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Interfacial Modification of Microcellular Carbon: Influence of Ceramic and Carbon Nanotube Coatings

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INTERFACIAL MODIFICATION OF MICROCELLULAR CARBON: INFLUENCE OF CERAMIC AND CARBON NANOTUBE COATINGS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering

By

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Microcellular carbon is an emerging ultra lightweight and efficient thermal management material, which also has great potential as a reinforcement material for selected composites. However, these porous materials exhibit relatively low mechanical properties, and are susceptible to degradation in oxidizing environment. The scope of this research is to investigate surface modification approaches that can address these issues. Two specific objectives were: (i) to develop ceramic coatings to improve the survivability of carbon foams in high temperature applications, and (ii) to develop and test modifications that can improve cellular composites involving carbon foam. It was seen that a mixed layer of BN and SiC on the foam improves its oxidation resistance at high temperatures to the same extent as pure BN layer. However, the mixed layer had improved microstructure, and presence of silica phase, that maybe useful in development of selected functionally gradient coatings in the future. For modification related to future cellular composites, it was seen that attachment of carbon nanotubes (CNT) on the surface can significantly improve its bonding with other phases, and therefore the mechanical behavior of composites made from this foam. The influence of CNT attachment on mechanical performance and failure mechanics of foam-epoxy composite
was investigated. Model studies were also carried out on planar graphite-epoxy interfaces using 3-point bending tests. It has been observed that the CNT attachment significantly improves the durability and toughness of the carbon-epoxy interface by preventing delamination.
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1. Introduction

1.1 Microcellular Carbon Structures

The constant demand for light weight, efficient, inexpensive, and multifunctional materials has lead to the development of many cellular structures. Examples of such structures are metallic, ceramic, polymer, and carbon foams. Cellular structures are traditionally divided into two types; closed cell and open cell structures. Closed cell structures consist of non connecting micron size air bubbles embedded inside a solid matrix, whereas open cell structures have interconnected pores distributed three dimensionally at fixed or varying intervals. Among the different open cell structures, carbon structures are of great interest for thermal and structural applications. Carbon foams are microcellular pores interconnected three dimensionally in a regular pattern with porosities ranging from 70 to 96%. Microcellular carbon is classified into two categories; vitreous (glassy) carbon foams and graphitic carbon foams. Vitreous carbon foams are predominately amorphous foams which have lower thermal, electrical, and mechanical properties, because of their lack of graphitization. Graphitic carbon foams have well-aligned graphitic planes along the ligament, which has many properties such as higher mechanical, electrical, thermal properties, and lower coefficient of thermal expansion, etc. Some of the potential applications of graphitic carbon foams are in the field of aerospace, electronics, bio-medical devices, communication satellites, and automobile industry. Many of the applications are primarily due to its low cost, high surface
area, open cell architecture, low density, controllable thermal and electrical conductivity, energy absorption, low coefficient of thermal expansion, and high corrosion resistance.

1.2 History of Carbon Foams

Carbon foam was initially developed by W. Ford in late 60’s [1]. After a few decades, researchers at Wright Patterson Air Force Base (WPAFB) first reported the creation of graphitic foams from mesophase pitch primarily to replace 3-D woven fibers. Several years later, Oak Ridge National Laboratory (ORNL) reported the first foams with specific thermal conductivities higher than that of copper. Later the process was licensed by Koppers Inc. and Poco Graphite Inc. for commercial production. The foams used in this study were developed by ORNL and licensed by Koppers Inc.

1.2.1 Graphitic Foam Used in this Study

Preparation process of the graphitic foam involves the following steps [2]:

- Pitch powder is loaded into the cylindrical and rectangular molds.

- Loaded molds are evacuated to less than one Torr and then heated to temperatures 50 – 100°C above the melting temperature of the pitch.

- At this point molds are pressurized to 1500 psi with nitrogen and the temperature of the system is raised to 1500°C at a rate of 5°C/min.

- After 15 minutes, the furnace is shutdown and cooled to room temperature at a cooling rate of 1.5°C/min.

- At this time pressure is also released at rate of 2 psi/min.

- Foams are heated to 1000°C for carbonized and 2800°C for graphitized foam.
The basic properties of the graphitic foams are:

- High thermal conductivity (ligament conductivity is greater than 1700W/m.K) up to 175W/m.K
- High specific surface area and low density
- Low coefficient of thermal expansion
- High acoustical absorption
- Good oxidation resistance in inert atmosphere

Potential applications include:

- Power electronics, brakes and clutch cooling
- High temperature structural applications
- Possible reinforcing materials for net-shaped composites
- Activated carbons for environmental and industrial applications

### 1.3 Microstructure Analysis of Carbon Foam

Microcellular structures are less studied and poorly understood structures compared to traditional carbon structures such as cylindrical fibers, graphite, and carbon nanotubes. Structures such as fibers and graphite have one or two dimensional alignment of graphitic planes, whereas cellular carbon foams are comprised of voids and a solid network consisting of stacked graphitic planes (graphitized foams) oriented along the ligament (Fig 1). Carbon foam nomenclature is explained in Figure 1. Microstructure, physical, chemical, and mechanical properties of carbon foam vary according to the
Figure 1: SEM images of microcellular carbon foam
processing parameters, type of precursor pitch, stabilized gasses used, and level of
graphitization. Graphitization improves the mechanical strength, density, and thermal
conductivity by creating the aligned hexagonal graphitic planes. On the other hand, it also
makes the foam brittle, hydrophobic, and susceptible to oxidation. Moreover, as the
degree of graphitization increases, properties become anisotropy. The combination of the
above effects makes these materials challenging to understand. Many groups have studied
the precursor pitch, temperature, and pressure effects on final microstructure of carbon
foam using scanning electron microscopy, X-ray diffraction (XRD), and X-ray
photoelectron spectroscopy (XPS) [3]. Optimization of strength, thermal conductivity,
and graphitization has been done but with limited success. In light of these problems,
over the last few years research has been conducted by this group focusing on the
development of various surface modification techniques. These include plasma and liquid
based coatings, and have proven to be effective in dealing with some of the
aforementioned problems. These coatings are based on tailoring the surface chemistry,
attaching particles, and growing nanotubes to the cell walls without damaging the
underlying graphite. These can help to solve issues related to surface area, surface
energies, and chemical potentials.

1.4 Surface Coatings

For many engineering applications the chosen materials (carbon foam in this study)
may not possess satisfactory surface properties and/or bulk properties. One way to impart
or enhance surface related properties is by utilizing coatings which are a form of surface
modification. Surface modification can be defined as deliberate process of
Table 1: Classification of coating techniques by deposition rates [4]
modifying structures on the outer regions (ragingly from 1nm - 1000nm) to enhance or impart the desired properties. Surface modification can be performed by either application of new materials onto the surface (coatings) or modification of composition of existing surface (etching, re-ordering, and alloying). Depending on the substrate material, function, desired durability, and deposition rates of the coating, there are different surface modification techniques available (table 1). Carbon foams have been subjected to various surface modifications techniques over the years for various applications. The application of protective coatings is an approach which dates back to the beginning of civilization. A coating can be defined as layer of any materials used as a cover, protection, decoration or finish. Examples include silicon oxide coatings, fluoro carbon coatings, surface etching, ceramic coatings, and CNT coatings. Most of the techniques used in this thesis are developed in-house and successfully employed on carbon foams. In this thesis, previously explored methods were further developed to make composite ceramic coatings for oxidation protection as discussed in the following section and CNT grafting for hybrid cellular composites to be discussed in later sections.

1.5 Oxidation Protection Coatings

Graphitic foams are being considered for high temperature thermal management material due to their combination of properties such as low density, high strength-to-weight ratio compared with respect to metallic foams, and their ability to retain mechanical properties at higher temperatures. Although an attractive material, graphitic foam tends to lose these unique properties due its inability to survive in oxidizing environment.
In this research, a dip-coating technique, developed in this group, has been used. Liquid based ceramic composite coatings have been developed to protect carbon foams from oxidation. A mixture of silicon carbide (SiC) and boron nitride (BN) together with poly-vinyl-pyrrolidone (PVP) binder has been dip coated onto the carbon foams. Performance of the coating was tested by heat treatment test, weight measurements, and referred as survivability of foam. Coating quality was analyzed using scanning electron microscopy (SEM) and surface chemistry is been studied by X-ray photoelectron spectroscopy.

1.6 Cellular Reinforcement for Composites

Performance of any composite system mainly depends on two things: characteristics of individual constituents and interfacial properties formed between the constituents. The typical reinforcement material for carbon-polymer composites are cylindrical micron-sized carbon fibers [5] and carbon nanotubes [6]. Carbon fiber reinforced composites possess excellent mechanical and thermal properties along the longitudinal direction, but have poor properties along its transverse direction. A change in properties with respect to direction is called anisotropy which has a significant impact on the performance of the composite. In light of these problems carbon foams have emerged as potential replacement due to their network-type architecture, surface area, isotropic properties, and substantial fiber-like properties. Though the carbon foam itself is a good reinforcement for net-shaped composites, its low density, complex geometry, presence of internal cracks, and graphite-like inert surface chemistry lowers the composite performance. Strength of the carbon foams can be increased by structural texturing such
as folding of graphitic planes, careful control of composition, and increased degree of
graphitization. Graphitization increases the strength, density and specific surface area
which is an important parameter for composites. Composite performance often depends
on available interfacial contact area between core and matrix, and interfacial shear
strength is regarded as directly proportional to this area. Researchers have been trying to
optimize graphitization levels and other properties by relating process parameters such as
temperature and pressure with porosity, pore sizes, etc. However, these do not help much
in terms of overall surface area as seen in the later sections.

1.6.1 Geometrical Modeling

Unlike two dimensional carbon structures such as carbon fibers or graphite, carbon
foams have a unique structure which makes it difficult to calculate properties such as
strength, conductivities, etc. The open cell architecture, high surface area, low density,
and unusual alignment of graphitic planes are features that can be exploited in reinforcing
many properties, but are difficult to calculate. Geometrical modeling of carbon foams can
help in the prediction of ligament and pore distribution from standard set of geometries.
Geometrical modeling may help to correlate the mechanical properties, thermal
properties and specific surface area of the foams with the structural parameters such as
pore radius, inter-pore diameter and ligament shape. With advancements in
computational modeling, researchers have developed various representative volume cells
(the smallest shape which will be repeated in three dimensional space to form a cellular
network) to model the carbon foam.
Geometric models such as tetrahedron, cylindrical, and cubic have been developed. Numerical methods such as Finite Element Modeling and Analysis were used to study the deformation characteristics, stress states, and thermal fields of the ligaments [7-8]. In this research, a simple solid geometrical model was enhanced. The body-centered-cubic arrangement of pores [9] initially combines with microstructure to predict a few surface related properties. Secondary electron micrographs and the previously developed analytical model have been combined to estimate changes in bulk properties such as specific surface area and porosity with the change in microscopic properties such as pore radius, inter-pore distance, and representative volume cell (RVC) length. AutoCAD was used to create geometrical models of a representative volume cell (RVC) and model carbon foam.

It is predicted from this model, that just changing the parameters (pore size and distribution) of the microcellular foam will not result in drastic changes in surface area. Hence, an additional approach may need to be investigated to enhance these materials. Addition of nano-sized structures to create a hierarchical structure is an option which will be investigated in the preceding section.

1.6.2 Hierarchical Structures for Cellular Composites

One approach common in natural biological systems and natural composites (e.g. cellulose aggregates in wood and collagen aggregates in cartilage) is the use of hierarchical structures. However, this was not done too much on synthetic materials because the challenge of controlling the interface of two dissimilar materials at different
length scales was found to be formidable. There are some reports of hybrid fibers (fibers grafted with carbon nanotubes) to improve the out-of-plane properties in fiber composites [10].

1.6.3 Carbon Nanotubes Grafting for Hierarchical Structures

Since the re-discovery of carbon nanotubes (CNT) in early 1990 by Sumio Iijima [11], they have found their way into the many applications including nanotechnology, optics, electronics, and other fields of materials science. A carbon nanotube can be viewed as a cylindrical nanostructure created by rolling a graphene sheet. The typical dimensions (width and length) of CNT changes with processing parameters and raw materials used. CNT have exceptional electrical, mechanical, thermal, chemical, and optical properties mainly due to their high aspect ratio, high surface-area-to-volume, and free $\pi$ electrons, etc [12-13]. CNT have been using in applied fields such as highly efficient field emitters, probes for scanning probe microscopy, high strength nano fibers for high performance composites, and micro-and-nano electronic devices. Because of the wide range of applications it can offer, extensive research has been going on to tailor the CNT growth mechanism to obtain specific kinds such as semi-conducting, conducting for electronic applications, and various shapes for structural applications. Currently there are a number of techniques available to synthesize carbon nanotubes, including arc discharge, laser ablation, and chemical vapor deposition. Among these, chemical vapor deposition (CVD) has proven to be advantageous, because it is able to produce nanotubes in relatively large quantities. Hydrocarbon sources such as methane, ethylene, and xylene
are decomposed over Co, Ni, Fe or other transition metal or alloys. Processing steps and parameters are discussed in detail in Chapter 5.

A layer of strongly attached CNT can enhance the surface properties (surface area) as well as the bulk properties of the substrate material because CNT offers high surface area, surface roughness, stress transfer channels, and mechanical interlocks needed at the core-matrix interface. There are reports of growing nanotubes on individual fibers, and fiber cloths [10, 14] to make composites (Fig 2). In addition, nanotubes are known for their exceptional load transfer and as an energy absorbing material, which makes them an ideal interface material between reinforcement and matrix in composite applications. Though it is clear that attaching CNT to the cellular core can be an effective way to improve the cellular composite performance, it has never been successfully attempted before.

Dr. Mukhopadhyay’s group has several publications [15-16] in grafting nanotubes on uneven surfaces such as carbon foams (Fig 2), which opens up the potential usage of the carbon foam for high performance composites. In this research, CVD method has been used for CNT grafting, and CNT-grafted carbon foams are used to make the composites by infiltrating them with epoxy. Epoxy-infiltrated foam is air cured for 10 days before being tested. Carbon nanotubes serve both as a load transfer medium between the epoxy matrix and carbon foam by forming a strong interface and also increases the toughness of the carbon foam itself by filling the micro-cracks which are already present.
Figure 2: Carbon nanotube grafting on carbon substrates
Developed composites were compression tested and compared with untreated foam composites or “control composites”.

These were also compared with previously proposed pre-coating [17] where the foam was coated with a nano-scale of oxide. This coating with nano-oxide was used as a pre-coating for CNT growth. A side study done earlier [18] had shown that this pre-coating by itself, without CNT attached, provides some improvement in the foam-epoxy interface. So, here it was considered appropriate to compare all the components: (i) untreated foam (ii) oxide pre-coated foam (iii) CNT attached foam composites. Each of these structural analyses has been repeated on flat graphite. Highly oriented pyrolytic graphite (HOPG) provides the plane interface for graphite and epoxy which can serve as a quantified model.

1.7 Objectives

The motivation for this research is to address the inability of carbon foams to survive high temperatures needed for thermal management, and lack of ductility needed for cellular net shaped composites. For investigating the former issue, a dip coating technique was used to develop composite ceramic coatings to improve survivability of carbon foams from oxidation in open air. For the later problem, methods for enhancing the interface that can enhance ductility of carbon foam for composites have been investigated. It must be emphasized that the focus of this thesis is not to develop one specific composite, but rather to focus on the possibility of creating a specific structure that can improve future composites based on these structures.
2. Literature

There has been a significant amount of research on carbon foam for tailoring the processing parameters, microstructure, and physical properties for specific applications. There is a variety of research papers available on micro structural studies, thermal, and mechanical studies which will be discussed in the following sections.

Since this materials inception in 1960, microstructural graphitic carbon has been evaluated as a possible core material for many engineering structures. The time line for evolution of this material can be summarized as follows [1-3]:

- In the late 60’s, W. Ford first reported production of vitreous (glassy) carbon foam from thermosetting organic polymer by a simple heat treatment process.
- Several decades later, researchers from Sandia National Laboratories first produced the carbon foam from natural precursor.
- In the early 90’s researchers from Air Force Research Laboratory (AFRL) and Oak Ridge National Laboratory (ORNL) produced the mesophase pitch derived graphitic foam, specifically to replace 3-D woven fiber for composites and to replace honeycomb primarily for structural composites.
- Researcher at ORNL developed inexpensive and high conductivity mesophase pitch derived carbon foams for thermal applications.
- Poco Graphite Inc. and Koppers Inc. adopted the process for commercial production.

Since these are relatively new and complex structures, understanding is somewhat limited. There are number of unresolved issues accompanied with these structures. Some of these are addressed below:

- Similar to other carbon structures such as fibers, graphite, and C/C composites, survivability of the carbon foam is low under oxidizing environments.
- Low compatibility with other phases of materials due to surface chemistry related issues.
- Not enough structural understanding and relatively low mechanical properties such as strength and work to failure needed for structural applications.
- Better correlation between void size, shape, density, porosity, thermal, electrical, and mechanical properties is needed.
- Optimization of precursor pitch, process parameters, and final microstructure needed for specific structural and thermal applications.

Based on the previous work done by the various groups, some of the issues addressed above were studied, few directly and few indirectly.
2.1 Microstructure Analysis and Geometrical Modeling

Carbon foams are considered to be an ideal alternative material for individual carbon fibers and metallic foams for selected applications. Some of them are reinforcing material for structural composites and core material for sandwich beams respectively. Because many unique properties of the graphitic carbon foam are due to their open cell architecture, alignment of graphitic planes along ligaments, and low density, researchers have been working on gaining control over the final microstructure, bulk thermal and mechanical properties. Some developments are: (i) high thermal conductivity graphitic foams without the traditional blowing, stabilization steps and studied the microstructural changes with the choice of pitch selected and changing processing parameters [3, 19-20]. (ii) Anderson et al from University of Dayton Research laboratory (UDRL) have developed the highest specific strength carbon foams to date from mesophase pitch and studied the density, volume expansion, strength, and thermal conductivities variation with temperature [21-22]. (iii) there are reports on the anisotropy of these materials in mechanical properties [23-24]. All the above efforts are focused on experimental studies. Researchers are trying to explore computational methods for structure property-process relations. First efforts to establish a solid-bulk property relationship is by Gibson and Ashby [25] followed by Bauer et al. Bauer et al first developed semi-empirical model and studied the thermal conductivity of porous mediums analytically and from that, draw a relation between solid properties to the bulk properties [26]. Balatrapu et al. [27] developed the analytical model consisting of mutually orthogonal cylindrical ligaments to predict the surface area and the thermal conductivity of open cell lattice structures. Sangwook and Roy [8] developed a tetrahedron model to predict the bulk properties of
the carbon foam finite element analysis on the tetrahedron shaped ligaments and also provided process-property relation. It must be noted that all the above mentioned research was targeted towards achieving optimum conductivity and strength with minimum cost but at the expense of excessive graphitization. However graphitic foams are inert, prone to oxidation, and brittle which needs to be addressed.

2.2 Composite Coatings for Oxidation Protection

Like every other carbon structure, graphitic foam is susceptible to oxidation at temperatures above 500°C and loses its unique combination of properties. Formation of refractory ceramic materials such as BN, SiC, Al₂O₃, Si₃N₄ or combination may provide some protection needed from surface oxidation. There is a variety of techniques available depending on substrate morphology, chemistry, cost, feasibility, intended application, and function. Some examples are SiC and glass multilayer coatings on C/C composites [28-29], SiO₂ and Al₂O₃ coatings on fibers by sol gel technique [30], and SiC coatings by chemical vapor deposition on graphite [31]. However, there is limited research available that targets coatings on carbon foam. Though researchers achieved significant success, the same materials and techniques may not work on carbon foams whose microstructure and morphology is quite different from the above mentioned carbons. James Klett et al. improved the oxidation resistance of the carbon foam by SiC coatings using trichlorsilane as a precursor [32]. This is a complex process involving toxic chemicals. The goal of the present project is to use benign chemicals, simple, and inexpensive processing route.
An earlier thesis in this group (D. N. Sharma, [33]) involves solution based, simple scalable dip technique for anti-oxidation coatings on carbon foams. The coating consisted of varying sizes of hexagonal BN particles forming a multi layer. This was done by dipping the carbon foam in a BN-containing precursor [33]. Double layer coatings however showed little improvement and issues such as adhesion and oxidation mechanisms were not addressed. In this thesis, some effort was made to advance the process to form a composite multilayer coating containing a mixture of SiC and BN particles. This would help in oxidation resistance and lay the groundwork for creating compositionally (and functionally) gradient coatings in future.

2.3 Carbon Foams for Cellular Composites

Cellular materials have distinct advantages over their solid counter parts because of the high specific strength, surface area, low cost, and versatility for selected applications. They are of great interest for reinforcement material in cellular composites and main core material in sandwich beam construction. They may be used in load-carrying structures and thermal management applications. Microcellular carbon structures can be a preferable choice over their metal counter parts in some cases because they are cheap, light, and versatile. Possibility of carbon foam as a core for sandwich panels has been tested with significant success [34-35]. However carbon foam based cellular composites showed poor mechanical properties because graphitic carbon foam is brittle [36]. Reasons cited are cell wall openings due to the precursor hardening at graphitization temperatures and graphite like surface chemistry which does not form any chemical bonds with the polymer matrix [37]. Enhanced interfacial bonding can be promoted by
surface etching, surface roughing, and attaching active groups. Earlier researches in this group have developed plasma enhanced silicon oxide coatings to improve core-matrix interfacial bonding with significant success [38-40]. There are reports of adding chopped fibers and clay to suppress the brittle fracture but this met with limited success [41-42]. However, one approach that can be used is the CNT grafting which will be discussed in the following section.

### 2.3.1 Carbon Nanotube Grafting

Synthesis of carbon nanotubes has been in practice for several years. There are number of techniques available and the choice of a specific technique depends on several factors such as desired yield, substrate morphology, targeted application, etc. Some of the techniques are arc discharge [43], laser vaporization [44], pyrolysis, and chemical vapor deposition [45-46] are successfully employed for wide variety of applications. Among the number of available techniques, chemical vapor deposition has demonstrated several advantages in growing carbon nanotubes. In addition, growth mechanisms are well studied [47-48] which opens up the possibility of hierarchical structures and successfully used for the multifunctional composites as stated earlier.

Hierarchical structure is a structure having components of different length scales. Though very common in natural biomaterials, it is not very common in synthetic materials because of the significant difficulties in fabrication [49]. Some of the hierarchical structures reported so far are grafting carbon nanotubes (CNT) on individual micron size fibers [50-51], fiber cloths [52], and/or ceramic fibers [53]. Composites made
with CNT grafted fibers or “Hybrid fibers” have shown improved fracture toughness. The reasons cited are improved interfacial bonding through mechanical interlocking, improved load transfer, improved interfacial contact area, and improved interfacial shear strength due to the presence of CNT reinforced matrix at the interface. However, grafting CNT on uneven substrates such as carbon foam is arguably the toughest task, as graphitic carbon foam has significantly more complex morphology.

Any composite performance depends on the individual components as well as the interfacial characteristics. Therefore specific surface area available for reinforcement-matrix interface is a very important factor. Hierarchical structures can increase this interfacial area significantly. In this study, an estimate of available specific surface area and its increase with CNT grafting is calculated using pre-developed geometrical models. This model is built upon analytical models developed by previous groups [9] as stated in earlier section. In this study, microstructure of the graphitic foam and its analytical model was combined to predict the specific surface area of the open cell structures. It can be seen that CNT grafting would increase the available specific surface area by three orders of magnitude [13].

Growing CNT layers have been limited to simple geometries. From earlier studies, it was seen that in order to have reliable growth and strongly attached CNT on any geometry, the critical step is the deposition of oxide layer. This was seen to improve catalytic activity [17]. Plasma enhanced silicon oxide nano-layers grown by this group for multifunctional applications have been used as the starting layer for the CNT growth
[17-18]. The parameters and process for growing carbon nanotubes was also optimized by earlier research [15]. In this thesis, an optimized process for growing carbon nanotubes on uneven surfaces such as carbon foam was used. Knowledge from the mechanical studies on carbon foams, nano composites, and hybrid fiber composites is combined together to study the failure mechanics of CNT grafted carbon foam reinforced cellular composite. The effects of CNT grafting on interfacial mechanics and failure mechanisms of carbon foam reinforced composites or “cellular composites” have been studied.

Further research was carried out by making CNT grafted graphite-epoxy- CNT grafted seam sandwiches for interfacial strength analysis. Three-point-bending test was used since samples were small and brittle and it was not feasible to grip them for tension tests [54]. The results have been compared to strength of the monolithic paralytic graphite tested this way [55].
3. Characterization Techniques

The various characterization techniques used in this thesis are discussed here. The equipments used were universal testing machine, field emission scanning electron microscope (FESEM), and X-ray photo electron spectroscopy.

3.1 Universal Testing Machine

A universal testing machine is a machine used to test various material properties. The machine used in this research was Instron 4505 series testing machine (Fig 3). Typical testing system consists of machine/test frame, control, and analysis software. Machine test frame consists of load cell and movable frame to measure force and displacement respectively. Load cell interchangeability, transducer recognition, and auto calibration makes this testing machine easy-to-use. There are wide ranges of load cells available ranging from 100kN to 500N (maximum load they can measure). Repeatability of the load cell is ± 0.25% of reading over a range of 0.4% to 100% of its full capacity. System electronics are designed in a way that they provide overload protection by stopping the test at 105% of full scale output. Control frame is to control the frame movement and test. Analysis software is to set the test procedure, parameters, and record the resulting data digitally.
Figure 3: Instron 4505 universal testing machine
Two kinds of tests were performed using the universal testing machine: compression and three-point-bending test. Compression test was to test the surface modifications that can improve cellular composites performance. Whereas, three-point-bending test was to test the model interfaces fabricated by attaching two flat graphite sheets with an epoxy. Detailed description of the tests is discussed in their respective sections.

### 3.2 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscope (FESEM) was one of the characterization techniques widely used in this thesis for microstructural failure analysis (Fig 4). Unlike regular SEM, field emission gun employs cold cathode, providing narrower probing beams at low as well as high electron energy. In addition, it has new technologies such as GB (gentle beam) mode for controlling the electrons irradiated from the specimen surface (especially non-conducting samples used in this work). This additional feature coupled with field emission (FE) gun improves spatial resolution while minimizing sample charging and damage. This system consists of four detectors: secondary electron detector, back-scattered electron detector, transmission electron detector, and X-ray detector, in order to acquire maximum information from the specimen. The complete set up is connected to graphical user interface (GUI) using windows based PC host.

The FESEM used here is JSM-7401F and its details are (Ref 56):

Primary function: surface microstructure, chemical composition
Source type: cold cathode type, FE electron gun

Resolution: 1.4nm at 1kV, 1nm at 15kV

Accelerating voltage: 100v to 30kV

Magnification: 25 to 1,000,000X

Maximum specimen size: maximum diameter is 150mm, optional is 200mm

Chemical composition: yes, provides through energy dispersive spectroscopy (EDS)

Chemical states: no

Other features: back scattered mode, transmission mode

### 3.3 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was the characterization technique used to study the surface chemistry of the oxidation resistance coatings (Fig 5). It can precisely reveal information about elemental composition, empirical formula, chemical state, and electronic state of the elements that exist within 10nm from the surface.

The XPS works under photoelectric effect. The sample surface is irradiated by X-ray source and knocks the electrons out from the outer shells of the surface atoms. Electronics in the system count the number of electrons coming out and simultaneously
plotting number of electrons on the Y-axis and binding energies on the X-axis. The quantitative formula of the photoelectric effect is:

\[ E_k = h\nu - E_b \]

Here \( h\nu \) is the energy of the X-ray photon, \( E_k \) and \( E_b \) are the kinetic energy and binding energy of the escaping electron respectively. The XPS used in this study was Kratos AXIS ULTRA and its characteristics are (Ref 57):

Primary function: elemental composition, chemical states, empirical formulas

X-ray source: Al monochromatic K-alpha or Mg X-rays

Vacuum: below \( 10^{-9} \) to \( 10^{-10} \) Torr

Escape depth: 10nm from surface

Sample surface: surface should be considerably flat

Sample size limits: 1×1 to 3×3cm

Element limitation: every element except hydrogen and helium.
Figure 4: JEOL field emission electron microscopy

Figure 5: X-ray photoelectron spectroscopy
4. Oxidation Resistant Coatings

4.1 Introduction

Cellular structures have distinct advantages over their solid counterparts in high temperature thermal management applications. Among different cellular materials available, graphitic carbon foam is a preferred choice as it has three-dimensional network type architecture, high porosity, high specific surface area, and higher bulk thermal conductivities. Despite numerous advantages of the graphitic carbon foam over the other cellular materials, they are prone to oxidation in open air above 500°C. In order to use this material at high temperature thermal management applications, it is important to protect them from being oxidized. These problems lead to the development of oxidation protection coatings, which are common on other carbon structures such as graphitic fibers, C/C composites, and graphite. The preferred barrier materials are refractory metal oxides such as Al₂O₃, ZrO₂, carbides, and nitrides. There are number of techniques available such as chemical vapor deposition (CVD), physical vapor deposition, plating (electro and electrolyses plating), sol-gel deposition, sputter deposition, ion implantation, plasma & thermal spraying, etc. However, most of the coatings are developed on simple geometries such as cylindrical fibers, flat graphite, and C/C composites. Moreover, some of the above mentioned techniques involve toxic chemical by products such as BCl₃, high processing temperatures, involve expensive equipment, and also restricted to simple geometries.
There is very limited research on oxidation resistance coatings on cellular carbon. An in-house developed liquid base dip coating proved to be effective on uneven faces like carbon foam hence it was selected for this research. Advantages include no toxic chemicals involved, affordable, versatile, and compatible for ceramics particles used in this study. Among different materials available, boron nitride and silicon carbide were chosen because they are chemically and thermally stable at high temperatures, structurally similar with graphite (hexagonal BN), and has close coefficient of thermal expansion with the graphite (Table 2). In this thesis, double layer composite coating involving BN and SiC was developed.

<table>
<thead>
<tr>
<th>Material</th>
<th>α-SiC</th>
<th>Al₂O₃</th>
<th>Y₂O₃</th>
<th>BN-hexagonal</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.T.E (r.t-1000°C)×10⁻⁶/K</td>
<td>4.8</td>
<td>7-8</td>
<td>8.1</td>
<td>3.8</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 2: Coefficient of thermal expansion of prospective barrier materials

4.2 Double Layer Composite Coatings

4.2.1 Materials

Boron nitride (BN) and Silicon carbide (SiC) were selected because of the individual properties they can offer for this kind of coating. Selection of hexagonal BN was based on its structural similarity with graphite and its proven ability to form continuous oxidation resistance barriers. Moreover, BN forms boron carbides on carbon substrates, an oxidation resistance material. Various sizes of BN particles were tried
initially and selected 0.7μm because they provided less pore free coatings. Silicon carbide is a well known material for oxidation protective coatings due to its excellent mechanical and thermal properties. SiC oxidizes at high temperatures and forms uniform crystalline silicon oxide layers, which, in turn, makes the substrate wet and promotes adhesion between substrate and the barrier material. Moreover, thermally grown crystalline silicon oxide (SiO$_2$) layers also acts as a barrier for oxygen penetration. Smaller sized (compared to BN particles) 0.3μm β-SiC particles were selected as they were intended to fill the gaps presented in the BN layer. Together, boron nitride acts as an intermediate layer to provide coherent interfaces with substrate and silicon carbide acts as supplier to form silicon oxide layers. To promote adhesion between substrate, BN, and SiC, poly-vinyl-pyrrolidone (PVP) was selected as binder. PVP cures during the heating process and was burned off eventually without leaving any unwanted by-products.

4.2.2 Carbon Foam Substrates

Different grades of carbon foams are supplied by Koppers Inc. Three types of carbon foam substrates, partially graphitized (L1a), partially graphitized (L1), and graphitized (D) foams. The microstructures of as-received carbon foams are shown in figure 6.

4.2.3 Coating Technique as Developed

As-received foams were cut into 5mm cubes and cleaned with methanol to remove loose flakes, carbon powder, and any kind of dust particles associated with them. Cleaned samples were placed on hot plate to dry them. Since this was a liquid based
Figure 6: Microstructures of received carbon foams
coating, 0.075g of binder PVP was added to 5ml of methanol to form PVP solution. The coating procedure (Fig 7) and binder compositions used were drawn from earlier thesis. 0.15g of boron nitride micro particles of size 0.7\(\mu\)m and 0.15g of silicon carbide micro particles of size 0.3\(\mu\)m were mixed together and the mixture was added to PVP solution to get PVP-(BN + SiC) dispersion. Cleaned 5mm cube samples were dipped in the dispersion for given amount of time and this process was repeated several times to make sure samples were completely coated with PVP-(BN+SiC) dispersion. Coated samples were then placed in box furnace and raised the temperature to 200°C and kept there for 1hr before it was turned off. Samples were allowed to cool in the furnace overnight. This process allows the PVP to polymerize and settles the coating. Similar procedure was followed for the second layer of coating to get double layer composite coating. It must be noted that, previously developed double layer BN coatings (without SiC) were also repeated on the current foams to evaluate double layer composite coating performance.

4.3 Testing and Results

Testing was done in open air for oxidation survivability. Multiple samples (maximum of three) were made and tested. Coated samples were inserted into the furnace at 700°C and heat treated for 1hr. Samples were removed after the 1hr. Samples were weighed before and after the heat treatment and difference in weight over initial weight termed as survivability. As-received or “uncoated foam” samples of same dimensions were also made and tested as control. Results are tabulated in table 3.

\[
\text{%Survivability} = \frac{\text{Weight}_{\text{befo}\text{r test}} - \text{Weight}_{\text{after test}}}{\text{Weight}_{\text{befo}\text{r test}}} \times 100
\]
Figure 7: Step wise coating procedure used for double layer composite coating
<table>
<thead>
<tr>
<th></th>
<th>L1a</th>
<th>L1</th>
<th>D1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BN+SiC</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double layer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coating</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(survivability)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uncoated (%)</td>
<td>23.7±3</td>
<td>29.6±4</td>
<td>85.4±3</td>
</tr>
<tr>
<td>Coated (%)</td>
<td>83.7±5</td>
<td>88.2±3</td>
<td>92.6±1</td>
</tr>
<tr>
<td>Improvement (%)</td>
<td>253±16</td>
<td>197±25</td>
<td>9±2</td>
</tr>
<tr>
<td><strong>BN</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double layer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coating</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(survivability)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uncoated (%)</td>
<td>23.7±3</td>
<td>29.6±4</td>
<td>85.4±3</td>
</tr>
<tr>
<td>Coated (%)</td>
<td>80.2±5</td>
<td>85.6±3</td>
<td>91.7±2</td>
</tr>
<tr>
<td>Improvement (%)</td>
<td>228±16</td>
<td>189±25</td>
<td>7±2</td>
</tr>
</tbody>
</table>

**Table 3: Survivability test results**
4.4 SEM Analysis on Model Flat Graphite

Coatings were repeated on highly oriented pyrolytic graphite (HOPG) which has similar surface chemistry to as-received carbon foams used in this research. From FESEM images, it was observed that the coating morphology was compact and continuous. However, there was observable porosity present (Fig 8-A, 8-B) because of the burning of the PVP during the heat treatment which releases gases, leaving the pores or “pin holes” in the coating. Higher magnification images also showed presence of few agglomerates (Fig 9-A) and cracks (Fig 9-B). Widely accepted reason for the agglomerates presence was due to the smaller sized particles and cracks were also expected due to the sudden entry into the 700°C furnace.

In summary, there was an observable improvement in the coating microstructure over the pure BN coatings previously developed. This improved microstructure was due to the addition of smaller size SiC particles (0.3μm) used in this current research. This result can serve as a base for developing functionally gradient composite coatings. In addition, survivability tests showed that, current coatings improved the survivability of foams significantly over uncoated foams (Table 3). However, this improvement was equal to or little higher than the improvement by pure BN coatings. This unexpected result was attributed to the pores presented in the current coating which allowed the oxygen to penetrate through the coating and strike the underneath carbon.
Figure 8: SEM images showing coating morphology after survivability test
Figure 9: SEM images showing coating morphology after survivability test
4.5 XPS Analysis on Model Flat Graphite

XPS spectrum was taken on the coating to analyze the coating surface chemistry. From the general scan (Fig 10), there was an indication of a few carbon-oxygen products shown by multiple carbon peaks at approximately 284eV possibly from the left over PVP binder. Pure boron nitride was also retained, indicated by both general scan and quantitative data (Table 4). It was also observed that the silicon peak was divided into two sub peaks hence fine scan was taken. Detailed analysis of silicon peak showed (Fig 11) original silicon carbide at 99eV and silicon oxide at 102.9eV. Formation of silicon oxide was due to the oxidation of silicon carbide and should have improved the survivability more than the result yielded. However, it was clear from the earlier studies [18-19] that, only thermally grown crystalline oxide layers can able to prevent the oxygen penetration. Oxides’ formed at room temperature or at 700°C may not act as prevention barrier. In summary, this coating was pure and presence of oxide phases opened up the other possibilities for future work.
Figure 10: General scan of composite coating after survivability test

<table>
<thead>
<tr>
<th>Element</th>
<th>B1s</th>
<th>N1s</th>
<th>Si2p-1</th>
<th>Si2p-2</th>
<th>C1s-1</th>
<th>C1s-2</th>
<th>O1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic concentrations (%)</td>
<td>24</td>
<td>26</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>2</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 4: Quantification data of the general scan

Figure 11: Fine scan of silicon peak
5. Cellular Composites

5.1 Introduction

Traditionally carbon fiber reinforced composites are of great interest in fields ranging from spacecrafts to sporting goods. However, individual fibers generally provide strength along its longitudinal direction only. In addition, pitch based carbon fibers are expensive, difficult to make, and developed from mesophase pitch which is the same precursor used for pitch based carbon foams. Carbon foams have graphitic planes folded into rigid shapes within the ligaments making them an excellent reinforcement material for net shaped cellular composites. The strength of the carbon foam (maximum compressive strength reported is approximately 50MPa) is lower compared to carbon fibers, but compares well with other cellular materials such as aluminum foam. Carbon foam is also compatible for densification with other materials such as metals, epoxy, and carbon for structural composites. Carbon foam based cellular composites offer isotropic properties, high strength to weight ratio, high surface area, low coefficient of thermal expansion, and low moisture absorption, etc.

However, high strength carbon foam often comes at the expense of excessive graphitization that makes structure brittle and inert. Moreover, graphitization also creates
internal cracks and anisotropy. All the aforementioned problems decrease the performance of the carbon foam based composites.

Two of the important factors that influence the composite performance are: Interfacial bonding between constituent materials and available contact area at the interface. An interfacial modification of carbon foam was done with considerable success [17-18]. In this thesis, it was found that CNT grafting was an ideal approach as it increases interfacial surface area. There are models to estimate the surface area which will be discussed in the following section.

5.2 Geometrical Modeling of Carbon Foams

5.2.1 Introduction

Carbon foam is a mixture of gas pores and continuous solid graphite. Porosity is the ratio of gas pores volume to the volume occupied by the solid graphite and often controls the final microstructure and properties such as surface area, density, thermal and electrical conductivities, and mechanical strength. Many attempts have been made to correlate the microscopic properties such as pore radius and inter pore distance with processing parameters to optimize the carbon foam without compromising the structural integrity of open cell architecture. Examples of such kind of efforts are solid geometrical modeling. Though the real microstructure has pores with uneven size and shape, most of the geometrical models assume uniform spherical pores distributed periodically over a set
distance. In this thesis, previously developed model was studied to estimate the specific surface area and how it varies with varying pore size and distribution.

Among the different models available, body centered cubic cell arrangement was selected because minimum porosity required for inter-connected network of this model was close to minimum open porosity of as-received foams (L1) (Table 5). Moreover, microstructure of as-received foam (L1a) was also similar to the cross sectional view of modeled foam developed using solid works (Fig 12). It must be noted that open porosities of as-received foams were estimates given by Koppers Inc (company who supplied the foams) and any future changes are completely subjected to the supplier.
<table>
<thead>
<tr>
<th>Model/cell</th>
<th>Body centered</th>
<th>Tetrahedron</th>
<th>Face centered</th>
<th>Hexagonal close packed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum porosity for interconnection</td>
<td>0.68</td>
<td>0.78</td>
<td>0.74</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 5: Minimum porosities required for interconnection for available models

<table>
<thead>
<tr>
<th>Foam</th>
<th>L1a</th>
<th>L1</th>
<th>D1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>0.39</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>Pore diameter (μm)</td>
<td>500</td>
<td>600</td>
<td>650</td>
</tr>
<tr>
<td>Porosity (Supplied)</td>
<td>0.78</td>
<td>0.70</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 6: Specifications of as-received foam
Figure 12: Microstructure of carbon foam (top), cross sectional view of solid model (bottom)
5.2.2 Body Centered Cubic Cell Model

The distribution and size of the pores in the real foam may be irregular, i.e., they may not follow any three-dimensional regular arrangement. This irregular arrangement makes surface area calculations difficult. To simplify the problem, a few basic assumptions were made.

Assumption 1: All the pores were assumed to have equal diameter.

Assumption 2: Each pore was separated by a set distance.

A representative volume cell (RVC) was (Fig 13) modeled based on the assumptions stated and body centered cell (BCC) arrangement [9]. If the minimum distance between two pores is less than the sum of the radius of two pores ($d < 2R_p$) then the pores intersect each other and form an open cell network. Let us assume

\[ a = \text{Length of the cube edge} \]
\[ R_p = \text{Radius of the pores} \]
\[ h = \text{Height of the spherical cap} \]
\[ d = \text{Minimum distance between the pores} \]

In this kind of arrangement the distance ($d$) between the center pore to corner pore is equal to the half of the length of the diagonal hence $d = a \times \sqrt{3}/2$

\[
\text{Porosity}(P) = \frac{\text{Volume of the voids}}{\text{Total volume}} \quad \text{Eq(1)}
\]

\[
\text{Volume of the voids} = 2 \times \frac{4}{3} \times \pi R_p^3 - 8V_{lens} \quad \text{Eq (2)}
\]

\[
= 8 \left( \frac{\pi}{3} R_p^3 - V_{lens} \right)
\]
Figure 13: Idealized representative volume cell (RVC)
Volume of the spherical cap = \( \frac{\pi}{3} h^2 (3R_p - h) \)

Lens is formed by the two Spherical caps

\[ V_{\text{lens}} = 2 \times \text{Vol. of the Spherical hollow cap} \]

\[ = 2 \times \frac{\pi}{3} h^2 (3R_p - h) \]

Substitute Eq. (3) in equation 2

After some mathematical manipulations, one obtains

\[ P = \frac{2\pi}{3} \left( \frac{12R_p^2 d - 12R_p^3 - d^3}{a^3} \right) \]

Equation valid only for \( 0.68 < P < 0.94 \)

Similarly for specific surface area or “surface area per volume” \((S)\)

\[ S = \frac{8(Scorner) + \text{Inside surface area}}{a^3} \]

\[ = \frac{8 \times \left( \frac{4\pi R_p^2}{8} - 2\pi R_p h \right) + 4\pi R_p^2 - 8 \times 2\pi R_p h}{a^3} \]

Solve the above equation (5)

\[ S = \frac{8\pi R_p^2 - 32\pi R_p h}{a^3} \]

Since \( h = R_p - d/2 \)

\[ S = \frac{8\pi R_p^2 - 32\pi \left( R_p - d/2 \right) R_p}{a^3} \]

for \( d = a \times \sqrt{3}/2 \), Eq (4) and Eq (7) becomes
\[
P = \frac{2\pi}{3} \left( \frac{12R_p^2d - 12R_p^3 - d^3}{8d^3 / 3\sqrt{3}} \right) \quad \text{Eq (8)}
\]

\[
S = \frac{8\pi R_p^2 - 32\pi (R_p - d / 2) R_p}{8d^3 / 3\sqrt{3}} \quad \text{Eq (9)}
\]

5.2.3 Analysis

Figure 12 showed the comparison between the microstructure of the foam and the cross sectional view of the solid model developed using AutoCAD. For a given carbon foam, porosity and radius of the pores are the measurable parameters that can be measured from density measurement (Eq 10) and electron micrographs respectively.

Porosity of foam \( P = \left( 1 - \frac{\rho_{foam}}{\rho_{graphite}} \right) \) \( \text{Eq (10)} \)

Substituted the pore radius \( R_p \) and porosity \( P \) in equation 8 and solved for inter pore spacing \( d \). By substituting the pore radius \( R_p \) and inter-pore spacing \( d \) in equation 9, specific surface area \( S \) was calculated. In the graph shown below (Fig 14) porosity of the foam was kept constant and surface area per volume \( S \) was calculated while changing the pore radius. There was no observable change in specific surface area \( S \) with porosities at higher radius (500-800μm) values while little improvement was observed with increasing porosity at lower radius values measured (<200μm).
Figure 14: Specific surface area variation vs. porosity and radius
However, the overall surface area was not significantly higher at any given point. Consider an intermediate point, $R_p=300\mu$m, (typical pore radius of the foam used in this study) the specific surface area ($S$) at 0.68 and 0.94 porosities are 6.80mm$^2$/mm$^3$ and 4.85mm$^2$/mm$^3$ respectively.

In summary, it was understood that once the porosity or radius of the foam was fixed, there was not much change in specific surface area without compromising structural integrity. In other words, specific surface area can not be increased significantly by process-property-parameters relations. This drawback motivates people to think beyond the usual geometrical modeling-property relationship to improve carbon foam’s surface area. One approach common in natural composites and less exploited in synthetic materials is grafting nano-structures for hierarchical materials. In light of this, CNT emerged as ideal materials for grafting since they possess high aspect ratio, high conductivities, high strength, etc. Grafting of carbon nanotubes can prove to be a more efficient way of increasing the specific surface area.

5.3 CNT Grafting

5.3.1 CNT Grafting on Idealized Model

The available specific surface area for CNT grafting was $S$ (Eq 9). If nanotubes were grafted over the foam cell walls then the increase in specific surface area was $\Delta S$. Model representation picture is shown in figure 15. Assume

$$r_n = \text{Radius of the nanotube}$$
\( l_n = \) Length of the nanotube

\( f = \) Percentage of nanotube coverage

Percentage nanotube coverage \( (f) \) was calculated from

\[
f = \text{Number of CNT per area} \times (2r_n)^2
\]

Total surface area per volume after nanotube coverage is

\[
S + \Delta S = \text{specific surface area of carbon foam + specific surface area of CNT’s}
\]

\[
\left( (1 - f) \times S + (4r_n^2 - \pi r_n^2) \times \frac{S \times f}{(2r_n)^2} \right) + \frac{S \times f}{(2r_n)^2} \times 2\pi r_n l_n \quad \text{……..Eq (11)}
\]

![Model representation of grafted CNT on foam](image)

**Figure 15:** Model representation of grafted CNT on foam

\[
\frac{(S + \Delta S)}{S} = \left(1 - \frac{\pi f}{4}\right) + \frac{f}{(2r_n)^2} \times 2\pi r_n l_n
\]

Since \( \Delta S \approx S \) and \( \frac{l_n}{r_n} \approx l \) re-arrange the equation 11

\[
\frac{S + \Delta S}{S} \approx \frac{\Delta S}{S} = \frac{f}{(2r_n)^2} \times 2\pi r_n l_n = \frac{\pi l_n f}{2r_n} \quad \text{……………………………………………………Eq (12)}
\]
<table>
<thead>
<tr>
<th>$P$ (mm)</th>
<th>$R_p$ (mm)</th>
<th>$d$ (mm)</th>
<th>$a$ (mm)</th>
<th>Surface area per volume ($S$) (mm$^2$/mm$^3$)</th>
<th>For 20% coverage ($S + \Delta S$) $S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.05</td>
<td>0.099</td>
<td>0.114</td>
<td>39.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.198</td>
<td>0.228</td>
<td>20.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.594</td>
<td>0.685</td>
<td>8.62</td>
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<td>1.371</td>
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<td>1256.63</td>
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<td>0.564</td>
<td>0.651</td>
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<td>1.066</td>
<td>1.230</td>
<td>5.006</td>
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*Table 7: Increase in specific surface area of carbon foam with CNT grafting*
For percentage coverage ($f$) of 20%, nanotube radius of ($r_p$) 5nm, and the length of 20μm, clearly the available specific surface area of the carbon foam was increased by three orders of magnitude with CNT grafting (Table 7). CNT grafting not only increases the specific surface area needed at the interface, but also provides load, thermal, and electrical transport channels between carbon foam and matrix. Moreover, it also increases surface roughness, fills the internal cracks, and encourages the ductility of carbon foams. However, the real challenge lies with attaching strongly bonded nanotubes to the carbon foam and this was successfully done with the in-house developed chemical vapor deposition technique.

### 5.3.2 CNT Grafting on Carbon Foams

Carbon foams used in this study were supplied by the Koppers Inc, Pittsburgh. Among the different grades received, L1a was chosen (Fig 6) which had average pore diameter of 550μm-600μm (measured approximation). According to the requirements of optimum growth of CNT, foams needed to have interconnected and uniform distribution of pores. Furthermore, the thickness of film (foam substrate) was needed to be 2mm for optimum growth of CNT all the way through thickness. CNT grafting was a two step processes and was optimized in-house.
5.3.2.1 Silicon Oxide Nano-coatings by Plasma Deposition

Silicon oxide nano-coating was the first step for CNT grafting and it was successfully built by earlier students from this group. Carbon foams were placed in a microwave plasma reactor and were exposed to mixture of hexa-methyl-disiloxane (HMDSO) and oxygen. Samples were placed in a way that the plasma reached into every surface of the foam. This pre-coating helps to increase the catalytic activity of the Fe which in turn increases the amount of nanotube yield per catalyst [15, 17-18].

5.3.2.2 CNT Grafting by Chemical Vapor Deposition (CVD)

In step two, oxide coated samples were moved to CVD furnace (Fig 16) for CNT grafting. Samples were cut into specific shape to fit into the tube to allow maximum amount of vapor flow pass through the sample. Mixture of ferrocene and xylene along with hydrogen and argon was allowed to pass through the sample at set temperatures. Ferrocene and xylene were first heated into vapor then thermally decomposed and reformed into CNT. The role of ferrocene here was to supply Fe catalyst which is the location for starting the nanotube growth. The role of argon here was to keep the oxygen out of the tube and keep atmosphere inert while the tube was hot. Hydrogen keeps the byproducts out of the sample and aids the nanotubes alignment. The processing parameters such as deposition time, temperatures, and flow rates have been optimized in-house [15]. Electron micrographs were taken prior to making the composite to verify the growth of CNT, and good CNT growth was observed at all levels of pores through thickness (Fig 17). Though there were concerns over possible loss of bulk mechanical
Figure 16: 2-Stage chemical vapor deposition furnace

Figure 17: Densely grafted CNT at different levels of pores through thickness
properties of carbon foam during the CNT grafting at high temperature, the foams used in this study showed good retention of properties at higher temperatures in inert atmosphere.

5.4 Preparation of Hybrid Cellular Composite

Hybrid cellular composite or “CNT composite” was prepared by infiltrating the CNT grafted carbon foam with epoxy resin. The epoxy resin system used for composite making was supplied by “MAS epoxies”. It must be noted that the goal of this research was not to develop CNT composite. Rather it was to explore the effects of CNT grafting on the interfacial failure mechanism. Moreover, the matrix is not restricted to polymers and can be expanded onto other materials such as metals. Some of the specifications of epoxy resin system used are shown in the below Table.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Function</th>
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<tr>
<td>Low viscosity epoxy resin</td>
<td>Main epoxy system</td>
</tr>
<tr>
<td>(supplier: MAS epoxies)</td>
<td></td>
</tr>
<tr>
<td>Medium epoxy hardener</td>
<td>Hardener</td>
</tr>
<tr>
<td>Mixing</td>
<td>Mechanically until bottom of the container gets hot</td>
</tr>
</tbody>
</table>

Table 8: Specifications of epoxy resin system
Epoxy resin and hardener were mixed in 2:1 ratios and were mixed vigorously until it gets hot, indicating the resin had started curing and was ready to use. Step wise procedure of making a composite was as follows:

- 2mm thick CNT grafted films were stacked on top of each other and placed on the vacuum mesh tube (Fig 18).
- Epoxy was pored on the stacks.
- Suction pressure was turned on to force the epoxy through the thickness of stacks.
- Suction pressure was optimized in such a way that the vacuum does not drag the epoxy completely out of the foam pores.
- This process was repeated several times until all the pores were completely saturated with epoxy liquid.
- Samples were dried in the open air for approximately 7 or 10 days and cut into different dimensions.
- All the edges were polished flat before the compression test to reduce the frictional effects on mechanical performance.

Figure 18: Vacuum tube to infiltrate the carbon foam with epoxy
- Above steps were repeated for making control composite or “Base composite”, by infiltrating the uncoated foam with epoxy.
- Oxide composite was also prepared by infiltrating silicon oxide plasma coated (section 5.3.2.1) foams with epoxy.

### 5.5 Composite Testing

Samples were tested in compression mode due to the sample dimensional restrictions. Instron 4505 universal mechanical testing machine with 100kN load cell was used for the compression test (Fig 3). Samples were tested at strain rates of 0.25mm/min. Samples were cut into specific dimensions and polished to flat surfaces to ensure they were flat and perpendicular to each other, as surface roughness also plays an important role as a failure mechanism. Since the stress–strain behavior of the samples was sensitive to the sample dimensions, various sample dimensions were tried to identify the reproducible data. Multiple samples (usually three each) were tested for reproducibility from each category, both along and across the stacks. Number of samples were tested from each category depends on repeatability of the load-extension curve.

Load-extension values were recorded, and hence, compression stress \( \left( \sigma = \frac{F}{A} \right) \) - strain \( \left( \varepsilon = \frac{\Delta L}{L} \right) \) were plotted (Note: No strain gages were attached to the sample as the extension in the loading fixtures were minimal compared to the sample’s compression). Here F, A, ΔL, and L are compression load, cross sectional area, cross head displacement and sample length respectively. Mean graphs were drawn by calculating mean stress at fixed strains all along the stress-strain graph.
5.5.1 Optimized Samples

Finally, it was observed that cube shaped samples with dimensions of 6×6×6mm yielded the most reproducible data therefore this geometry was selected for final testing. Since CNT grafting was best optimized to 2mm thick foam for through thickness grafting, three 2mm foam samples were stacked on top of each other to get 6mm thickness. Samples were tested both along and across the stacks (Fig 19). Both control composite and oxide composite were also tested at each step to analyze the performance of the CNT composite. Incase of control composite, the test was stopped whenever a sudden drop of load was observed, whereas for oxide and CNT composite test was continued to a point where the sample dimensions and shape no longer relate to their original counterparts. Note: Red line in stress-strain graphs represents individual sample and black line indicates average graphs calculated over number of samples tested in that particular category.
Figure 19: Schematic representation of loading directions in optimized samples.
5.6 Results

From the figure 20 it was understood that control composites failed predominantly by brittle fracture both along and across the stacks, indicated by sharp decrease in stress after the maximum stress was reached. Digital photographs taken after the test also showed that (Fig 24) the samples were shattered into many pieces (almost powder), which are a signature of the brittle fracture.

In case of oxide composite, samples were plastically deformed both along and across the stacks before it finally fractures catastrophically. Work-to-failure was increased to several times and no rapid drop of load was observed at any point on the stress-strain graph until its final failure (Fig 21). Sample broke into two or more pieces as shown figure 24. Initial observations indicated that, sample posses both ductile and brittle behavior possibly due to the increased interfacial bonding between the carbon foam and epoxy.

Whereas, in case of CNT composite, samples showed completely different behavior over control composite and oxide composite. Samples behaved like truly ductile material as they were simply bulged laterally and became shorter and thinner (Fig 24) as the compression test continued. Samples became tougher and stress-strain curve never seems to drop at any point in the stress-strain curve (Fig 22). Samples showed huge amount of plastic deformation both along and across the stacks, and all failure
mechanisms indicated ductile failure. Chevron patterns have been also observed on the loading surface which is a clear indication of ductile material.

From summarized figure 23, it is clear that the work-to-failure is significantly higher in CNT composite compared to other two composite systems. Although the strain to failure was quite different from one another, the other properties such as yield strength and compression modulus of elasticity fall within too small a range to give any conclusions on other mechanical properties. The change in material behavior with the addition of CNT can be attributed to the increased interfacial matrix volume, increased interfacial contact area, better distribution of the load, and possible bridging of carbon foam-epoxy through mechanical interlocking or chemical bonding.
Figure 20: Stress-strain behavior of control composite
Figure 21: Stress-strain behavior of oxide composite
Figure 22: Stress-strain behavior of CNT composite
Figure 23: Summarized stress-strain graphs
Figure 24: Before compression (1st row), after compression along the stacks (2nd row), and across the stacks (3rd row)
5.7 SEM Analysis

SEM failure analysis was carried out for samples before and after the compression test. It must be noted that, since there was no difference in stress-strain behavior of the samples tested both along and across stacks, SEM images were only taken on samples that were tested along the stacks. From the images taken before the compression test, it was observed that all most all the pores are infiltrated with epoxy.

It was observed that the primary mode of failure in control composite was carbon-epoxy interface delamination. Interface delamination was attributed to the lack of interfacial bonding (Fig 25, 26). Traditionally, carbon foams are hydrophobic and do not form good adhesion with the polar fluids such as epoxy. Under compression, as soon as the stress reaches the yield strength of the sample, carbon-epoxy delamination starts and grows along the weak interface, resulting in catastrophic failure of the composite. This was shown by stress-strain graphs and microstructure of failed samples.

In case of oxide composite, the crack was initiated at both the interface and carbon foam itself, possibly due to the increased interfacial bonding (Fig 25, 26). It was already showed that [18] surface modification of carbon using silicon oxide nano layer can increase the interfacial bonding which makes interface strong and resist the crack growth. The images showed below indicates multiple crack initiation locations (both at the interface and within the carbon foam) unlike base composite system. After stress reached the yield strength of the sample, epoxy starts deforming and was forced out of
the carbon core. Since the interface was relatively stronger, epoxy pulled the core along and broke the core. This mechanism continued until the deformation reaches to point where it no longer sustained additional deformation and end up falling apart.

In the CNT composite, the crack had to propagate predominately in the graphite region due to the further improvements in interfacial bonding between the foam and epoxy (Fig 25, 26) under the compression loading. The sample bulged because the interface was much stronger resulting in both carbon and epoxy deform together. Delayed fracture is mainly due to the strong interface which enables epoxy to stretch like a pure plastic material. Due to the presence of CNT at the interface, interface got stiffer and continued to take high loads. The shear stresses developed at the interface eventually transformed to the foam core ligaments caused them to fail. The sample finally fractured at a point where further deformation created huge cracks in graphite.

Since the interfaces are curved in carbon foam, two sets of micrographs are presented: one at junction (Fig 25) and another at ligament (Fig 26).
Figure 25: Failure mechanism at the junction after the compression test
Figure 26: Failure mechanism at the ligament after the compression test
5.8 Role of CNT on Failure Mechanism

There are three interfaces were formed in making CNT composite: carbon-oxide interface, oxide-CNT interface, and CNT-epoxy interface. Microscopic failure can initiate within carbon foam or at the any of the mentioned three interfaces. It was already discussed in the earlier section that the crack initiated in the carbon foam ligament during the compression test due to the strong interfacial bonding. In addition, higher magnification (above 20000x) electron micrographs also revealed additional information on CNT role as an interfacial reinforcement material. Since interfacial failure mechanism may changes from location to location due to complex structure of the carbon foam, electron micrographs were taken from various locations. From the electron microscopic images taken from the various locations of the failed samples, it was understood that CNT were forming a bridge across the graphite-epoxy interface and preventing any delamination that may occurred (Fig 27-A). However, with the excess stretching of interface graphite flakes were pulled away from core and ended up sticking to the epoxy (Fig 27-B). Majority of the nanotubes were remained strongly attached to the graphite even after failure (Fig 27-B). This was only possible by strong bonding between carbon-oxide layer, oxide-CNT, and CNT-epoxy. However, CNT does not form any chemical bonds with the epoxy as they are so inert. If it is not chemical bonding, only CNT kinks can foam mechanical interlock with polymer chains. CNT with curves contribute greatly to the bridging the carbon foam and epoxy.
Figure 27: Interfacial failure mechanism
There are few areas where broken nanotubes are dangling from graphite core (Fig 28-A). Though there was no clear evidence showing the ends of the broken CNT due to the charging effects caused by the non-conductive epoxy, nanotubes dangling at the delaminated interface were shorter than average length (approx 20µm) of CVD grown nanotubes. It was also showed that the CNT with no significant kinks or defects were forced out of the epoxy due to their extremely smooth surfaces (Fig 28-B). This mechanism was seen from the nano-sized holes presented on the epoxy surface. However, this claim had lacked solid proof. Considering the nature of CNT and epoxy CNT pullout is very much a possibility.

In summary, CNT bridging, breaking, and CNT pullout all contributed to the delayed fracture. It was clear from the analysis that, there were more elements (graphite ligaments, CNT slippage from epoxy, CNT braking) got involved in the failure process. Bridging helped the delayed fracture whereas CNT breaking and pullout helped the composite to absorb more energy during its failure. Though it was concluded that, CNT composite performance was due to the strong interface, there was no quantitative analysis that can be done because of the complex morphology of the carbon foam. To analyze in detail interfacial strength, study was carried out on CNT coated flat graphite coupled with epoxy.
Figure 28: Interfacial failure mechanism
6. Interface Characterization

6.1 Interface Fabrication

The structure of the carbon foam is too complex and any quantitative analysis on the carbon-matrix interface makes the further analysis difficult. Geometry issues such as radius of curvature can be eliminated by producing graphite-epoxy flat interfaces using HOPG graphite. HOPG graphite surface chemistry was similar to carbon foams used in the earlier study. Details of making flat interfaces are followed:

- 3.15mm thick graphite samples were grafted with CNT similar to the way carbon foam was grafted.
- Two of the CNT grafted graphite samples were attached together with epoxy (same epoxy used for composite making) to make “CNT seam”.
- CNT seam was cured in the open air for 10days.
- It must be noted that length of the sample (2×3.15mm+ thickness of epoxy) was restricted to 6.32 due to 3.15mm thickness HOPG sheets.
- Even though, ideally one would like to do tension test on fabricated seams, the seam length was too small to hold in the tension fixtures, hence the three point bending test was selected.
- Samples were cut into 6.32mm×2.5mm×2.5mm for three point bending test to enable the seam to failed by tension (Note: Anything smaller than 2.5 mm width
and thickness was effected by machine sensitivity and also in addition, smaller samples were quite difficult to make.

- Similar dimension “control seam” fabricated by attaching two uncoated graphite sheets with an epoxy was made.
- “Monolithic graphite” uniform graphite with no epoxy attachment was also made.

6.2 Experimental Setup

Small beams of 6.32mm×2.5mm×2.5mm size were prepared for the three point bending test. Instron 4505 universal testing machine with 1kN load cell was used (Fig 29). Seams were tested at a rate of 0.5mm/min. Schematic representation of bending test has been showed in the below figures (Fig 30). The three point bending test was designed to break the seam at carbon–epoxy interface and measure the load required. The flexural load and extension were recorded from the machine transducer and cross head displacement respectively. The maximum loads and corresponding deformations are recorded and maximum flexural strength and corresponding strains were calculated from

Maximum flexural stress \( \sigma_{\text{max}} = \frac{3P_{\text{max}}l}{2bt^2} \) .................................................Eq (13)

Flexural strain \( \gamma = \frac{\delta l}{L} \) .................................................................Eq (14)

\( P_{\text{max}} = \) the maximum force recorded by the testing machine

\( \delta l = \) distance moved by the cross head during the testing

\( l = \) Span length = 4.52 (6.32-width of the supports)
Figure 29: Three point bending test set up

Figure 30: Schematic representation of testing method
In equation 13, $b$ and $t$ are width (2.5mm) and thickness (2.5mm) respectively. Using equations 13 and 14, flexural strength was taken on Y-axis and flexural strain was taken on X-axis.

### 6.3 Results

The resulting flexural load-extension plots (RAW data) are shown below for all tested samples (Fig 31). Since the sample dimensions were too small compared to traditional beam dimensions (length to thickness 16:1), strains recorded were too small to make any observations hence were neglected for the final analysis. Maximum flexural strength of the seam was calculated from equation 13. It was observed that the recorded maximum strength varies from sample to sample hence multiple samples were tested. The maximum strength of control seam varies in between 11MPa to 15MPa and averaged to 13MPa over six samples. For the CNT seam maximum strength varies from 43MPa to 47MPa and averaged to 45MPa over eight samples which was almost over 2.5 times the average strength of the control seam. Flexural strength of the monolithic graphite was 54MPa, which was close to the strength of CNT seam. Therefore, introduction of the epoxy joint affected the original strength of graphite as expected. Incase of control seam, graphite lost almost 75% of its original flexural strength whereas, in case of CNT seam it was only 20% (or it retained almost 80% of its strength). Strength of the seams tested is also shown in figure 32. All the failure load and strength results are tabulated in the table 9.
Figure 31: RAW data of three-point-bending test
Figure 32: Stress-strain graphs for base interface and CNT reinforced interface

<table>
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<tr>
<th>Type</th>
<th>No of samples</th>
<th>Fracture load (N)</th>
<th>Flexural strength (MPa)</th>
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</thead>
<tbody>
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<td>Control seam</td>
<td>6</td>
<td>31±6</td>
<td>13±2</td>
</tr>
<tr>
<td>CNT seam</td>
<td>8</td>
<td>107±8</td>
<td>45±2</td>
</tr>
<tr>
<td>Monolithic graphite (HOPG)</td>
<td>8</td>
<td>129±8</td>
<td>54±2</td>
</tr>
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</table>

Table 9: Strength of control seam, CNT seam, and monolithic graphite
6.4 SEM Analysis

From the SEM images (Fig 33) it was clear that CNT reinforcement at the interface had changed the interface failure mechanism. The reasons cited were same as the ones stated earlier section 5.8. Carbon nanotubes were well attached to the graphite through chemical bonding, and these bonds were stronger than van-der-wall forces between graphite flakes. Though the high aspect ratio of CNT was vulnerable to fiber pull out from epoxy, nanotube entanglement with epoxy polymer chains during curing of epoxy provided a mechanical interlock needed for strengthening mechanism. Formation of high surface contact area increases interfacial shear strength between CNT and epoxy significantly. Kinks and irregularity of nanotubes were other contributing factors for mechanical interlock. There were also signs of fiber pull out (Fig 34) from the epoxy which was helped to absorb some energy during the mechanical testing. Considering the nanotube growth density, effect of fiber pull out on the strengthening mechanism was minimal. In summary, CNT Seam had failed by graphite-graphite failure whereas control seam had failed by graphite-epoxy delamination.

To conclude, irrespective of the surface geometry, CNT reinforcement increases the interfacial bond strength significantly. This type of failure mechanism opened up number of future applications.
Figure 33: Microstructure failure mechanism of control (left) and CNT seam (right)

Figure 34: CNT-Epoxy interface failure
7. Summary and Conclusions

In this thesis, two types of interfacial modification techniques have been used to enhance surface properties of microcellular foam. A dip coating technique was applied to create composite ceramic layers for oxidation resistance. A chemical vapor deposition (CVD) technique was used to attach Carbon Nanotubes (CNT) on the foams in order to improve their bonding with matrix materials, so that advanced cellular composites can be fabricated in the future. Geometric and structural investigations of carbon foams have also been carried out in order to estimate its specific surface area as a function of microstructural parameters such as pore radius and percentage porosity.

It was seen that a mixed layer of BN and SiC helped to improve the oxidation resistance of the foam only to the extent that a pure BN layer would help. However, microstructural improvement in terms of reduced porosity was observed, that can be further optimized in future. This combination layer may also lead to functionally gradient coatings in the future.

Geometrical calculations proved that total surface area per unit volume cannot be improved drastically by changing geometric parameters such as radius and porosity. On the other hand, grafting of nanotubes can improve surface area and related applications by several orders of magnitude. This was seen relevant to cellular composites made from
foam. Foams with and without carbon nanotubes grafted on the surface of pores were fabricated into composites and their mechanical response compared under compression loads. It was observed from the stress-strain plots that for normal foam-epoxy composites without nanotubes, failure was predominately brittle as the composite shattered into several pieces. Composites made with CNT attached foam deformed in a ductile manner without shattering. Electron microscope images revealed that, in the case of CNT-treated core, there was a strong bonding between carbon core and epoxy matrix which prevented delamination at the interface. No such bonding was observed and the carbon core was delaminated from epoxy upon its failure.

For quantification, the three point bending test was performed on planar graphite-epoxy interfaces. Such an interface was formed by attaching two CNT graphite sheets together using epoxy, Epoxy-bonded graphite with and without nanotubes attached were compared by measuring their interface failure loads at the joint. Flexural strength of untreated graphite-epoxy seam was 13MPa compared to 43MPa for seam containing CNT-grafted graphite. As a baseline, this test was also performed on monolithic graphite (without seam) and that had a flexural strength of 54MPa. Hence, it is clearly proven that carbon nanotubes attached to the graphite at a graphite-epoxy interface improves its interfacial strength, load transfer, shear strength irrespective of the surface geometry of the core. This opens up the possibility for many future applications. It must be noted that this work can be extended to other matrix materials such as metals, bio tissues, etc.
8. References


11. Marc Monthioux and V. Kuznetsov, "Who should be given the credit for the discovery of carbon nanotubes?", Carbon 44 (2006) 1621.


40. Raja sekhar V. Pulikollu Dissertation “Nano-Coatings on carbon structures for interfacial modification” Mechanical and Materials Science Engineering Department, Wright State University, 2005


43. Seung Jong Lee, Hong Koo Baik, Jae-eun Yoo, and Jong Hoon Han, “Large scale synthesis of carbon nanotubes by plasma rotating arc discharge technique” Diamond and Related Materials 11 (2002) 914–917.


