mesophase pitch for highly graphitic carbon fibers
- Fats and proteins Research Foundation (FPRF/ACREC), "*Extrusion & Molding of Animal Coproduct-based Proteins for Geostructural Applications",* $39,940; 07/01/08-06/30/12; Relationship – No relationship with DOE-EPSCoR project
- United Soybean Board, "Continuous Calendaring-Extrusion Route for Melt-Processing of Films and Fibers Derived from Soy Proteins", $ 119,480; 7/2011 -6/2012; Relationship – No relationship with DOE-EPSCoR project
- NSF, "ERC-Small Business: Micropatterning of Film Extrusion Die Surfaces", $ 200,000, 10/2011-9/2013, Relationship: No relationship with DOE-EPSCoR project

American Ceramic Technologies, "Tungsten Powder-Filled Polyethylene Fibers and Nowoven Webs", $ 15,000, 7/2011-6/2012, Relationship: No relationship with DOE-EPSCoR project

Pending:

"Mechanism of Neutron Damage in Carbon Fibers", Pre-proposal from ORNL submitted in response to Program Announcement LAB 12-603, Topical Area (3) Divertor plasma facing components, PI: Dr. Timothy D. Burchell, Group Leader, Carbon Materials; Collaborator:

Clemson PI Amod A. Ogale; (Total Proposed Budget: $ 750,000, Clemson budget: $ 165,000). This pre-proposal is directly motivated by the DOE-EPSCOR grant.

10. Cost-Status:

Category	**Budgeted** Amount	**Expended** Amount
Graduate stipend	$61,122	$60,582
OTHER (Tuition, supplies, etc)	$30,315	$30,782
WAGES (undergraduate and post-doctoral)	$87,733	$117,179
FRINGE	$51,254	$47,920
Participant Support	$2,368	$2,368
TRAVEL	$10,000	$3,562
Faculty salary	$64,088	$44,486
Total Direct Costs	$306,880	$306,880
Indirect Costs	$143,120	$143,120
DOE TOTAL	**$450,000**	**$450,000**
Clemson Cost-sharing	$45,000	$52,083

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