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# Oxidation of Carbon-Carbon Composite

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# OXIDATION OF CARBON-CARBON COMPOSITES

by

Weishen Yee

B.S., Southern Illinois University, 2013

A Research Paper

Submitted in Partial Fulfillment of the Requirements for the  
Master of Science

Department of Mechanical Engineering and Energy Processes  
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RESEARCH PAPER APPROVAL

OXIDATION OF CARBON-CARBON COMPOSITES

By

Weishen Yee

A Research Paper Submitted in Partial

Fulfillment of the Requirements

for the Degree of

Master of Science

in the field of Mechanical Engineering and Energy Processes

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29<sup>th</sup> of April, 2016

## AN ABSTRACT OF THE RESEARCH PAPER OF

WEISHEN YEE, for the Master of Science degree in MECHANICAL ENGINEERING, presented on 29<sup>th</sup> OF APRIL, 2016, at Southern Illinois University Carbondale.

TITLE: OXIDATION OF CARBON-CARBON COMPOSITES

MAJOR PROFESSOR: Dr. Jarlen Don

This paper reviews the research and development efforts on oxidation in CC composites. CC composites are widely used in the aerospace industry especially in airplane brakes due to its favorable properties, however carbon is particularly susceptible to oxidation at elevated temperature and thus oxidation protection in CC composite plays an important role in the advancement of CC composites to allow the replacement of a lightweight, high strength and high modulus structural materials. A vast knowledge on properties and compositions of carbon, carbon fiber and matrices in a macro and microscopic level is needed in order to fully understand the effects of oxidation on CC composites at different temperature. Analysis techniques used to study the microstructure is briefly discussed to allow for a better understanding of the effect of oxidation. Methods that could assists the inhibition of the oxidation process in CC composites include, microstructural modifications of carbon, addition of inhibitors, application of protective layer coatings and surface treatment with aqueous mixtures.

Keywords: carbon-carbon composites, microstructural analysis, oxidation resistance

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## CHAPTER 1

### INTRODUCTION

A composite material is formed by combining two or more reinforcing materials with different chemical and physical properties, that when combined together through various processes, produces a characteristic different from when either is used alone [1]. Composite materials are favored because it combines materials of different properties to form an overall structure that is better suited to the characteristics needed.

Carbon-carbon (CC) composites are categorized under the graphite/epoxy family of polymer matrix composites [2]. They consist of carbon fiber reinforced in a matrix graphite. The element carbon is well recognized as having some anomalous properties, including its ability to embrace the three major divisions of materials science; polymers, ceramics and metals. Carbon forms strong inter-atomic bonds with itself, leading to organic chemistry and polymers; the element in either of it forms, allotropic, diamond or graphite is highly refractory and possesses a relatively high melting point compared to ceramics, whilst the graphite crystal form has a high electric and thermal conductivity similar to those of typical metals [3].

CC composite consists of a fibrous carbon substrate in a carbonaceous matrix. The properties of carbon fibers can vary over a wide range depending on the precursor and processing conditions it undergoes. At present, graphite fibers are mainly produced from three precursor materials: rayon, polyacrylonitrile (PAN), and coal-tar or petroleum-based pitch. There are two distinct methods for forming the carbonaceous matrix. The first method is based on liquid carbonaceous materials which are coated on to or

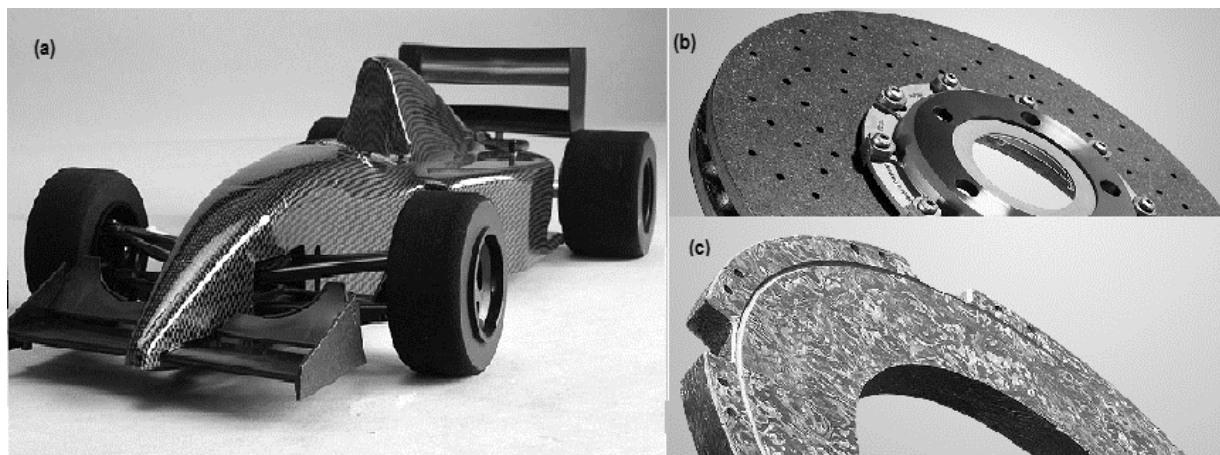
impregnated into fiber tows and subsequently converted into a residue of carbon by heating in an inert atmosphere. The alternative method is chemical vapor deposition (CVD) or chemical vapor infiltration (CVI) which involves the thermal decomposition of carbonaceous gases or vapors on to heated carbon fibers [1] [2].

Many applications of CC composites come from the aerospace industries, particularly in military aerospace where the performance capability are more important compared to the production cost. Products such as, jet engine nozzles, turbine wheels, leading edges for missiles and the Space Shuttle (shown in Figure 1), wind-tunnel models, sporting goods such as rackets and golf clubs, aircraft and race car brake discs and also surgical implants such as bone prostheses and dental implants also utilizes the favorable characteristics of a CC composite. [1] [3]. Some examples of the application of CC composite are shown in Figure 2. The reasons for the application of CC materials in these products mainly comes down to it possessing one or a combination of the desired properties, whether it being mechanically stable, light weight, thermal or electrically resistant or chemically inert.



*Figure 1. CC composite used on the nose cone of the space shuttle by NASA.*





*Figure 2. Applications of CC composite. (a) Body of a Formula one race car. (b) Race car disk brake. (c) Airplane disk brake.*

Even though CC composites are chemically inert to most chemicals that are corrosive to other materials, carbon is particularly susceptible to oxidation at elevated temperature especially at 500°C and above [4]. It is vital to tackle the issue of oxidation in CC composite to still be able to allow the use of CC composites as a lightweight, high strength and high modulus structural material.

The objective of this paper is to review the research and development activities conducted over the past few decades on the oxidation of CC composites and solutions developed to inhibit the oxidation on CC composites in high temperature and high pressure environments especially for airplane brakes, where oxidation is a common issue that leads to the premature removal of carbon brake discs.

## CHAPTER 2

### REVIEW

#### 2.1 History

The first carbon filament discovered by Thomas Edison and Joseph Swan were used in incandescent lamps in 1880s. It was then valued more for its electrical properties instead of its high strength and thermal characteristics which relates to CC composites in the modern world. By 1910, tungsten had superseded carbon filament in lamps and most research on carbon filaments were halted [3]. CC composites were put back into practical use in the late 1950s, where space shuttle programs required thermal protection materials which possess characteristics such as light in weight, high thermal shock resistance, low coefficient thermal expansion, maintenance of high strength at high temperatures, high impact resistance and an oxidation resistance sufficient to limit strength reduction [2] [3] [5].

Extensive research and development in the area of CC technology in the 1980s include improvements in the carbon fibers and carbon matrix precursors, new carbon fiber reinforced polymer composites technology, the hot isostatic press (HIP) technology and the chemical vapor deposition (CVD) technology. The high fracture toughness and thermal conductivity properties possessed by CC composite allow them to grow into different sectors although the major concentration is still in the aerospace industry [5].

#### 2.2 Carbon fiber

The properties of carbon fibers can vary over a wide range depending on the organic precursor and processing conditions used [2]. Carbon fibers are highly

anisotropic, which means that they are directional dependent, and depends greatly on the direction of the fibers [6]. Graphite fibers are produced from three precursor materials: rayon, polyacrylonitrile (PAN), and petroleum pitch. Fibers having low modulus (27.6 GPa) are formed using a rayon precursor material that may be chemically pretreated by a sequence of heating steps. The fiber is first heated above 400°C to allow cellulose to pyrolyze (decomposition or chemical change by thermal conversion of organic materials to carbon and graphite). The fiber is left to undergo carbonization (continued heating of organic material to initiate ordering of the carbon structures produced by pyrolysis) at above 1000°C. Finally, the fiber is graphitized (continued heating of carbonized organic materials to produce a 100% graphite-ordered crystal structure) at above 2000°C. A flow diagram for the production of carbon fiber reinforced carbon is shown in Figure 3.

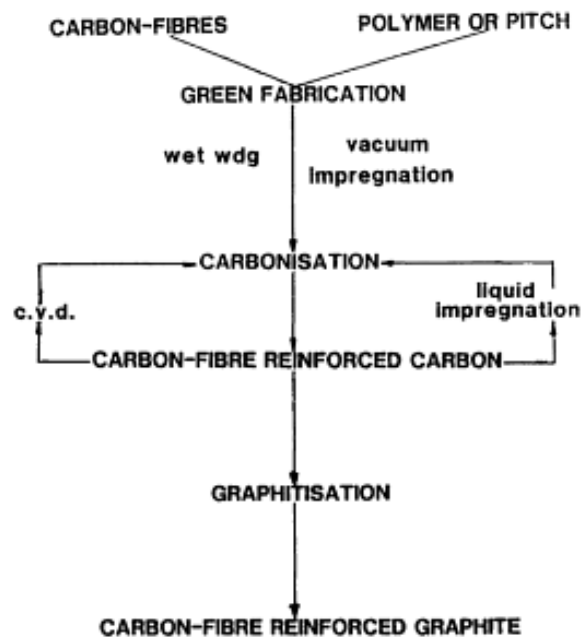


Figure 3. Flow diagram for production of carbon fiber reinforced graphite. [2]

On the other hand, high modulus (344GPa), high strength carbon fibers are typically made from PAN or, in some cases, mesophase pitch precursors. Its process involves a three-stage operation as PAN fibers are initially stretched and then stabilized while still under tension in an oxygen atmosphere at 200°C and above [2]. This treatment causes the PAN fiber to become nonplastic, to ensure it will be able to withstand the higher temperature treatments that follows [7]. This stabilization process is time consuming and is one of the limiting factors of PAN-based carbon production [1, 2]. The carbonization process takes place at about 1000°C and finally the graphitization process takes place at above 2500°C [1] [2].

Mesophase pitch fibers undergo the same processing procedure as PAN fibers but do not require an expensive stretching process during heat treatment as they form thermotropic crystals which means that at high temperature they become and isotropic liquid, while at lower temperatures they remain as a glass phase, to maintain a preferred alignment of crystallites. According to Huang, the structure and composition of the precursor affect the properties of the resultant carbon fibers significantly. He also states that although the essential processes for carbon fiber production are similar, different precursors require different processing conditions in order to achieve improved performance [8]. Mesophase pitch have a high degree of preferred orientation and are readily graphitizable which makes it an attractive carbon fiber precursor [1] [9], however, they are restricted for thermal insulation because of their mechanical properties. PAN-fibers are therefore, the carbon fiber most used as a structural reinforcement at present [2].

### 2.3 Matrix

The matrix acts as a binder to maintain the alignment and position of fibers and fiber bundles in a predetermined arrangement. It helps bond together laminates and fill the interstices that exist in multidirectional composites [10]. The matrix in a CC composite provides compressional strength and fracture toughness to the material and at the same time serves as a stress distributor, transferring the external load applied to the composite as a whole to the individual reinforcing filaments [1] [10]. It also acts as a barrier, protecting the carbon fibers against chemical attack especially in CC composites where carbon is susceptible to oxidation at elevated temperature [10].

Three methods of fabricating matrices are pitch-based (thermoplastic), resin-based (thermosetting), and depositing carbon into a fibrous preform through CVI [1] [10]. The choice of fabrication method depends largely on the geometry of part being processed. The CVI method is used in thin section production as this method tends to preferentially deposit in and on the surface layer while thermosetting and thermoplastic tends to be chosen while fabricating thicker sections.

Pitches are complex mixtures of many organic compounds, with a high aromatic character and are usually derived from coal-tar or from petroleum residues [10]. The basic fabrication method for producing pitch matrix CC composites is to use pressure to force pitch into an evacuated cavity that contains the dry fiber preform. The infiltration and carbonization cycle can be performed at atmospheric pressure or at pressures up to 210MPa. Carbonization of isotropic coal tar or petroleum pitch produces a 50 to 60 percent coke yield under atmospheric conditions. The coke yield would increase to 70 to 80 percent if the process is performed very slowly under the high pressure [11].

According to White and Sheaffer, up to 92% yield can be achieved if the mesophase pitch, first produced from an initially isotropic pitch, is stabilized (oxidized) before carbonization [12].

Phenolics and epoxy resins are two types of commonly used thermosetting resins [13]. Resin matrix composites are cured prior to carbonization. In a typical process, multiple layers of prepreg fabric which consists of fiber and resin, are laid up on a mold before being pressed at a given temperature and pressure for several hours. Resin densification takes place several times under low pressure by repeated infiltration and carbonization cycles [13] [14]. Resin matrix precursors do have the advantages of low viscosity at low processing temperature and pressure, and better purity and consistency of composition than pitch precursors [1].

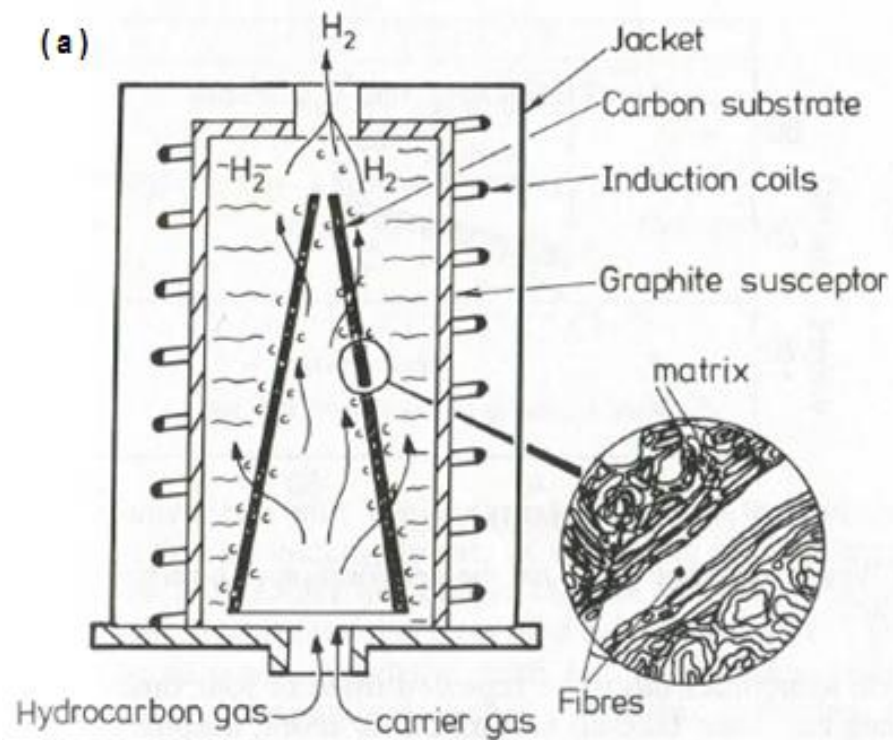
Both matrix aforementioned involves liquid phase infiltration process while CVI/CVD would be conducted in the gaseous phase. The CVI/CVD process uses volatile hydrocarbon compounds such as methane, propane, or benzene as precursor gases. The thermal pyrolysis of these gases is achieved over a hot substrate onto which the carbon product is deposited. If the gas is allowed to infiltrate into a carbon fiber preform the deposition will take place at the internal fiber surfaces, so leading to densification of the composite [1] [10] [13]. Under isothermal conditions, pyrolytic carbon deposits preferentially on the surface, making the filling of internal pores difficult as it changes open porosity to close porosity in the composite [13]. According to Kotlensky, this effect can be reduced by conducting the deposition process in lower temperatures as studies indicate that low temperature tend to limit reaction while having relatively little effect on diffusional transport [15]. CVI has a number of advantages over other methods

of composite fabrication, for example, it improves fiber/matrix bonding [6], provides higher strength and flexibility as well as enhancing the erosion resistance of the CC composite [16]. However, the downside is the process is time consuming and expensive [17] [18].

There are several methods of infiltration used in CVI, isothermal (I-CVI), thermal gradient (TG-CVI), isothermal-forced flow (IF-CVI) and thermal gradient-forced flow (F-CVI) [13] [19].

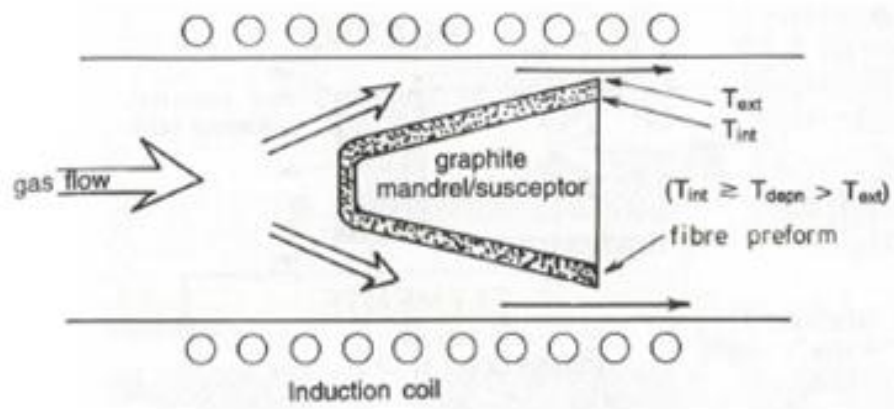
- The isothermal-isobaric (I-CVI) shown in Figure 4(a), is the oldest ‘hot wall’ technique that is still widely used, as it is rather easy to control its parameters and bulks of complex preforms can be densified together. A main drawback however is the long processing time with a very slow rate of deposition associated with a very low overall precursor efficiency [20]. The effects of the CVI parameters of temperature and total pressure can be clearly seen in the review by Naslain [21].
- In the (TG-CVI) process the preform is kept at a temperature gradient. The vapor precursor diffuses through the preform from the cooler surface to the hotter inside regions. The precursor decomposes and deposits in the hotter region. This method allows better densification due to prevention of early closing at the surface pore [13]. A schematic drawing of the (TG-CVI) method is shown in Figure 4(b).
- The third method shown in Figure 4(c), the (IF-CVI), utilizes forced flow (pressure gradient) of the hydrocarbon precursor penetrating into the uniformly heated preform depositing into the pores of the preform.

- A more efficient method shown in Figure 4(d), the F-CVI process combines the effects of both temperature gradient and forced flow enhancing the infiltration of the vapor precursor while reducing the densification time. Vaidyaraman et al., [22] has shown that F-CVI has been found to be very effective in rapidly fabricating uniformly dense SiC/SiC composites. According to Probst et al., [23] the F-FCVI developed at Oak Ridge National Laboratory overcomes the problems of slow diffusion and restricted permeability, and has demonstrated a capability to produce thick-walled, simple-shaped SiC-matrix components in times of the order of hours.

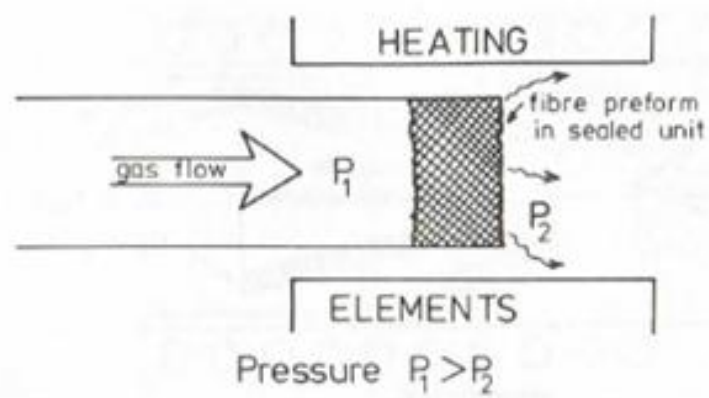




(b)



(c)



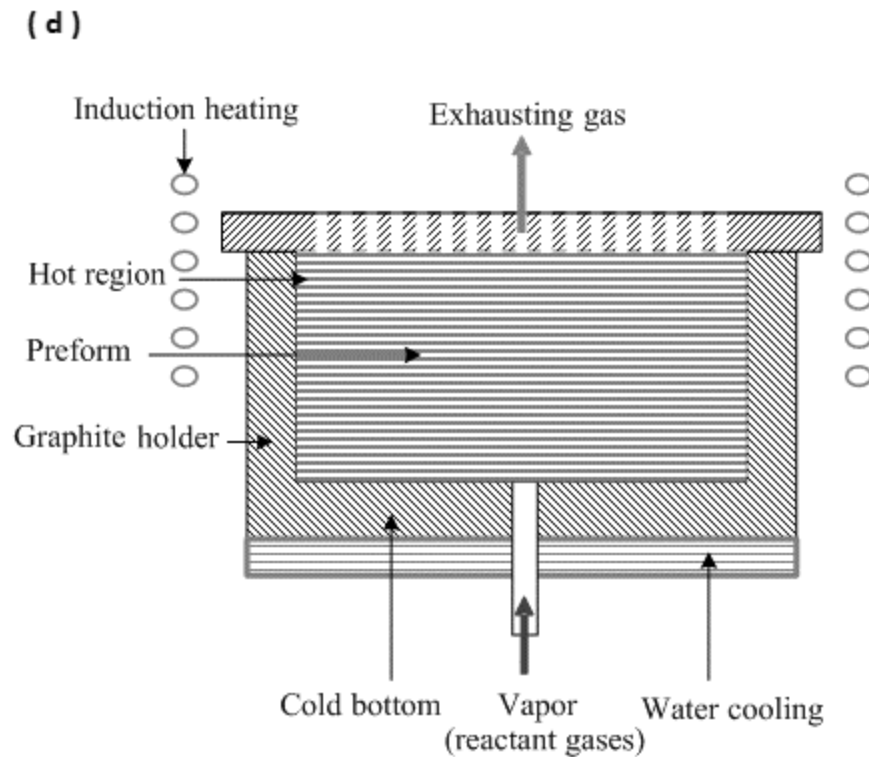


Figure 4. Schematic diagram of methods of infiltration used in CVI. (a) isothermal method; (b) thermal gradient method; (c) pressure gradient method; (d) isothermal-forced flow method. [24] [25]

## 2.4 Microstructural Analysis

Understanding the microstructural features of a CC composite is an integral part in determining the effects of oxidation towards the composite and the ability to provide a better understanding to overcome it. Microstructural evaluation of CC composite ranges from simple determination of certain parameters such as grain size, coating thickness through porosity and pore structure, surface deposits, or development of interfaces on reaction, to full characterization of multi-component systems or evaluation of degradation or failure mechanisms. Various analysis techniques could be applied to understand the microstructural features of CC composites. Optical microscopy which is

one of the oldest analysis techniques, electron microscopy such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which are capable of identifying surface features on the level of a few hundred angstroms, more advanced techniques such as the scanning tunneling microscopy (STM) and atomic force microscopy (AFM), which utilizes a scanning probe tool, as well as X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), which gives an elemental analysis of surfaces and depth profiling, are all used either partially or in combination to determine the microstructural features of a CC composite [13]. The primary difference between optical and electron microscopy is that the former uses light as a probing beam while the latter uses an electron beam, having a much lower wavelength than light, resulting in much better resolution. Figure 5 shows a schematic diagram of various important components in an optical microscope.

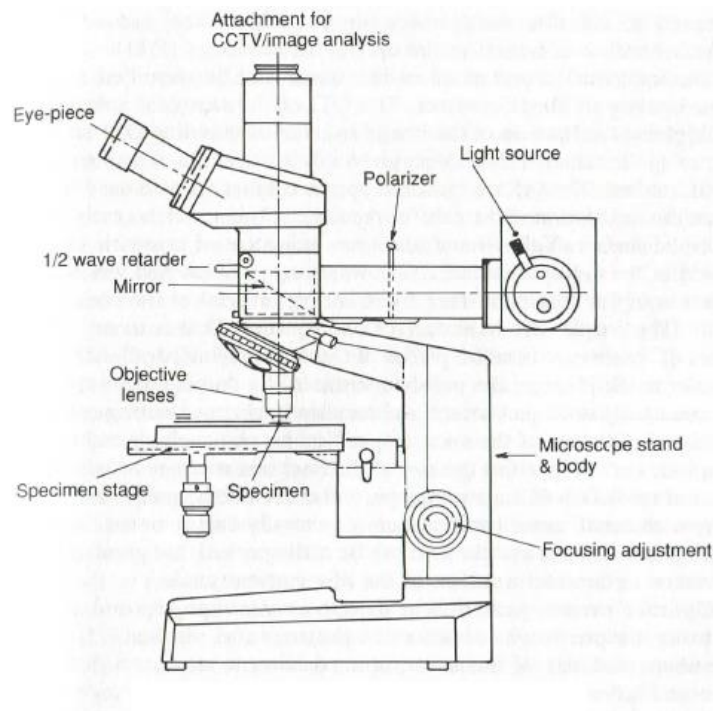


Figure 5. A schematic diagram of a light optical microscope. [24]

In SEM, a condenser lens focuses electrons emitted from a source (electron gun) to a desired spot on the surface of a sample. These primary electron beams strike the surface of the sample, and its energy is converted into different forms such as X-rays, back-scattered electron (BSE), Cathodoluminescence and secondary electrons. Particularly the secondary electrons and BSE are most useful in determining the microstructure of the sample. Lower energies emitted by the secondary electrons are easily attracted to a collector mesh which could produce a final image of the sample. The BSE is collected by another collector commonly located some position above the sample, and BSE images are extremely useful in metallographic studies as the contrast of the images is sensitive to elemental composition. [26] A schematic diagram of a scanning electron microscope is shown in Figure 6.

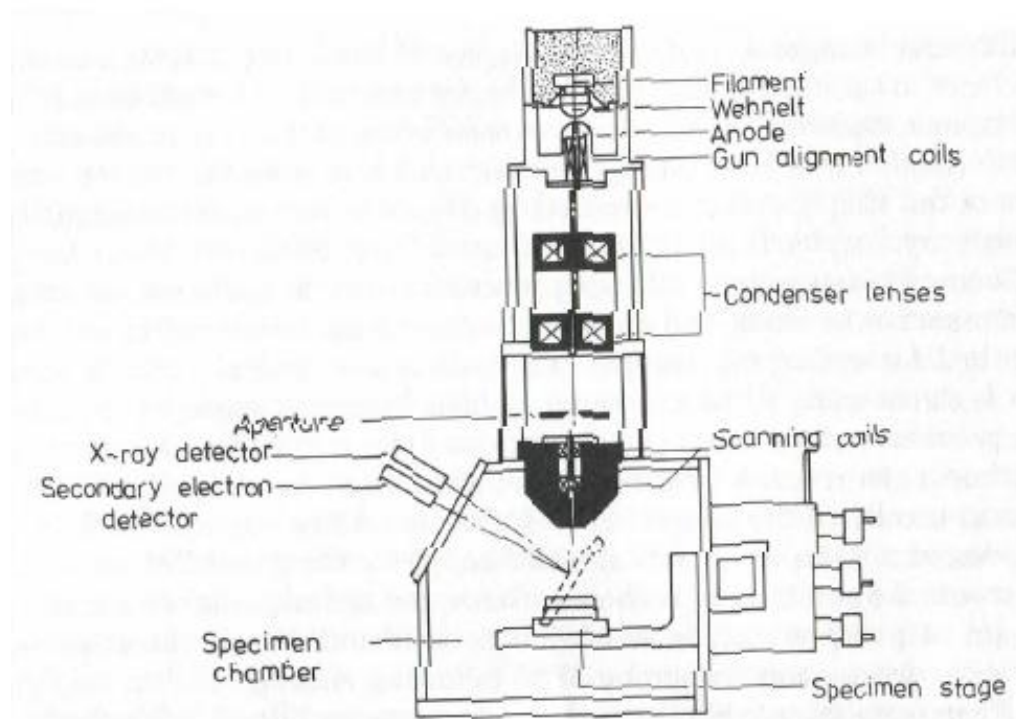


Figure 6. A schematic diagram of a SEM analyzer [24]

In XRD, a beam of monochromatic x-ray is directed on to sample and the diffracted x-rays are observed at various angles with respect to the incident beam angle. A schematic diagram of an XRD is shown in Figure 7. The interplanar distance,  $d$  of the sample can then be calculated through Bragg's equation shown in Equation 1.

$$\lambda = 2d\sin\theta/n \quad (1)$$

where,  $\lambda$  denotes the wavelength of the x-ray beam,  $2\theta$  denotes the angle of diffraction, and  $n$  is the order of diffraction. It is possible to identify and characterize each compound in the sample as each crystalline structure have to an extend a unique diffraction pattern, in terms of diffraction peaks, position and width.

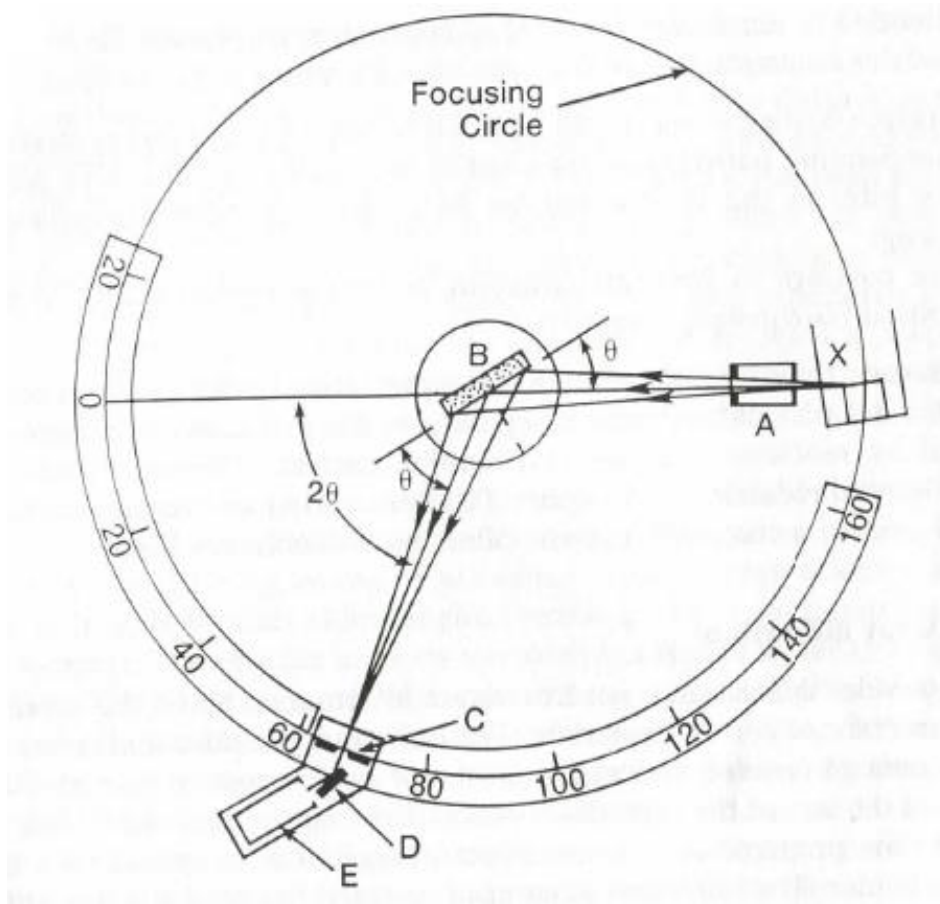


Figure 7. A schematic diagram of an X-ray diffractometer. X, X-ray source; B, crystalline sample; C, slit; E, detector [24]

## 2.5 Oxidation of CC composite

It is a known fact that carbon reacts with oxygen in air to produce carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). This chemical property that carbon possesses inhibits its ability to resist oxidation reactions especially at high temperature. Such oxidation reactions can occur on the external surfaces as well as in numerous internal pores, which are usually introduced during the fabrication processes of the composite [27] [28]. CC composites are comprised of multiphase carbons, i.e., carbon fibers with different microstructures and crystalline order and carbon matrix with varying crystalline order and porosity. All of these variations in the constituents will influence the oxidation behavior of CC composites [29], and thus the oxidation rate is a rather complex matter which could not be directly known by adding the reactivities of each of its components [29] [30].

Many researchers have since placed extra emphasis on understanding the relationship between the compositions and structure properties of CC composites and their oxidation behavior. Luthra [31] supported by Chang and Rhee [32] proposed that there are different oxidation mechanisms operating at different temperature. Jones et al. [33] have observed that the structure of the constituent fibers directly effects the gasification behavior of CC composites. On the other hand, Fischbach and Uptegrove [34] have observed that the microstructural characteristics of the matrix, such as crystallographic order, preferred orientation, and morphology, also have great influence on the gasification of CC composites. They also discovered that high temperature treatment reduces the amount of impurities present in the matrix which otherwise would act as a catalyst for oxidation, thus reducing the gasification of CC composites.

Rodriguez-Mirasol et al. [35], have proposed new methods of improving the carbon structure in CC composites based on their observation that porosity developed in the fibers prior to composite preparation improves the oxidation resistance of the composite. They discovered that by optimizing the porosity of the fibers to promote fiber-matrix adhesion and enhance carbon graphitization will improve the oxidation resistance of CC composites.

According to studies conducted by Thrower et al. [36], oxidation will reduce the overall compressive strength on graphitic materials. They also found that the oxidation rate varies with different type of reactant gas ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ) and dopant material used. Crocker and McEnaney [37] observed that during oxidation, oxygen attacks at the fiber/matrix interfaces within fiber bundles, resulting in decoupling of fiber and matrix. Their experimental results show a reduction in elastic modulus and flexural strength by 30% and 50% respectively, after a 10% of weight loss at high temperature due to oxidation. Zao et al. [38], conducted similar experiment but at low temperature in the order of  $600^\circ\text{C}$ , found a decrease in strength by about 60% and Young's modulus by about 75% with a 20% oxidative weight loss which could be seen in Figure 8.

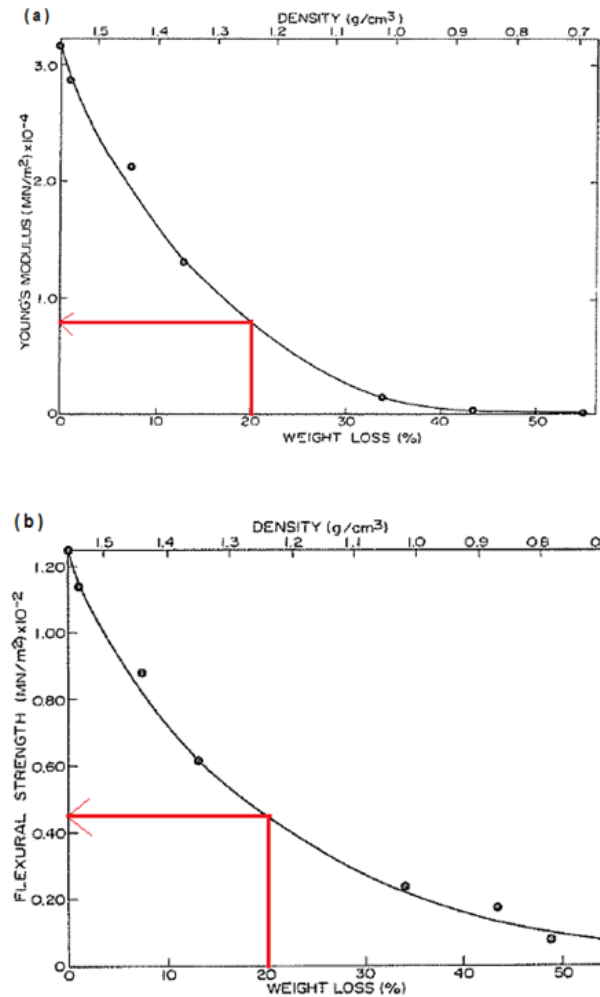


Figure 8. Decrease in (a) young's modulus by 70% and (b) flexural strength by 60% against 20% oxidative weight loss at 600C. [38]

Ahearn and Rand [39], took pitch-based matrix composites fabricated from Pan-based fibers and were mildly oxidized in air at temperatures of 420°C and 730°C. They found that material loss occurred primarily at the fiber-matrix interfaces at the edge regions of the composites and, in the case of the lower temperature, in the areas close to internal pores and cracks. Also, the mode of failure of the lower temperature sample showed a change from a totally brittle mechanism to a pseudo plastic “graceful” failure mode as seen in Figure 9.



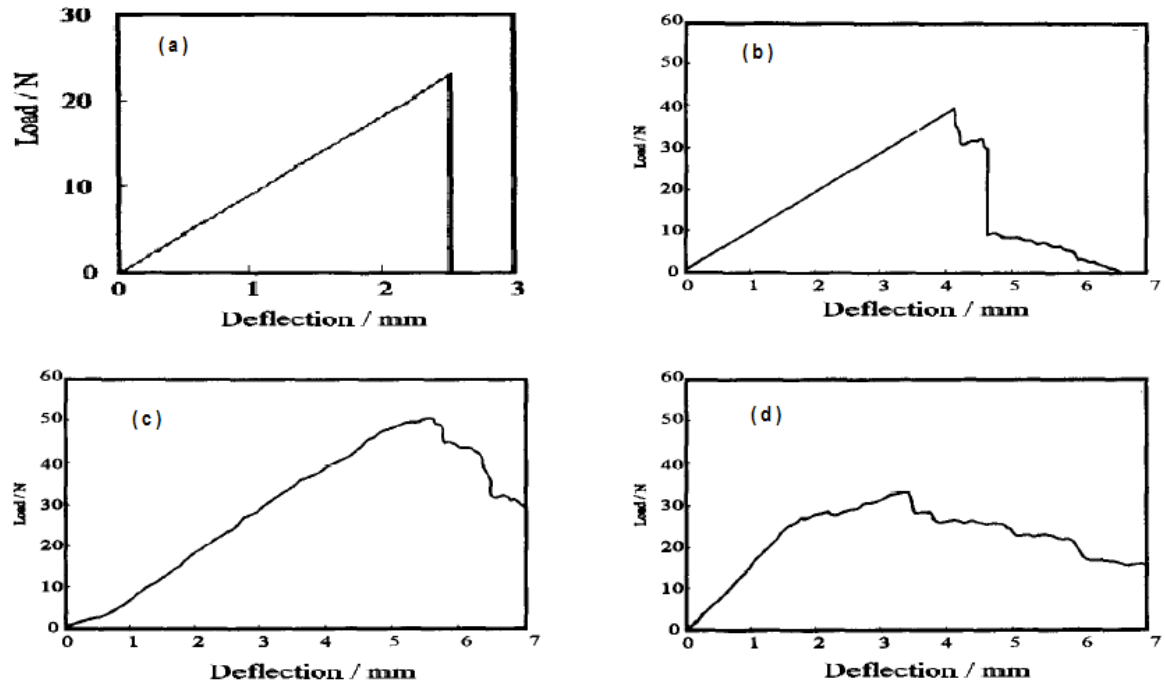


Figure 9. Load extension curve of composite (a) unoxidized; (b) oxidized to 0.4% weight loss (c) oxidized to 1.4% weight loss (d) oxidized to 2.2% weight loss. [39]

Chang and Rusnak [40] investigated the effects of oxidation on the wear of CC composites for aircraft brake materials. They found that wear rate on the composite increases with increasing oxygen partial pressure especially in air compared to in an inert atmosphere which was at least 4.5 times more reactive. They also concluded that oxidation induced major weight loss on the composite through two methods; direct removal by conversion of the solid to CO and CO<sub>2</sub> and the weakening of the surface and subsurface, which in turn facilitated material removal by mechanical action at the contact interfaces.

On the contrary, Jin et al. [41] studied the effects of ozone method treating carbon fibers on mechanical properties of CC composites and concluded that the ozone treatment of carbon fiber improved the interfacial adhesion between fibers and matrix, which leads to the increase of compressive strength and flexural strength of the CC

composite. However, ozone decomposes rapidly at higher temperature to oxidize the carbon fibers and thus the decrease in strength in Figure 10.

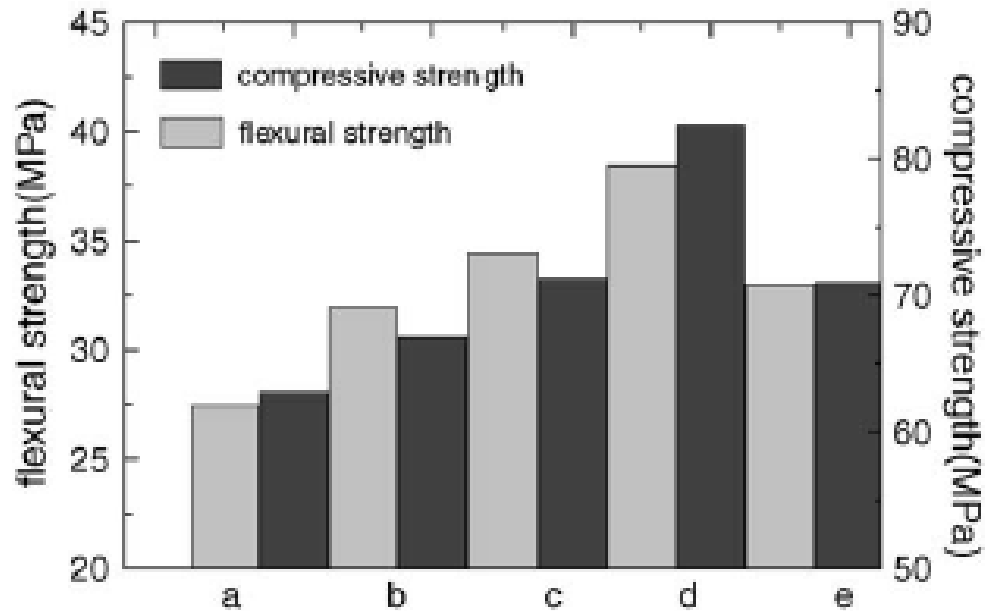


Figure 10. The compressive strength and flexural strength of the carbon/carbon composites: (a) untreated carbon fiber; (b) the 100 °C for 6 min ozone method; (c) the 120 °C for 3 min ozone method; (d) the 120 °C for 6 min ozone method; (e) the 160 °C for 6 min ozone method. [41]

An AFM study was conducted and they observed that ozone treating increases the surface roughness of carbon fiber that aids in the interface bonding between carbon fiber and matrix.

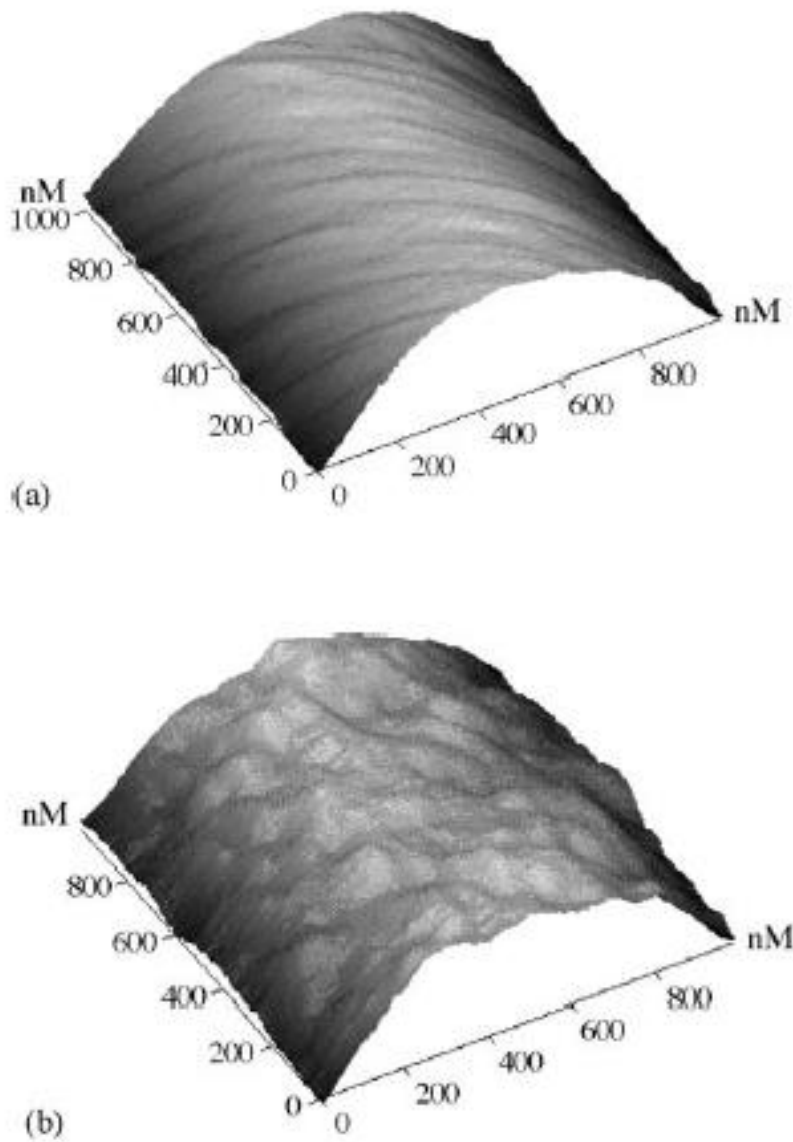


Figure 11. AFM image of (a) untreated carbon fiber, (b) after 120C for 6min ozone method treatment. [41]

The ozone treating method also improved the wettability of carbon fibers and changed the graphitization degree of carbon fiber surface, as well as increased the carbonyl functional group which improved the overall strength of the CC composite which could be observed with the aid of the scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and the micro-laser Raman spectroscopy which were used in their research.

## CHAPTER 3

### OXIDATION PROTECTION

Oxidation resistance is an important characteristic that must be improved in order to continue the advancement of CC composites in replacing high strength and high modulus structural materials especially in elevated temperature and pressure conditions. Various techniques and oxidation protection methods of CC composite have been studied widely in recent years and these studies have been focused in

1. microstructural modifications of carbon
2. addition of inhibitors
3. application of protective layer coatings (pack cementation and CVD)
4. surface treatment of oxidation inhibiting aqueous solution

The more notable researchers in this field of study include, Honeywell International Inc., Goodrich Corp., HITCO Inc., Rolls-Royce plc, and many more.

#### 3.1 Microstructural modification of carbon

Research over the years have concluded that the microstructure which includes the fiber, matrix and interfaces of CC composite has a great effect on its oxidation resistance [31] [32] [33] [34] [35]. Fabrication methods (pyrolysis, carbonization, graphitization, etc.) and the control of the process parameters (time, pressure, temperature, etc.) alters the microstructure of a composite and have huge impact on its oxidation resistance. A strong bond between the fiber and matrix interface results in better oxidation resistance, however it degrades other desirable properties of the CC composite as a consequence [28].

### 3.2 Addition of inhibitors

The addition of Boron or Phosphorous during the fabrication of prepregs have shown significant improvement in the oxidation resistance of the composite [42]. Boron forms stable oxide glass (melting point 450°C, boiling point 2040°C) on its own in dry air. In order to increase the viscosity of boric oxide, McKee [42] proposed to add silica compounds to form borosilicate glass to reduce its susceptibility to water vapor. A similar experiment was conducted and patented by Marin [43], where fine powders of silica and boron nitride were dispersed in a thermosetting resin which is painted onto the surfaces to be protected and cured. Similarly, during the oxidation process, these compounds oxidizes and form a glaze on the surface of the composite.

Wu and Radovic [44], investigated the inhibition effect of high temperature boron-doping on the catalytic oxidation of CC composites. It was evident in their experiment that boron-doping at high temperature (2500°C), improves the oxidation resistance of catalyst loaded composites due to graphitization and active sites blockage by the formed boron oxide. Research on the addition of inhibitors in prepregs has since been studied extensively as it plays a major role in improving the oxidation resistance of the composite [45] [46] [47].

### 3.3 Application of protective coating layer

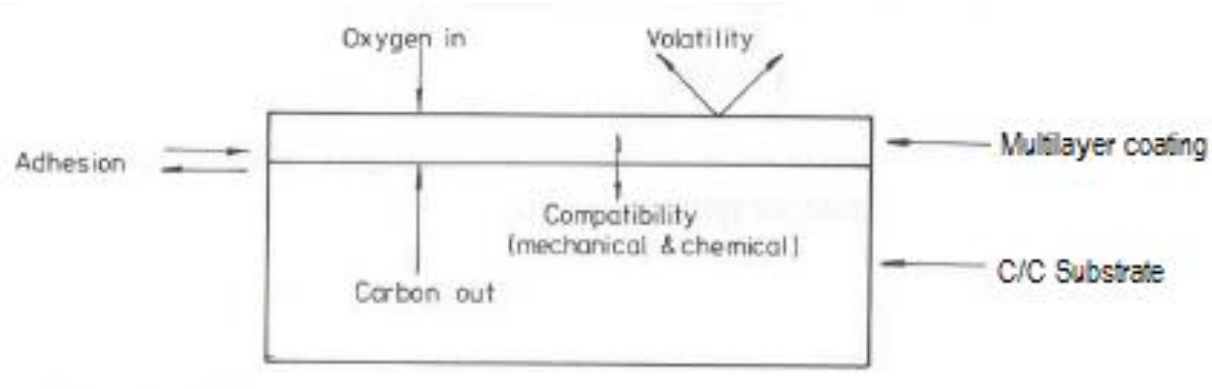


Figure 12 Considerations when designing a CC oxidation protection system. [24]

The application of a protective coating layer to inhibit oxygen from reaching the carbon material is another method that is widely used and an illustration of the application is shown in Figure 12. Thermal expansion mismatch occurs between the protective coating barrier and the CC composite as both have different coefficient of thermal expansion (CTE). Initial stages of applying protective coating is done by a two-layer coating system of a porous SiC inner layer sealed with SiO<sub>2</sub> and an outer coating of alkali silicate glass filled with SiC particulate [48]. A problem with this protective coating however is the rate of alkali volatilization from SiO<sub>2</sub> becomes significant in the 1200°C to 1300°C range, allowing the loss of the fluxing agent over periods of hours to compromise the compliancy and sealing characteristics of the glaze [49]. SiC and Si<sub>3</sub>N<sub>4</sub> are among the top outer barrier protective coating used in CC composites due to its relatively low CTE values, excellent oxidation resistance up to at least 1700°C and it serves as an erosion-resistant bearing surfaces that cover the inner layers to inhibit vaporization of the glass sealants. As seen in (Eq.2 and Eq.3) however, Si<sub>3</sub>N<sub>4</sub>

undergoes simple thermal decomposition and SiC by interaction between itself and the protective layer of silica, where both begin to degrade at higher temperature.



Elemental boron, boron carbide, and several configurations of mixed boron compounds with and without SiC and elemental silicon are constantly under evaluation as a replacement for inner layers protective coating. The main purpose of the inner layer is to form a borate glass by oxidation through the cracks in the outer coating as illustrated in Figure 13.

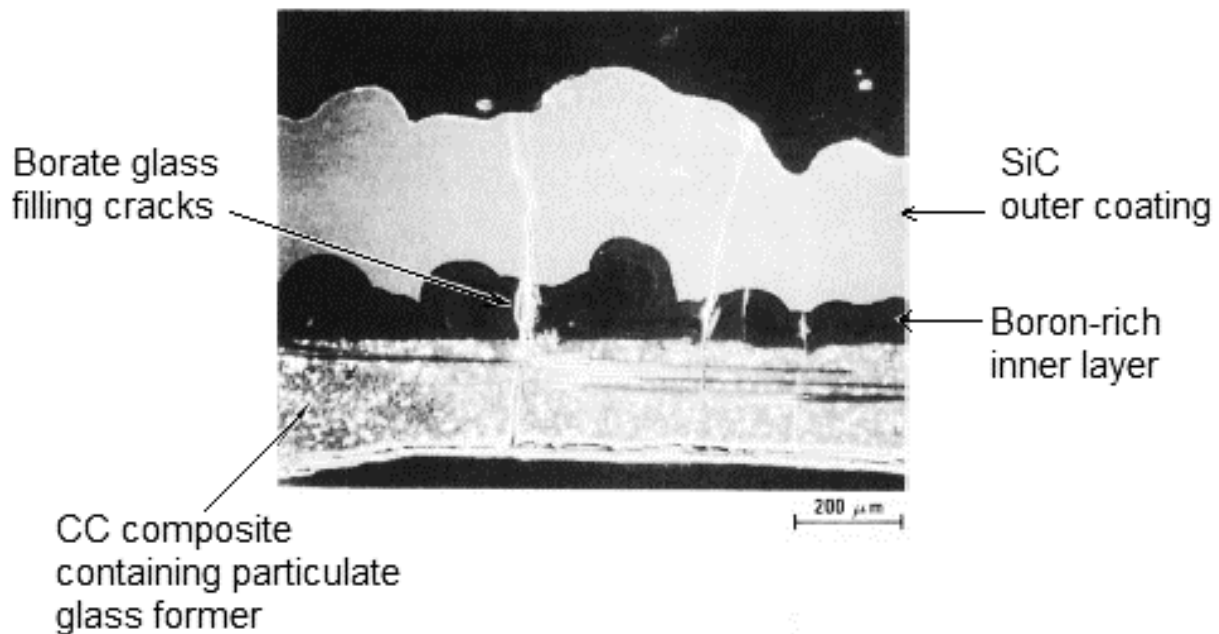


Figure 13. CC composite with silicon based outer coating and a boron-rich inner layer coating concept. [49]

Extensive research to find the best oxidation protective coating for various CC composites include; Fu et al. [50], proposed a multi-layer protective coating, using SiC as an internal buffer layer along with  $\text{MoSi}_2$ , which has a high melting point and



excellent oxidation resistance as the outer-layer material. Manocha and Manocha [51] coated CC composites with silica and zircon prepared by sol-gel technique together with a preceramic polymer. They concluded based on their observation in Figure 14 that oxidation in zircon coatings (d) begins at 850°C and only a 10% weight loss at temperatures up to 1200°C which is an improvement in oxidation resistance in silica coatings.

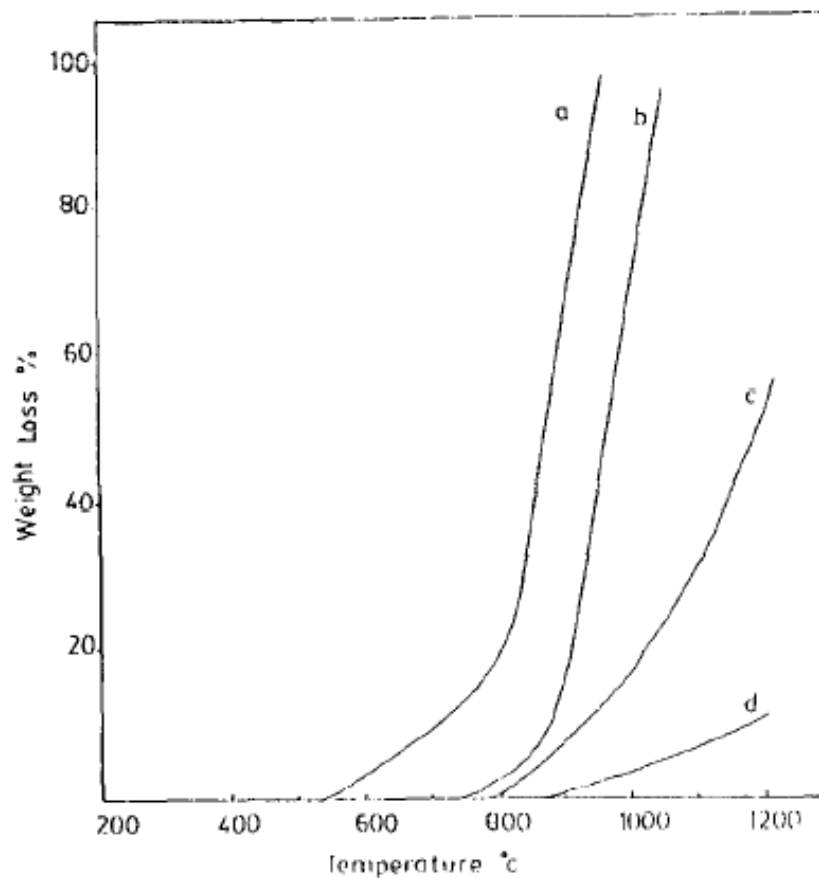


Figure 14. TGA curves of CC composite in air (a) Uncoated; (b) coated with silica; (c) coated with silica by multiple dip; (d) coated with zircon by multiple dip. [51]

Dhami et. al. [52] reported that Si-based coatings with cracks generated during thermal cycling due to mismatch of CTE are filled with boron oxides sealants provides an effective oxidation protection of up to 1500°C. Hoffman and Phan [53] enhanced the

effectiveness of oxidation protection coatings for CC composite with the nucleation and growth of silica deposited by CVD. They suggested the use of a technique – catalytic silver oxidation to increase the number of active sites concentration and distribution to enhance deposition uniformity which enhances the silica deposition rate on carbon.

Jacobson and Curry [54] from NASA research center studied the oxidation microstructure of CC composites and concluded that CC composite with SiC conversion coating exhibits limited attack at low temperatures (500 – 700°C) due to kinetic barriers to carbon oxidation, shows oxidation voids formed in cracks below the interface at temperatures (900 – 1300°C) and limited oxidation at higher temperature (1500°C) when the SiC coating and glass sealants are intact. However, they also observed that when the protective layer is damaged, oxidation of the composite becomes extensive and proceeds through matrix cracks, creating denuded fibers on the edges of the cracks. In a different experiment conducted by Wu and Raadovic [55], they studied the oxidation behavior of phosphorus deposited on CC Composites catalyzed by potassium or calcium acetate. They concluded that the presence of P groups bonded to carbon sites causes the site blockage that encourages its oxidation resistance. Research involving multilayer protective coating is still being conducted vastly to further understand the complicated relationship between the oxidation behaviors towards CC composite.

### 3.3.1 Application technique

#### Pack cementation method

Among the many ways to apply protective layer coatings on to CC composite which will be discussed here includes the pack cementation and CVD technique. Pack

cementation technique as illustrated in Figure 15, converts the surface carbon layer to ceramic. In this process, a powder composition of ceramic usually Si, graphite, and a penetration enhancer  $\text{Al}_2\text{O}_3$  to promote the diffusion reaction is packed together in a graphite crucible and are baked at low temperature followed by heating at high temperature ( $1700^\circ\text{C}$ ) in an inert gas (Argon) for several hours until a SiC inner coating is formed. [28]

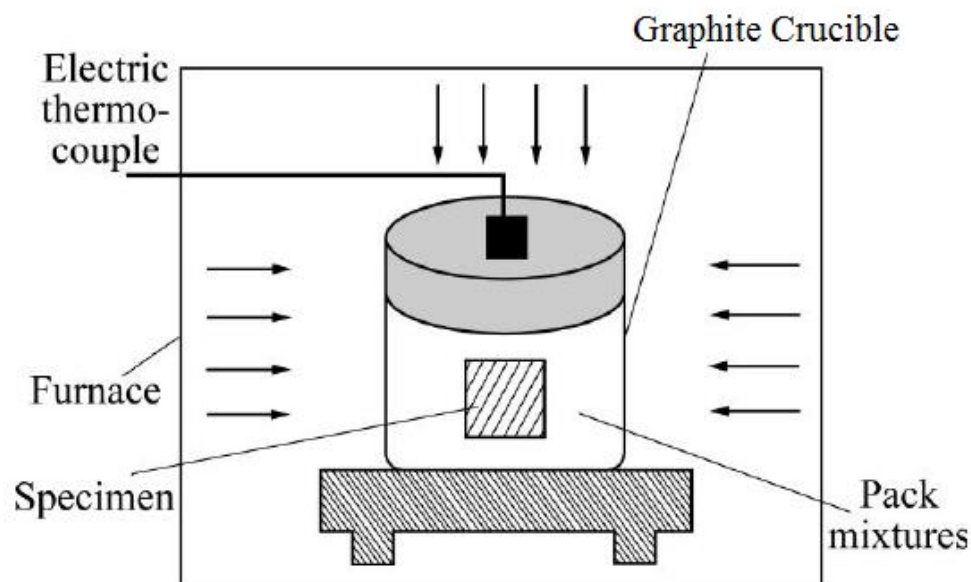


Figure 15. Schematic diagram of a pack cementation device [56]

#### Chemical vapor deposition (CVD) method

The CVD method as shown in Figure 16, begins with vaporizing a precursor compound followed by an introduction of an inert gas known as the carrier gas to carry the vaporized precursor vapor through a column to the reactor chamber where the CC composite substrate is located. In the reactor, the substrate is kept at a constant temperature that is sufficiently high for the precursor vapor to decompose and form a layer of coating on to it. [28]

Recent experiments have combined both techniques to form a two-step method of pack cementation followed by a low pressure CVD process to provide an external protection layer that could effectively inhibit the oxidation reaction on CC composites.

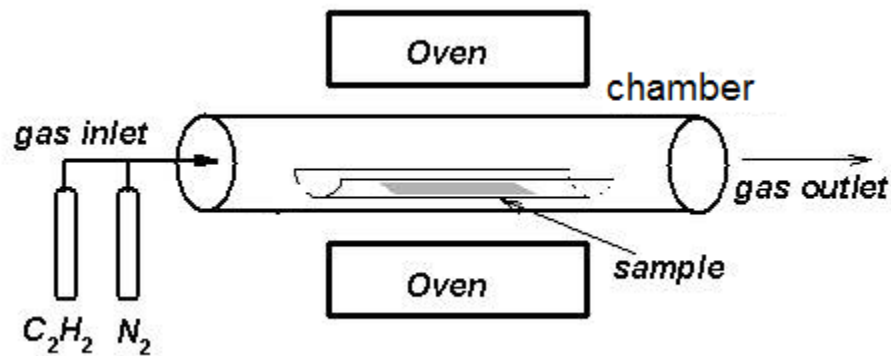


Figure 16. Schematic diagram of a CVD process.

### 3.4 Surface treatment of oxidation inhibiting aqueous solution

This method utilizes a phosphoric based penetrant salt solution containing ions formed from the combination of  $\text{H}_3\text{PO}_4$ ,  $\text{MnHPO}_4$ ,  $\text{Al}(\text{H}_2\text{PO}_4)_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Zn}_3(\text{PO}_4)_2$ , and alkali metal mono-, di-, or tri-basic phosphate that is brush painted, sprayed or other painting techniques to form a stable complex with active sites at the base of the cracks to prevent oxidation. Honeywell International Inc. currently holds the patent on the composition of penetrant salt solution followed by curing the surface treated CC composite in Nitrogen gas to a temperature of about 500 to 900°C. Improvements of the original composition have been made throughout the years and have been patented by the inventors T. B. Walker and L. A. Booker. [57] Following up with their research on inhibiting the oxidation process, they discovered that the use of phosphoric acid-based penetrants starts to degrade at peak operating conditions for a CC composite airplane brake disk. Walker et al. suggested using a Bi- or tri-layer anti-oxidation system for CC composite brakes in which they recommend the use of the phosphoric base penetrant

salt solution as an inner coating and later applying a silicon based overcoat protective layer consisting of particulate silicon carbide, water-miscible silicate binder component and a pH modifier. [58]

## CHAPTER 4

### CONCLUSION

A significant amount of research work has been done on understanding the effects of oxidation towards CC composites at various temperature. Oxidation reactions can occur on the external surfaces as well as in the internal pores of the composite and variations such as composition and structure properties, porosity, structure of constituent fibers, crystalline order, carbon fiber and matrices precursors, degree of graphitization of carbon and surface roughness plays a role in exciting or inhibiting the oxidation process. Emphasis on studies towards the microstructural analysis of composites proved to be useful in understanding the effects of oxidation towards CC composites in the microscopic level. Techniques and oxidation protections methods have to be studied and developed in order to allow the replacement of CC composite as a lightweight, high strength and high modulus structural material especially in an elevated temperature and elevated pressure environment. The major areas focused in inhibiting the oxidation process involves microstructural modification of carbon, the addition of inhibitors and application of a protective layer coatings and surface treatment with aqueous solution. Strong bonding between fiber and matrix, addition of inhibitors during fabrication of prepregs, active site blocking, application of multi-layer protective coating and filling cracks caused by mismatch of thermal expansion with sealants have all proven to be particularly useful inhibiting the oxidation process in CC composites.

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