The surface chemistry and topography of carbon fiber surfaces have been probed using a variety of surface analytical tools in order to understand the processes that effect the oxidation of carbon-carbon composites. Core and Valence Band X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and other techniques were used to monitor the surface chemistry and topography of carbon fibers, with and without oxidation protective coatings. A special high vacuum apparatus was built to study surface oxidation at elevated temperatures in a chamber directly attached to a surface spectrometer. The valence band XPS spectra were interpreted by calculations that modelled the fiber surface and interfacial chemistry. The results of the project provide a better understanding of the interfacial chemistry associated with carbon fiber surface oxidation and protection. Protective films for the outer surface of the composite, and coupling agents that improve the oxidation resistance of the carbon fiber-carbon matrix interface are reported.
Final Report
for
Grant F49620-92-J-0144

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Objectives

Grant F49620-92-J-0144 was awarded to support a project that used a novel combination of core and valence band X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and other techniques to monitor the surface chemistry associated with carbon-carbon composites and their oxidation protection. The approach is aimed at developing an understanding from which better oxidation protection approaches can be developed.

Status of Effort

The project has achieved the goals set in the original proposal, with details given in the next section. A special apparatus for treating carbon fibers with protective coatings and for producing "mini" carbon-carbon composites has been developed and used. Surface chemical information has been obtained from various surface analytical tools, especially core and valence band photoemission. These studies have allowed the interfacial chemistry to be identified, and this interfacial chemistry related to the oxidation behavior. X-alpha and ab initio calculations, performed on IBM RISC/6000 workstations, allowed the valence band XPS region to be interpreted, and greatly assisted its use in detecting subtle differences in surface film composition and in investigating interface chemistry. The work has shown how important chemical considerations are when the question of carbon-carbon oxidation protection is considered.

Accomplishments/New Findings

All the papers listed below have been submitted to AFOSR, thus detailed information about this work is readily accessible in published form. The description below provides a summary of this work which relates these studies to the overall goals of the project.

Progress under the grant

Most of the goals of the initial proposal have been achieved. So far, twenty four papers have been published\textsuperscript{1,24}, and two papers are in preparation.\textsuperscript{25,26} The most notable accomplishments on the planned program of study were in the following areas:

\textit{Analytical Probes}: The range of analytical probes of surface chemistry and topography has been extended from that originally envisaged. Core and valence band XPS, XRD and scanning electron microscopy (SEM) has been used as originally planned. In the second year of the project the principal investigator (PI) placed an electron microprobe into operation. This apparatus serves as an SEM, but also has both energy dispersive and wavelength dispersive X-ray capabilities. An important feature of this equipment is the ability to map even light elements (C, O, and N) with high intensity by using a new state-of-the-art synthetic crystal in the monochromator for X-radiation from light elements. We have shown that this allows elemental mapping of the surface of carbon fibers, with and without potentially protective films on them.\textsuperscript{15,17} Recently (since January 1994) the PI has had the use of an AFM and STM apparatus, purchased with funds from ARO for Professor
Klabunde's research. This has allowed us to obtain effective AFM pictures of carbon fibers with and without protective films on them, showing significant topographical changes.\textsuperscript{21}

\textit{Construction and Operation of a Special High Vacuum Apparatus:} The grant provided equipment for the construction of a high vacuum apparatus, attached to one of our XPS instruments, that allows carbon fibers to be coated with protective films and organic materials for carbonization to make a "mini" carbon-carbon composite.\textsuperscript{15} The chamber allows a sample to be treated in various gas atmospheres or at different vacuum levels in the chamber. Carbon fiber samples can be heated to over 2000°C by passing up to 20A of dc current through the fiber, and the temperature of the fiber can be monitored by an optical pyrometer mounted just outside the viewport of the chamber. The gas phase in the chamber can be analyzed by a quadrupole mass spectrometer. The sample can also be bombarded with an ion gun.

\textit{Reporting Accurate XPS Data for Carbon and Carbon Fibers:} Thirteen papers\textsuperscript{2-14} have been published in \textit{Surface Science Spectra} that report accurate XPS data for carbon and carbon fibers. \n
\textit{The Investigation of Potentially Oxidation Protective Films:} Five types of potentially protective films have been investigated to date. Oxidized magnesium and aluminum films have been prepared on carbon fiber surfaces in the special apparatus discussed above.\textsuperscript{15} These films have been shown to adhere to the fiber surfaces even at high temperatures (1300°C). The three other types of film studied have been prepared externally by chemical vapor deposition (CVD) using an apparatus in the KSU chemical engineering department. Films of Si\textsubscript{3}N\textsubscript{4} have been found to be susceptible to cracking, as a result of heating, from argon ion and oxygen ion etching, and by sample biasing.\textsuperscript{17} Films of SiC and SiO\textsubscript{2} appear to be less susceptible to cracking.\textsuperscript{21} We have examined the preparation of aluminum nitride films by nitrogen ion implantation\textsuperscript{23} and hope to be able to develop aluminum nitride protective films on carbon fibers in future studies. We are currently examining a new boron-silicon-nitrogen material that has been developed by Bayer. This work is being carried out with the support of Bayer, and they have provided us with the necessary material to treat fiber surfaces. A special apparatus has been developed to coat the fibers, and we have successfully coated a number of fiber surfaces, and performed surface analysis on these films. We hope to publish this study soon, and a preliminary report of this work has been submitted to AFOSR.

\textit{Monitoring Resistance to Oxidizing Environments:} Oxygen ion etching has been used as an oxidizing environment to investigate the effect of oxidation on fibers coated with potentially protective films. The extent to which a particular coating can cause enhanced oxidation resistance has been examined by investigation of the mass loss resulting from heating in air using thermal gravimetric analysis (TGA).\textsuperscript{16,20} The extent to which this method is effective has also been monitored by taking into account effects such as oxidative attack along the fiber axis, and through cracks in the protective films.

\textit{Improvement of Carbon Composite Preparations by Enhancement of Interfacial Chemical Interactions:} We have investigated methods for enhancing the interaction of carbon fibers with the resin precursor. The effect that surface treatment has on the fibers has been monitored\textsuperscript{16,20} and it has been found that prior fiber surface treatment leads to better oxidation resistance of the resulting carbon-carbon composites. Interfacial chemical reactions between the treated fiber and precursor resins (phenolic resins) have been examined, and the chemical interaction enhanced by using coupling agents that react with both the surface treated fiber and the phenolic resins. The interface chemistry has been monitored by core and valence band XPS using a thin film technique.\textsuperscript{16,20} We have found titanium alkoxide to be a very effective coupling agent that can lead to a substantial
improvement in oxidation protection.\textsuperscript{22} We found an unusually high affinity of oxidized surfaces for sodium ions during these studies.\textsuperscript{24}

**Building up a "mini" Carbon-Carbon Composite:** We have been able to prepare a "mini" carbon-carbon composite on magnesium oxide and aluminum oxide protected fibers. This was achieved by coating the magnesium or aluminum oxide covered fibers (prepared in the special apparatus described above) with a phenolic resin (whose thickness was controlled by dipping the fibers into a solution of resin), and then carbonizing the coated fibers by electrical heating in the special apparatus in the presence of an inert atmosphere. These experiments have shown that it is possible to get a uniform coverage of carbon over the coated fibers, and illustrate how this approach provides a "step-by-step" probe of the carbon-carbon composite preparation process.\textsuperscript{25}

**Calculations:** Many calculations have been performed in order to interpret the core and valence band spectra of resin precursors and the interface between these resin precursors and surface treated carbon fibers.\textsuperscript{16,20} The calculations have shown how core and valence band photoemission can reasonably detect changes in the chemistry at this interface region, allowing cases where chemical interaction has occurred to be identified. Most calculations have been carried out using \textit{ab initio} Hartree-Fock calculations, which we have used successfully in the study of other polymer systems. Valence band photoemission has been found by us and others to be especially valuable in this area.

**Personnel Supported**

The grant has supported a number of graduate students and postdoctoral fellows.

**Faculty**

Professor Peter M.A. Sherwood

**Ph.D. Students supported**

Tiejun Wang (Ph.D.) 1995 (Jan)
Michael Rooke (Ph.D. expected in May 1996)
Nathan Haercraft (1st year Ph.D. student)
Hema Viswanathan (1st year Ph.D. student)

**Postdoctoral fellows supported**

Dr. Yaoming Xie (1992-1994)
Dr. Cara Weitzsacker (1994)
Publications

Publications acknowledging support from F496620-92-J-0144


Interactions/Transactions

a) Participation/presentations at meetings, conferences, seminars, etc.

The work discussed at these meetings has in most cases been either solely or partly concerned with this project.

March 27th 1992  Department of Chemistry, University of Illinois, Urbana-Champaign. Invited Seminar

April 17th 1992  Department of Chemistry, University of Southern Illinois at Carbondale. Invited Seminar

April 24th 1992  Department of Chemistry, University of California, Irvine Invited Seminar


May 25th 1992  American Carbon Society, Atlanta Meeting. Invited Speaker

September 3rd 1992  Department of Chemistry, Analytical Institute, University of Bari, Italy. Invited Seminar

September 4th 1992  Department of Chemistry, Analytical Institute, University of Bari, Italy. Invited Seminar

September 9th 1992  12th International Symposium on Microchemical Techniques Cordoba, Spain Keynote Lecture


November 16th 1992  Department of Chemistry, Emporia State University Invited Speaker

Feb. 10th 1993  Department of Chemistry, Wichita State University Invited Speaker

Feb. 22nd 1993  NASA Langley Research Center. Presentations made by self and Dr. Weitzacker, and M. Bellamy.

March 31st 1993  American Chemical Society, National Meeting, Denver 30 minute talk. Members of the group made two other oral presentations, and four poster presentations.

April 23rd 1993  Materials Research Center, University of Pittsburgh Invited Seminar
June 29th 1993  Wright Patterson Air Force Base, AFOSR Materials Meeting  Invited Seminar

Oct 18th 1993  Air Force Contractors Meeting, Irvine California  Invited Seminar

Oct 26th 1993  Materials Research Center, Southern Illinois University  Invited Seminar at Carbon Conference

Nov 17th 1993  American Vacumm Society, National Meeting  Oral presentation made by Dr. Cara Weitzsacker (postdoc with group)

May 20th 1994  Raychem Research Laboratories, Palo Alto, California  Invited Seminar


September 21st 1994  Department Seminar, Wichita State University

October 2nd 1994  FACCS Meeting St. Louis  Invited Seminar on Industrial Funding during meeting of past and present federal Program Officers


November 15th 1994  Invited Seminar - Alcoa, Pittsburgh, PA

May 1995  Moderator for Data Processing Session "AES: From Physics to Data" French Vacuum Society, near Grenoble, France

July 17 1995  NASA Langley "Presentation on Studies of Carbon Fiber Surfaces"

August 24th 1995  American Chemical Society National Meeting. Invited Paper

b). Consultative and advisory functions to other laboratories and agencies

See AFOSR and Air Force Meetings in list above.
c) Transitions

Discussions with industry have included Dupont, Amoco, Alcoa, Raychem. These discussions often included discussion of work funded by this project.

New Discoveries, inventions, or patent disclosures

The conclusion of many of the published studies promise to be important in the development of new oxidation protection approaches for carbon-carbon composites.

Honors/Awards

During Grant Period

Sc.D. Degree from the University of Cambridge in England (1995). This degree is awarded after submission of a complete set of publications for evaluation of "distinction by some original contribution to the advancement of science or of learning".

Prior to Grant Period

Fellow of the Royal Society of Chemistry (1982)
Salters Company Fellow (1970-1972)
Forrester Prize and Irvine Jubilee Medal (1967) (Best first class honors degree in Chemistry, St. Andrews University, Scotland)
Finlayson Prize and W.J. Matheson Bursar (1965)