NANO-COATINGS ON CARBON STRUCTURES FOR INTERFACIAL MODIFICATION

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By

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Abstract


Surface modification of materials is a rapidly growing field as structures become smaller, more integrated and complex. It opens up the possibility of combining the optimum bulk properties of a material with optimized surface properties such as enhanced bonding, corrosion resistance, reactivity, stress transfer, and thermal, optical or electrical behavior. Therefore, surface functionalization or modification can be an enabling step in a wide variety of modern applications. In this dissertation several surface modification approaches on carbon foam and carbon nano-fibers will be discussed. These are recently developed sp² graphitic carbon based structures that have significant potential in aerospace, automotive and thermal applications. Influence of surface modification on composite formation and properties have also been investigated. Two types of property changes have been investigated: one for enhancing the surface reactivity and another for surface inertness. Characterization techniques such as X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), Contact Angle Measurement, Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and mechanical testing are used in this study to find out the influence of these coatings on surface composition, chemistry and morphology. Mechanical testing has been performed on composites and stand alone foam to study the influence of surface
modification on physical and mechanical properties of the composite materials. The effectiveness of these coatings on metallic/graphite interface has also been investigated for metal-matrix composite related applications. Additionally, the influence of plasma coatings on nucleation and growth of nanotubes on larger carbon structures (to produce multiscale, multifunctional materials) have also been studied.

It is seen that the liquid phase activation treatment introduces oxygen functional groups on the surface, but may cause severe enough degradation that damages the ligaments and cell walls of carbon foam. This results in higher elastic modulus but lower strength. So, to get any benefit from such approaches the optimization window may be very narrow and marginal in controllability. An alternative solution would be to synthesize ultra thin film coatings without etching the surfaces. It is observed that plasma assisted coatings having thickness in the range of few nanometers (4-5nm) are completely covering the graphite substrates. The coating surface chemistry and morphology information is based upon XPS and AFM studies on pyrolytic graphite substrate. Two types of plasma surface modification techniques have been attempted: one is to make the surface more reactive for structural components and the other is to make the surface more inert for stand-alone structures. In order to achieve these goals plasma assisted oxide and fluorocarbon coatings are studied in detail. The synthesized oxide and fluorocarbon coating chemistries are comparable to conventional silica (SiO₂) and polytetrafluoroethylene (PTFE, –CF₂–).
It is seen that the fluorocarbon coatings provide moisture resistance to graphitic foam by making the surface inert at the nanometer scale. On the other hand, plasma assisted oxide coating is a feasible and effective means of improving the wettability and dispersion of foam and nanofibers in organic polymer matrix material. Surface analysis as well as microstructural studies and mechanical tests have shown encouraging results. The interface reactions between graphite (coated and uncoated) and epoxy have also been studied in detail.

Nano-scale plasma coatings have also been applied for metal matrix composites and semiconductor related applications. The fluorocarbon coating promote delamination/exfoliation of the metal on graphite, hence may be used for patterning or lithography. Oxide coatings seem to enhance the adhesion and metallic diffusion between graphite and metal, hence can be used for the development of metal matrix composites. Additionally, oxide coating seems to enhance the length and density of nanotubes synthesized on carbon structures, desired for the design of advanced nano-composites.
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Dedication

This dissertation is dedicated to my family members
1. Introduction

1.1 Surface Modification of Materials

Surface modification refers to modification of surface composition or surface structure of a solid to enhance its properties. The "surface" region can be defined as the outer skin having a thickness ranging from few angstroms to few mm (depending on application). In general, traditional applications involved thicker regions (µm) and modern nanoscale applications need control of the outer surface at atomic scales. Therefore surface modification methods need very accurate control. Several approaches which are generally used to modify the surface are listed below:

a. Traditional mechanical modification (e.g. sandblasting to roughen the surface, shot peening to create built in stresses).

b. Traditional thermal treatments (tempering, annealing etc.).

c. Heating the surface in a controlled (often inert) environment.

d. Bombardment by charged particles or energetic beam such as laser to introduce surface defects, roughness, localized annealing, and restructuring.

e. Controlled chemical reaction to change the surface composition or to form surface functional groups (includes use of liquid phase and plasma reactions)\(^1\).
This project involves the last approach i.e. chemical modifications involving etching and coating. These approaches is complicated at the nanoscale, therefore need to be investigated clearly.

1.2 Materials Used in this Study

Carbon core structures are focus of the study. Traditionally, they have been used as micron – mm size fibers. Recent applications involved more complex shapes such as carbon foam, nanofibers, nanotubes and fullerenes. We have focused our work on two of these structures i.e. carbon foam and nanofibers. These materials are chemically identical to sp² carbon². Therefore detailed surface/interface modeling studies have been performed on flat graphite surfaces.

1.2.1 Carbon Foam

Micro-cellular foam prepared from Mitsubishi synthetic pitch using the AFRL patented (US patent No. 5868974) technique have been used in this study. Initial development of carbon foam was made primarily to replace expensive 3-D woven fiber preforms in polymer composite materials³. Cellular foams of carbon and graphite are made of pitch-type precursors such as coal-based precursor, chemically synthesized pitch etc. The foam made of synthesized pitch was observed to have porosity as much as 96% and hence it can be used for the processing of lightweight structural components. Processing of a pitch foam involves (a) pressing a quantity of a pitch and placing it in a pressure vessel, (b) introducing an inert gas into the pressure vessel under an elevated pressure and temperature 10-40°C above the melting temperature of the pitch (c) venting the pressure vessel to atmospheric pressure provides a porous foam (d) stabilizing the
porous foam at an elevated temperature in an oxygen-containing environment, and (e) cooling the resulting, stabilized porous foam to ambient temperature. Porous carbon foam can be obtained by heating the pitch foam in an inert atmosphere to a temperature sufficient to carbonize the pitch. Graphitic foam is synthesized by heating the carbon foam in an inert atmosphere to a temperature sufficient to graphitize the pitch\textsuperscript{2, 4}. This study focuses on carbon foam.

Figure 1 shows the SEM microstructure of carbon foam and other types. The following features were observed from the microstructure:

- It is highly porous and the size of the cells varies between 50 – 150 µm
- The cell structure is rough and less uniform and the cell walls have an open, interconnected cell structure.
- In fully graphitized foam, the cell walls and ligaments (intersection regions of cell walls) consists of layered graphitic planes.

Some of the advantages of carbon foam:

- Highly ordered graphitic ligaments have the following potential of providing graphite like properties
- Dimensionally stable – low coefficient of thermal expansion
- Open porosity – most probably permeable to many fluids
- Excellent thermal management material
- Ability to absorb tremendous amounts of impact energy

Due to the as mentioned advantages, carbon foam of interest has potential aerospace and thermal applications\textsuperscript{3, 5, 6}:
Figure 1: SEM Images of Microcellular Foam

- Smooth walls (Graphitic plane parallel)
- Planes of stacked graphite
- Carbon Pore
- Ligaments
1.2.2 Carbon Nanofibers

Vapor grown carbon nanofibers (VGCF’s) were used in this study. Figure 2 shows the SEM and TEM images taken on carbon nanofibers and it was observed that the nanofibers were entangled with each other due to high van der Waals forces of attraction between them. The nanofibers have diameter ∼70-200nm which is one or more order of magnitude smaller than conventional carbon fibers (5 – 10 microns), but larger than single walled carbon nanotubes (1-10 nm).

These fibers possess excellent mechanical and physical properties, and very high electrical and thermal conductivity\textsuperscript{7-9}. Especially, nanofibers are being used for reinforcing polymer matrices to improve the mechanical, thermal and electrical properties. Some of the typical applications of carbon nanofibers composites are\textsuperscript{10}
Entanglement of Carbon Nanofibers
Figure 2: SEM and TEM Images of Vapor Grown Carbon Nanofibers
Aerospace applications

- Aircraft braking systems
- Thermal management

Automotive uses

- Fuel systems
- Mirror housings
- Interior parts
- Bumpers & fenders
- Tires

Industrial applications

- Silicon wafer production
- Batteries and fuel cells
- Disk drive components

1.3 Surface Modification of Carbon Structures for use in Composites

Composite materials are multiphase materials obtained by combination of different materials to attain properties that the individual components cannot attain. Carbon reinforced polymer composites have received considerable attention in the scientific and industrial communities due to their interesting mechanical and thermal properties and numerous applications. These composites offer high stiffness, strength and dimensional stability, and more importantly high strength to weight ratios. They can be processed by conventional processing techniques providing for low cost composite
manufacturing. In addition, carbon structures are expected to serve as mechanical reinforcements as well as electrical conductor in composite systems, leading to multifunctional composites \(^\text{11}\).

Effective reinforcement requires sufficient wettability of the matrix on the carbon as well as optimum bonding between the carbon and the matrix material. In addition, very good infiltration of the matrix material is crucial for the formation of void-free composite structure. The carbon structure should be in intimate contact with the matrix i.e., the matrix must be able to wet the surfaces of the carbon structure. However, carbon surfaces by themselves do not possess good wettability for organic and metallic matrices \(^\text{12}\). Hence, formation of strong chemical bonds at the interface is necessary in order to produce composites with acceptable mechanical properties. If the fiber-matrix adhesion is poor then composite may fail at the interface reducing the strength of the composite.

In this dissertation, methods to enhance wetting and chemical bonding for carbon structures have been studied. This includes liquid phase oxidative treatments as well as plasma enhanced oxide coating that create a nanometer-scale outer layer without oxidizing or etching the bulk carbon. Liquid chemical oxidation is described in chapter 4 and nano-scale oxide coatings are shown in chapters 5, 7, 8, 9 and 10.

Mechanisms of carbon-matrix bonding are as follows:

a. Chemical bonding: this can provide a large bonding force, provided the density of chemical bonds across the carbon-matrix interface is sufficiently high. This
density can be increased by surface modification to enhance reactive sites/functional groups.

b. Mechanical interlocking between the carbon and the matrix: This provides an important contribution to the bonding. This can be enhanced by increasing the surface roughness. The carbon foam has a three-dimensional network and its surface is inherently rough, therefore offers good mechanical interlocking. In nanofibers, the degree of mechanical interlocking is expected to depend upon surface roughness and chirality, which can vary from fiber to fiber$^1$.

c. Van der Waals forces influence agglomeration and clumping, play a minor role in determining the interface strength.

1.4 Surface Modification for Stand-alone Structure Applications

In addition to composite formation, there may be applications where stand-alone carbon structures will be useful (such as lightweight sandwich structures or thermal dissipation materials). In such cases, treating the surfaces for corrosion/degradation resistance will be important.

In this project, coating to make the surface more inert has been studied. These are discussed in chapters 6, 7, 8 and 9.

1.5 Research Objectives

The main objective of this research is to investigate the influence of surface treatments and coatings on the surface properties of complex and uneven carbon
structures [microcellular solid (carbon foam) and carbon nanofibers], at the nano-scale. In order to accomplish this goal, several primary components of this research were identified as follows:

- To enhance the surface reactivity and wettability of carbon structures using surface treatments
- To enhance the surface inertness of carbon structures for stand-alone structure related applications
- To investigate the chemical and micro-structural effects of surface treatments on carbon structures
- To determine the chemical reactions taking place at the interface of nanoscale coatings and carbon structures
- To study the influence of surface treatments on carbon reinforced polymer matrix composites mechanical performance
- To study the influence of nanoscale coatings on metallization process for metal-matrix composite related applications
- To apply the nanoscale coatings for synthesis of nanotubes on larger carbon structures

In order to meet these objectives the following tasks were designed:

- To study the effectiveness of liquid phase oxide treatments on physical and chemical properties of microcellular foam.
- To evaluate the performance of liquid phase oxidative treated carbon foam reinforced polymer matrix composite.
- To explore the capability and the limitations of utilizing the plasma reaction technique for effective surface modification of carbon structures at the nano-scale.

- To study the chemistry, layer thickness and growth rate of nano-scale plasma oxide and fluorocarbon coatings on flat carbon substrates.

- To evaluate the durability and performance of nano-scale plasma coatings for high temperature related applications.

- To determine and correlate the changes in physical and chemical states of the carbon surface, modified due to plasma treatments.

- To study the chemical reactions at the interface of uncoated and plasma coated carbon structures reinforced polymer matrix composites and their mechanical performance.

- To evaluate the performance of plasma assisted surface inert coatings for stand-alone structure related applications.

- To investigate the influence of nano-scale coatings on dispersion and wettability of carbon nanofibers in organic matrix medium.

- To study the performance of plasma surface modified carbon nanofiber reinforced polymer matrix composite.

- To determine the effectiveness of plasma assisted coatings in metallization process and patterning of metal interconnects.

- Additionally, the studies related to growth and characterization of nanotubes on carbon structures has also been performed.

  In this dissertation, the approaches used to accomplish these tasks and the results are explained in detail.
1.6. Dissertation Overview

The detailed work has been presented in seven parts. (1) The study of influence of liquid phase activation (Nitric acid and hydrogen peroxide) on surface and interface properties of stand-alone carbon foam and polymer matrix infiltrated carbon foam composite (chapter 4). (2) Details of surface chemistry and morphology of oxide thin films as they grow on pyrolytic graphite (chapter 5). (3) The study of chemistry, layer thickness and growth rate of fluorocarbon thin films as they grow on graphite (chapter 6). (4) Effectiveness of plasma thin films on carbon foam surface properties and carbon-core structures (chapter 7). (5) The study of influence of plasma coatings on dispersion and wettability of nanofibers in organic matrix medium (chapter 8). (6) The study of effect of plasma coatings on carbon-metallic interfaces (Chapter 9). (7) The study of influence of nano-scale plasma films on the distribution density, growth and properties of nanotubes synthesized on carbon structures (Chapter 10).
2. Literature Review

There is a large variety of literature available on carbon foam, fiber, nanotubes, etc. which form the foundation of the carbon made composites and graphitic materials. The following is a brief review of literature specific to this study.

Organic and carbon based foams were first developed in late 60’s for thermal insulation and carbon fibers in late 70’s for new composite materials, since then many questions have been raised related to the following:

- control and prediction of the structure of carbon foam and fibers by changing the precursor used in the process of manufacture
- produce cost effective solids (precursor, processes etc)
- study the influence of carbon foam and fiber surface and structure on its performance
- being used in many advanced applications such as lightweight aerospace structures and thermal usage.

A closer look is needed on several of these earlier aspects, and at a much more controlled level. The proposed research work looks on some issues relating to surface chemistry and interface of these materials.
2.1 Carbon Foam and Nanofiber Structure and their Applications

Carbon foams are basically classified into two types: glassy and graphitized. Glassy (reticulated vitreous) carbon foam was first produced by Ford\textsuperscript{13} in late 60’s by carbonizing thermosetting organic polymer foams through a simple heat treatment process. Glassy foam lacks high thermal, electrical and mechanical properties, as it is predominately in amorphous form and cannot be crystallized with heat treatments, due to which it is mainly used as a thermal insulating material. In the early 1990’s, researchers at AFRL and ORNL produced multifunctional graphitized carbon foam, which is a ultra-lightweight solid made of interconnected ligaments and cells, having potential for structural thermal management applications\textsuperscript{14}. Two types of pitch-type precursors, chemically synthesized pitch and coal based precursor are available. The porosity of the carbon foam obtained from the latter is only about 50\%. The former precursor, synthetic pitch is of our interest as it has high porosity (80-90\%) made of interconnected ligaments (where cell walls meet) and cells, and can be used in lightweight structural components\textsuperscript{2}.

Due to randomness and complexity in carbon foam properties, only few research groups concentrated on studying its structure and performance. Sangwook and Roy [ref 6, 2004] attempted to model and predict the bulk properties of carbon foam. They developed a model in which they first characterized the cell ligaments and tried to correlate the micro-structural configuration with bulk performance of carbon foam using finite element method. The model provides relationship between process and properties. Haung and Gibson [ref 15, 1993] carried an optimization analysis of brittle foams to determine their appropriate structural density and cell size to fit certain applications.
Their objective function was weight, which was subjected to stiffness, compressive strength and fracture toughness constraints. Mora and Waas [ref 16, 2002] combined the knowledge of brittle failure (size effect) and mechanical behavior of foams to explain load-carrying capabilities of brittle open-cell foams, like carbon foam. The study based upon rigidly interconnected segments of graphite indicates that the foam like systems cover the structural phase space extending from hexagonal diamond to graphite. Hence, the carbon foam is considered to be metallic, stable, and structurally rigid, desired in lightweight composites [ref 17, 2001].

Due to continuous graphitic network, carbon foam reinforced composites are expected to have enhanced mechanical properties. However, carbon foam does not posses good wettability to both polymer and metal matrices which lead to poor interfacial adhesion in carbon foam core composites. Due to this, not much data was available on carbon foam reinforced polymer/metal matrix composites. In order to overcome this problem, oxygen-containing groups can be added on to the surface of carbon foam which leads to the enhancement in interfacial bond strength leading to property improvement of composite materials.

Traditional carbon fibers (micron size or higher) have been available for many applications. Vapor grown carbon fibers (VGCFs) are relatively new fibers which can be made with diameters between several tens of nanometers and several tens of microns depending on the preparation conditions. The ones in the nanometer scale (typically for 100 nm) are often called nanofibers. Due to their potentially low cost of production,
VGCFs have been receiving increasing attention in recent years in the search of their possible applications, principally as reinforcement in composite materials [ref 18, 2003]. Serp Ph and his research group [ref 19, 1998] has shown that the thermal and electrical conductivity properties of VGCFs surpass those of other conventional carbon fibers such as PAN-based and pitch-based. Paredes [ref 20, 2001] is the first person who performed scanning tunneling microscopy (STM) surface characterization studies at submicron level on VGCFs and observed that they have relatively smooth topography, and there is no indication of an extensive porosity. Composites with excellent mechanical properties made up of VGCFs and polymeric matrices have also been prepared and studied recently [ref 21, 1999]. Patton et al. [ref 22, 1999] reported a large increase in flexural strength and decrease in maximum strength when they performed tensile test on VGCFs reinforced with epoxy matrix. The loss in maximum strength can be attributed to voids, residual thermal strains, or uncertainties about fiber strength, fiber-matrix bonding and the degree of fiber dispersion.

However, enough data was not available to show the advantages of using nanofibers over conventional carbon fibers as a core structure in composite materials. The problem is due to the smooth surface and non-uniform dispersion of nanofibers in matrix medium [ref 23, 2003; ref 24, 2002]. If the nanofiber surface is modified appropriately, it will improve its wetting, dispersion and interfacial bond leading to enhancement in composite properties.
2.2 Surface Modification of Carbon Foam and Nanofibers for High Performance Composites

Composite performance mainly depends on the interface between carbon structures and matrix material. Optimum bonding is responsible for maximum static and dynamic mechanical properties and environmental resistance. Adhesion of carbon structures to a matrix material results from mechanical, physical, and chemical interactions at the interface. A basic understanding and control of the interface is essential for optimized composite properties. Therefore substantial research has been directed toward the development of surface treatment techniques to improve and optimize the interfacial bond as discussed below.

2.2.1 Liquid Phase Oxidative Treatments

Surface treatments of commercial carbon fibers are classified into oxidative and non-oxidative treatments. Oxidative treatments are further divided into dry oxidation in the presence of gases, plasma etching and wet oxidation (using liquid-phase oxidizing agents like nitric acid, hydrogen peroxide, ammonium bicarbonate etc.). Deposition of more active forms of carbon, such as highly effective whiskerization, plasma polymerization, and grafting of polymers are considered to be non-oxidative treatments of carbon fiber surfaces\(^{25}\).

As reported by Scolar, [ref 26, 1974] nitric acid and hydrogen peroxide generally increase the surface area, surface functionality and surface oxide content. It is observed by Donnet and Ehrburger [ref 27, 1977] that these treatments generally cause an
appreciable weight loss and smoothing of the carbon fiber surface by removing surface irregularities. An oxidative treatment increases the oxygen contents on the surface in the form of carboxyl and hydroxyl groups [1974, ref 26 1978, ref 28]. Scolar [1974] has attributed the large increase in interlaminar shear strength (ILSS) to the surface reactivity of the treated carbon fiber. Ko, Y.S [ref 29, 1982] showed better retention of the composite strength with oxidized fibers when subjected to hygrothermal ageing. When a weak surface layer was removed, an increase in shear load is observed by Drzal [ref 30, 1983]. In this work liquid phase oxidative treatments were first experimented on carbon foam.

2.2.2 Plasma Assisted Coatings

Most of the previous work was concentrated on developing surface treatment methods of oxidative nature to improve stress transfer through increased interfacial bonding. However, improvements in composite strength are often achieved at the expense of fracture toughness and impact resistance [ref 31, 1991 ; ref 32 1986]. An acid treatment, H$_2$SO$_4$/HNO$_3$ mixture, gives good dispersion of entangled nanotubes/nanofibers in water by effectively severing them. However, damage to the cell walls is unavoidable [ref 33, 2003]. A coating that deposits oxygen functional groups on the carbon structures without etching can be an alternative method to achieve high strength and good fracture toughness.

Interest in the plasma organosiloxanes (Hexamethyldisiloxane, HMDSO) have been popular for transparent oxide coatings, especially so because high deposition rates
can be realized when utilizing a microwave power, they are non-toxic and have a relatively high vapor pressure at normal temperature (98 mbar at 310 K) [ref 34, 2003]. In addition, the inclusion of oxygen in microwave sustained plasmas of HMDSO enables glass-like and scratch resistant coatings with a good substrate adhesion [ref 35, 1993]. Kettle et al. [ref 36, 1997] successfully applied microwave plasma assisted coatings onto carbon fibers using HMDSO/O₂ gas mixture. These coatings are about 0.5µm thick and proved to be effective in stress transfer between epoxy matrix and carbon fiber. They obtained a simultaneous increase in fracture toughness and strength. Benitez et al.[ref 37, 2000] observed that the presence of 400 nm thick silica (SiO₂) layer on substrates obtained from a mixture of HMDSO and oxygen gas in a DC glow discharge reactor enhances the surface wettability. The microwave-plasma assisted deposition of plasma oxide polymer film of thickness 1 µm in HMDSO/Ar/H₂/O₂ plasma provided good wettability of Al substrates [ref 38, 1998]. Paredes et al. [ref 39, 2002] is the first research group to perform STM studies on oxygen plasma-modified VGCF’s and it is shown that they preserve their general smoothness upon plasma oxidation. Their results pointed to the addition of oxygen functionalities rather than the development of surface roughness as the main source of potential improvements in VGCF-matrix adhesion upon plasma oxidation of the fiber. Alexander et al. [ref 40, 1999] has shown that the stoichiometry of the SiOₓ film is strongly related to plasma composition. Increasing the oxygen flow has an appreciable effect on the silicon chemical environment. Hence, the desired surface chemistry can be obtained by optimizing the plasma parameters.
Polytetrafluoroethylene [PTFE, (-CF₂-), Teflon] has good temperature stability, chemical resistance, low dielectric constant, a low friction coefficient, low surface energy, and high impact strength. These properties have led to many applications, especially as protective coatings for industrial, electronic, and biomedical applications (ref 41, 1989). By conventional coating techniques, adhesion of the fluorinated coatings to the substrate is often poor [ref 42, 1997]. Liston and his research group [ref 43, 1994] observed that the plasma deposited fluorocarbon films produces low surface energy and water resistant coatings better than conventional coatings. Plasma fluorocarbon coatings offer the hydrophobicity of linear fluorocarbon polymers, such as PTFE, without the disadvantage of having mobile hydrophobic groups that can move away from a polymer surface that is exposed to humid air or water [ref 44, 1990 and ref 45, 1988]. Ultra thin (few nm) fluoropolymer films containing more –CF₃ groups were deposited by using rf plasma reactor, from mixtures of hexafluoropropylene (C₃F₆) and octafluoropropane (C₃F₈) precursors. The deposited layer is a mixture of –CF, -CF₂, and CF₃ [ref 46, 1998].

It is observed that CF₄, C₂F₆, C₃F₈, and C₄F₁₀ monomers are generally used in combination with carrier gases like H₂ to deposit chemically inert fluorocarbon layer. One among these monomers will be selected based upon the surface chemistry, quality, thickness, and degree of wettability that they are going to provide to the carbon structures. For this study, ultra thin homogeneous fluorocarbon coating with clean surface chemistry is desired.
At present, the plasma coating chemistries and its interactions with the substrates are almost unknown. An understanding of the basics in these areas is of importance for optimizing the functionality of the coating, and for process and quality control. If the coating thickness obtained using microwave plasma is within few nanometers, it will have a very wide range of applications. Homogeneous nano-scale coatings can be successfully used in modifying complex and uneven structures as it can reach the intricate surfaces which are hard to modify using traditional coating techniques. These types of issues, which have not been systematically addressed to date, have been investigated. Additionally, in this dissertation, effectiveness of these coatings on complex and uneven structures will be presented.
3. Characterization Techniques

The characterization techniques used in this study are briefly introduced here. The details of each experiment are outlined in their respective chapters.

3.1 X-Ray Photoelectron Spectroscopy (XPS)

XPS is the main characterization technique which has been extensively used in this work as it can detect elements present on the top few atomic layers (5-70 Å) very precisely and it can also identify their chemical bonding states, therefore ideal for this type of analysis. The working principle of XPS is based on photoelectric effect (shown in Figure 3). In this process a photon of known energy ($h\nu$) transfers all of its energy to a bound electron in an atom, causing the ejection of it.

The energy of the outgoing electron is

$$E_K = h\nu - E_B$$

where $E_K = \text{Kinetic energy}$

$E_B = \text{Binding energy}$

Since the binding energy is a characteristic property, the measurement of photoelectron kinetic energies enables elemental analysis. Only the electrons from the top few atomic layers escape from the surface. Hence, it is a very surface sensitive technique.
The electrons leaving the sample are detected by an electron spectrometer according to their kinetic energy. The analyzer normally is operated as an ‘energy window’, accepting only those electrons having energy within the range of this fixed window, referred to as the pass energy. The analysis spot can be adjusted. In this study data is collected using an analysis spot size of 110 x 110 µm. Electrons are detected as discrete events and the number of electrons for a given detection time and energy is stored digitally.\textsuperscript{47,48}

Few characteristics of XPS are:

1. Range of elements: all except Hydrogen and Helium
2. Destructive: no, for most materials. Extremely X-ray sensitive or liquid samples may be damaged, due to vacuum environment
3. Elemental analysis: yes, semiquantitative without standards; quantitative with standards.
4. Chemical state information: yes
5. Depth probed: 5-50 Å
6. Depth profiling: yes, initial 50 Å or so can be profiled by angle-resolved analysis. Greater depths require sputter profiling which involves surface damage
7. Depth resolution: a few to several tens of Å, depending on conditions
8. Lateral resolution: 5mm-75µm; down to 10µm in special instruments, such as the one used in this study
9. Sample requirements: all vacuum-compatible materials; flat samples best; size accepted depends on holder instrument
10. Main uses: determinations of elemental and chemical state compositions in the top 30Å.\textsuperscript{49} It can provide direct signal to differentiate chemical states of the
Figure 3: XPS Photoelectric Effect

Figure 4: Signals Available from the Sample in Electron Microscope
surface elements (e.g. C – F bond Vs C – C bond for carbon, Si – O bond Vs Si – Si bond for Silicon etc.)\textsuperscript{39}.

3.2 Scanning Electron Microscopy (SEM)

SEM is one of the major techniques for micro-structural characterization. Electron microscopy is analogous to optical microscopy except that electrons are used to image instead of light. Here, electromagnetic lenses control the beam instead of glass lenses. In SEM when electron probe is rastered across the surface of the specimen it results in several emissions as shown in the figure 4. Of these emissions backscattered electrons, secondary electrons or X-rays are used to form the image on the Cathode ray tube by mapping their intensity as function of position of the incident beam. The intensity of the characteristic X-ray is used to form compositional image\textsuperscript{50, 51}.

Few characteristics of SEM are:

1. Main use: high magnification imaging and composition (elemental) mapping.
2. Destructive: generally non destructive, some electron beam damage in sensitive materials
3. Magnification range: 10 ×, 100,000 ×, 300,000 × is the typical operating range
4. Beam energy range: 500 eV to 50 eV; typically, 20-30 keV
5. Sample requirements: minimal, occasionally must be coated with a conducting film; must be vacuum compatible
6. Sample size: less than 0.1mm, upto 10cm or more
7. Depth sampled: varies from a few nm to a few µm, depending upon the accelerating voltage and the mode of analysis
8. Lateral resolution: 1-50 nm in secondary electron mode
9. Bonding information: no
10. Chemical information: provides information for heavy elements
11. Depth profiling capabilities: only indirect

3.3 Transmission Electron Microscope (TEM)

Transmission electron microscope (TEM) is one of the most powerful techniques for obtaining information on the surface morphology at nanoscale, crystal structure on a micro-scale and defect structure of crystalline materials. TEM was extensively used in this work to study the surface morphology of carbon nanofibers, nanotubes, and plasma assisted coatings. Generally, it requires slow and specialized specimen preparation. However, the samples used in this study do not need any special sample preparation techniques as their thickness is \( \leq 200 \) nm. The sample for TEM analysis is placed on copper grids. The specimen is bombarded in vacuum with a highly-focused, monoenergetic beam of electrons (100 kV). The beam is of sufficient energy to propagate through the specimen. Due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample, the transmitted image from small regions of the sample contains contrast. The analysis of these images provides information about the structure and surface morphology of the carbon structures and coatings. Hence, TEM is ideal for this study.
KODAK Electron Image Film SO-163 TEM negatives were used for this study. Kodak D-19 developer, Fixer and Photo-flo 200 solutions were used to develop the negatives by following the standard procedure. The developed negatives were then scanned using a high-resolution scanner.

Characteristics of TEM\textsuperscript{49}:

Range of elements: TEM does not specifically identify elements measured

Destructive: yes, during specimen preparation

Chemical bonding information: sometimes, indirectly from diffraction and image simulation

Quantification: yes, atomic structures by diffraction; defect characterization by systematic image analysis

Accuracy: lattice parameters to four significant figures using convergent beam diffraction

Detection limits: one monolayer for relatively high-Z materials

Depth resolution: none, except there are techniques that measure sample thickness

Lateral resolution: better than 0.2 nm on some instruments

Imaging/mapping: yes

Sample requirements: solid conductors and coated insulators. Typically 3-mm diameter, < 200-nm thick in the center

Main uses: atomic structure and microstructural analysis of solid materials, providing high lateral resolution

Instrument cost: $300,000-$1,500,000
3.4 Atomic Force Microscopy (AFM)

This technique utilizes the atomic forces of attraction or repulsion between a sharp tip and the sample surface (Figure 5). The contact area between the tip and the surface is extremely small. Inter-atomic repulsive forces which are short range are observed at this point due to the penetration of electronic shells of the tip and the substrate atoms. Since the inter-atomic repulsive force is influenced by the total electron density around an atom this force can be used to map the topography of the surface down to atomic dimensions. The tip is mounted on a cantilever beam. The force is measured in term of the deflection of cantilever beam. This can be measured by large number of methods like tunneling current, optical laser, interferometry, and capacitance. The lateral resolution of the image can be as small as the tip radius (typically 5-15 nm), and the vertical resolution can be on the order of angstroms. Some of its applications are:

- To investigate surface processes like thin film growth, corrosion, crystal growth etc.
- It is used for imaging on areas larger than 100 µm in square.
- Used in metrological field due to its ability to give an image which contains direct depth information.
- A wide variety of organic, biological, and inorganic insulators can be studied.\textsuperscript{49,52}

3.5 Contact Angle Measurements

Wettability is the term used to describe the extent to which a liquid would spread on a solid surface. The wettability of carbon foam by a polar fluid (water, epoxy etc.) can be measured using contact angle measurement by considering the equilibrium of forces in
Figure 5: Schematic view of forces encountered when the AFM tip touches the sample surface

Figure 6: A Liquid Drop on a Solid Surface
a system consisting of a polar fluid drop resting on a carbon foam surface in the right atmosphere. The polar fluid drop will spread and the wet the carbon foam surface completely only if this results in a net reduction of the system free energy. For example, figure 6 shows a portion of the solid-vapor interfaces is substituted by the solid-liquid interface. So, for complete wettability

\[ \gamma_{LS} + \gamma_{LV} < \gamma_{SV} \]

where \( \gamma \) represents the specific surface energy while the subscripts S, L and V denote solid, liquid, and vapor, respectively. If this process of substitution of the solid-vapor interface involves an increase in the free energy of the system, then complete spontaneous wetting will not result. Under such conditions, the liquid will spread until a balance of forces acting on the surface is attained, i.e. partial wetting. The angle \( \theta \) that the liquid drop makes with the solid surface is called contact angle. From equilibrium of forces (Young’s equation),

\[ \theta = \cos^{-1}\left(\frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}}\right) \]

For \( \theta = 180^\circ \), the drop assumes spherical shape and no wetting occurs. Conversely, a \( 0^\circ \) contact angle represents perfect wetting. For \( 0^\circ < \theta < 90^\circ \), a partial wetting occurs. So, contact angle measurements provide information about the nature of surfaces\(^{53,54}\).
4. Liquid Phase Surface Activation of Carbon Foam

4.1 Introduction

In this chapter, the effect of liquid phase surface treatments on surface chemistry and physical properties of the microcellular foam is studied in detail. Liquid phase surface treatment involving acidic solutions falls in the category of oxidative treatments, as it deposits oxygen containing functional groups on the surface. By investigation of work on carbon fibers (Jimmy C. M. Peng et al), it was noted that such treatments increase the interlaminar shear strength (ILSS) in some composites due to enhanced interfacial bond caused by increased chemical interaction and mechanical interlocking. An increase in surface reactivity and surface area was also observed. Some had observed etching and degradation of a few mechanical properties of the fiber, but improvement in the overall composite strength\textsuperscript{25, 1}. The influence of this treatment on a microcellular carbon structure such as foam will be of interest, but has not been studied earlier, to the best of our knowledge.

Surface characterization techniques, X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were used. As liquid phase treatments deposits oxygen functional groups on the surface, they should improve the polar fluid infiltration
such as epoxy and water. Finally, the influence of liquid phase treatments on the performance of carbon foam infiltrated with epoxy matrix composite is investigated.

4.2 Experimental Details

Three samples were prepared in this experiment for comparative study.

- Untreated carbon foam
- Carbon foam dipped in aqueous Nitric acid (70% concentrated)
- Carbon foam dipped in aqueous Hydrogen peroxide (30% concentrated)

The carbon foam pieces were immersed in aqueous solutions for specific time (10 minutes). These samples were analyzed using SEM to study the influence of oxidizing chemicals on foam surface. Water absorbability experiment was performed on carbon foam pieces to study its surface property changes with liquid treatments. The carbon foam piece was soaked in distilled water for different times (5, 10, 15 and 20 minutes) and placed on absorbent paper for 5 minutes in between the time periods, so that it catches the dripping water. The change in weight is measured using a microbalance which gives a qualitative measure of water absorbed.

Composites were processed by infiltrating epoxy 828 resin along with curing agent in untreated and 70 % HNO₃ treated carbon foam under vacuum. The composites were cured for 2 days at room temperature. Block compression test was performed on these samples. Figure 7 shows the block compression testing equipment at WPAFB, where a cube of the material was subjected to block compression in a rigid fixture with a
Figure 7: Block Compression Testing Set Up at WPAFB

Figure 8: Comparative C 1s Scans of Carbon Foam and Single Crystal Graphite
swivel head. The purpose of the swivel head was to relieve eccentricity in the applied load that might occur if the specimen loading face is not perpendicular to the loading axis\textsuperscript{55}. The ram travel speed is approximately 0.508 mm/min. This work is done in collaboration with WPAFB (Dr. A.K. Roy and Erik Ripberger). In this experiment 25.4 mm cube of the material is used for compression testing.

The XPS analysis spot used is 110 \(\mu \text{m}^2\). The photoelectron signals received from carbon foam surface will be very weak as the analysis spot might be at cell wall region, ligaments, inside the pore etc. The weak peaks obtained from these rough surfaces were not quantifiable. Figure 8 shows the comparative scans taken on flat single crystal graphite and carbon foam. The carbon photoelectron peak is much stronger for single crystal graphite compared to carbon foam due to difference in their surface geometry, but the elemental composition seems to be same for both the samples\textsuperscript{2}. So, in order to perform the accurate XPS chemical analysis of the carbon surface, identical single crystal graphite surfaces were prepared.

4.3 Liquid Phase Surface Modification of Carbon Foam

4.3.1 SEM Analysis

SEM images were taken on untreated, \(\text{H}_2\text{O}_2\) treated, and \(\text{HNO}_3\) treated carbon foam samples, but the surface changes observed due to \(\text{H}_2\text{O}_2\) treatment were minimal, so those images are not included here. From SEM images shown in Figure 9, it can be seen that \(\text{HNO}_3\) increase the surface roughness due to etching effect. Increase in surface
Figure 9: SEM Images of Untreated and 70 % Nitric Acid Treated Carbon Foams

Table 1: Absorbability Test Results of Treated and Untreated Carbon Foam

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Weight increase of foam after soaking in water for given time (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated Foam</td>
</tr>
<tr>
<td>5</td>
<td>32.3</td>
</tr>
<tr>
<td>10</td>
<td>33.0</td>
</tr>
<tr>
<td>15</td>
<td>34.5</td>
</tr>
<tr>
<td>20</td>
<td>47.7</td>
</tr>
</tbody>
</table>

Table 1: Absorbability Test Results of Treated and Untreated Carbon Foam
roughness may cause increase in the ILSS of any composite formed with carbon foam, as it increases the mechanical interlocking.

4.3.2 Absorbability Test

The carbon foam surface affinity for polar fluids can be measured based upon its water uptake capacity. Table 1 shows the water absorbability test results taken on untreated and treated carbon foams. The water uptake capacity of bare foam saturates at 52% (30 minutes) and for comparative studies the tests were performed until 20 minutes as by then the treated foam absorbability capacity is getting saturated. Compared to untreated carbon foam, HNO$_3$ treated carbon foam has 1.6 times higher water uptake capacity. This shows that HNO$_3$ is increasing the surface reactivity and wettability of carbon foam. Hydrogen peroxide causes insignificant increase in water uptake capacity compared to untreated foam.

4.3.3 XPS Analysis

XPS analysis was performed on untreated and treated graphite. Figure 10 shows the comparison of O 1s and C 1s peaks taken on untreated and HNO$_3$ treated single crystal graphite samples. Compared to untreated graphite, there is an increase in O 1s peak and decay of C 1s peak observed in HNO$_3$ treated sample. Table 2 indicates that there is a significant increase in atomic concentration of oxygen when it is treated with HNO$_3$ and the effect of H$_2$O$_2$ on the graphite surface is minimal. This shows that Nitric acid causes increase in oxygen functional groups which improves wettability and surface reactivity of carbon foam surface.
Figure 10: Carbon and Oxygen photoelectron peaks on flat crystalline graphite:

Comparison of untreated and HNO$_3$ treated surfaces
4.4 Effectiveness of Liquid Phase Treatments on Mechanical Properties of Carbon Foam and its Composites

4.4.1 Compression Test of Carbon Foam

The treated and untreated carbon foams are compression tested using the block compression testing equipment at WPAFB (Figure 7). The schematic representation of compressive stress vs strain for a carbon foam sample is shown figure 11, where the compressive modulus is taken from the linear region and compressive strength is taken at a point where the crushing starts. The obtained compression test results on treated and untreated samples, average of five tests are shown in Table 3. There is no significant change observed in compressive modulus with liquid phase treatments. When compressive modulus values were compared, there is no change observed with H$_2$O$_2$ and HNO$_3$ (30% Conc.) treatments, but HNO$_3$ (70% Conc.) leads to a drop in strength. This indicates a structural degradation like damage to cell walls, ligaments etc., when carbon foam is excessively etched.

4.4.2 Compression Test of Treated and Untreated Carbon Foam Infiltrated with Epoxy Matrix Composite

The chemical structure of an epoxy resin and curing agent (Jeffamine D 230 Polyoxypolylenediamine) used is shown in figure 12. Epoxy resins are characterized by having two or more epoxy groups per molecule. The ring groups are able to absorb both mechanical and thermal stresses. These epoxy groups are highly reactive functional groups. The curing reaction between epoxy and Polyoxypolylenediamine is as follows
Table 2: Variation of Oxygen (At %) with Liquid Phase Treatments

<table>
<thead>
<tr>
<th>Liquid Phase Treatment</th>
<th>Oxygen (At %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>1.2</td>
</tr>
<tr>
<td>H₂O₂ (30%) treated</td>
<td>1.6</td>
</tr>
<tr>
<td>HNO₃ (70%) treated</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Figure 11: Schematic Compressive Stress Vs Strain Curve for a Carbon Foam specimen

<table>
<thead>
<tr>
<th>Foam</th>
<th>Max Load (Kg), S.D</th>
<th>Modulus (Gpa), S.D</th>
<th>Strength (MPa), S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unetched</td>
<td>34.06, 6.96</td>
<td>0.27, 0.10</td>
<td>2.20, 0.43</td>
</tr>
<tr>
<td>Peroxide</td>
<td>34.88, 2.06</td>
<td>0.30, 0.03</td>
<td>2.30, 0.14</td>
</tr>
<tr>
<td>33% HNO₃</td>
<td>37.33, 2.82</td>
<td>0.32, 0.12</td>
<td>2.44, 0.21</td>
</tr>
<tr>
<td>70% HNO₃</td>
<td>29.98, 3.36</td>
<td>0.30, 0.15</td>
<td>1.96, 0.21</td>
</tr>
</tbody>
</table>

Table 3: Mechanical Properties of Treated and Untreated Carbon Foam in Compression (average of 5 tests)
In this reaction, the epoxy rings are opened and hydrogen atoms from the diamine form –OH groups which are reaction sites for further cross-linking. There is no by-product given off in this reaction.\textsuperscript{58}

The results of the compression test on epoxy-foam composites are shown in figure 13 (average of five tests). Compared to untreated carbon foam/epoxy composite, there is a decrease in compressive strength and minimal increase in modulus observed in HNO\textsubscript{3} treated carbon foam/epoxy composite.\textsuperscript{59}

In summary, this study indicates that Nitric acid treatment on carbon foam produces oxygen functional groups and increases micro-roughness by etching the surface. These two effects contribute to increase in polar fluid infiltration and wettability of the carbon foam surface. However, this treatment may be severe enough that it damages the ligaments and cell walls of carbon foam making it weak and resulting in a weaker composite. So, to get any benefit from acid etching approach, the optimization window may be very narrow and marginal in controllability. A better option may be to activate the surface without etching or degrading the surface in anyway. That will be the focus of the next few chapters where one of the plasma enhanced coatings discussed can enhance reactivity without degrading the structure.
Epoxy Resin

Curing Agent (Polyoxypropylenediamine)

Figure 12: Chemical Structure of Epoxy Resin and Curing Agent
Figure 13: Comparison of Compressive Strength and Modulus: Untreated and HNO₃ Treated Carbon Foam Infiltrated with Epoxy Matrix Composite
5. Chemical Structure and Growth of Nano-scale Oxide Coatings

5.1 Introduction

From the plasma of volatile organic compounds, highly adherent and conformal coatings can be deposited with novel chemistries and physical properties\textsuperscript{40}. Plasma is a partially or fully ionized gas containing electrons, ions, and neutral atoms or molecules, also called the fourth state of matter\textsuperscript{60}. The technology of microwave plasma thin film deposition is of vital importance to several manufacturing industries due to its potential applications, including protection (e.g. anti-corrosion), interfacial adhesion promotion, optical modifiers and diffusion membranes\textsuperscript{61}. Plasma coating is evolving as a modern technology due to its ability to excite gaseous atoms and molecules into transient and non-equilibrium conditions with very high densities\textsuperscript{62}. Plasma thereby alters the normal pathways through which surface modification is performed and thus enables production of novel materials.

The coating thickness obtained by traditional surface modification techniques (liquid phase oxidative treatments, chemical vapor deposition, sand blasting, spray painting etc) often roughen the surface, complicates deposition process, deposits thick coatings (\(\mu m - mm\)) and may be hazardous. For example, when liquid phase oxidative
treatment (concentrated nitric acid, NaClO etc.) is used to modify the surface of a sample, the equipment used must have good corrosion resistance and the acid absorbed onto the sample surface must be properly removed. The waste of acid solution also needs to be treated properly to avoid polluting the environment. Moreover the oxidation etchants may even degrade the material being surface treated. Therefore microwave plasma coating may be an attractive option.

Hexamethyldisiloxane [(CH₃)₃SiOSi(CH₃)₃: HMDSO], tetraethoxysilane [Si(OC₂H₅)₄: TEOS] and chlorotrimethylsilane [Si(CH₃)Cl: CTMS] have been used for the growth of silicon dioxide films due to their chemical stability at room temperature. Interests in the plasma organosiloxanes (HMDSO) have been popular for transparent oxide coatings, especially so because high deposition rates can be realized when utilizing a microwave power, they are non-toxic and have a relatively high vapor pressure at normal temperature (98 mbar at 310 K). In addition, the inclusion of oxygen in microwave sustained plasmas of HMDSO enables glass-like and scratch resistant coatings with a good substrate adhesion. Even though several research groups have explored the applications of plasma assisted silicon dioxide coatings, fundamental issues have not been resolved, and there are still several important unanswered questions that need to be addressed, like:

- What are the actual bonding states of the atoms/ions in the coating
- How does this coating start and grow. What is the minimum coating thickness of oxide coating required to completely cover the substrates and how does it grow?
- How effective are these coatings at nano-scale? Most of the earlier studies dealt with micron-scale or large materials. When the intended substrates are nanoscale solids, the effectiveness of this coating at the atomic scale become a crucial question that needs fundamental study.

- Can oxide coatings withstand high temperatures treatments customary of composite fabrication?

This work is mainly focused to address these questions. The primary goal of this work is to determine and correlate the changes in physical and chemical states of the graphite surfaces as the plasma oxide layer evolves from few atomic clusters to a complete effective coating. Techniques such as XPS and AFM have been used for this study. The secondary goal is to explore the capability and limitations of utilizing the plasma reaction techniques for effective surface modification of nanostructured materials. Durability and high temperature applications of oxide coating have also been studied and will be discussed in detail.

5.2 Experimental Details

Highly oriented pyrolytic graphite, HOPG ZYH grade (supplied by Molecular Imaging) substrate was used for this study. A microwave plasma chamber manufactured by PlasmaTech Inc was used for coating deposition. In the instrument, the 8 cm × 16 cm rectangular microwave coupling quartz window is located on top of a 25 cm × 25 cm aluminum square vacuum chamber. The low-pressure microwave (2.45 GHz) plasmas are of high chemical activity due to the high generation rate of reactive atoms or molecules.\(^{38}\)
Samples were ultrasonically cleaned using isopropyl alcohol before keeping them in the plasma chamber. Plasma assisted oxide coating was generated using plasma deposition chamber.

There are three sub-processing steps in depositing oxide coating:

a. Ultra high purity O$_2$ gas (99.99%) is allowed to enter the plasma chamber at a flow rate 50 ml/min, chamber pressure 48 Pa and microwave power 225 watts. Due to the high microwave frequency carrier gas gets ionized and it cleans and activates the surface of the sample to be coated. This process was carried out for 180 seconds.

b. O$_2$ carrier gas (flow rate 50 ml/min) was passed inside the chamber (pressure 56 Pa) along with monomer hexamethyldisiloxane, HMDSO (flow rate 2 ml/min) at a microwave power of 250 watts. This mixture was used to deposit oxide layer on the surface which makes it highly reactive. The chemical structure of HMDSO is shown in figure 14.

c. O$_2$ carrier gas (flow rate 50 ml/min) was allowed to enter the chamber (pressure 48 Pa) at a microwave power of 150 watts for 60 seconds to stabilize the oxide coating deposited on the sample surface.

Surface chemistry and morphology of the coating formed from the microwave sustained HMDSO plasma have been analyzed using X-ray Photoelectron Spectroscopy (XPS, Kratos Axis Ultra System) and Tapping Mode Atomic Force Microscope. XPS analysis was carried out using monochromatic AlK$_\alpha$ (1486.6 eV) X-radiation in ultra high vacuum environment (~ 10$^{-9}$ torr). The X-ray source was run at a power of 140 W (14 kV
Figure 14: Microwave Plasma Polymerization of HMDSO and Oxygen Mixture
with a 10 mA emission current. Survey scans (BE: 0-1000 eV) were collected to identify the elements present on the sample surface and high resolution scans for the selected elements were acquired using analyzer pass energy of 80 eV. Two scans were collected in an area of 110 µm (analysis spot size) and then added together. Charge neutralization value of 2.6 eV was employed that leads to very uniform and consistent neutralization of charge build-up on the sample surface during the analysis.

In order to understand the durability of the coatings in heat treatment conditions, the changes in surface chemistry of oxide layer deposited on pyrolytic graphite substrates have been studied after heat treatments at different temperatures (100°C, 300°C, 400°C, 500°C, 700°C, 900°C, 1000°C, 1125°C, 1200°C). The samples were heat treated under ultrahigh pure argon gas (99.99%) environment.

5.3 Results and Discussion

5.3.1 XPS Analysis of Chemical States and Interfacial Reactions

Oxide coated and uncoated HOPG samples were prepared for this study. XPS survey scans and high resolution scans were acquired for qualitative and quantitative analysis. Figure 15 shows the comparison of XPS scans taken on uncoated and oxide coated HOPG samples. These scans indicate that the untreated sample contains mainly graphitic carbon (B.E = 284.75 eV) and minimal oxygen which is basically from ambient atmospheric contaminants. On oxide coated sample, coating deposits contain
Figure 15: XPS Scans of Plasma Oxide Coated HOPG and Uncoated HOPG
predominately silicon and oxygen, and minimal presence of carbon. The small carbon peak on the oxide coated surface can be from contamination on the deposited layer due to the delay in transferring the sample from plasma chamber to XPS ultra high vacuum chamber.

Previous studies have indicated that higher oxygen flow rate reduces the carbon content of the deposits i.e. carbon associated with the silicon within the oxide layer, and it is not possible to remove all of the carbon from the deposits simply through the addition of oxygen. It is expected that the carbon is not present as simple hydrocarbon, but is mostly associated with silicon. When the oxygen gas is added to the plasma chamber along with HMDSO monomer, the radicals generated in the plasma are saturated by the additional oxygen. The chemical environments such as SiO2 (shown in figure 14), (CH3)2SiO2 and (CH3-)3Si-O can be expected in the deposited oxide layer on HOPG substrate.

Plasma oxide coatings were deposited on highly oriented pyrolytic graphite (HOPG) substrates for various time duration (7, 15, 30, 45, 60, 90, 120, 150, 180, 210 and 240 seconds) in order to study the growth rate and interfacial reactions as the film grows. These samples were then analyzed using XPS. Quantitative chemical analysis was performed on XPS high resolution scans of carbon, silicon, and oxygen elements.
Figure 16 shows the variation of full-width at half maximum (FWHM) of the Si 2p, C 1s and O 1s signals with deposition time. If there is any change in the chemical states of the elements present on the sample surface, it will result in shift of their binding energies and change in FWHM value. No detectable change in chemical environments of silicon and oxygen elements was found. On the other hand, very drastic change in FWHM values of C 1s peak with deposition time was observed. Initially the photoelectrons will be emitted from the substrate (C-C). As the deposition time increases the chemical states $\text{C}_3\text{H}_3\text{-Si}$ and C-O-X from the oxide layer and interfacial reactions may contribute to the C 1s peak. When the coating thickness exceeds the escape depth of carbon 1s photoelectrons i.e. from the substrate and interface chemical environments, then the presence of C 1s peak is mainly due to the carbon chemical states present within the oxide layer. The variation in FWHM values of C 1s peak can be attributed to the changes taking place in chemical environment of C 1s peak. As a result, entire C 1s peak cannot be used as a charge-corrector source due to the change in chemical state of C 1s peak with deposition time.

The information related to chemical states of the elements is completely relied on the accuracy of the measured spectral binding energy positions. The experiment was repeated on silicon substrates for 15, 30, 60, 90, 120, 150, 180, 210 and 240 sec deposition times, to find out the right source for charge-correction whose chemical state does not change with the variation in the oxide coating time. Table 4 shows the data collected on the silicon samples using XPS. As expected there is shift in Si 2p and O 1s peak positions due to differential charging. Initially there is no presence of carbon peak at
Figure 16: Change in FWHM of Si 2p, C 1s and O 1s peaks with increase in deposition time
<table>
<thead>
<tr>
<th>Deposition Time, Sec</th>
<th>Si 2p B.E (eV)</th>
<th>C 1s B.E (eV)</th>
<th>O 1s B.E (eV)</th>
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</table>

Table 4: XPS Si 2p, C 1s and O 1s peak binding energy values (non-charge-corrected) obtained from Oxide Coated Silicon Substrates
284.4 eV on the silicon substrate and with the increase in the deposition time an enhancement in the carbon atomic percentage (∼ 9 atomic %) is observed. The presence of C 1s peak is due to the carbon environments, mainly $\text{C} \text{H}_3 \text{- Si}$ present in the oxide layer, which appears at 284.4 eV (shown in figure 17). In ref. 61, all the C 1s spectra were charge corrected using the C 1s chemical state at 284.4 eV. When the spectra have been charge corrected using this C 1s peak, Si 2p and O 1s peaks appeared at their standard binding energy values of 103.2 eV and 532.1 eV as shown in table 4. These results indicate that charge correction can be accomplished using C 1s spectral component at 284.4 eV for HOPG samples.

Figure 18 and 19 shows the variation of C 1s, O 1s and Si 2p peak intensities, and their atomic percentages with deposition time. Figure 18(a) shows the decay of C 1s spectra with the increase in deposition time. From figure 18(b) it is observed that there is no presence of silicon on untreated graphite surface and with the increase in deposition time there is an increase in Si 2p peak intensity, which is basically from the oxide coating. The same trend can be seen in the case of O 1s peak (figure 18c).

Figure 20 shows the resolved components of C 1s spectra obtained from selected specimens. These have been fitted with four spectral components $\text{C} \text{H}_3 \text{- Si}$ (284.4 eV), C-O-X (285.8 eV), C-Si (283.1 eV) and C-C (284.75 eV). C-C is basically from graphite, C-O-X is always present on graphite surface exposed to air and $\text{C} \text{H}_3 \text{- Si}$ came from the plasma since HMDSO has $\text{C} \text{H}_3 \text{- Si}$ groups. Decay of C 1s substrate component (284.75 eV) and enhancement of C 1s coating component (284.4 eV) is observed with the
Figure 17: Resolved C 1s peak of 90 seconds Oxide Coated Silicon
(a) Decay of Substrate Peak

(b) Increase in Coating Peak
Figure 18: Variation of (a) C 1s and (b) Si 2p (c) O 1s Peaks Intensity with Oxide Coating Time
Figure 19: Change in Atomic % of Elements on the HOPG Surface with Oxide Coating Time
60 seconds Oxide Coated HOPG

C 1s Spectra

C-C

C-O-X

30 seconds Oxide Coated HOPG

C 1s Spectra

C-C

C-O-X

Uncoated HOPG

C 1s Spectra

C-C

C-O-X

60 seconds Oxide Coated HOPG

C 1s Spectra

C-C

C-Si

CH₃-Si

C-O-X
Figure 20: XPS Resolved C 1s peaks for (a) 0, (b) 30, (c) 60, (d) 90, and (e) 240 seconds Oxide Coated HOPG Specimens
increase in deposition time. There is no presence of C 1s substrate component (284.75 eV) after 3 minutes coating time, which shows that silica layer has completely covered the graphite substrate with a layer several times thicker than the escape depth of C 1s photoelectrons from C-C environment. The spectral binding energy positions (shown in table 5) were determined after making charge-corrections using C 1s component at 284.75 eV for the samples with deposition time’s \( \leq 90 \) seconds. C 1s component at 284.4 eV was used to charge-correct for the samples with deposition times ranging between 90-240 seconds. When the spectra have been charge corrected, Si 2p and O 1s peaks were observed at their standard binding energy positions (shown in table 5) in agreement with the results obtained on silicon samples. Figure 21 shows the comparison of XPS scans collected on standard SiO2 sample and plasma oxide coated HOPG sample for accurate interpretation of the data. From the binding energy positions of Si 2p (B.E = 103.2 eV) and the O 1s (B.E = 532.1 eV) peaks, it can be concluded that the film is comparable to SiO2.

It is interesting to observe the component of C 1s at the low binding energy (283.1 eV) side due to the presence of C-Si bonds. This peak appeared only in the spectra collected on 60 sec and 90 sec oxide coated samples, as shown in figure 20. If the C-Si chemical environment is present within the oxide layer then it should appear along with \( \text{C}_3 \text{H}_3 \)-Si and C-O-X spectra components for higher deposition times, which is not the case observed here. This component cannot be observed at higher deposition time oxide coated silicon sample, when the coating is thick enough to cover the signals from the interface (figure 17). This peak is absent in uncoated graphite, therefore, not from the
<table>
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<tr>
<th>Deposition Time, Sec</th>
<th>Si 2p B.E, eV</th>
<th>C 1s B.E, eV</th>
<th>O 1s B.E, eV</th>
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Table 5: XPS Si 2p, C 1s and O 1s peak binding energy values (non-charge-corrected) obtained from Oxide Coated HOPG Substrates
Figure 21: XPS Comparison of Oxide Coated Graphite and Standard Silica Sample
HOPG substrate. This implies that the observed C-Si bonds are due to the interfacial reactions taking place in between the substrate (C-C) and the oxide layer (SiO₂). So, from figure 20, it can be concluded that the chemical states C₃H₃-Si within the oxide layer and C-O-X from atmospheric contamination, C-Si bonds at the interface, and C-C bonds from the substrate contribute to the C 1s peak. This result is consistent with the Si 2p peak chemical state data shown in table 5. A binding energy shift of ~ 0.3-0.4 eV (102.8-102.9 eV) was observed in the Si 2p peak within 45-120 sec deposition time range, as carbon atoms from the substrate bonded with silicon atoms present in the oxide layer.

5.3.2 Nondestructive Evaluation of Average Over-layer Coating Thickness Using XPS

For quantitative analysis it is important to determine the escape depth: the distance that electrons of a well-defined energy can travel without losing energy. The incident radiation, X-ray photons in this case, is sufficiently energetic so that it penetrates deeply into the solid. The output signal is from low energy electrons which have very limited penetration capability in solids and those from the outermost atom can reach the detector without attenuation. Electrons that undergo inelastic collisions lose energy in transport from the point of excitation to the surface. These electrons leave the solid with a lower energy and contribute to a background signal or tail that can extend several hundred eV below the main signal peak.

The inelastic mean free path (IMFP) of the electron is defined as the mean distance an electron of particular energy could travel in any particular material before losing energy in an inelastic collision⁶⁴, ⁶⁵. It depends on the kinetic energy, and the
nature of the solid. Although x-ray penetrates deep into the solid, a typical photoelectron may only travel 5-70 Å (IMFP) without being scattered or suffering energy loss. This phenomenon gives the XPS technique its characteristic surface sensitivity. The intensity of an XPS peak detected depends on composition of material and number of electrons emitted from that material and reaches the detector. By substituting the values of peak intensities obtained from XPS analysis and IMFP value in equation (1), the estimated average over-layer coating thickness can be calculated.

\[
I = I_o e^{-x/\lambda}
\]

\( I = \text{Intensity of photoelectron peak from the coated surface} \)

\( I_o = \text{Intensity of photoelectron peak from the uncoated surface} \)

\( \lambda = \text{Escape depth of the photoelectron} \)

\( x = \text{Estimated average over-layer coating thickness} \)

The number of electrons that can escape from the surface of the deposited absorber film then decreases exponentially with film thickness\(^{35}\). Wagner, Davis and Riggs\(^{66,67}\) proposed the inelastic mean free path (IMFP) values for C 1s and Si 2p peaks through an average solid to be 27 Å and 25 Å, respectively.

Figure 22 shows the estimated average over-layer coating thickness (calculated using equation (1) and XPS results shown in figure 18), as a function of plasma oxide deposition times (15, 30, 45 and 60 seconds). It is observed that the oxide coating growth rate is \( \sim 4 \text{ nm/min} \). Average over-layer coating thickness values can be calculated until a complete layer is formed. After that saturation will occur as the coating gets substantially thicker than the escape depth. The XPS analysis was averaged over an area of 110 \( \mu \text{m}^2 \).
Figure 22: Estimated Average Over-layer Coating Thickness Vs Oxide Coating Deposition Time
5.3.3 AFM analysis of oxide coating growth rate with coating time

Tapping Mode Atomic Force Microscope was used to study the surface morphology of the oxide coating as it grows on HOPG substrates. The AFM topographic images of as received HOPG, and 15 and 60 seconds oxide coated HOPG are shown in figure 23. The line profiles generated on selected area of these three samples are shown in figure 24. The bare HOPG has an average surface roughness of less than 0.5 nm, ideal for this type of study. AFM surface morphology studies of plasma oxide coatings on HOPG substrate indicates that the substrate was partially covered for 15 seconds coating time and completely covered for 60 seconds coating time, as shown in figure 23. AFM line profiles show that the islands present on 15 seconds coated sample are of height 4-5nm, whereas there are no presence of these islands on 60 seconds coated sample. By correlating the topographic images and line profiles, it is observed that SiO₂ film start as 4-5 nm high islands which become complete layers, and subsequently grow as overlayers. This shows when an average coating thickness is about 4-5 nm, the substrate is completely covered. In figure 24, the line profile generated on completely covered HOPG (coated for 60 seconds) shows that the coating forms a uniform layer, as the surface roughness measured is less than 1 nm.

5.3.4. High Temperature Applications

XPS results show the formation of Si-C bonds between the SiO₂ layer and HOPG substrate. This indicates that the coating may be strongly bonded to the substrate and opens up wide rage of applications of oxide coating for potential aerospace, thermal, and electronic industry applications. For instance, plasma assisted oxide coating can be used
Bare HOPG Substrate

(a)

15 sec Oxide Coated, Partial Coverage

(b)
Figure 23: AFM Topographic Images of (a) Uncoated, (b) 15 seconds Oxide Coated and (c) 60 seconds Oxide Coated HOPG Samples
Bare HOPG, Line Profile for the Selected Area

15 sec Oxide Coated, Line Profile for the Selected Area
Figure 24: AFM Line Profiles Generated on Selected Area of (a) Uncoated, (b) 15 seconds Oxide Coated and (c) 60 seconds Oxide Coated HOPG Samples
to successfully modifying complex and uneven micro and nano structures like foam, nanofibers etc. These structures have potential applications as a core reinforcement for polymer matrix and metal matrix composites. For some applications, the coating may even get exposed to high temperatures during the operating conditions. In this case, the coating should be able to retain its chemistry in the operating temperature.

Sequence of experiments was performed on oxide coated HOPG samples by varying the temperatures in the range of 100-1200 °C, as most of the operating conditions fall in this range. The samples were heat treated in ultrahigh pure argon gas (99.99%) environment, so that there won’t be any oxygen contamination from the air. The samples were maintained at the desired temperature for 2 hours and latter samples were allowed to cool to room temperature in flowing argon gas.

XPS chemical analysis was performed on heat treated samples. Figure 25 shows the variation of C 1s, Si 2p and O 1s atomic percentage with increase in temperature. It is observed that the coating is stable until 1000 °C and degrades after that. There are no signs of degradation and chemical changes observed in SiO₂ layer within 0-1000°C temperature range, a good sign for high temperature applications.

In summary, the following key observations were made on the oxide coatings by correlating the results obtained from XPS and AFM analysis:

- In XPS resolved scans of C 1s (shown in figure 20), graphite substrate photoelectron peak (C-C, 284.75 eV) was present even for 60 seconds coating
time when AFM indicates complete coverage with the silica layer. This proves that the oxide coating thickness is well within 1-3 times the escape depth of carbon photoelectrons (2.7 nm) even when the surface is completely covered. This is therefore truly a coating at the nanoscale.

- Presence of C-Si peak appears after 45 seconds and can be detected upto 90 seconds of coating. Beyond that, as the coating thickness increases, it disappears. This indicates that the C-Si component is confined to the interface of the graphite and coating.

- Plasma assisted oxide coating can withstand temperatures upto 1000 °C without degradation.
Figure 25: Change in At % of Silicon, Oxygen and Carbon with Temperature
6. Characterization of Nano-scale Fluorocarbon Coatings

6.1 Introduction

The purpose of this work is to obtain nano-scale fluorocarbon coatings combining the characteristics such as low surface energy, chemical inertness, and good physical and chemical properties desired for stand-alone structure applications. If the coating deposited is comparable to polytetrafluoroethylene (PTFE), then this coating will have many potential applications, especially as protective coatings for industrial, biomedical and electronic applications\textsuperscript{42,46,68,69}. Fluorocarbon thin films generated by traditional techniques have some disadvantages listed below\textsuperscript{42,68,69}:

- It may contain significant concentration of dangling bonds, detrimental to the properties of the deposited film. Since the dangling bonds are reactive free radicals, reaction with atmospheric contaminants might result in oxidative aging that effects the thin film properties with time.
- The adhesion of the coating to the substrate is often poor
- Environmental problems due to the presence of the solvent in the film
- Disposal of significant amount of toxic liquids created as by-products.

The microwave plasma approach overcomes most of the drawbacks associated with traditional methods\textsuperscript{70}. The advantages will be pointed out as apparent in the present chapter and in chapters 7 and 8. Initially, Tetrafluoromethane (CF\textsubscript{4}), Hexafluoroethane (C\textsubscript{2}F\textsubscript{6}) and Octafluoropropane (C\textsubscript{3}F\textsubscript{8}) gases were tried to produce films comparable to
PTFE. In order to produce films with low surface energies, it is necessary to introduce a high concentration of CF$_2$/CF$_3$ groups onto the sample surface$^{42, 71}$. Earlier studies indicated that by using C$_3$F$_8$ as process gas, fluorocarbon film with highest CF$_2$ density and minimal dangling bonds can be obtained$^{72}$. Hence, C$_3$F$_8$ have been studied in detail and outlined below.

In the previous chapter, detailed XPS and AFM analysis performed on plasma assisted oxide coating was used to show that the thickness of the silica layer required to completely cover the substrate is 4-5 nm. The main goal in this work is to similarly study the chemistry, layer thickness and growth rate of the microwave plasma fluorocarbon coating to understand how it nucleates and grows and what thickness is needed for effectiveness.

6.2 Experimental Details

The same microwave plasma system described earlier was used for these coatings. The chemical structure of octafluoropropane, (C$_3$F$_8$) process gas is shown in figure 26. The flow rate of the gas was controlled using mass flow controller. For all the experiments, the C$_3$F$_8$ gas flow was held constant at 50 ml/min and microwave power at 150 watts. The same chamber can be used to deposit a large number of different functional coatings. Therefore, to avoid cross contamination, the chamber was cleaned with O$_2$ carrier gas and isopropyl alcohol whenever there is a change in the coating chemistry. The inner surface of the chamber is completely covered with aluminum foil and it is changed frequently. Contamination check was performed regularly using X-ray
Figure 26: Microwave Plasma Assisted Fluorocarbon Layer Deposition

Microwave Radiation

---

Octafluoropropane
\((C_3 F_8)\)

\(\text{(CF}_2)_n \text{ Functional Group}\)
photoelectron spectroscopy (XPS, Kratos Axis Ultra System). XPS was also used for
chemical analysis of the coating deposits formed from the microwave sustained C\textsubscript{3}F\textsubscript{8}
plasma.

6.3 XPS Analysis of Chemical States and Deposition Rate

Pyrolytic graphite substrates (supplied by Minteq Inc.) were used as model flat
surfaces for initial surface study. Uncoated and fluorocarbon coated graphite samples
were compared using XPS. Figure 27 shows the comparison of chemical states present on
uncoated and fluorocarbon coated samples. The following observations can be made from
the XPS data:

- Uncoated sample mainly contain carbon due to C-C bonds (B.E: 284.75 eV) in
graphite and small, but detectable oxygen (B.E: 532.65 eV) from the atmospheric
contamination.

- Fluorocarbon coated graphite contains mainly fluorine and a higher binding
energy carbon peak (B.E: 291.5 eV) in the overall spectrum.

- Even when the coated sample is exposed to the same atmosphere as the uncoated
graphite, there is no presence of oxygen on the fluorocarbon coated graphite
surface. This is observed even when the sample is left in the open lab
environment for several days indicating that the coating makes the surface inert to
atmospheric contamination.

XPS analysis was conducted on conventional PTFE, for accurate interpretation of
the data. Figure 28 displays survey, C 1s and F 1s spectra (688.3 eV) comparison of
Figure 27: XPS Chemical State Comparison of Uncoated and Fluorocarbon Coated Graphite
Figure 28: Survey, C 1s, and F 1s Spectra of the Fluorocarbon Film and Conventional PTFE
fluorocarbon deposited film and conventional PTFE. The fluorocarbon peak shapes are identical and therefore can be used as a standard peak for charge correction. The peaks are charge-corrected based upon the binding energy position of F 1s peak at 688.3 eV. The main C 1s component located at 291.5 eV is due to the –CF₂– functional groups. This B.E value has been reported by other authors [46, 69, 71]. The binding energy difference between C 1s component and F 1s peak of PTFE sample is 396.9 eV. In this study, this binding energy difference is ~ 396.8 eV. The primary carbon peak in our fluorocarbon film is identical to the carbon in PTFE i.e. (–CF₂–)ₙ, which verifies the deposition of predominantly –CF₂– functional groups on the graphite surface. In additional, there are two small components on the film which are discussed later. Hence, the chemistry of the deposited film is comparable favorably to that of PTFE with respect to the CF₂ functionality.

The plasma fluorocarbon coating was deposited on graphite substrates for various deposition times (15, 30, 45, 60, 120, 180, 300, 420, 540, 660, and 900 seconds). These samples were analyzed using XPS. Figure 29 shows C 1s and F 1s spectra of the plasma polymerized film for different deposition times. It is observed that with the increase in coating time, there is an increase in CF₂ functional group and F 1s peak from the deposited film and a decay of substrate peak (C-C). Figure 30 illustrate the elemental atomic percentage changes observed as a function of deposition time. Initially, there is ~ 4 At % of oxygen element present on the uncoated graphite substrate due to the atmospheric contamination and it dropped to 0 At % when the fluorocarbon film
Figure 29: (a) C 1s and (b) F 1s Spectra of the Fluorocarbon Film for 60, 180, 300, 540, and 900 seconds Deposition Times
Figure 30: Atomic Percentage of Elements as a Function of Fluorocarbon Layer Deposition Time

At % of Elements Vs Deposition Time

Fluorocarbon Film Deposition Time, Seconds

At %

Absence of Oxygen

(CF₂)n Functional Group

C-C

O 1s

F 1s

Figure 30: Atomic Percentage of Elements as a Function of Fluorocarbon Layer Deposition Time
deposition time increased from 15 to 900 seconds. This proves that the film is making the surface inert to the atmosphere.

High resolution C 1s spectra were deconvoluted to analyze the carbon bonding environments in the deposited film. Figure 31 displays the deconvoluted C 1s XPS spectra of the fluorocarbon film for the selected deposition times (0, 60, 180, 300 and 900 seconds). The uncoated graphite has only C-C (284.7 eV) and C=O (285.7 eV) chemical environments. For 60 seconds coated sample, the fit shows that 75.5 % of carbon atoms are present in C-C chemical state (i.e. from the substrate) and the remaining in CF₂ and C-O-X (285.7 eV) chemical states. The percentage of carbon atoms from the CF₂ chemical state increased with the increase in coating time. Minimal presence of CF₃ functional group was observed at 293.5 eV in 180 seconds coated sample. In the case of 900 seconds fluorocarbon coated sample, absence of C-C peak shows that fluorocarbon coating has completely covered the graphite substrate with a layer several times thicker than the escape depth of C 1s photoelectrons from the C-C chemical state. The percentage of various structures present in this film is 82.4 % (CF₂), 7.9 % (CF₃) and 9.7 % (hydrocarbons, 285.4 eV). The presence CF₃ of is a bonus in this case because it adds to hydrophobic behavior. The origin of the CₓHᵧ component is unexpected. However, it is clearly present and could be from trace contamination in the carrier gas (C₃F₈) or gas chamber components.

Figures 32 illustrates the estimated average over-layer coating thickness (calculated using equation (1) in chapter 5 and XPS results shown in figure 29), as a
Fluorocarbon Coated Graphite

(a) 60 seconds Fluorocarbon Coated Graphite

(b) 180 seconds Fluorocarbon Coated Graphite

Uncoated Graphite

(c)
Figure 31: Deconvoluted C 1s XPS Spectra for (a) 0, (b) 60, (c) 180, (d) 300, and (e) 900 seconds Deposition Time

900 seconds Deposition Time
Figure 32: Estimated Average Over-layer Fluorocarbon Coating Thickness Vs Deposition Time

Fluorocarbon Coating Thickness Vs Deposition Time

Graphite

Silicon

Deposition Time, seconds

Average Over-layer Coating Thickness, mm

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

0 10 20 30 40 50 60 70
function of plasma fluorocarbon coating times (15, 30, 45 and 60 seconds). The deposition rate of fluorocarbon film produced on graphite is 0.88nm/min, averaged over an area of 110 µm. The deposition rate appears to be low as compared to other studies\textsuperscript{4}. This is due to the absence of co-reactant gas along with the fluorocarbon feed gas. Earlier studies indicated that addition of hydrogen or hydrocarbon co-reactant gas can increase the deposition rate of fluorocarbons but at the same time it even alters the final composition of the film\textsuperscript{42}. Moreover, handling of some of the co-reactants like H\textsubscript{2} is difficult and hazardous. Hence, to maintain purity and avoid handling of hazardous gases, co-reactant gases were not used in this study. The obtained fluorocarbon film is comparable to PTFE with the absence of dangling bonds, and some additional of the beneficial CF\textsubscript{3} group.

Flat single crystal silicon having an average surface roughness of 1 nm was used for model AFM analysis to study the coating growth morphology with deposition time. Silicon samples were plasma fluorocarbon coated along with graphite samples. Graphite and silicon samples were used for XPS analysis, and silicon samples were used for AFM analysis. Extensive work has been done by this group\textsuperscript{72} on the nucleation and growth of the fluorocarbon coating on silicon substrate and it is shown that these films start as 4-5 nm high islands which become complete layers, and subsequently grow as overlayers.

The aspects observed by correlating the XPS and AFM results were outlined below:
- AFM surface morphology studies of plasma fluorocarbon coatings on silicon substrate (shown in figure 33) indicate that the substrate was partially covered by 45 seconds coating time and completely covered by 3 minutes.

- From Figure 32, compared to silicon substrate (0.74 nm/min), the fluorocarbon coating growth rate is higher on graphite substrate (0.88 nm/min), which indicates that the graphite substrate should have been completely covered with – CF$_2$ – functional groups for 3 minutes fluorocarbon coating time.

- XPS scans in figure 31(b) displays the presence of graphite substrate photoelectron peak (C-C) even after 3 minutes deposition time which implies that the coating thickness is with 1-2 times the escape depth of carbon 1s photoelectrons (2.7 nm).

- Hence, it can be expected that the plasma fluorocarbon coating having thickness less than 5 nm is completely covering the graphite substrate.

- The ability of C$_3$F$_8$ to produce predominantly –CF$_2$– and minimal CF$_3$, as compared to a mixture of CF, CF$_2$ and CF$_3$ obtained using traditional techniques, makes this appear more favorable for pure and reliable nanoscale coatings.
Figure 33: AFM Topographic Images of (a) 45, and (b) 180 seconds Fluorocarbon Coated Silicon Samples (Courtesy: Pratik Joshi Ph.D., Dissertation)
7. Nano-scale Plasma Coatings for Carbon Foam

As discussed in chapter 4, the liquid phase chemical treatment can damage the surface of the carbon foam, and may weaken the composite in some cases. It is proven in chapters 5 and 6 that the plasma assisted oxide and fluorocarbon coatings of thicknesses in the 4-5 nm range can completely cover the graphite surface. Chemically, pyrolytic graphite and carbon foam have the same structure [chapter 4, figure 8]. Therefore, the chemical behavior of plasma coatings on graphite substrates should be comparable to that of on foam surface.

In this chapter, the effectiveness of nano-scale coatings on the physical and chemical behavior of carbon foam has been shown. The influence of nano-films on the mechanical behavior of polymer matrix composites has also been investigated. Quantitative analysis was performed using contact angle measurements, water absorbability test and compression test. The foam-polymer matrix adhesion was qualitatively studied using scanning electron microscope (SEM).

7.1 Effectiveness of Coatings on Contact Angle Measurements

Three Carbon foam samples uncoated, oxide coated and fluorocarbon coated (coating thickness ∼4-5 nm) were prepared for water contact angle measurements. As
shown in figure 34, de-ionized water droplets were placed on the surfaces. Contact angles of the droplets on those three carbon foam pieces were measured. Contact angle made by the water droplet on uncoated foam is 77° as the surface is partially reactive. On the other hand, in the case of oxide treated foam it is measured as 0°, due to the presence of silica layer on the foam surface which makes it hydrophilic in nature. Water contact angle measured on the fluorocarbon coated foam is 141° comparable to that of commercial teflon, as the carbon foam surface behaves hydrophobic. These observations indicate that nanometer scale coatings formed on the surface (as described in chapters 5 and 6) are effective on property modification of uneven microporous surfaces.

7.2 Water Absorption of Microporous Structure

Water absorption experiment was performed on plasma treated and untreated carbon foam specimens in order to study the influence of surface chemistry. In a microporous surface such as carbon foam, an estimate of surface affinity for polar compounds can be made from the amount of water absorbed in a given time. In this experiment, three carbon foam samples: untreated, oxide treated, and fluorocarbon treated was prepared of equal known weights. The procedure of the test is described in section 4.2. The results shown in Table 6 indicate that the foam treated with oxide plasma absorbs more water compared to untreated and fluorocarbon treated foam. This supports the hypothesis that the presence of silica layer deposited by oxide plasma enhances the wettability and polar fluid infiltration. Compared to untreated foam, oxide plasma treated foam has significantly higher (2.3 times) water infiltration in 20 min. The fluorocarbon treatment,
Figure 34: Contact Angle of Water Droplets on Uncoated and Coated Foams
(Performed at Plasmatech)

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Weight increase of foam after soaking in water for given time (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated Carbon Foam</td>
</tr>
<tr>
<td>5</td>
<td>32.3</td>
</tr>
<tr>
<td>10</td>
<td>33.0</td>
</tr>
<tr>
<td>15</td>
<td>34.5</td>
</tr>
<tr>
<td>20</td>
<td>47.7</td>
</tr>
</tbody>
</table>

Table 6: Water uptake capacity of uncoated, oxide coated and fluorocarbon coated carbon foam
on the other hand reduces the water uptake capacity significantly to about an order of magnitude lower than that of untreated foam\textsuperscript{73}.

### 7.3 Permeation of Coating into Inner Layers of Carbon Foam

In order to study the permeation of plasma coatings through the pores of the carbon foam, stacks of five cubic samples of about 12.7 mm were prepared. Each stack was covered from all the sides using aluminum foil and a tape, leaving only the top surface uncovered for plasma coating. So, the only way the plasma coating could enter the stack is through the top layer. Each stack would then be plasma oxide treated for a certain time. After coating, water absorption experiment was performed on each layer of carbon foam in the stack and the results are as shown in the figure 35. It is observed that the water uptake capacity of the top layer is comparable to the bottom layer for both 3 and 5 minutes coating time. This proves that the plasma oxide coating is able to permeate through the porosity in the top layer all the way to the bottom layer through the carbon foam pores of size \(\sim 100 \, \mu \text{m}\).

### 7.4 Influence of Coatings on Polymer Matrix Composites Reinforced with Carbon Foam (In Collaboration with Dr. Roy, AFRL)

#### 7.4.1 Composite Formation

Foam-epoxy composites were prepared as described below.
Figure 35: Permeation of Plasma Coating through the Pores of Carbon Foam
The chemicals used in this study are:

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epon 828</td>
<td>Miller-Stephenson Chemical Company</td>
</tr>
<tr>
<td>JeffAmine D-230</td>
<td>Hunts Man</td>
</tr>
<tr>
<td>Releasing Agent</td>
<td>Buehler</td>
</tr>
<tr>
<td>5 minute Epoxy</td>
<td>Hardman</td>
</tr>
</tbody>
</table>

The steps followed in the process of composite formation are as follows:

- Releasing agent was applied inside the container and it is allowed to settle for 5 minutes.
- Small amount of 5-minute epoxy was placed on the bottom surface of the carbon foam and it is placed at the bottom of the container to cure.
- Resin was mixed with hardener at a ratio of 75% epoxy and 25% hardener (Ex, 25g of resin to 8.75g of hardener).
- Epoxy and hardener mixture was poured in the container, allowing carbon foam to be submerged.
- The epoxy resin/carbon foam was degaussed in a vacuum chamber for 20 minutes to remove the air bubbles formed in the mixture. During this process, it was made sure that the resin settles and will not overflow out of the container.
- The composite formed was removed from the vacuum chamber and allowed it to cure for 2 days at room temperature.
- Using the high speed diamond cutter, excess resin from foam was removed.
- 0.5 in (12.77 mm) cube composite with flat and sharp edges is used for compression testing.

The influence of surface treatments on mechanical behavior of the epoxy/carbon foam composite was studied in compression-mode loading under the same experimental conditions as mentioned in chapter 4.2.

7.4.2 Composite Testing

The following three samples were prepared for the compression test:

Sample A: Uncoated carbon foam infiltrated with epoxy resin
Sample B: Plasma oxide coated carbon foam infiltrated with epoxy resin
Sample C: Plasma fluorocarbon coated carbon foam infiltrated with epoxy resin

The test was performed by using the same experimental set up mentioned in chapter 4.2. This work was done in collaboration with AFRL (Dr. Ajit K. Roy). The load (lbs) and deformation (in.) data was obtained during the test. The test was stopped when there is a drastic drop in the load applied. Using this data and the dimensions of the composite, stress vs strain was plotted.

7.4.3 Results and Discussion

The obtained stress vs. strain plots for all the three samples are shown in figure 36. The compressive modulus, maximum stress and the percentage of compression to failure values obtained from the tests are shown in Table 7. The compressive modulus values are determined by taking the stress-strain values in the low strain linear regions. The maximum stress is determined from the peak in stress-strain plot. The maximum strain value in the plot gives the percentage of compression to failure.
Figure 36: Compression Stress Vs Strain Plot of Carbon Foam Composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compressive Modulus, $\sigma$ (GPa)</th>
<th>Maximum Stress, $\sigma$ (Mpa)</th>
<th>Failure Strain, $\sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated (Sample A)</td>
<td>4.12 (±0.20)</td>
<td>101 (±3.20)</td>
<td>4.00 (±0.15)</td>
</tr>
<tr>
<td>Oxide Coated (Sample B)</td>
<td>4.14 (±0.34)</td>
<td>108 (±4.12)</td>
<td>9.0 (±0.1)</td>
</tr>
<tr>
<td>Fluorocarbon Coated (Sample C)</td>
<td>4.7 (±0.22)</td>
<td>116 (±3.46)</td>
<td>3.8 (±0.12)</td>
</tr>
</tbody>
</table>

Table 7: Block Compression Test Results of Carbon Foam Composite
The compressive test results show that the performance of the composite depends on its interface as it functions as a transmitter of forces between epoxy and carbon foam. It is seen that the plasma oxide coating increases the failure strain of the composite significantly (2.25 times) compared to uncoated sample. From water contact angle and water absorbability test results, it is observed that plasma oxide coating improves the wettability of polar fluids (water, epoxy etc) on carbon foam surface. XPS detected the presence of strong Si-C bonds at the interface. Therefore, the enhancement in mechanical performance can be correlated to the improved wettability and interfacial bonding of the oxide coated foam by the epoxy resin.

On the other hand, compared to epoxy/untreated carbon foam, the wettability of fluorocarbon treated foam by epoxy is expected to be weaker. At this time, there is no clear understanding of how much effect the reduced bond strength or reduced infiltration should have. For continuous fiber composites, fiber pull-out could be an issue, but this is a 3-D microcellular foam. More detailed study will be needed here. However, there is no significant degradation of composite behavior. In fact, there appear to be a slight improvement in strength, no effect on deformation. This will be studied in detail in future.

Detailed SEM analysis was performed on failure surfaces of the composites. Failure analysis was done by correlating the SEM images with the compressive test results. Figure 37(a) shows the SEM images taken on sample A. It is observed that some
Regions not infiltrated with Epoxy

Cracks Propagating through the graphitic Layers

Cracks Propagating through the interfaces
Crack seem to Propagate within the graphitic regions.

(b)
Figure 37: SEM Failure Surface Images of (a) Uncoated (b) Oxide Coated and (c) Fluorocarbon Coated Carbon Foam Infiltrated with Epoxy Resin
regions are not infiltrated with epoxy, as the carbon foam surface consists of a large number of graphitic planes, they do not possess good wettability to epoxy matrix. The interface between the untreated carbon foam and epoxy matrix is weak, due to which cracks were propagated both in the graphitic layers and along the interfaces. The mode of failure observed in sample A is brittle in nature.

Figure 37(b) shows the failure surface of sample B. Very good infiltration of epoxy matrix because of enhanced surface activity of the oxide coating is observed. Cracks seem to propagate only within the graphitic regions but not through the interfaces which shows that the interfacial bonding is strong. This might be the possible reason for the increased toughness observed during the compressive test. The mode of failure in sample B is comparatively more ductile, probably because the interface doesn’t delaminate.

Figure 37(c) shows the SEM images taken on compressive tested sample C, which indicates reduced infiltration of epoxy matrix (due to inert coating) and catastrophic crack propagation. It is observed that the crack is propagating through the graphitic layers, interfaces and cell wall regions.

7.4.4 Interfacial Reactions

The interface chemical reactions presented here were based upon theoretical approach and experimental data. In this study, three carbon foam specimens were considered: uncoated, plasma oxide coated and fluorocarbon coated, all infiltrated with epoxy/hardener mixture. The interface between epoxy and carbon foam is modified by
plasma oxide and fluorocarbon coatings [figure 38(a)]. The graphical representation of the interfacial chemical reactions taking place in the epoxy infiltrated uncoated, oxide coated, and fluorocarbon coated carbon foam composite materials are shown in figure 38(b). At the interface of uncoated carbon foam/epoxy composite, carbon atoms on the carbon foam surface bonds with the reactive sites in the epoxy resin. On the other hand, in the case of oxide coated graphite, detailed XPS analysis indicates that there is a formation of strong Si-C bond between silica layer and graphite substrates (chapter 5). Chemically, foam is comparable to the structure of graphite. Therefore, the same interaction can be expected between foam and SiO$_2$ nano-layer. Oxygen atoms from the coating are expected to interact with the reactive sites (epoxy group) in the epoxy resin and silicon atoms from the coating bonds with the carbon atoms on the carbon foam surface, forming strong Si-C bonds. The formation of Si-C bonds is desired at the interface due to their chemical stability and excellent mechanical properties, especially at high temperatures$^{74-76}$. Plasma fluorocarbon coating deposits –CF$_2$- functional groups on the surface and it is not yet clear how may carbon atoms in –CF$_2$- group are available to bond with the reactive sites in epoxy.

In summary, plasma oxide coatings are effective in increasing the fluid infiltration and good for surface reaction whereas fluorocarbon coatings prevent fluid infiltration and good for surface inertness. Oxide coatings seem to increase the toughness in carbon foam/epoxy resin composite. These results encourage use of plasma oxide coatings on other uneven carbon structures such as vapor grown nanofibers. The influence of these coatings on carbon nanofibers is discussed in next chapter.
Figure 38: Expected Interface Chemical Reactions in Epoxy Infiltrated Uncoated, Oxide Coated, and Fluorocarbon Coated Carbon Foam Composites
8. Coatings for Nano-fibers

Several fundamental processing challenges must be overcome before nanofibers can effectively provide reinforcements in composites. Because of the intrinsic van der waals attraction of the carbon nanofibers with each other, they are held together as bundles and ropes (as shown in figure 2 in Chapter 1), having very low solubility in most solvents. The lack of dispersion becomes crucial when nanofibers are blended into the polymer. They tend to remain as entangled agglomerates, rather than forming a homogeneous dispersion. Dispersion enhancement will allow the manufacturing of smaller precision parts possessing high strength, stiffness, thermal stability and uniform surfaces. Furthermore, because of the atomically smooth non-reactive surface of nanofibers, the reduced interfacial bonding limits load transfer from the matrix to nanofibers⁹,⁷⁷.

In chapter 7, it was already proven that plasma coatings are successfully modifying the surfaces of carbon foam having pores of size ~100 µm and proved to be very effective at nanoscale. The plasma coatings were tried on carbon nanofibers, as they have thickness ranging 70-200 nm. In this study, the influence of plasma enhanced coating (which are effective in 5 nm scale) on dispersion and wettability of nanofibers in organic matrix materials have been studied.
8.1 TEM Characterization of Nanofibers

8.1.1 Uncoated Nanofibers

Figure 39 shows the bright field TEM images of the as-received nanofibers. The fibers are entangled and curved with some surface-surface attractions [figure 39(a)]. Very rarely we can see the two ends of the nanofibers as the length of the fibers is \( \sim 50-100 \) \( \mu \text{m} \). Figure 39(a) shows the presence of metal catalyst particle inside the hollow cylindrical fiber. Majority of the fibers have cylindrical surface morphology [figure 39(b)], where as some fibers have bamboo-type morphology [figure 39(c)]. The nanofibers surface appears to be smooth with an outside diameter \( \sim 70-200 \) nm and inside hollow diameter \( \sim 30-80 \) nm.

8.1.2 Silica Coated Fibers

The TEM images of the nanofibers after plasma oxide coating are shown in figure 40(b) and 40(c). An ultra thin amorphous silica layer can be seen on the outer layer. Detailed TEM observations illustrate that the nanofibers are uniformly coated with silica layer. The thickness of the nano-film is \( \sim 4-6 \) nm covering the entire outer nanofiber surface. The coating thickness value obtained from TEM analysis is an excellent match with the results obtained from XPS and AFM analysis [chapter 5]. No trace of damage caused by the plasma oxide coating on the fiber surface was observed. The surface roughness of the deposited silica layer appears to be less than \( \sim 1\)nm. Hence, plasma oxide coating can be useful in modifying the surfaces of much smaller nanofibers i.e. multiwalled nanotubes.
Figure 39: TEM Images of As-received Nanofibers
Figure 40: TEM Images of (a) Uncoated and (b, c) Oxide Coated Nanofibers
8.2 Dispersion Studies

8.2.1 Experimental Procedure

The experimental set up used for the dispersion studies is shown in figure 41. In
1.5 ml nitrocellulose (1 % concentration in amyl acetate, supplied by Ernest F. Fullam.
Inc.), 0.003 grams of carbon nanofibers were dispersed ultrasonically. A square glass
substrate was taped at the center of the rotating disk. 10 μL of the solution mixture was
taken in a pipette and placed exactly at the center of the square glass plate. The speed of
the rotating disk was set to 300 rpm. The solution was released from the pipette onto the
glass substrate and left it to dry in air for 10 minutes. A circular thin film, which is a
mixture of nitrocellulose and carbon nanofibers, is formed on the glass substrate. This
circular thin film was analyzed using SEM.

8.2.2 Surface Modification of Carbon Nanofibers

Carbon nanofibers were dispersed in organic medium to find the effectiveness of
plasma coatings. The following three samples were prepared for this study:

Sample A: Uncoated nanofibers dispersed in nitrocellulose
Sample B: Plasma oxide coated nanofibers dispersed in nitrocellulose
Sample C: Plasma fluorocarbon coated nanofibers dispersed in nitrocellulose

Using the as-mentioned experimental procedure, thin layers of coated and
uncoated nanofibers dispersed in organic medium were prepared on the glass substrates.
These samples were analyzed using SEM and the low and high magnification images are
shown in figure 42. In sample A,
Figure 41: Experimental Set Up for Dispersion Studies
(a) Low Magnification Images

- **Uncoated**
- **Oxide Coated**
- **Fluorocarbon Coated**

- **Entangled Nanofibers**
- **More Agglomeration of Nanofibers**
- **Less Agglomeration of Nanofibers**
Figure 42: SEM (a) Low and (b) High magnification Images of Uncoated and Coated Nanofibers Dispersed in Organic Medium
- The nanofibers are still agglomerated.

- Nitrocellulose is not completely able to penetrate into the lumps of nanofibers and cause wetting. Beads of solidified nitrocellulose are visible.

- The distribution density of nanofibers in the matrix is not uniform.

In sample B,

- There is less agglomeration of nanofibers observed in the matrix medium.

- Nitrocellulose is able to penetrate into the clusters of nanofibers and no beads are seen.

- Uniform distribution of nanofibers in the matrix medium is observed

Where as in sample C,

- Compared to sample A, more agglomeration of nanofibers is observed.

- Nitrocellulose is unable to penetrate inside nanofiber clusters and beading is higher than in untreated film.

- The distribution of nanofibers in the matrix medium is highly non-uniform.

8.3 Mechanical Testing of Composites (In collaboration with Ohio University; Dr. M.K. Alam Group)

8.3.1 Experiment Details

Vapor grown carbon nanofibers (VGCF) were blended with epoxy resin, and later epoxy hardener was added to the mixture. Composite samples were kept in a vacuum chamber for several minutes to remove the air bubbles. The mixture was cured in room
temperature for about 24 hours, and then oven cured at 150 °F for more than 8 hours. Cylindrical samples were produced from the composites. MTS 810 Material Test System is used for compression test with crosshead speed of 2.5 mm/min. Composites having different volume percentage of VGCF were prepared.

8.3.2 Influence of Plasma Coatings on Composite Performance – SEM Analysis

From the dispersion experimental results, it is clear that plasma oxide coating enhances the wettability of carbon nanofibers in a polar organic medium. It can be expected that the oxide coating may improve the interfacial bonding between carbon nanofibers and epoxy resin matrix as it enhances the nanofiber surface reactivity. Compression test was performed on uncoated and coated nanofibers/epoxy resin matrix composites, to find the influence of plasma coatings on their mechanical behavior. The following sets of samples were compared for compression testing:

Set 1: Composites containing 2.0 vol. % VGCF prepared at OU
Set 2: Composites containing 3.2 vol. % VGCF prepared at WSU
Set 3: Composites containing 5.0 vol. % VGCF prepared at OU

Since blending and preparation issues can be important, processing and testing of composite samples at two independent labs will be beneficial in adding confidence to these results. The main difference between different sets of samples is expected to be blending speed, amount of fiber chop and viscosity of epoxy. Several samples were then prepared to verify the reproducibility of the observations. The absolute value of the properties (compressive strength and yield stress) varied somewhat from run to run in each set of samples but the percentage change caused by oxide coating was surprisingly
constant. The values of compressive yield stress for three sets of samples are tabulated in table 8.

Detailed SEM analysis was performed on compression tested specimens (5 % fiber volume) to correlate the microstructure of the composites with their mechanical performance. Figure 43(a) shows that sample A has high beading up of epoxy resin in between nanofibers. In the case of sample B, the fractured surface has less beading up of epoxy resin. Figure 43(b) shows the formation of more amounts of voids in sample A than in sample B due to poorer dispersion. This implies that agglomeration of fibers leads to formation of porosities within the structure which influence the mechanical properties of the composites. More uniform wetting of nanofiber surface by epoxy resin was observed in sample B than in sample A due to the presence of silica layer on fiber surface which enhances its wettability [figure 43(c)]. Hence, the presence of silica layer on the surface of nanofiber is enhancing its surface reactivity and wettability. These results show an excellent match to the results that are obtained from dispersion studies [discussed in section 8.7.2].

In summary, plasma coatings successfully modified the surface of carbon nanofibers and proved to be effective at nanoscale. Based upon dispersion results, plasma oxide coating enhances the dispersion and wettability of carbon nanofibers in organic matrix medium, whereas fluorocarbon coating reduces it. In the next chapter, the applicability of these coatings for metal matrix composites is discussed in detail.
Table 8: Compressive Yield Stress Values obtained from Compression Test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uncoated, MPa</th>
<th>Oxide Coated, MPa</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1 (2 Vol %)</td>
<td>60</td>
<td>68</td>
<td>13.33</td>
</tr>
<tr>
<td>Set 2 (3.2 Vol %)</td>
<td>30</td>
<td>36</td>
<td>20</td>
</tr>
<tr>
<td>Set 3 (5 Vol %)</td>
<td>50.5</td>
<td>69.5</td>
<td>37.62</td>
</tr>
</tbody>
</table>
Sample A  Beading up of Epoxy

Sample B  Less Beading up of Epoxy

(a)
Sample A  Non-Uniform Dispersion of CNF’s in Epoxy

Sample B  Uniform Dispersion of CNF’s in Epoxy
Figure 43: SEM Images of Compression Tested Uncoated and Coated Nanofibers

Reinforced Epoxy Matrix Composites
9. Coatings for Metallization

9.1 Introduction

Carbon-core metal matrix composites have potential aerospace and commercial applications as it combines the desired mechanical-thermal and electrical properties. The adhesion of metallic phases to the carbon structures is very poor due to low surface reactivity and lack of inter diffusion between them. The weak interfacial bond is one of the main drawbacks in using carbon structures as a core material in metal matrix composite. Previous studies have shown that interfacial adhesion not only influence the mechanical performance of the composite but also its thermal conductance along the interface.\textsuperscript{78, 79} Strong interfacial bond that enhances the mechanical performance and reduces thermal and electrical resistance at the interface in the composite will be desirable for use as structural and heat-sink components in electronic, tribological and future fusion reactors applications.\textsuperscript{78-81}

Earlier research work has been done in analyzing the influence of surface treatments on the interface and performance of carbon-core metal matrix composites.\textsuperscript{78-86} The main focus in this work is to study the changes in surface chemistry, morphology and adhesion of metallic phase on carbon structures caused by the presence of nano-scale plasma coatings at the interface. Investigations have been performed on model flat graphite substrates. The same outcome can be expected when other carbon structures
such as foam, nanofibers and nanotubes are reinforced by metal matrix. Metallic films can be obtained by conventional methods like physical vapor deposition (PVD), chemical vapor deposition (CVD), and electro-deposition (electroplating and electroless plating). We have employed pulse electroplating process to deposit thin metallic layers on graphitic substrates as it is inexpensive and offers high deposition rates. This part was accomplished in collaboration with Jenny Sun at Faraday Technology.

The two different coatings discussed in the earlier chapters oxide coating for enhancing surface reactivity and fluorocarbon coating for inertness have been used in this study. It was shown in chapter 7 that oxide coating can enhance the interfacial bond in carbon-core polymer matrix composites. On the other hand, fluorocarbon coating protects the carbon structure surfaces from degradation caused by atmospheric moisture, pollutants etc when used in stand-alone structures. This chapter shows that the same oxide coatings can be useful for enhancing the interfacial bond strength of metal-matrix composites and fluorocarbon coating can be used for masking or patterning of metal interconnects on carbon structures.

9.2 Experimental Details (In Collaboration with Faraday Technology Inc.)

Model flat graphite substrates (supplied by American Graphite Co.) were used in this study. Oxide and fluorocarbon coatings were obtained in microwave plasma by the same procedure described earlier. The information regarding processing, growth, and characterization of these nano-coatings at the atomic level are explained in detail in chapters 5 and 6. Three samples as shown in figure 44 and one partial fluorocarbon
Figure 44: Copper plated on (a) uncoated, (b) oxide coated, (c) half uncoated and half fluorocarbon coated graphite
coated sample were prepared to study the effectiveness of plasma coatings on surface chemistry, morphology, diffusion, and adhesion of electroplated copper films on graphite substrates.

Electrolytic solution used for these experiments is an amalgamation of de-ionized water, Copper sulphate, and sulphuric acid. hydrochloric acid and polyethylene glycol were used as carriers to control the Cu deposition on the graphite substrate. When a potential difference is applied between cathode and anode which are dipped in electrolytic solution, acids and salts are broken up or dissociated into ions. Thus copper Sulphate, CuSO₄, is dissociated into the metal copper and the acid radical SO₄. The copper, like all metals carries a positive charge and is therefore deposited on the cathode, the free SO₄ attacks the copper of the positive anode, to which it has been attracted; and fresh copper Sulphate is formed which replaces that removed from the solution by electrolytic action, restoring it to its previous composition. These experiments were performed at Faraday Technology Inc. (Clayton, OH). The apparatus used for this experimental set up is Dynatronix model DPR 20/5/10 (Pulse Reverse Power Supply), as shown in figure 45.

The graphite sample (0.75 in × 0.75 in × 0.125 in) to be copper plated was placed in a rotating disk electrode (RDE) and dipped in the electrolytic solution. The sample acts as cathode and the copper grid immersed in electrolytic solution acts as anode in the electrolytic cell, as shown in figure 45. The RDE is rotated at a speed of 210 rpm. To get
Figure 45: (a) Electroplating Experimental Set Up. (b) Rectangular Pulse Electrodeposition
the best plating, a current density of about 10 ASF (Average Current Amp/Square Foot) was used for these experiments. The coating growth rate was set at 0.4 µm/min. Rectangular pulse deposition technique was used in this experiment in order to improve the distribution, and leveling of the copper deposit. The pulse is 7 ms ON and 3 ms OFF. The copper ions were deposited on the surface of the sample for an experimental time of 15 minutes. After electroplating process, the sample was taken out from the RDE and it is cleaned with de-ionized water and dried subsequently.

The characterization techniques such as X-ray photoelectron spectroscopy (XPS) with Al Kα monochromatic source and Scanning Electron Microscopy (SEM) were used to study the effectiveness of microwave plasma treatments on copper plated graphite substrates. Scratch tests were performed on copper plated samples using a diamond stylus to determine the influence of modification of interfaces on copper films adhesion and integrity.

9.3 Results and Discussion

9.3.1 Characterization of Copper Electroplated Samples Using SEM

Figure 46 shows that the graphite substrate has open cracks on the surface. SEM was used to reveal the surface morphology of electrodeposits. Figure 47 shows that the copper deposition is indeed influenced by the presence of nano-coatings at the interface. In uncoated sample, due to less surface reactivity, the copper deposition is not uniform and gaps in the coating are visible at few places on the surface. In oxide coated sample, uniform copper deposits is observed as oxide particles behave as grafting sites and
Figure 46: SEM (a) Low and (b) High Magnification Images of as-received Graphite
Partial Fluorocarbon Coated
Oxide Coated
Uncoated

(i) Partial Fluorocarbon Coated
Oxide Coated
Uncoated

(ii) Partial Fluorocarbon Coated
Oxide Coated
Uncoated

(iii) Partial Fluorocarbon Coated
Oxide Coated
Uncoated
Figure 47: SEM Low and High Magnification Images of Copper Deposits on (i) Uncoated, (ii) Oxide Coated and (iii) Partial Fluorocarbon Coated Graphite
enhances the surface reactivity. On the other hand, in the case of partial fluorocarbon coated sample, uniform distribution of copper with fine microstructure is observed for small coating times (which can easily peel off). For higher deposition times there is no copper deposited.

The samples were sliced at the center using a low speed diamond cutter. The cleaved sides were analyzed using SEM to study the metallic diffusion in the graphite substrate and to estimate the copper layer thickness formation. Figure 48 shows that the copper layer formed on the uncoated graphite is very thin and superficial ~ 2.2 µm. In oxide coated graphite, the copper layer appears to be inter-diffusional and thick (on an average ~ 14 µm) due to the metallic diffusion through the open cracks on the graphite surface. The significant infiltration of the copper ions is due to the presence of silica layer at the interface which enhanced the wettability and surface reactivity of the graphite substrate. On the other hand, in partial fluorocarbon coated sample, the adhesion is very poor due to the presence of -CF₂- functional groups on the graphite surface, which restricts the chemical reaction between the copper layer and the substrate. The copper layer if formed spontaneously flashes off from the sample surface. This coating may be useful in situations where metal adhesion is to be avoided.

9.3.2 Nano-scale Coatings for Patterning of Metal Interconnects

As shown in figure 44, sample c was prepared to apply nano-scale fluorocarbon coating for patterning/lithography related applications. Half of the sample was masked with aluminum foil and the exposed half was then plasma fluorocarbon coated. This
Figure 48: Cross-sectional SEM images of copper layer thickness and its diffusion in Uncoated (i), Oxide Coated (ii) and Partial Fluorocarbon Coated (iii) Graphite
sample was copper electroplated under the same experimental conditions and then characterized using XPS and SEM.

Figure 49 shows the absence of copper deposits on fluorocarbon coated half, where as the uncoated half shows the presence of copper electrodeposits. Figure 50 shows XPS general and high resolution scans taken on model flat graphite. It is observed that the surface mainly contains carbon (C-C) and minimal oxygen (due to the atmospheric contamination). Figure 51 show the XPS data collected on the sample c. It is observed that there is a presence of -CF₂- functional groups and absence of oxygen and copper elements on the fluorocarbon coated half of the sample. Hence it can be concluded that plasma assisted fluorocarbon coatings can be used in the fabrication industry (semiconductors, automotive, decorative applications etc) for masking areas that does not need to be metallized.

9.3.3 Scratch Adhesion Test Analysis

Scratch adhesion test was performed on uncoated and oxide coated samples using a diamond stylus for qualitative assessment of the influence of plasma oxide coating on interfacial bond strength. The scratches were laid by moving the stylus from left to right in a uniform motion. Different areas along the scratched contours were then analyzed using SEM (shown in figure 52). Scratches were laid once on the surfaces of uncoated and oxide coated samples. Uncoated sample exhibits copper flakes along the scratched edges as the graphite substrate was exposed, which shows poor adhesion of the copper layer. On the other hand, in the case of oxide coated sample, graphite substrate is
Figure 49: SEM comparison of copper electro-deposit on half uncoated and half fluorocarbon coated graphite
Figure 50: XPS General and High Resolution C 1s and O 1s Spectra of Graphite
Figure 51: XPS peaks comparison of copper electrodeposits on half uncoated and half fluorocarbon coated graphite
Figure 52: SEM qualitative scratch test adhesion analysis of copper thin film on uncoated and oxide coated graphite. (a) Scratched once and (b) Scratched twice in the same region on oxide sample.
unexposed. There is a presence of copper deposits inside the scratch track. In order to expose the substrate, scratches were laid twice in the same region on oxide sample. In this case, the copper layer is completely removed along the track and the graphite substrate is exposed. There is no presence of copper flakes observed along the scratch contour. The scratch edges are relatively smooth when compared to the scratches on uncoated sample. This indicates that the interfacial bond between copper and graphite is so strong on the oxide coated substrate that no delamination occurred during the test. This can be attributed to the presence of C-Si-O-Cu bonding at the interface and mechanical interlocking caused by the interpenetration of copper through the open cracks on the substrate.

In summary, plasma oxide coating proves to be effective in metallization process. Oxide coating not only improve the interfacial bond in carbon reinforced-polymer matrix composites (as shown in chapter 7) but also in carbon reinforced/metal matrix composites. The fluorocarbon coating on graphite promotes delamination /exfoliation of the metal, hence may be used for patterning of metal interconnects.
10. Nano-coatings for Nanotube Growth on Complex Structures

10.1 Introduction

The discovery of fullerene and carbon nanotubes in the early 1990’s by Iijima has stimulated intensive research in their synthesis, characterization, and applications. This opened new field in material science i.e. nanotechnology. One-dimensional carbon nanotubes have fascinating molecular structure, good electrical conductivity, and extraordinary mechanical and chemical stability. These make them potential and promising candidates for advanced applications in many fields. Exceptionally high tensile strength, stiffness and aspect ratio of these structures have aroused particular interest and promoted research into the fabrication of nanotube structural components. The price of the nanotubes and limitations in their reliable large volume production are some of the important factors that inhibited the commercialization of nanotube technology. Many research efforts have thus been focused in controlling the physical and chemical properties and producing high purity nanotubes in large quantities.

Arc-discharge, laser ablation, gas-phase catalytic growth from carbon monoxide, and chemical vapor deposition (CVD) from hydrocarbons are some of the main synthesis methods for the formation of nanotubes. The electric arc and laser methods are inherently impossible to scale up. An economic way to produce bulk nanotubes is by
CVD and it is possible to scale up this process for industrial applications. Many recent results pointed to the flexibility and power of the CVD technique\textsuperscript{92-94}. It can be operated at very low pressure and moderate temperatures and gives very high selectivity to multi-walled nanotubes\textsuperscript{95}. Many research groups have successfully produced nanotubes on silicon crystals, quartz glass, porous silicon dioxide, and aluminum oxide substrates. Nanotubes collected from these substrates were mainly used to make carbon nanotube composites, electrical devices, and for electrochemical storage\textsuperscript{90, 92, 94}.

If one can grow nanotubes on larger engineering structures such as micro-sized fibers and other composite core materials, it will be possible to fabricate truly multi-scale composite that provide reinforcements and property enhancements at all length scales. With these types of applications in mind, the goal in this project is to study if any of the functional coatings developed here can be used to catalyze nanotube/nanofiber growth on engineering materials.

Many of the recent results pointed to the dependency of CNT growth on the presence of SiO$_2$ nano-layer on the substrates [ref. 91, 92, 94, 96, 97]. It is observed that silica layer enhances the length and growth rate of CNT’s. A minimum SiO$_2$ thickness of $\sim$5-6 nm is necessary for its presence to be felt, as the catalyst particles may diffuse through this thin layer and react with the substrates, making it ineffective. SiO$_2$ layer (thickness $\sim$ 6-24 nm) reduces the diffusion of Fe particles through it, and promotes the retention of active pure gamma ($\gamma$) iron (FCC Fe) catalyst nano-particles, which is conductive for seeding CNT growth\textsuperscript{91, 96}. The SiO$_2$ deposition methods such as thermal
CVD used by several research groups are complicated, tedious and time consuming. By using plasma oxide coating (as discussed in chapter 5), we can deposit very conformal, ultra thin and reliable silica layers within a few minutes. There should not be any problem with the high temperature working conditions (main furnace, 800°C) as silica nano-layer can withstand a temperature of upto 1000°C, without degradation (as discussed in chapter 5, section 5.3.4).

To coat any structure with carbon nanotubes for enhanced surface and related properties, nanotubes were fabricated on the carbon core structures (microcellular carbon foam, carbon nanofibers, pyrolytic graphite) by CVD process through the catalytic decomposition of the xylene (C₈H₁₀) – ferrocene [Fe (C₅H₅)] mixture. The surface of the carbon foam and nanofibers were modified at the nano-scale using plasma oxide coating, which deposits silica layer on the substrates and nanotubes were subsequently deposited on them. Our desirable goal is to study the influence of the silica layer on the distribution density, growth and properties of nanotubes synthesized on carbon structures. These unique structures can be used to make high performance structural composites. The results obtained from this study indicate that nanotubes formation can be enhanced and controlled by the silica coatings. Detailed study related to optimization of the processing conditions to synthesize nanotubes of desired physical and chemical properties on carbon structures will be performed in the future.

10.2 Experimental Procedure

Microcellular carbon foam and nanofibers were used as substrates for this study.
The experimental equipment (shown in figure 53) was designed to fabricate bulk and high purity nanotubes at low cost. The experimental procedure is somewhat like that described in other journal papers [ref. 89, 90, 95]. It is a simple design consisting of a mullite process tube (inner diameter 32 mm and 750 mm long) with in a two-stage reactor (preheater and main furnace). Ferrocene was dissolved in xylene to obtain a solution of 0.12 g/ml. The substrates were placed inside the mullite tube, at the middle of the main furnace. Ultra high pure argon gas (99.99%) was flown into the tube from one end while the preheater and main furnace was heated to 175 °C and 800° C. Ferrocene (sublimation temperature, ∼140° C) has been shown to be a good precursor for producing Fe catalyst particles which can seed nanotubes growth, and xylene acts as the hydrocarbon source since it boils (boiling point, ∼140° C) below the decomposition temperature of ferrocene (∼190° C). Once the preheater and main furnace reaches the set temperatures, the xylene/ferrocene mixture was fed into the preheater as small liquid drops through a stainless steel tube (ID 0.254 mm) using a syringe pump. Simultaneously, H₂ gas at 150 sccm and argon at 900 sccm were flown inside the mullite tube. When a drop of the solution passes the outlet of the stainless steel tube, xylene would volatize soon, while the remaining ferrocene gradually sublimed and get carried by flowing gases to the reaction zone (800° C) of the tube where ferrocene would decompose into numerous Fe particles. After the reaction time of half an hour, preheater and the furnace were allowed to cool to room temperature in flowing argon gas. Carbon nanotube deposits were formed on the walls of mullite furnace tube and on the carbon substrates. Scanning electron microscope (SEM) and transmission electron microscope
Figure 53: CVD Experimental Set Up
(TEM) were used to characterize carbon nanotubes grafted on the foam and nano-fiber substrates.

**10.3 Results and Discussion**

**10.3.1 Nanotubes on Nanofibers**

Nanotubes and nanofibers are promising candidates for mechanical, electronic, and chemical devices. If carbon nanotubes are synthesized on nanofibers, the nanotubes may alter the characteristics of the nanofibers and add functions that might be of an advantage, especially for the production of structural components. A previous study has shown that nanotubes can be grown on SiO$_x$ nanowires by a simple CVD process. The SiO$_x$ nanowires are of diameter 100 nm, mass produced by the thermal evaporation and oxidation of Si wafers at 1050$^\circ$C$^{96}$. In another recent study, nanotubes were successfully synthesized on carbon nanofibers containing Fe nanoparticles. The diameter of the precursor electrospun nanofibers ranged from 100 to 300 nm$^{93}$. However, large-scale synthesis of nanotube on nanofibers still remains a big challenge. In this study, we tried to produce high density nanotubes grafted on nanofibers by a simple CVD process.

Nanotubes were synthesized on vapor grown fibers having a thickness in the range of 70-200 nm. TEM was used for surface characterization of nanotubes grown on nanofibers. The curled and long nanotubes seem to be grown along the nanofiber surface and also at its tip (figure 54). Very sparse growth of nanotubes on nanofibers was observed. This is due to the fact that low numbers of iron nanoparticles can attach on the inert nanofiber surface and subsequently nucleate nanotube growth.
Figure 54: TEM Images of Carbon Nanostructures on Nanofibers

(a)

(b)

Figure 54: TEM Images of Carbon Nanostructures on Nanofibers
To overcome this problem, either Fe particles can be deposited on the surface of nanofibers by chemical treatments [e.g. using a mixture of dimethylformamide (DMF) and Fe(acetylacetonate)$_3$] or by enhancing the surface reactivity of nanofibers. In the case of first option, some Fe particles may get embedded into the nanofibers, which add to the Fe content without participating in the growth of nanotubes. For composite related applications, it is better to have less number of Fe particles present in nanotubes and on nanofibers. So, the best option is to enhance the surface reactivity by using nano-scale plasma oxide coating which already proved to be a success [chapter 8].

Ultra thin layer of silica was deposited on nanofibers using plasma oxide coating. Carbon nanotubes were synthesized on silica coated fibers by using the CVD equipment under the experimental conditions mentioned in section 10.2. Figure 55(a) represents TEM low magnification images taken on uncoated and oxide coated samples. The nanotubes grafted on silica coated fiber have higher distribution density of nanotubes along the entire lengths of fibers, in comparison with nanotubes grown on uncoated foam.

An enlarged image [figure 55(b)] shows that the nanotubes are uniformly distributed along the oxide coated fibers. This can be attributed to the uniform distribution of Fe nanoparticles on the surfaces of oxide coated nanofibers. The nanotube growth is generally defined by tip growth and root growth mechanisms. In tip growth, the Fe particles detach from the substrate and move at the head of the growing nanotubes. On the other hand, in the case of root growth, the nanotube grows upwards from metal particles that remain attached to the substrate. Detailed TEM observations illustrate
(a)
(b)
Figure 55: TEM Images of Nanotubes Grown on Uncoated and Oxide Coated Nanofibers
that most of the nanotubes are formed by tip growth mechanism. Tip growth is favorable for the formation of nano-composites, as it leads to the formation of an interfacial bond between carbon nanotube and SiO$_2$ layer. Metal catalyst is also found within the core of the nanotubes. It appears that its content can be reduced by decreasing the amount of ferrocene fed along with xylene. Optimization of the process and detailed nucleation and growth studies of nanotube growth will be important and will be performed in the future.

Figure 55(c) shows that the grown nanotubes are multiwalled carbon nanotubes. There is no observable difference in the diameters of nanotubes grown on uncoated and oxide coated nanofibers. Hence, the presence of SiO$_2$ layer on the nanofiber is increasing the nanotube growth rate and length, but does not have any effect on its diameter. The form of nanotube produced is closely related to the physical dimensions of the metal catalyst. This hypothesis is based upon the considerable volume of research that has been conducted from the past few years$^{98}$. The properties and temperature of the substrate will influence the iron particle size apart from the percentage of ferrocene used in the process. So, the diameter of the nanotube can be controlled by optimizing these process parameters.

10.3.2 Nanotubes Synthesized on Carbon Foam

Synthesis of nanotubes on carbon foam was also attempted. This unique structure can be used as a core in lightweight composites. The effective utilization of the nanotubes grafted foam in composite applications depends strongly on homogeneous distribution of
nanotubes on the foam surface. In this study, the influence of silica layer on the distribution of nanotubes has been investigated.

Figure 56(a) shows a typical SEM image of the cell wall and ligament of carbon foam. After CVD growth of nanotubes for 30 minutes, SEM observation (figure 56 b) reveals that nanotubes grafted on carbon foam were formed. It is interesting to observe the simultaneous multi directional growth of nanotubes on foam surface. The nanotubes are grown vertically on the ligaments and horizontally along the cell walls. Figure 56 (c) shows a SEM image of CNT’s growing almost normal to the cell wall surface and forming a bridge along the pores. The synthesized nanotubes are 10-20 µm long, although not vertically well defined. The nanotubes are slightly bent and entangled. From SEM images it is very hard to see the nanotubes grown vertically on the ligaments due to high distribution density of the nanotubes grafted on its surface, where crowding limited the nanotube propagation. There are some traces of shower like growth of nanotubes on the CNT’s grafted uncoated sample [shown in figure 57(a)]. This can be attributed to the surface inertness of carbon foam. For uniform growth of nanotubes, the foam surface can be modified using a thin SiO$_2$ coating which can enhance its surface reactivity.

SiO$_2$ layer was deposited on carbon foam surface by following the same experimental procedure mentioned in chapter 5. Silica layer is expected to act as grafting sites for nanotube growth. CNT’s were then synthesized on plasma surface modified foam following the same experimental procedure. After 30 minutes treatment time, the
Carbon Nanotubes Grown on Foam

(a)

Carbon Nanotubes Grown on Foam

(b)
Figure 56: SEM Images (a) before and (b, c) after synthesizing Nanotubes on Foam
sample was analyzed using SEM [figure 57 (b)]. Compared to uncoated foam, oxide coated foam has high density and uniform distribution of CNT’s as the silica layer nucleates the nanotube growth all over the surface. Due to the limitation in the magnification range and high growth rate of nanotubes on the oxide coated foam surface, no other useful information was able to be produced using SEM. The distribution density of nanotubes can be controlled by adjusting the CVD growth temperature and ferrocene to xylene ratio. It is observed that sparse CNT’s can be obtained when the CVD is performed at a higher temperature range. It is also shown that the nanotube diameters and total carbon yield decreases with decreasing ferrocene concentration due to the formation of smaller iron clusters²⁹, ⁹⁶, ⁹⁹.

In summary, studies related to growth and characterization of nanotubes on carbon structures has been performed. Multiwalled nanotubes were successfully synthesized on complex and uneven carbon structures like carbon foam and nanofibers. Silica layer nucleates nanotube growth on the entire carbon structures where as uncoated carbon structures have shower like growth of nanotubes. SiO₂ layer seems to enhance the length, density and uniformity of nanotubes synthesized on oxide coated carbon structures. This unique nanotube grafted carbon structures are expected to have potential aerospace, automotive and thermal applications. In particular, the presence of nanotubes on carbon structures enhances the surface area to volume ratio, desired for the design of reinforced composites.
Figure 57: SEM Images of Nanotubes Grafted (a) Uncoated and (b) Oxide Coated Foam
11. Summary and Conclusions

Detailed investigation of chemical and micro-structural effects of surface treatment on carbon structures has been performed. The results obtained from the liquid phase activation treatment indicate that exposure to acidic solutions deposit oxygen functional groups and improves micro-roughness. These can indeed increase the polar fluid infiltration and wettability of the carbon foam surface. However, this treatment may be severe enough that it damages the ligaments and cell walls of carbon foam making it weak and results in a weak composite. So, to get any benefit from such approaches the optimization window may be very narrow and marginal in controllability.

Plasma assisted coatings having thickness in the range of few nanometers (4-5 nm) can completely cover graphite substrates. Plasma oxide coating chemistry is comparable to pure SiO$_2$ that enhances the surface reactivity and wettability. Presence of strong Si-C chemical environment is observed at the silica-graphite interface. These coatings can withstand temperatures upto 1000 °C without degradation, hence suitable for high temperature applications. In the case of plasma fluorocarbon coating, the chemistry of the synthesized nano-layer is comparable to the conventional polytetrafluoroethylene (PTFE, -CF$_2$-). This coating enhances the surface inertness of the substrates.
When plasma coatings were used for surface modification of microcellular solids such as carbon foam, they were able to pass through the pores (∼ 100 µm) and modified the cell walls and ligaments. Plasma oxide coatings proved to be effective in increasing polar fluid infiltration, surface bonding, and the toughness in carbon foam/epoxy composite.

On the other hand, plasma assisted fluorocarbon coatings have the opposite effect. Fluorocarbon coatings applied to foam reduced oxygen contamination, and fluid infiltration. The effects were found to last over long periods at room temperature. Fluorocarbon coatings seem to have potential applications in the field of stand-alone carbon structures to prevent moisture, degradation, etc.

Plasma coatings successfully modified the surface of vapor grown carbon fibers (size 70 - 200 nm) and proved to be effective at nanoscale. The plasma coated nanofibers are smooth and there are no traces of damage caused by the nano-coatings. Plasma oxide coating enhances the dispersion and wettability of nanofibers in organic matrix whereas fluorocarbon coating reduces it.

Plasma coatings proved to be effective in metallization process. The plasma oxide coatings not only improve the interfacial bond in carbon reinforced-polymer matrix composites, but also in carbon reinforced/metal matrix composites. The fluorocarbon coating on graphite promotes delamination/exfoliation of the metal, hence may be used for patterning of metal interconnects.
It was also found that nanotube formation on base structures can be enhanced and controlled by the plasma oxide coating. Silica layer enhances the nanotube length and distribution density synthesized on carbon structures, hence can be used for fabrication of nanotube structural components.
12. Future Study

- It will be interesting to optimize the processing conditions of nanotubes to obtain the desired physical and chemical properties. Controlling the nanotube growth on carbon structures will be instrumental in achieving multiscale composites.

- Further application of plasma coatings in modifying much more complex and uneven structures such as nanowires, multi-walled carbon nanotubes (MWNT), and single-walled carbon nanotubes (SWNT) will open more areas of its applications.

- In the future, studies related to the mechanical performance of nanotube grafted oxide coated carbon foam/nanofiber reinforced polymer matrix composite will help to produce multifunctional materials.

- Detailed XPS analysis indicated the presence of Si-C bonds at silica-graphite interface. This will enable to effectively design and perform model studies of the interface in oxide coated carbon core polymer/metal matrix composite.

- In the future, the influence of plasma coatings on 3-dimensional carbon-metal composites needs to be studied in detail.
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