A NEW FABRICATION METHOD OF CONTINUOUS FIBER REINFORCED METAL MATRIX COMPOSITES

By

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ABSTRACT

A NEW FABRICATION METHOD OF CONTINUOUS FIBER REINFORCED METAL MATRIX COMPOSITES

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The existing fabrication methods of continuous fiber metal matrix composites face many problems such as, excessive interfacial reaction, poor wetting, uneven fiber distribution, high cost and time consuming. This thesis demonstrates a new fabrication method which is the modification of the continuous fiber polymer matrix composite technique developed by the Composite Materials and Structures Center at Michigan State University. The new technique was investigated with carbon/aluminum system. The carbon fiber reinforced aluminum matrix composites were produced by fiber spreading and aluminum powder fluidizing to make precursors and subsequent vacuum hot pressing of the precursors. The experimental results showed that the thermoplastic polymer serves well as the binder between the fibers and the metal powders. The mechanical test and microscopy examination demonstrated preliminary success of this process. The investigation proved that the new fabrication method is potential to produce high quality continuous fiber metal matrix composites by a continuous process with low cost.

DEDICATION

To my parents, my wife and my daughter.

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Chapter 1

Introduction to Metal Matrix Composites

1.1 Definition of Metal Matrix Composites

Metal matrix composite (MMC), in general, consist of at least two components: one is the metal matrix, and the second component is a reinforcement. Metal matrix composites are broadly classified into two categories [1]:

1. Fiber reinforced composites. This class is further subdivided into continuous or discontinuous fibers with uni-directional or bi-directional reinforcement.
2. Particle or whisker reinforced composites. Here the subdivision is based on random or preferred orientation of the whiskers or particles.

MMCs have several advantages that are very important for their use as structural materials. These advantages include many of the following properties [1-4]:

1. High specific strength
2. High specific modulus
3. High toughness and impact properties

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4. Low sensitivity to temperature changes or thermal shock
5. High surface durability and low sensitivity to surface flows
6. High electrical and thermal conductivity
7. High service temperature
8. Good wear and seizure resistance
9. Resistance to moisture
10. Ability to be coated, joined, formed and heat treated by conventional metallurgical processes.

Figure 1.1 and 1.2 compare MMCs to other materials in terms of specific strength, specific modulus and high temperature capabilities.

For a composite structure the environmental stability of the matrix at elevated temperature is emphasized, since the required mechanical strength and stiffness can be obtained from the reinforcement. The shear strength requirements of the matrix are nominal because the matrix serves only to transfer load into the filaments in continuous filament composites. However, the matrix strength is very important in discontinuous metal matrix composites.

Numerous metals have been used as the matrix, for example aluminum, magnesium, copper, lead, titanium, titanium aluminizes, nickel, nickel aluminizes, nickel-based superalloys, and various alloys of iron. The aluminum matrix alloy composites are the only ones that have become widely

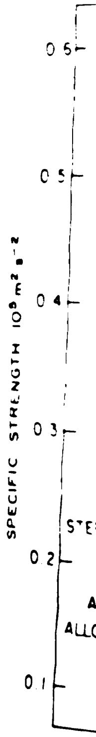

Figure 1
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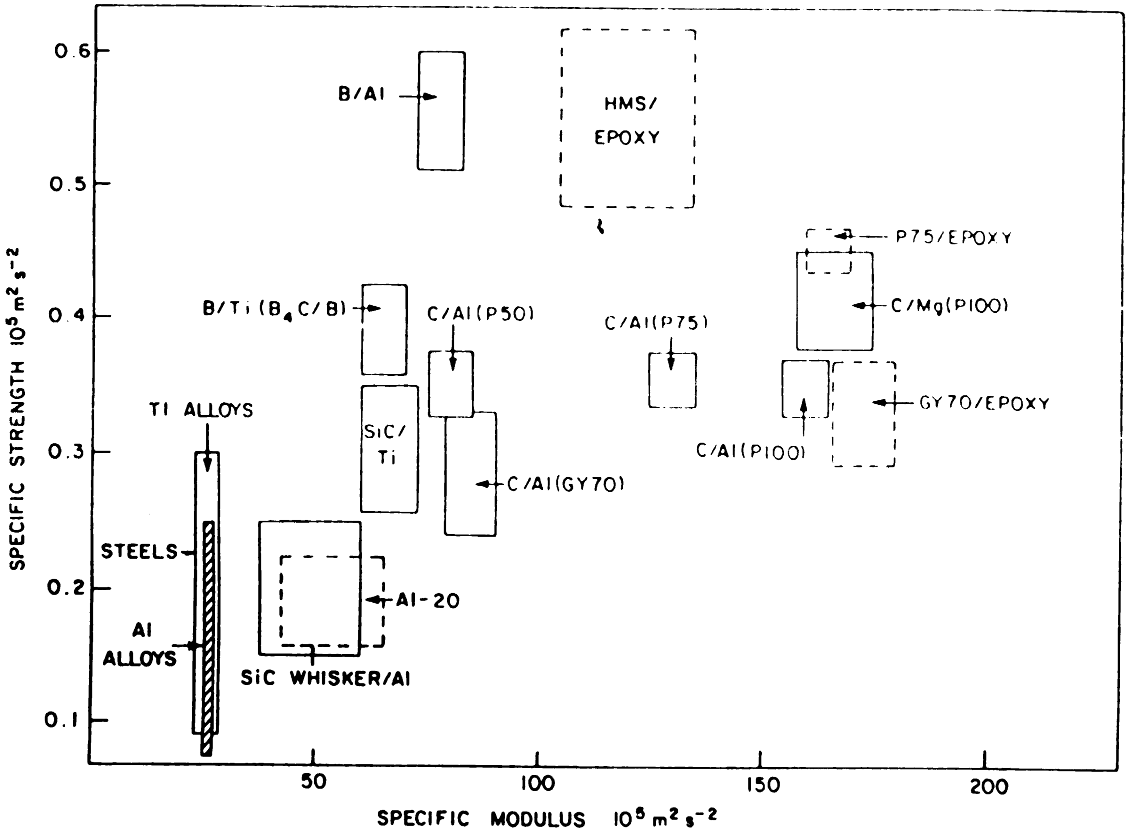

Figure 1.1 Specific strength and modulus of some metal matrix composites compared to some other materials [1].

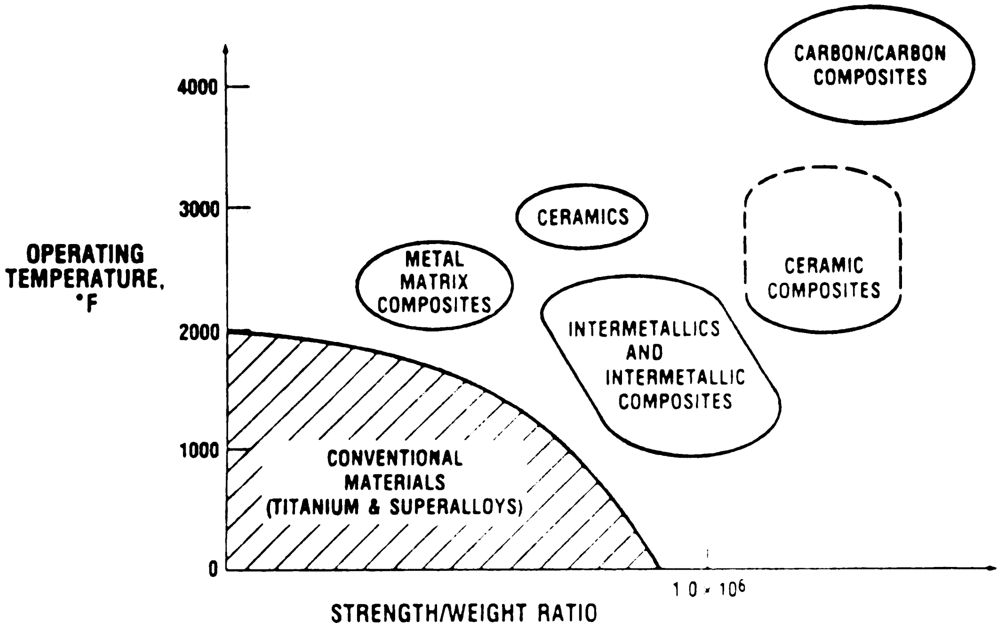

Figure 1.2 Performance map of various high-temperature engine materials in terms of operating temperature (°F) and strength/weight ratio [2].

available [2, 7].

The reinforcements can be divided into two major groups, discontinuous and continuous. The most prominent discontinuous reinforcements have been SiC, Al_2O_3, and TiB_2 in both whisker and particulate form. In terms of continuous reinforcements most are non-metals, such as carbon, silicon, boron, boric, alumina, although continuous metal filaments like tungsten and stainless steel are also being used as reinforcements. However in this thesis, particular attention will be given to continuous fiber reinforced metal matrix composites, especially continuous carbon fiber reinforced aluminum matrix composites.

1.2 Historic Development of Continuous Fiber Reinforced Metal Matrix Composites

The development of continuous fiber reinforced metal matrix composites (CFMMC) dates back to the late 1950s when NASA first reported its results of tungsten wires reinforced copper alloy matrix composite [8]. From 1960 to 1970 a large effort was made to develop continuous fibers reinforcements and the progress was carried out mostly by the aerospace industry because performance was more important than the cost of the material. So few commercial applications involved CFMMC for a period of twenty years. In 1960s boron monofilament of 140 microns in diameter were made to reinforce aluminum alloys and were used in the space shuttle as a tubing for cargo bay stiffeners [9]; however, the only structure that has found its way into service is a tube [7]. Boric fibers (SiC-coated boron fibers) reinforced aluminum alloys were also found applications as structural components in spacecraft and airplanes [10]. Silicon carbide and alumina whiskers were used as reinforcements for aluminum, magnesium, titanium, etc, but the high cost of these whiskers limited the continued development of these systems. Carbon fibers were considered as potential reinforcement for aluminum alloys due to their much lower cost as compared to the boron fibers. In 1970 researchers at the Aerospace Corporation successfully produced graphite fiber/aluminum composites [11]. However, early work showed that the wetting problem of carbon by molten aluminum and the excessive reaction between the fibers and the matrix are major problems for the development of this system.

In 1980 researchers at Lockheed Missiles and Space Corporation developed an aluminum-based composite with almost zero thermal expansion, high thermal conductivity and very high stiffness combination of properties. The known commercial application of this composite is the big antenna booms used by NASA for its space telescope [7] where thermal stability and high stiffness are major concerns. Much of efforts of the 1980s have been to improve the mechanical properties, develop cheaper reinforcements and simple processing methods to find commercial applications in areas other than the aerospace and the

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the defence industries. But the improvements came slowly due to the price of CFMMCs and certain disadvantages of CFMMCs. The disadvantages include thermal fatigue, lower fracture toughness than the matrix alloys, and shear, compression, traverse strength limitations.

Despite the fact that CFMMCs have some disadvantages, they are still considered to be a reliable high temperature and high performance material system. The direction of CFMMC is toward minimizing the cost of fabrication and optimizing the processing parameters to control the interfacial reactions and improve the mechanical properties. This thesis follows the trend by investigating a new fabrication method for continuous fiber reinforced metal matrix composites.

Chapter 2

Existing Fabrication Methods of Continuous Fiber Reinforced Metal Matrix Composites

In the production of continuous fiber metal matrix composites (CFMMC), most technological schemes include two stages [12]. The first stage is usually the production of precursor wire which is similar to the well-known prepregs in the fiber reinforced plastics technology. The precursors are then cut into desired lengths, aligned in mats, and consolidated by diffusion bonding to form simple shapes in the second stage. Although the direct liquid phase hot pressing method was used, it will not be reviewed in this thesis because that process faces some serious and unresolved problems [4], such as, 1) the presence of voids after solidification due to poor infiltration, shrinkage of the matrix; 2) uneven distribution of the fibers as a result of the formation of metal channels during solidification; 3) uneven matrix concentration with a solute-rich microstructure near the interface.

2.1 Fabrication of Composite Precursors

2.1.1 Metal Melt Process

The most common method of the production of precursor wire is the metal-melt (liquid-infiltration) process because of its simplicity and continuity. Figure 2.1 is a example of this method. The composite precursor cable is produced by pulling a fiber bundle through a bath of molten metal. This process faces two serious problems: poor wetting of fiber by molten metal and excessive reaction between fibers and metal due to the high temperature (above the melting point of the matrix metal). In addition, uneven fiber distribution is an unresolved problem.

A. Wetting

For fibrous composites, the extent to which the melt will infiltrate into the fiber bundle or preform will depend on the ability of the liquid metal to wet the solid surface of fiber. This is known as wettability. That is the ability of a liquid metal to penetrate a fibrous body and cover all the surface area of the fiber, which is dependent on the contact angle θ as shown in figure 2.2, and in equilibrium it is given by Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad (2\text{-}1)$$

Where γ_{sv} = surface energy of the solid

γ_{sl} = solid/liquid interfacial energy

γ_{lv} = surface tension of the liquid

If the contact angle θ is less than 90°, then the liquid metal wets the solid fibers spontaneously. However, most molten metals do not wet most inorganic fibers, which is the case $\theta > 90°$ [13-16]. Without wetting, infiltration is not possible [17], and therefore wetting must be improved by:

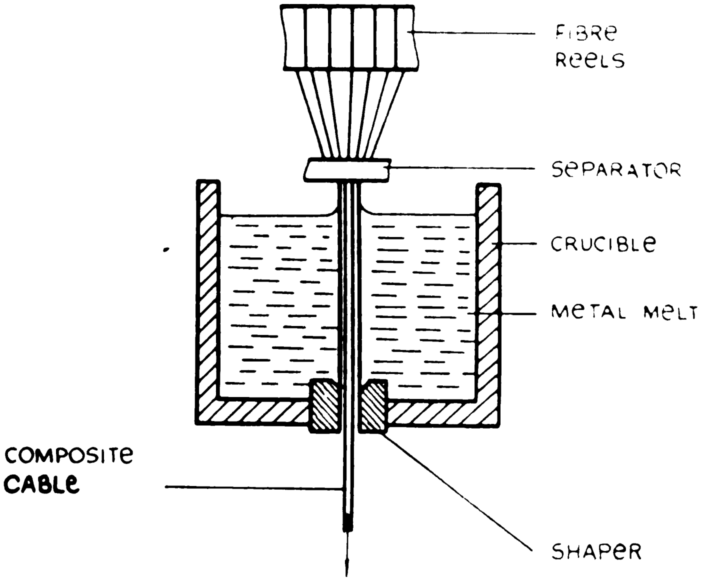
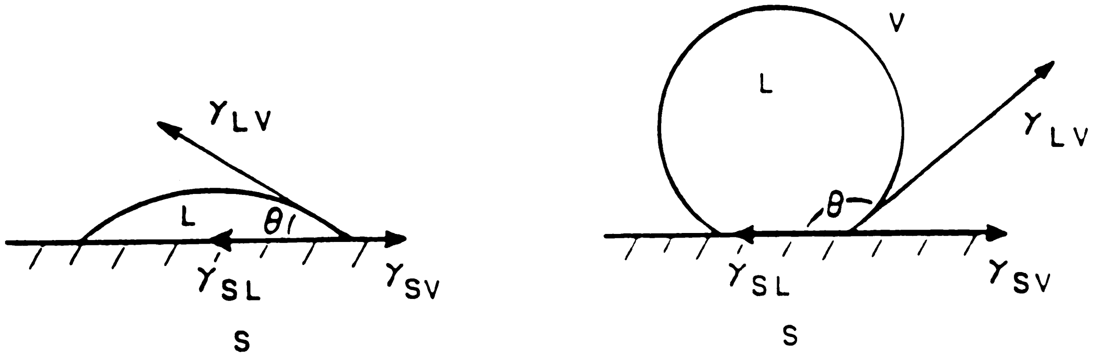


Figure 2.1 A scheme of producing a composite cable by pulling a fiber bundle through a matrix melt [12].

Fig



$\theta < 90^0$

GOOD WETTING

$\theta > 90^0$

POOR WETTING

Figure 2.2 Schematic of sessile drop on solid surface [7].

a) Modification of the chemical composition of the surface of the fibers

b) Modification of the chemical composition of the liquid matrix

c) Increasing the working temperature

d) Modification of the working atmosphere.

B. Interface Reactions

The composite interface may be defined as follows [18]: An interface is the region of significantly changed chemical composition that constitutes the bond between the matrix and reinforcement for transfer of loads between these members of the composite structure.

Three general classes of interface have been proposed for metal matrix composites. The three classes are:

Class I, filament and matrix mutually nonreactive and insoluble.

Class II, filament and matrix mutually nonreactive but soluble.

Class III, filament and matrix react to form compound(s) at interface.

Table 2.1 gives examples of each type. However, the interface reactions in class III interface result in compound formation and may lead to loss of strength and ductility of the composite, if the compound is brittle. Interface reactions can be prevented by:

a) Modification of the chemical composition of the surface

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Table 2.1 Classification of composite systems

Class I	Class II	Class III
Copper–tungsten	Copper(chromium)–tungsten	Copper(titanium)–tungsten
Copper–alumina	Eutectics	Aluminum–carbon (>700°C)
Silver–alumina	Columbium–tungsten	Titanium–alumina
Aluminum–BN coated B	Nickel–carbon	Titanium–boron
Magnesium–boron	Nickel–tungsten[a]	Titanium–silicon carbide
Aluminum–boron[b]		Aluminum–silica
Aluminum–stainless steel[b]		
Aluminum–SiC[b]		

[a] Becomes reactive at lower temperatures with formation of Ni_4W.

[b] Pseudo-Class I system.

of the fibers

b) Modification of the chemical composition of the matrix

c) Lowering the working temperature

d) Modification of the working atmosphere.

2.1.2 Other Methods for Making Precursors

There are many other methods for making precursor materials. Some of these methods are described next.

A. Electroplating

It starts by winding fibers on a mandrel (or bobbin) and placing them in a solution containing the ion of the desired material in the presence of an electric current. The fibers represent the cathode while the matrix material serves the anode. Positively charged metal ions move toward the cathode and deposit onto the fibers. A uniform coating of the matrix material is usually obtained with no voids. Nickel, copper, aluminum and lead were successfully deposited the electroplating [19,20]. However, this process exhibits some problems. First, only a limited numbers of alloy matrices are available to choose from. Second, the adherence of the deposit to the fiber may be poor, especially for carbon fibers.

B. Spraying

A typical spray operation consists of winding fibers onto a foil-coated drum and spraying molten metal onto them to form a monotape. Compressed hot air pushes small droplets of the molten matrix toward the fibers at very high speed. The liquid droplets freeze instantly when they contact the cold fibers. The rapid rate of solidification causes a fine matrix microstructure to form around the fibers, and reduces the fiber surface area that could have been wetted in the case of a moderate cooling rate [21]. But this instant freezing generates voids and causes lower mechanical properties. Microcracks are also formed during the rapid solidification due to thermal stresses[22].

C. Chemical Vapor Deposition (CVD)

CVD process begins by heating chemical components until vaporization. A vaporized component decomposes or reacts with another vaporized chemical, and the desired species are deposited on the fibers while the rest of chemicals escape the system as gases. This process is used more frequently to coat fibers with wetting agents or with diffusion barrier coating against fiber/matrix interactions. It has been used to coat carbon fibers for Al-based composites [19,23-26]. Some of these coating include TiB, Cu, Ni, TiC, TiN and SiC. CVD is highly dependent on the precursor chemicals and the temperature of the reaction chamber. Another disadvantage of CVD process is that the process is slow and expensive.

D. Physical Vapor Deposition (PVD)

PVD process is similar to CVD. The matrix material is de

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deposited on the fibers in the vapor phase but without the help of chemical components. Three basic PVD processes can be utilized to form metal matrix composites: evaporation, ion plating, and sputtering. Aluminum-carbon composites were made by this process [27,28]. The primary advantage of PVD is versatility in composition and microstructure of the coating. Deposits can be made as pure metal compounds, or alloys from alloy targets. An additional benefit is that No pollutants or effluants are created or used in the processes. However, like CVD, the process is slow and expensive.

2.2 Consolidation by Diffusion Bonding

In the final stage of the primary manufacturing of CFMMCs, the precursor wires are consolidated into simple shapes by diffusion bonding. Figure 2.3 is a flow chart of metal-matrix composite fabrication based upon diffusion bonding.

Diffusion bonding is solid state process which is used to join the same or dissimilar metals by applying heat and pressure. It requires the formation of strong adhesive bonds between asperities. The temperature ranges from 50 to 90% of the melting point of the metal matrix. The pressure should be well below the yield stress of the matrix to avoid excessive plastic deformation of the bulk material. A bond is formed when new grains appear at the interface region and when small pores remaining at the joint line are few. The mechanical

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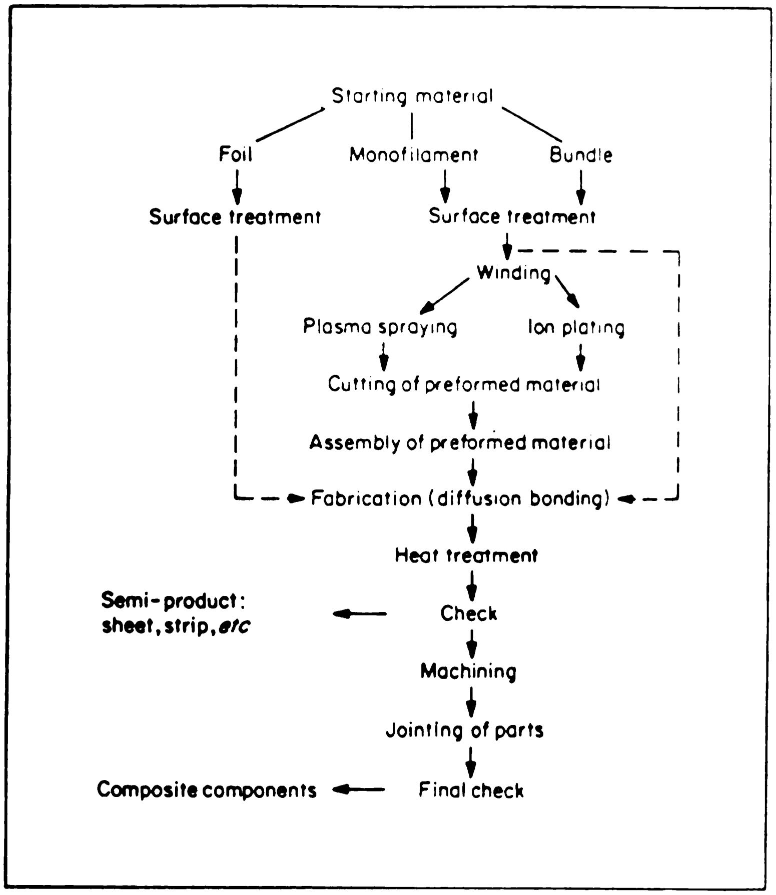

Figure 2.3 Flow chart for composite fabrication by diffusion bonding.

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properties depend on the consolidation method and processing parameters: temperature, pressure and time. For the consolidation of powders, the best consolidation parameters give low flow stress and high ductility of the matrix material and at the same time retain the fine microstructure obtained from the use of powders.

2.2.1 Mechanisms of Diffusion Bonding

Many researchers have studied the mechanisms and the practical aspects of diffusion bonding [29-34]. Derby and Wallach are the first authors to suggest that diffusion bonding consists of five mechanisms. (1) plastic deformation of surface asperities, (2) power-law creep of the surface, (3) diffusion of matter from interfacial void surfaces to growing necks, (4) diffusion of material from bonded regions on the interface to the growing necks, and (5) bond formation by mass transfer in the vapor phase. The most important mechanisms are those involving bulk, grain boundary, surface diffusion and plastic deformation by creep. Vapor phase transport is the least important because of the low vapor pressure of metals during typical bonding conditions. These mechanisms will be active at different times and in different combinations during a diffusion bonding cycle, depending on the interfacial geometry and the thermodynamic driving force of the system.

A bonding cycle can be divided into three stages. The initial stage is the combination of first two mechanisms, plastic deformation and power-law creep. It involves the plastic deformation of surface asperities and the fracture of surface oxide layers. The desired goal is to increase the contact area between surfaces and produce an intimate contact between oxide-free and freshly formed surfaces. Breaking the oxide film is important especially for powder consolidation because the surface area of powder is very large. During this stage, most of the oxide films are broken by shear displacements between two asperities in contact as a result of the applied pressure, and by dissolution or spherodization of the oxide layers as a result of the diffusional flow at high temperature. At the end of the first stage, the bonded area contains a lot of voids. The second stage is dominated by the third mechanism, neck growth by diffusion. In this stage, long prismatic voids spaced along the bonding interface are converted to smaller circular or lenticular voids by diffusion of matter across the bonding interfaces. The driving force for the shrinkage and the spheroidization of these pores is the difference in the chemical potentials in the growing neck and the region away from the neck. Finally, in the third stage, these voids contract while maintaining their geometry until they disappear. Since the shrinkage and the elimination of these pores may take a long time, the growth of the interaction compounds at the interface must be considered when optimizing consolidation parameters.

In composites, two additional factors must be considered. First, the matrix must deform around any reinforcements present in order to make contact with other matrix material. Composite consolidation reduces the role of surface asperities in the initial stage of contact, and increases the role of plastic deformation in breaking tough, adherent surface oxides or other adsorbate films in order to expose clean metal surfaces. Second, a fiber/matrix interface must be created as the closure process progresses. As the fiber get embedded in the matrix, the arc of fiber/matrix bond changes. This means that the contact time and bond strength can vary as a function of position on the fiber surface during the initial stage of consolidation. In composite systems with reactive matrices or reactive fibers, fiber degradation caused by an interfacial reaction may take place before matrix-to-matrix bonding can be completed.

2.2.2 Processing Techniques

There are many different diffusion bonding processing techniques for metal matrix composites. Some methods will be reviewed next.

A. Vacuum Hot Press (VHP)

Vacuum hot pressing is the quintessential diffusion bonding process for metal matrix composites. A typical VHP process is illustrated in Figure 2.4. Once the precursor

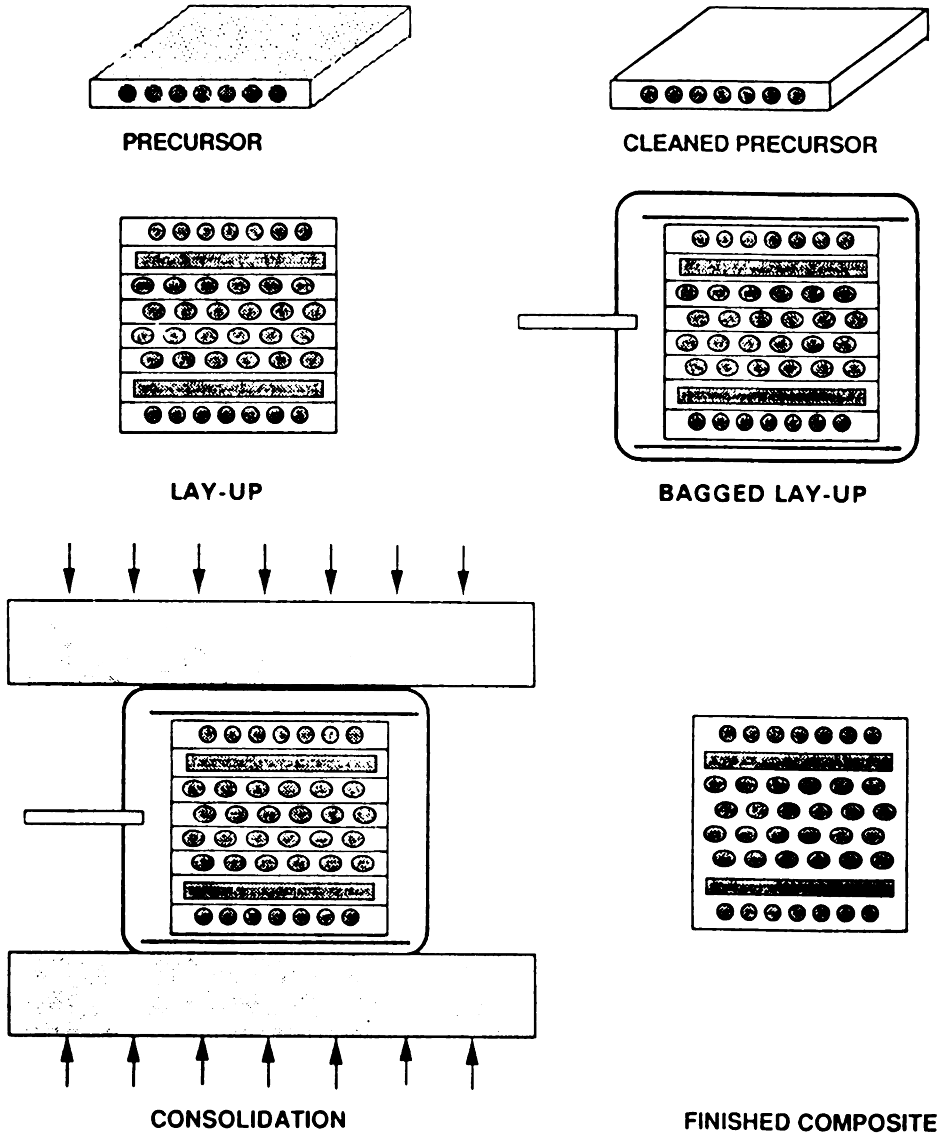

Figure 2.4 Steps performed during a generic MMC diffusion bonding operation [7].

materials are cleaned from residual organic materials, greases or thick oxide layers, they are cut and stacked to form the desired lay-up. To prevent bonding of the lay-up to the vacuum bag, foils with stop-off material are included. A vacuum is drawn to remove reactive gases such as oxygen, hydrogen and water vapor, because vacuum can prevent oxidation of the metal matrix and the fibers and the formation of undesirable products. If fugitive binders are used, a hot degassing operation must be performed before VHP in order to evaporate the binders. Once these preliminary works are completed and the desired vacuum level has been reached, the vacuum-bagged sample is placed between platens. Pressure is then applied at the bonding temperature for a given hold time. Finally, the consolidated composite plate is extracted from the vacuum bag, trimmed to eliminate unconsolidated material at the edges, and cleaned to remove the stop-off materials.

VHP has good control over all the fabrication parameters and it is quick, simple, inexpensive and it yields yield high-quality materials. However, it lacks the capacity to form large and complex shapes.

B. Step Pressing

Step pressing is a variation of the standard VHP technique. It involves performing repeated VHP cycles by moving, or stepping the bagged lay-up in the platens after each cycle. By step pressing, parts which are larger than the hot-press platen size can be fabricated.

C. Hot-Die Molding

In hot-die molding, the flat platens of VHP process are replaced by shaped dies [35]. By this process, complex parts can be fabricated. Furthermore, the die sidewalls can prevent excessive lateral deformation of the part.

D. Hot-Roll

Hot-roll is a semicontinuous technique which can be used to consolidate composite sheets [36]. Precursor lay-ups are placed in packs for maintaining fiber alignment. The packs are heated in a furnace to the desired rolling temperature and then passed through a standard rolling mill. Important roll-bonding parameters include temperature, rolling pressure, speed, heating atmosphere, and pack material.

Other processing techniques include hot drawing, hot isostatic pressing and superplastic forming, etc.

2.2.3 Processing Parameters and Parameter Optimization

The consolidation method and the processing parameters directly determine the mechanical properties of a composite material. Unfortunately, processing parameters are some of the least reported items of information in the open literature. This is caused by two factors. First, most of MMC research is sponsored by the government and this information is considered as vital to the national security interests. Second, commercial composite fabricators classify the processing parameters under proprietary information in order to keep their competitive edge. Therefore, optimum processing parameters have to be achieved through experimental trials.

The primary variables of in diffusion bonding are temperature, time, and pressure, but other variables such as vacuum level, the use of stop-offs and fugitive binders, and type of deformation may also be significant under certain circumstances. It is obvious that there should exist an optimal set of temperature, pressure and pressing time, but selecting the best consolidation parameters is difficult. The most common technique for parameter optimization is the one-variable-at-a-time approach. For example, keeping time and pressure constant, it is easy to obtain the maximum in tensile strength from the variation of the tensile strength with hot pressing temperature. This technique is simple but deficient because that the interactions between consolidation parameters are ignored, which, in fact, should not be ignored.

A better technique for parameter optimization is to simplify optimization problem from three parameters, time, temperature and pressure, to two parameters, time and temperature. The response surface in Figure 2.5 represent the ultimate tensile strength of composite fabricated at every conceivable temperature-time combination. First, a one-variable-at-a-time "optimization" is performed while holding time

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time constant and varying temperature, and a curve is obtained by the intersection of a plane containing the fixed time value and the response surface. Then, the second "optimization" is performed at the maximum of the first curve by holding temperature fixed and varying time, and a second curve is generated. The maximum of the second curve is then considered the "optimum" processing condition according to the one-variable-at-a-time technique. But it is not exactly the true optimum fabrication conditions. Response surface analysis [37] can be used to find the exact optimum conditions. It works by calculating the gradient of a small portion of the response surface, and following the gradient to a new section of the surface. The process is repeated until the optimum conditions are found. However, optimization would be performed in at least three dimensional processing space, with the response in a fourth dimension.

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Chapter 3

Continuous Carbon Fiber Reinforced Aluminum Matrix Composites

Aluminum matrix composites with continuous reinforcing fibers of carbon will be reviewed in this chapter due to two reasons. First, the aluminum matrix composites are the only ones that have become widely available. Second, the new fabrication method for continuous fiber reinforced metal matrix composites will be demonstrated by investigating the carbon/aluminum system.

3.1 Carbon Fibers

Carbon fibers are generally produced by thermal decomposition of various organic fibers. Based on precursor material, carbon fibers can be classified as rayon base, polyacrylonitrile (PAN) base and pitch base fibers. Table 3.1 lists the properties of some selected carbon fibers available in USA.

Rayon base carbon fiber have been widely used with aluminum matrix [38,39], and have provided the most consistent behavior in terms of dispersion within the aluminum matrix and in terms of composite properties. Unfortunately, rayon base

Table 3.1 Properties of carbon fibers available in USA

Manufacturer	Fibre Name	Precursor	Tensile Strength GPa	Tensile Modulus GPa	Density g/cm^3
Great Lakes	Fortafil 3	PAN	2.48	207	1.71
Corp. USA	Fortafil 5	PAN	2.76	331	1.80
Celanese	Celion GY-70	PAN	1.86	517	1.96
Corp. USA	Celion 6000	PAN	2.76	234	1.76
	Celion 3000	PAN	2.76	234	1.76
	Celion 1000	PAN	2.48	234	1.76
	Celion 12K, 3K	PAN	3.24	234	1.77
Hercules	AS	PAN	3.10	220	1.77
Incorp.	HTS	PAN	2.76	248	1.80
USA	HMS	PAN	2.34	344	1.86
Union	Thornel 50	Rayon	2.20	393	1.67
Carbide	Thornel 300	PAN	2.65	227	1.75
USA	Thornel 75	Rayon	2.65	524	1.82
	Thornel B	PAN	3.2	290	1.71
	P 55	Pitch	2.07	379	—
	P 75	Pitch	2.07	517	—
	P 100	Pitch	2.07	689	—

fiber is very expensive and the production is being taken off the market [40,41].

Pitch base carbon fiber tows (or bundles) are the cheapest and most easy to infiltrate with molten aluminum, and the composite wire produced from them posses sound structure with a uniform fiber dispersion [38]. However, the strength values of the composite are quite low because of the current low strength of this kind of fibers. Higher strength pitch base fibers may be available in the future.

PAN base fibers are further subdivided on the basis of their mechanical properties into the following three general types:

a) Type 1, high modulus fibers
b) Type 2, high strength fibers
c) Type 3, lower cost variants

PAN base carbon fibers react somewhat unpredictably when incorporated in aluminum matrix. For instance, PAN base carbon fiber T-300 reacts extensively with aluminum alloy resulting in fiber degradation and lower strength composites, while HM-3000, which is also a PAN base fiber, yields some very high strength composites. The reactivity of PAN base fiber is believed to be controlled by the final graphitization temperature used during their production. T-300 is a relative low modules fiber with high relativity which results from the relative low final heat treatment temperature, while HM-3000 is a

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is a high modulus fiber with good chemical stability which was carbonized at relative high temperature. However, PAN base carbon fibers GY-70, T-300, HM-3000, and Celion HT have all been used as reinforcing agents with various aluminum alloys.

3.2 The Matrix

The matrix material has the dual function of maintaining the component shape and the transference of load to the fiber via shear processes at the interface. Aluminum is extremely attractive for use as a matrix material because of its low density, low cost and availability.

The most common aluminum alloys used with carbon fibers are: 201, 6061 and 1100. Pure aluminum, 356, 413, 5056, 5154, Al-5Mg, Al-10Mg, Al-13Si and Al-12Si have also been used as matrices [1]. Table 3.2 shows the properties of some aluminum alloys.

3.3 Manufacturing Problems of C/Al composites

The objective of a fabrication process is to combine the fibers and the matrix with three essential requirements:

a) The fibers are introduced in the matrix without mechanical damage.

b) The fibers are aligned and distributed uniformly.

c) Adequate bonding between fiber and matrix is obtained

Table 3.2 Properties of some aluminum alloys

Aluminium Alloy	Density gm/cm^3	Modulus GPa	Tensile Strength MPa	Thermal Expansion Coefficient X 10^{-6} 20-100°C
Pure Al	2.71	69.0	82.8	13.2
1100	2.71	69.0	89.7	13.1
2024	2.77	73.1	186.3 (annealed) 448.5 (T3)	12.9
5052	2.69	70.3	193.2 (annealed) 262.2 (H34)	13.2
5056	2.63	71.07	289 (annealed) 414 (H38)	13.4
6061	2.71	69	124.2 (annealed) 310.5 (T6)	13.0
7075	2.80	71.7	227.7 (annealed) 572.7 (T6)	13.1
201	2.80		448.5 276 (T6)	10.7

without any detrimental chemical reaction at their interfaces.

However, the fabrication of carbon/aluminum composites faces some problems. The major problems are:

a) Poor wetting of carbon fibers by molten aluminum

b) Reaction between aluminum and carbon.

These problems will be discussed in this section.

3.3.1 Wetting

The melting point temperature of aluminum is 660°C. Liquid aluminum does not wet carbon fiber, as measured by contact angle θ, below about 1000°C. The contact angle θ between molten aluminum and carbon fibers is greater than 90° and may exceed 150°, in some cases. Above 1000°C, θ decreases to less than 90° (Figure 3.1). Below 1000°C, stable aluminum carbide (Al_4C_3) is formed, θ may decreases to less than 90°C as a function of time [3]. However, the formation of the brittle intermetallic components is detrimental to the mechanical properties of the composite. Therefore, the interfacial reaction must be controlled and the ways to improve the wetting are fiber coating and matrix alloying, which will be discussed in details later.

3.3.2 Interface Reactions

It is well established that aluminum reacts with carbon

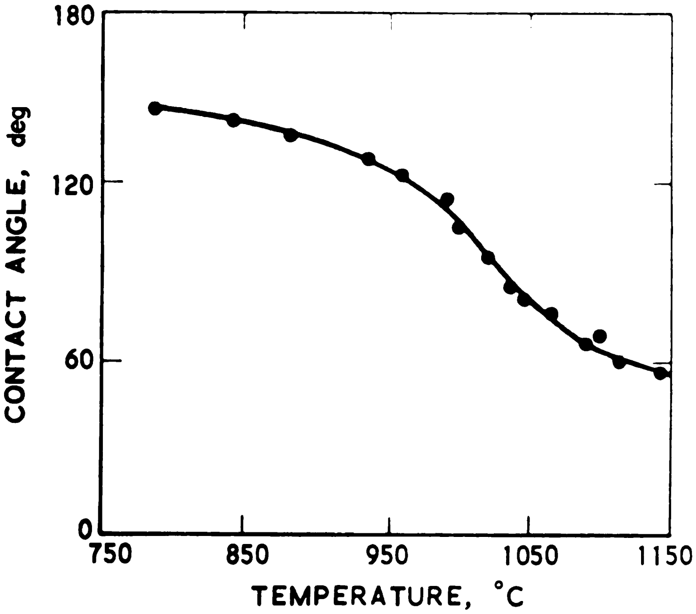

Figure 3.1 Contact angle of aluminum on carbon as a function of temperature [3].

fibers to form aluminum carbide (Al_4C_3) at high temperature. This interface reaction can degrade the mechanical properties severely and must be controlled.

A. Mechanism and Kinetics

The reaction at the carbon/aluminum interface occurs in two stages [42]. The first stage is interface-controlled and involves three steps. First, carbon atoms dissociate from the surface of the fibers. Second, the "free" carbon atoms diffuse through the aluminum oxide layer and other interphases. Third, carbon atoms react with aluminum atoms to form aluminum carbide. At this stage, understanding the first step is very important. It is the presence of oxygen that catalyze the dissociation of carbon atoms from the surface of the fibers. This model is based on the oxidation of graphite in air studied by Long and Sykes [43]. The second step is easy to understand because the microstructure of the interface shows that aluminum carbide forms on the aluminum side of the interfacial oxide. This implies carbon , rather than aluminum, as the diffusing species.

Maruyama et al [44] studied the effect of water vapor on the interfacial reaction. They concluded that the formation of aluminum carbide at glassy carbon/aluminum interface is catalyzed by the presence of as little as 500 Langmuirs (10^{-6} Torr-s) of water vapor at 410°C. This implies that the formation of aluminum carbide in carbon/aluminum composites may be catalyzed because of the levels of Water vapor found in typical consolidation environments.

The second stage of the reaction is the growth of the interfacial layer (aluminum carbide), which is diffusion-controlled because the mass transport across the interface becomes the limiting step in the aluminum carbide formation. As the interfacial layer grows, carbon atoms have to diffuse through longer distances and this requires more time. The growth rate of thickness of the reaction layer at the interface exhibits a square root dependence with time and is given by the following equation:

$$X = A_0 \exp(-Q/KT)\ t^{1/2} \tag{3-1}$$

Where X = The thickness of the reaction layer

A_0 = Constant

Q = Activation energy

K = Boltzman constant

T = Temperature

t = Time

In fact, all such reactions begin with interface-controlled kinetics, at least for a short time, and eventually change to diffusion-limited growth [45].

B. The Effect of Temperature, Pressure and Atmosphere on The Formation of Aluminum Carbide

In last 30 years, many researchers studied the effect of temperature, time, pressure and atmosphere on the formation of aluminum carbide. Unfortunately, The results are not in accord. Jackson et al. observed that aluminum carbide is formed at temperature above 400°C [46]. During stress-rapture test, Khan [47] concluded that chemical reaction occurs at aluminum-graphite interfaces at temperatures above 500°C. Lo et al.[48] reported that formation of aluminum carbide at aging temperature above 550°C was observed. Baker et al.[49], in compatibility test, showed that the carbide formation occurs at temperatures above 600°C. Upp et al.[50], in short time high temperature tensile test observed no interaction between the graphite fibers and the aluminum matrix at 560°C or degradation of the composites. Harrigan and French [51] reported no degradation of the composites at 465°C.

Motoki et al.[52] studied the reaction between high strength carbon fiber and vacuum evaporated pure aluminum. The study showed that aluminum carbide formed after vacuum annealing for four hours at 550°C or above and for one hour at 620°C or above. Baker et al.[53] reported that the degradation in the ultimate tensile strength of aluminum-coated carbon fibers was associated with the formation of aluminum carbide during annealing treatments for 100 hours in vacuum at temperature 475°C or above for high tensile fibers and 550°C or above for high modules fibers. Pepper et al.[54] exposed rayon base T50 fibers with coatings of aluminum alloys A13, 220 and 6061, to high temperature for five minutes, and reported no degradation in strength below 680°C.

Asanuma et al.[55], while investigating the use of roll diffusion bonding process for carbon/aluminum composites, reported that degradation of high strength PAN base fibers in air begins at 450°C, and at 600°C the strength was decreased by 50% in just one hour. Oxidation of the fibers was reported to be the cause. Shorshorov et al.[56], in a study of the interface reaction in carbon/aluminum composites fabricated by vacuum-compression infiltration of a carbon tape by Al-12%Si alloy, reported that increasing infiltration pressure, time and temperature increases the quantity of aluminum carbide at the interface, and temperature has the most significant effect. Maruyama et al.[44] determined that the formation of aluminum carbide is catalyzed by the presence of as little as 500 Langmuirs (10^{-6} Torr-s) of water vapor. Yoon et al.[57] studied the interfacial reaction between PAN base and pitch base carbon fibers and pure aluminum. Aluminum carbide was observed by TEM after a four hour heat treatment at temperatures above 550°C, and 600°C, for aluminum coated PAN base and pitch base fibers, respectively. It was further proven that the reactivity on the interface varies with the surface structure of the carbon fiber.

In summarizing the work described in the literature cited above, the following conclusions can be drawn:

1) The formation of aluminum carbide depends on temperature, time, pressure, atmosphere, the composition of the matrix and the characteristics of the fiber. Increasing pressure, time and temperature increases the quantity of aluminum carbide. Temperature and atmosphere (oxygen and water vapor) have significant effect.

2) The temperatures reported when aluminum carbide begins to form are different because the conditions of the experiments are different in these studies, especially for the reaction time (varying from a few minutes to hundreds of hours).

3) Optimum conditions may be different for different processes in order to control the formation of aluminum carbide.

C. The Microstructure of Aluminum Carbide and The Effect of The Interface Reaction on The Mechanical Properties

Some researchers studied the microstructure of aluminum carbide formed at the interface between carbon fibers and the aluminum matrix. Baker et al.[47] found that the aluminum carbide initiated on the fiber surface as fineplatelets with a random orientation. TEM investigations were used [58,59] to determine the size, the shape and the amount of aluminum carbide. In the case of pure aluminum matrix, aluminum carbide formation is random and dependent on the time of contact between the liquid aluminum and the graphite fibers. When the contact time minimized, only a few isolated aluminum carbide precipitates form on the surface of the fibers. These precipitates have a needle shape and range from 0.15 um to 0.40 um in size. The amount of aluminum carbide increases drastically as the contact time increases, and tangles of aluminum carbide precipitates are formed throughout the interface. These partially connected precipitates would grow to form a continuous layer of aluminum carbide if the fibers continue to be exposed to molten aluminum [60].

Khan [47] performed quantitative experiments on reaction kinetics. Electron diffraction observations showed that aluminum carbide has a hexagonal structure. Using SEM to observe the reaction rate, he found that the reaction zone thickness at the interface varies linearly with the square root of the reaction time, and increasing temperature increases the rate of the reaction (Figure 3.2). The thickness ranges from 1 to 10 microns with heat treatment temperatures of 650 to 800°C and times of 1 to 10 hours. This further confirms that the reaction process is diffusion controlled. Khan also studied the effect of the interface reaction on the mechanical properties of the composite. He concluded that the carbide growth on the graphite fibers causes surface damage, resulting in degradation of fiber strength and hence the composite strength.

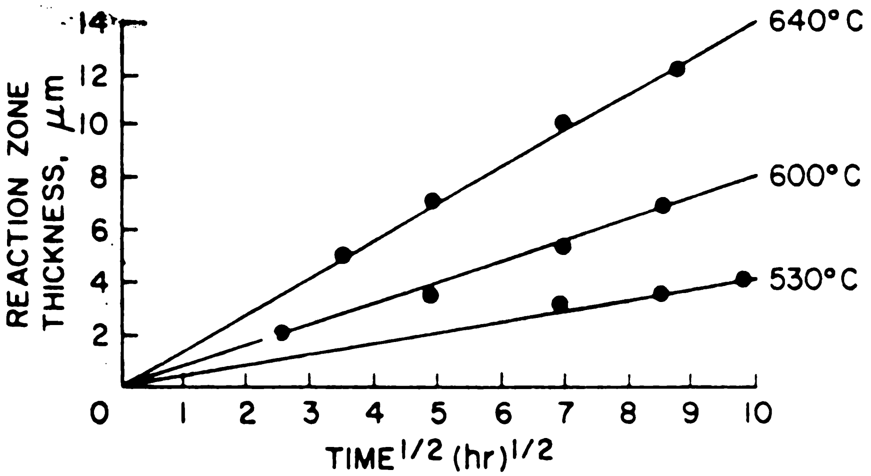

Figure 3.2 Thickness of the reaction zone as a function of temperature and time for Al-Gr systems.

Generally, the interface in continuous fiber composites plays two important roles. First, the interface transfers the load to the fibers through good interfacial bonds. Second, it provides toughness to the composite by allowing crack propagation along the interface before fracture. The last phenomenon is called the interface fuse mechanism [61] and requires "not too strong" interfacial bonds. In carbon/aluminum composites, aluminum carbide formation causes interface brittleness and results in premature failure which changes the mode of fracture. Crack propagation is no longer along the interface, but from one fiber to the next one by passing through the aluminum carbide phase. This is accomplished by the presence of very strong aluminum carbide bond at the interface. Under this condition, the interface fuse mechanism can not operate and low fracture toughness is to be expected. Furthermore, the brittle carbide phase can serve as sites for crack initiation. Another disadvantage of interfacial reaction is that the formation of aluminum carbide damages the fiber surface and causes significant decrease in strength of the fiber and the composite [62].

On the other hand, the formation of aluminum carbide increases the interfacial bond strength and could be beneficial to the overall strength of the composite when the interfacial thickness is controlled. It is possible that there is a threshold level of aluminum carbide before the degradation affects the composite strength [59]. It is believed that when the total amount of carbide exceeds 1000 ppm, a decrease in composite strength can be expected [3].

3.3.3 The Solutions for Manufacturing Problems of Carbon/Aluminum composites

Much work has been done to improve the wetting and control the interfacial reaction in liquid fabrication processes [62-71]. Modification of the chemical environment is the key to solve the problems. The most successful modification strategies are fiber coating and matrix alloying.

A. Fiber Coating

Carbon fibers are generally coated with metallic or ceramic layers using techniques like electroplating, electroless plating and chemical vapor deposition. An electroless plating technique was adopted and perfected to provide a homogeneous silver coating on the carbon fiber surface in an attempt to improve the wettability between molten aluminum and carbon fiber infiltration [68]. It was found that silver coating promoted the wetting between aluminum and carbon fibers, particularly with PAN base carbon fibers. However, interfacial reactions between aluminum and carbon fibers were still observed. Nickel coating was used in aluminum composites to protect carbon fibers from the molten metal. However, a Brittle intermetallic compound, $NiAl_3$ formed at the interface while aluminum carbide was not found [69].

The Ti-B coating applied by chemical vapor deposition was regarded as the most successful coating for making carbon fibers wettable with aluminum alloying [19]. Himbeault et al. [70] reported that aluminum alloy-titanium carbide coated fiber composites have been successfully produced by liquid infiltration method. Patankar et al. [71] tried a different approach by pre-treatment of the carbon fiber with K_2ZrF_6 that improved fiber wetting and results in good matrix-fiber interfacial bonding in the carbon/aluminum composite. Kitahara et al. [72] reported that eleven metals, Cu, B, Zr, Si, Ta, Cr, Mo, Fe, Ni, Al, could improve the wetting and bonding ability between carbon fibers and aluminum as fiber coating materials. But all the metals except Cu react with carbon fibers and all metals form brittle intermetallic compounds with Al after heating at 600°C. Other possible coating include TiN, SiC, B_4C, CaO, MgO, Al_2O_3, etc.

There are some other fiber coating methods for the technology of liquid metal infiltration (LMI). Figure 3.3 is known as the sodium process. Sodium is one element that wets graphite at reasonably low temperatures, and this fact became the foundation of the sodium process [19]. However, this process encountered some problems with maintaining a consistent volume fraction and with infiltrating T-300 PAN-base fibers without degrading their properties. Interfacial studies showed that some of the sodium remained in the fibers of the composite and the presence of a thin interfacial layer

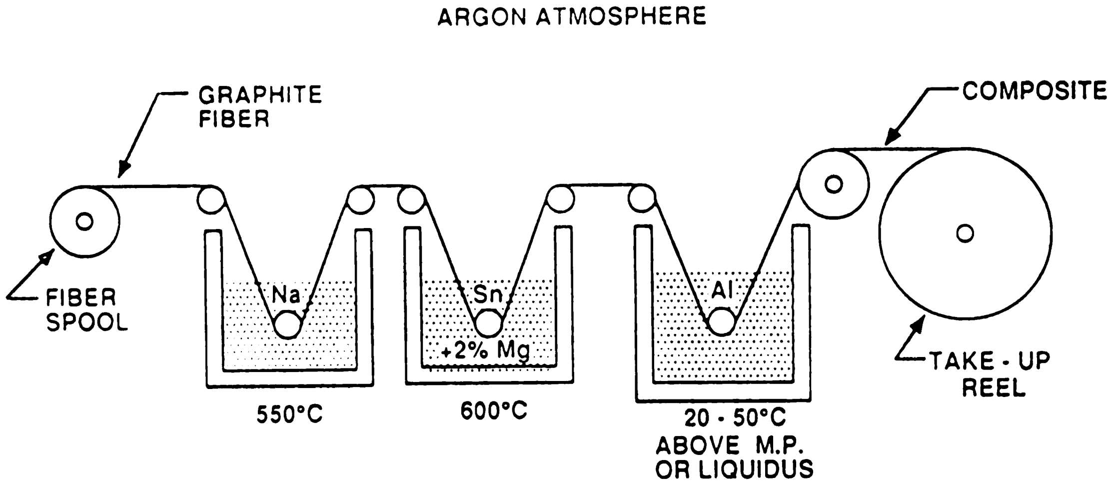

Figure 3.3 The sodium for infiltrating carbon fiber tows [19].

containing sodium, tin and magnesium. Figure 3.4 is a similar technique but the carbon fibers are coated by titanium boride instead of sodium. The titanium boride coating was formed from a chemical vapor deposition of $TiCl_4$ and BCl_3. Much of work on LMI of graphite fibers has used titanium boride as a barrier coating to liquid aluminum alloy because that the titanium boride barrier coating provided the most consistent results upon graphite fibers from a rayon precursor [73].

B. Matrix Alloying

It has well established that matrix composition has a large effect on the matrix-fiber reaction. The enrichment of alloying element at the interface changes the interfacial composition and affects the formation of the interfacial phase [74]. Addition of special elements to the metal matrix to reduce the aluminum carbide formation is often used in carbon-aluminum composites. Ti and Si are added to aluminum to reduce the activity of carbon in molten aluminum and slow the rate of the aluminum-carbon reaction. TEM examination of graphite fiber- reinforced Al-7%Si matrix shows Si segregation at the interface which inhibits carbon diffusion into aluminum. Cheryshova [60] reported that 58 mg of aluminum carbide was formed for 1 g of carbon fiber in pure aluminum and only 13.3 mg of aluminum carbide for 1 g of carbon fiber in Al-7%Si alloy. A SiC layer may form at the interface and as a diffusion barrier. Chen et al. [74] reported that an appropriate amount of magnesium (about 5 wt.%) added to the

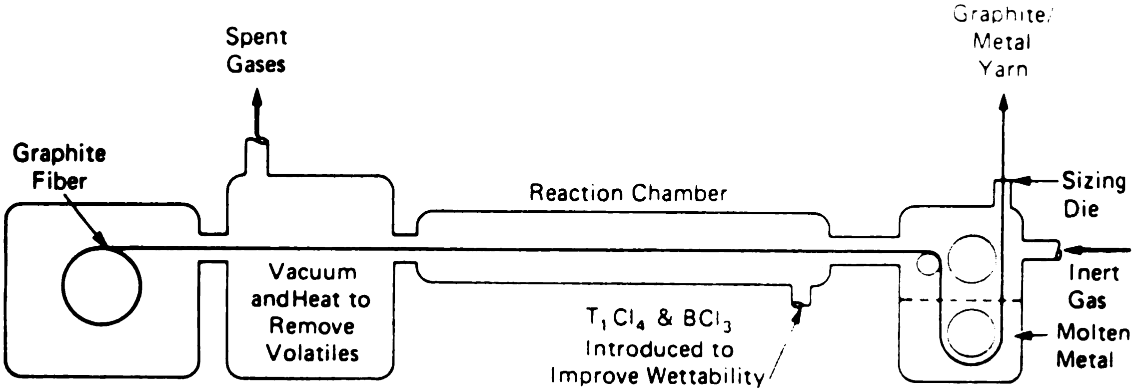

Figure 3.4 Schematic process of graphite fiber tow impregnated with metals [73].

aluminum matrix results in a remarkable strengthing effect on the tensile strength of carbon/aluminum composites. He et al. [75] showed that the graphite fiber reinforced composites with Al-Ti matrix had excellent tensile properties, even after heat-treatment at 600°C. Lithium, which is more known for promoting wetting in Al_2O_3 fiber-Al matrix composites, can also be used with carbon fibers. Li helps weaken the aluminum oxide layer and therefore promotes wetting at lower temperatures [76].

However, limited success has been achieved via fiber coating and matrix alloying. Although liquid infiltration technique is in expensive, it has many difficult problems such as poor wetting, interfacial reaction and uneven fiber distribution.

3.4 Processing Parameters and Mechanical Properties of Consolidated Carbon/Aluminum Composites

3.4.1 Processing Parameters

The mechanical properties achieved by any composite system are the direct result of the choice of consolidation method and parameters. For certain composite system and consolidation method, parameter optimization is primary. Hot-isostatic-pressing diagram technique, which was developed by Ashby [77], may be a useful method to select the optimal conditions. But at present this procedure has been carried out mainly in empirical fashion, known as one-variable-at-a-time approach.

Although processing parameters are the least reported items of information, some results have been reported in the open literature. The most commonly used process for the consolidation of carbon/aluminum precursor wire is vacuum hot pressing. Various temperatures have been used for this process. Generally, pressing at higher temperature may cause excessive reactions between aluminum and carbon fibers; pressing at lower temperature below solidus requires the use of higher pressure, which may cause fragmentation of fragile carbon fibers. Both cases degrade the strength of the composite. Pepper et al. [54] reported that pressing above the liquid temperature resulted in segregation of the fibers in the composite, a large amount of shrinkage porosity and in some cases degradation of the carbon fibers. Satisfactory composites have been obtained by partial liquid phase hot pressing [54, 78], in which the precursor wire is bonded under pressure at temperature above the solidus temperature in the two phase solid/liquid state in vacuum. However, it was also reported that satisfactory properties can be obtained in carbon/aluminum composites produced by solid state diffusion process in vacuum [27, 47, 79]. Masson et al. [79] reported that the best carbon/aluminum composite properties were found at processing parameters of 600°C for 30 minutes. Ohsaki et al. [27] studied the properties of carbon fiber reinforced aluminum composites formed by the ion-plating process and vacuum hot pressing. It was found that the optimal conditions were between 520 and 540°C with a pressure of more than 6 Kg/mm^2 for 1 hour. Figures 3.5 and 3.6 show the effect of the temperature and pressure respectively of hot pressing on the flexural strength of the composite. Other processes that have been used for the consolidation of carbon/aluminum precursor wire are the roll bonding and hot drawing.

3.4.2 Mechanical Properties

The mechanical properties of CFMMCs can be predicted by the rule of mixtures (ROM). The rule of mixtures is expressed as the contribution to the strength and modulus of the composite by the fibers and the matrix based on their relative volumes. This rule, as usually applied, assumes that there is no interaction effect between the components and is expressed as:

$$\sigma_c = V_f \sigma_f + (1 - V_f) \sigma_m \tag{3-2}$$

$$E_c = V_f E_f + (1 - V_f) E_m \tag{3-3}$$

Where σ_c = Strength of the composite

σ_f = Strength of the filament

σ_m = Strength of the matrix

V_f = Volume fraction of the filaments

E_c = Modulus of the composite

E_f = Modulus of the filament

E_m = Modulus of the matrix

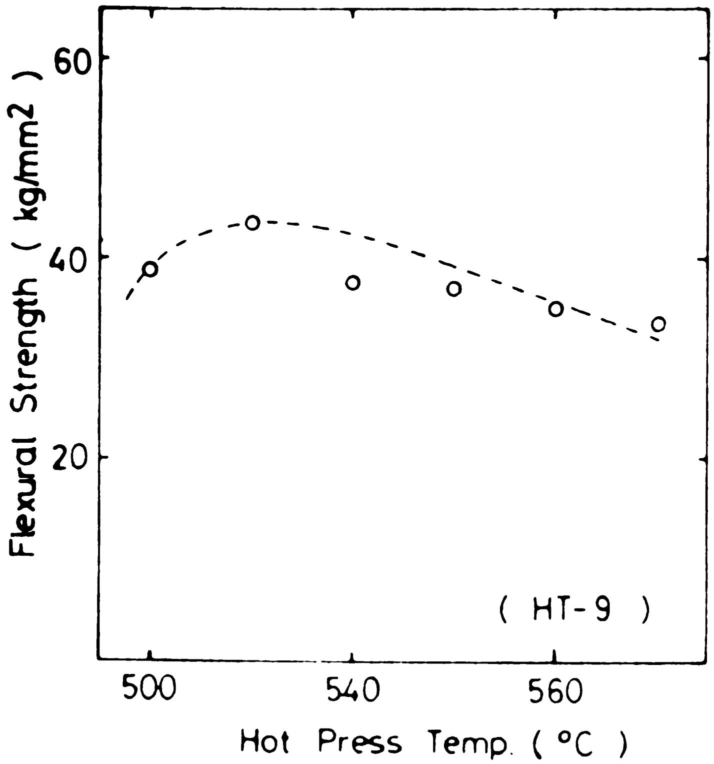

Figure 3.5 Effect of the pressure of hot pressing on the **flexural strength of the composite:** v_f =28; 9 kg/mm^2; 1 h [27].

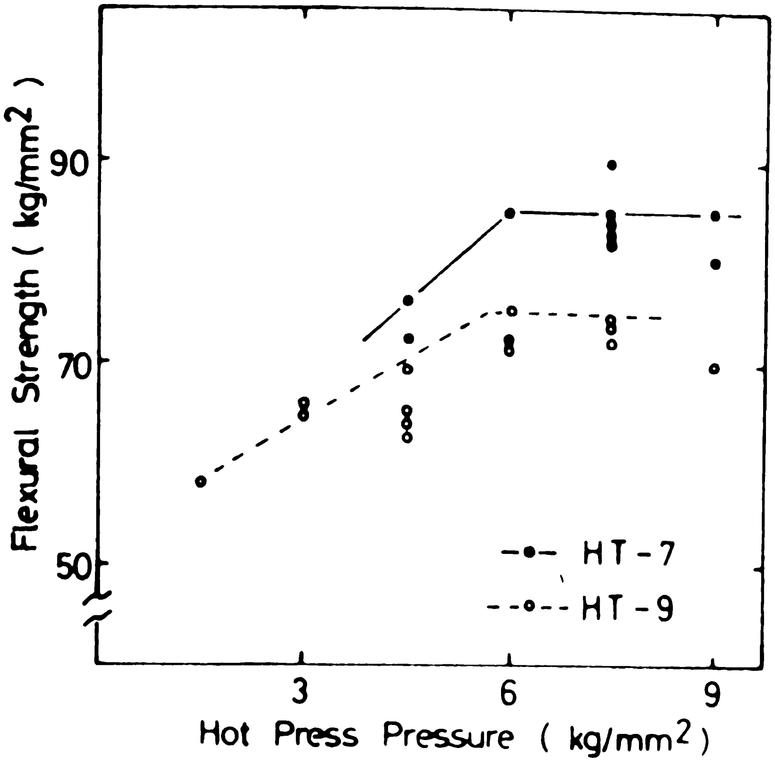

Figure 3.6 Effect of the pressure of hot pressing on the **flexural** strength of the composite: v_f =40; 540°C; 1 h [27].

Most of the tension test data on composites has been presented in light of this rule of mixtures, and the composites are rated in terms of the percentage of the rule of mixtures strength that they have achieved. A review of carbon/aluminum composites [1] summarized much of the consolidation parameters and the mechanical properties of the composites. In table 3.3, the tensile properties of the consolidated composites produced by hot pressing are listed along with the consolidation parameters. It can be seen that consolidation temperatures both in the solid state and in the two phase (solid/liquid) regions have been utilized. Maximum tensile strength of 1014 MPa was obtained in HM3000/201 composite (fibers coated with TiB_2), when the pressing was done at 568°C for 25 minutes at 24 MPa pressure. This corresponds to a value of 98% rule of mixtures strength.

Ohsaki et al.[27] reported the properties of carbon fiber reinforced aluminum composites formed by ion-plating process and vacuum hot pressing with 40 Kg/mm^2 (v_f:0.40) in tensile strength. Patanker et al.[71] fabricated carbon fiber reinforced Al-12% Si alloy composite by pre-treating the fibers with K_2ZrF_6 followed by molten alloy infiltration and subsequent hot pressing of the performs. The fiber volume per cent of was found to result in composite tensile strength of about 240 MPa. Asanuma et al.[80] produced carbon fiber reinforced aluminum composites by the plasma spray and roll diffusion bonding method. It was found that the tensile

Table 3.3 Consolidating parameters and the mechanical properties of the consolidated carbon/aluminum composites

Consolidation Parameters	Tensile Strength MPa	Fiber Content %	Al_4C_3 Content ppm	% ROM Strength	Reference (As listed in [1])
T50/356 (Ti-B)					
626°C, 2.76 MPa, 10 min.	296-407	37-57	800-3000	30-31	26
T50/A413 (Ti-B)					
598°C, 4.14 MPa, 10 min.	269-365				26
T50/6061 (Ti-B)					
575°C, 21 MPa, 40 min	434	27			30
615°C, 4.14 MPa, 10 min.	490-676	28-33	300-1000	63-77	26
615°C, 0.15 MPa, 5-10 min.	586	30	1145		35
615°C, 0.25 MPa, 5-10 min.	449	32	772		35
615°C	558	31	625		36
621°C, 20.7 MPa, 30 min.	379-517	26-32	250-500	52-61	26
626°C, 4.14 MPa, 10 min.	559-724	41-50	750-2500	53-59	26
630°C	560	45	1600		36
670°C, 3.4-6.9 MPa	631	42.5			34
675°C, 3.4-6.9 MPa	440	26.7			34
685°C, 33.4-6.9 MPa	517	30.0			34
690°C, 3.4-6.9 MPa	291	26.0			34
T50/201 (Ti-B)					
555°C, 21.0 MPa, 40 min.	531	27			30
560°C, 20.7 MPa, 30 min.	517-586	28-32	400-800	66-69	26
570°C, 24.0 MPa, 25 min.	743	32	1012	84	8
604°C, 4.14 MPa, 10 min.	552-690	29-34	340-700	68-77	26
T50/5056 (Ti-B)					
621°C, 20.7 MPa, 30 min.	331	22.3	1050-1450	50	26
T50/1100 (Ti-B)					
587°C, 20.7 MPa, 40 min.	276	35	4150	30	26
643°C, 13.8 MPa, 5 min.	303	42	2015	28.5	26
T50/5154 (Ti-B)					
598°C, 4.14 MPa, 10 min.	524	27	250	76	26
615°C, 4.14 MPa, 10 min.	524-600	37-40	600-750	55-58	26
T50/A13					
645°C, 3.4-6.9 MPa	396-676	36-46			34
650°C, 3.4-6.9 MPa	584	43.9			34
T50/220					
645°C, 3.4-6.9 MPa	573	26.6			34
650°C, 3.4-6.9 MPa	588-677	27-37			34
T300/201 (Ti-B)					
568°C, 24 MPa, 25 min.	212	36	3280	19	8
T Pitch/201 (Ti-B)					
568°C, 24 MPa, 25 min.	313	34	1568	61	8
HM 3000/201 (Ti-B)					
568°C, 24 MPa, 25 min.	1014	40	369	98	8
HM 3000/6061 (Ti-B)					
596°C, 24 MPa, 25 min.	692	34	203		8
HM 3000/1100 (Ti-B)					
607°C, 24 MPa, 30 min	621	30	176		8

strength of C/Al composite remarkably varied depending on the fabrication conditions of roll diffusion bonding, and it attained to 312 MPa (V_f:0.12) by selecting favorable conditions.

Chapter 4

New Fabrication Method

Fabricating composites from tow-based fibers has always presented difficulties to material producers. If the fiber was wetted by the matrix material, liquid-infiltration technique could be the first choice because of it's simplicity and continuity. If the fiber was not wetted by the matrix material, a suitable fiber coating or matrix alloying addition had to be found first. In either case, interfacial reaction was hard to control due to overexposure to molten metal. Besides, uneven fiber distribution is a unsolved problem. Other methods, such as electroplating, spraying, chemical vapor deposition and physical vapor deposition, could be able to get high quality composites, but they are time consuming and expensive. Furthermore, these techniques are not suitable for commercial large-scale production because that they are not a continuous process. Therefore, a new fabrication method will be described in this chapter.

4.1 The Original Process

The new fabrication method of CFMMC is the modification of the continuous fiber-reinforced polymer matrix composite technique, which was originally developed by the Composite

Materials and Structures Center at Michigan State University [81,82].

In the original process, a unsized carbon fiber tow goes through different chambers to make a prepreg tape of a polymer matrix composite. This process is shown in Figures 4.1 and 4.2. A fiber tow is driven by a D.C. motor from a fiber spool to pass above a speaker (Figure 4.3). The sound waves coming off the speaker spread the fibers apart. The spread fibers are held in position by ten stainless steel shafts spaced one inch apart and placed on the top of the speaker. Figures 4.4 and 4.5 show the spreader and the spreading operation. After spreading, the fibers pass through an optional pre-treatment chamber to modify the fiber surface or to apply a thin coating of binder material to improve adhesion with the matrix. Then, the fibers enter an impregnation chamber, called aerosolizer (Figure 4.6), where small polyamide particles (about 10 microns in diameter) are suspended by the effect of a vibrating rubber membrane placed on top of a speaker, which works as a bed of polymer powders. The powders are attached to the fibers by electrostatic force generated from the static charges held by the fine polymer particles. After coating with polymer particles, the fibers pass the oven chamber for about 15 seconds. The particles are heated by convection and radiation until sintering occurs between adjacent particles to form a thin film (Figure 4.7). The impregnated fibers are then wound on a take up drum. Sequences of the same events make up

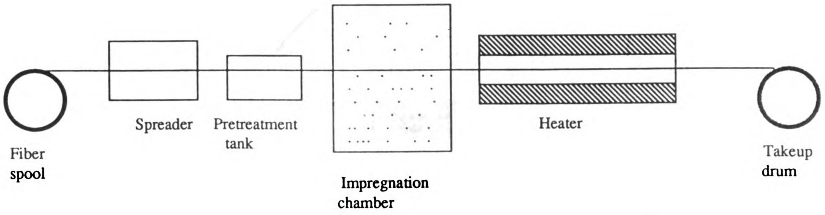

Figure 4.1 Design of powder prepregging process [82].

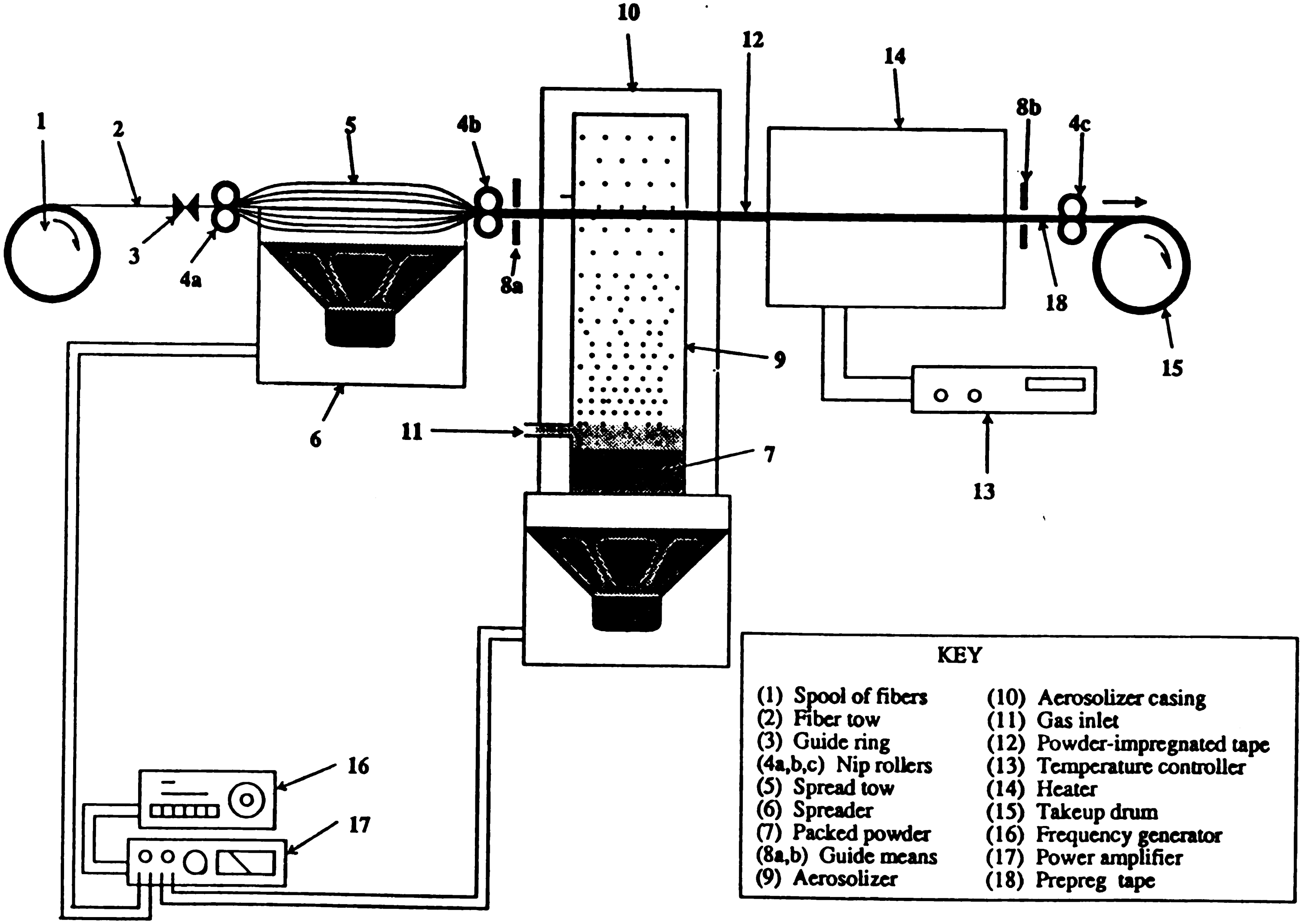

Figure 4.2 Schematic of powder prepregging process [82].

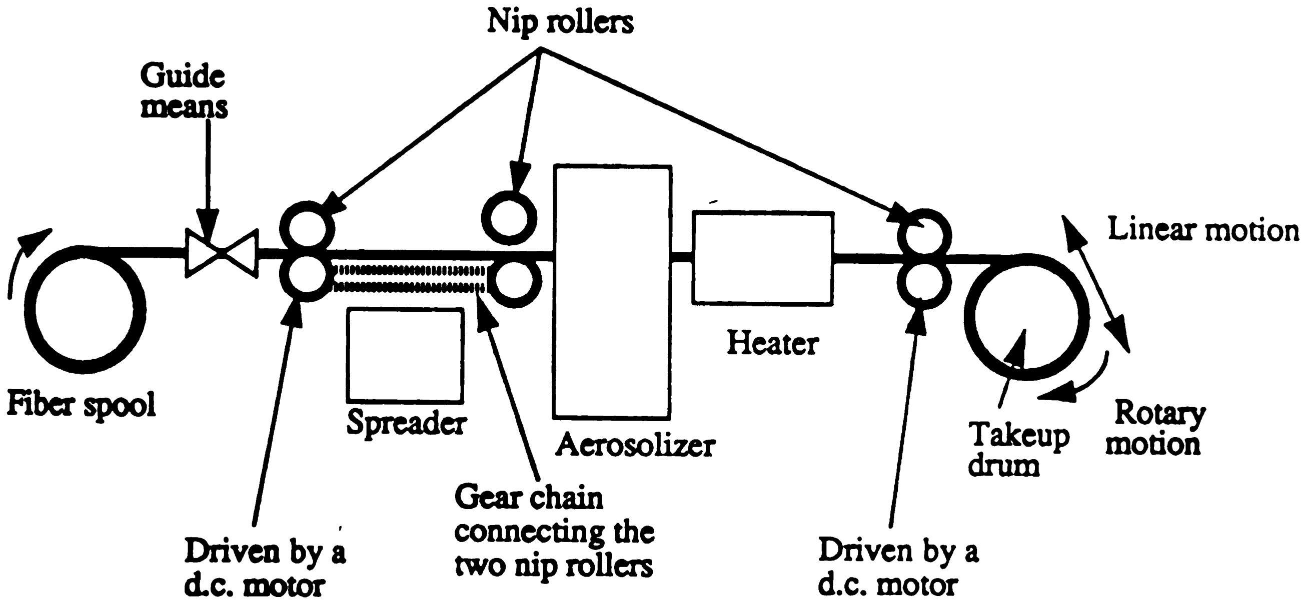

Figure 4.3 Fiber motion in the powder prepregging process [82].

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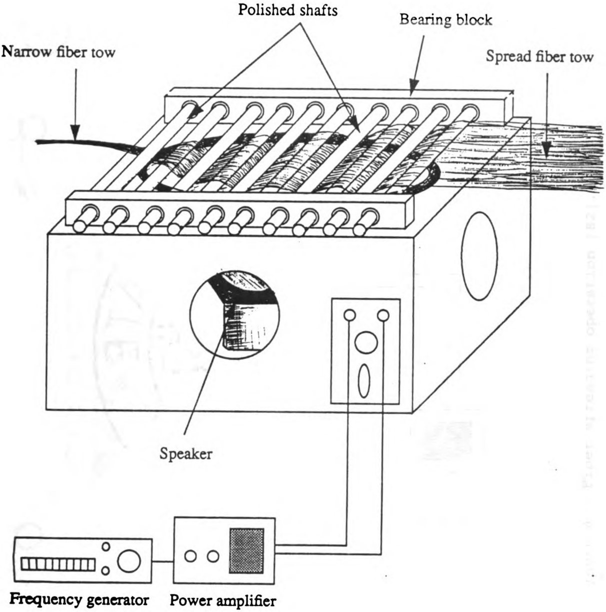


Figure 4.4 Spreader [82].

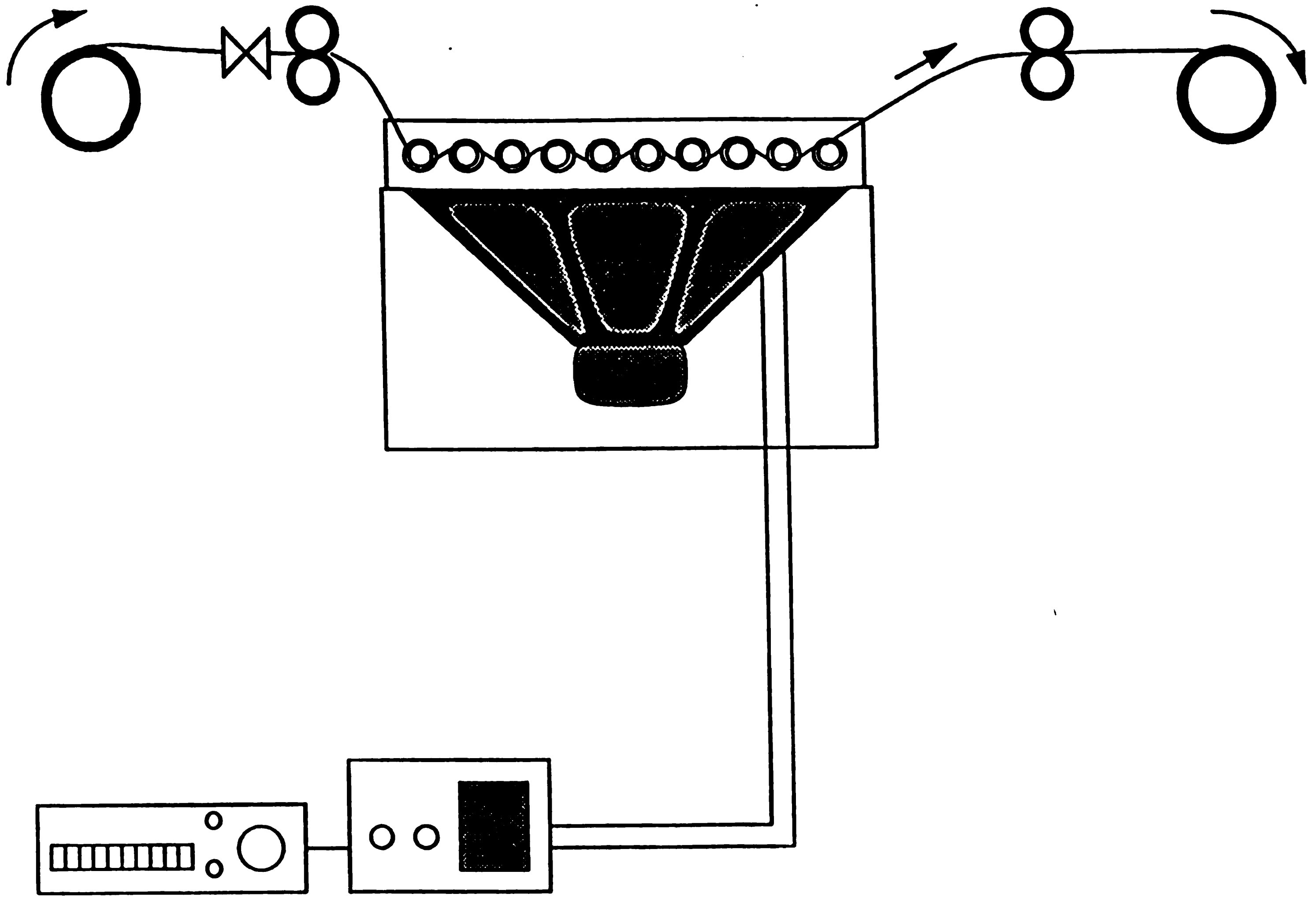


Figure 4.5 Fiber spreading operation [82].

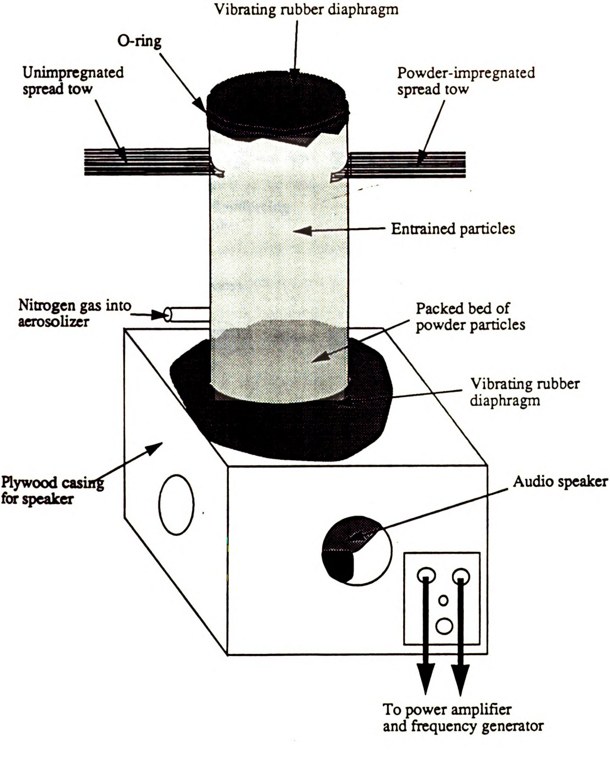


Figure 4.6 Aerosolizer [82].

Figure

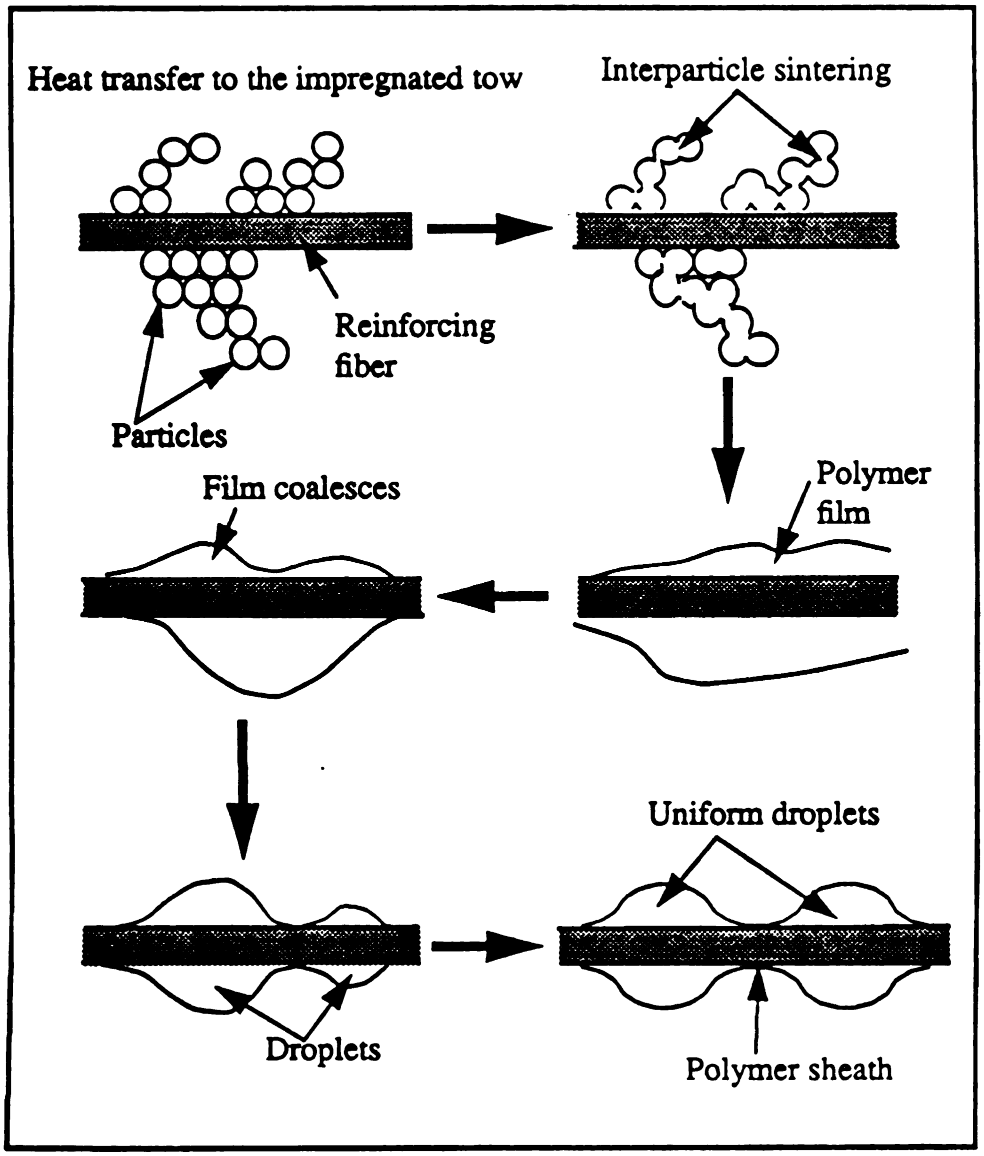


Figure 4.7 Coalescence in the heater [82].

a single run of this continuous process. After one run, the resulting prepreg tape is cut into pieces to a desired length and are laid-up in a rectangular stainless steel mold for hot pressing according to a pressure-temperature-time profile. A sheet of continuous fiber-reinforced polymer matrix composite material is thus formed and can be evaluated.

4.2 The Modification of The Original Process

In order to manufacture CFMMC, the original process needs to be modified by adding a new coating chamber with fine metal powders. The modified process will appear as shown in Figure 4.8. In this new process, the fibers coated with sticky polymer, which will serve as the binder between fibers and fine metal powders, leave the oven chamber and enter the new chamber where they will be coated with fine metal powders (matrix material). This coated prepreg will be called the precursor of the CFMMC. The precursor is then cut into pieces and laid up for hot pressing.

4.3 Advantages of The Proposed Process

The proposed process has many of advantages comparing with the existing CFMMC fabrication techniques:

1) It minimizes undesired interface reactions because the precursor is produced at much lower temperature.

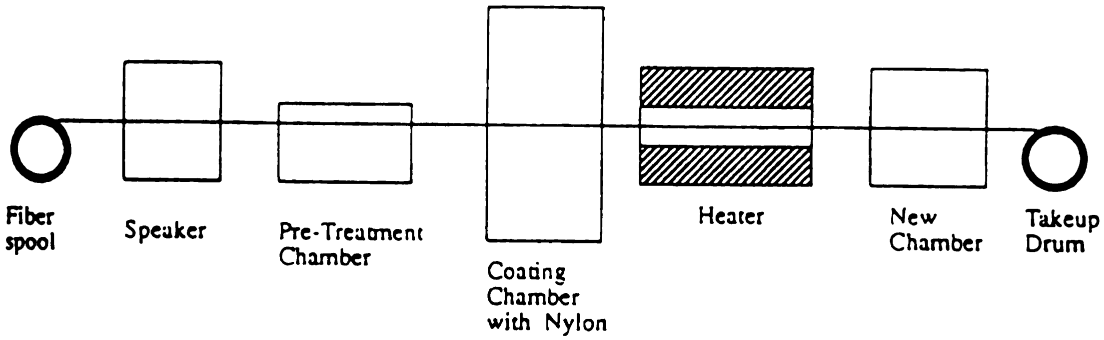


Figure 4.8 Design of the modified process.

2) Fibers are evenly distributed throughout the composite by spreading operation. This reduces fiber damage usually caused by fiber-to-fiber contact.

3) Uniform distribution of the matrix around each fiber is achieved from the use of the aerosolizer and fine metal powder with smaller size (5.5 microns in diameter) than the diameter of the fibers (8.0 microns).

4) High fiber volume fraction can be obtained due to the effective use of the spreader and fine metal powders.

5) High quality composites can be made using the new process because of homogeneous fibers and matrix distribution, high fiber volume fraction, reduced interface reactions.

6) The new method is far less expensive than most of the existing CFMMC fabrication techniques because of its simplicity, continuity and automation.

Chapter 5

Experimental Procedures

5.1 Experimental Chamber System

The new experimental chamber is made of plexi-glas material because the fluidization of the powders requires visual adjustments to determine the appropriate frequency of the speaker. The chamber has similar dimensions to those of the original aerosolizer, so it can be added to the whole system once good results are obtained. However, before adding the new chamber to the original system, it must be shown that the fibers can be coated well with fine metal powders in the new chamber. Therefore, as the first step, at present the precursor will be produced in an independent experimental chamber outside the whole system.

The new chamber is made of a closed plexiglas tube containing a speaker, a speaker wood box, a glass tube, a heating system and an aluminum flange which connects the speaker, lower membrane and the glass tube. Figure 5.1 gives an overall view of the chamber.

The outside tube has two lids made of aluminum for the top

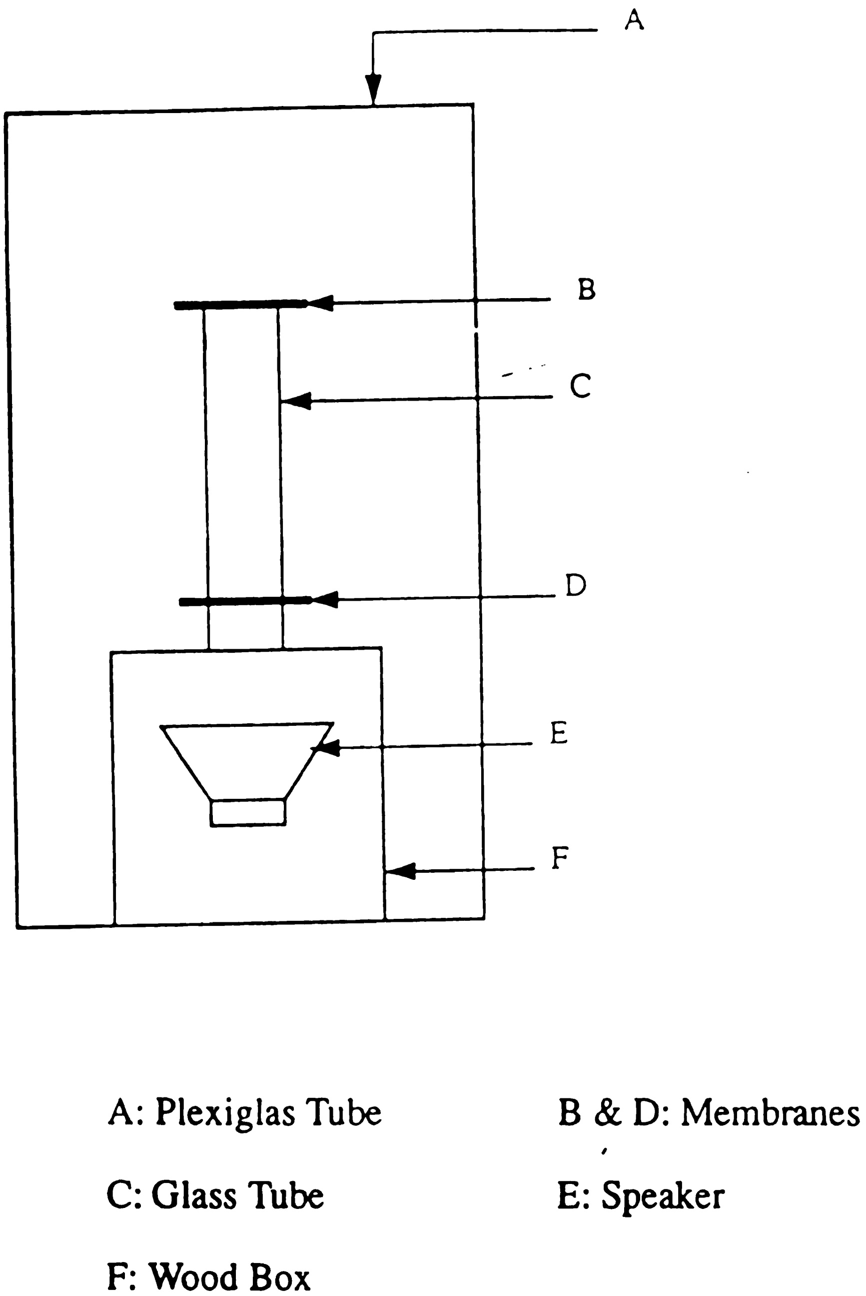
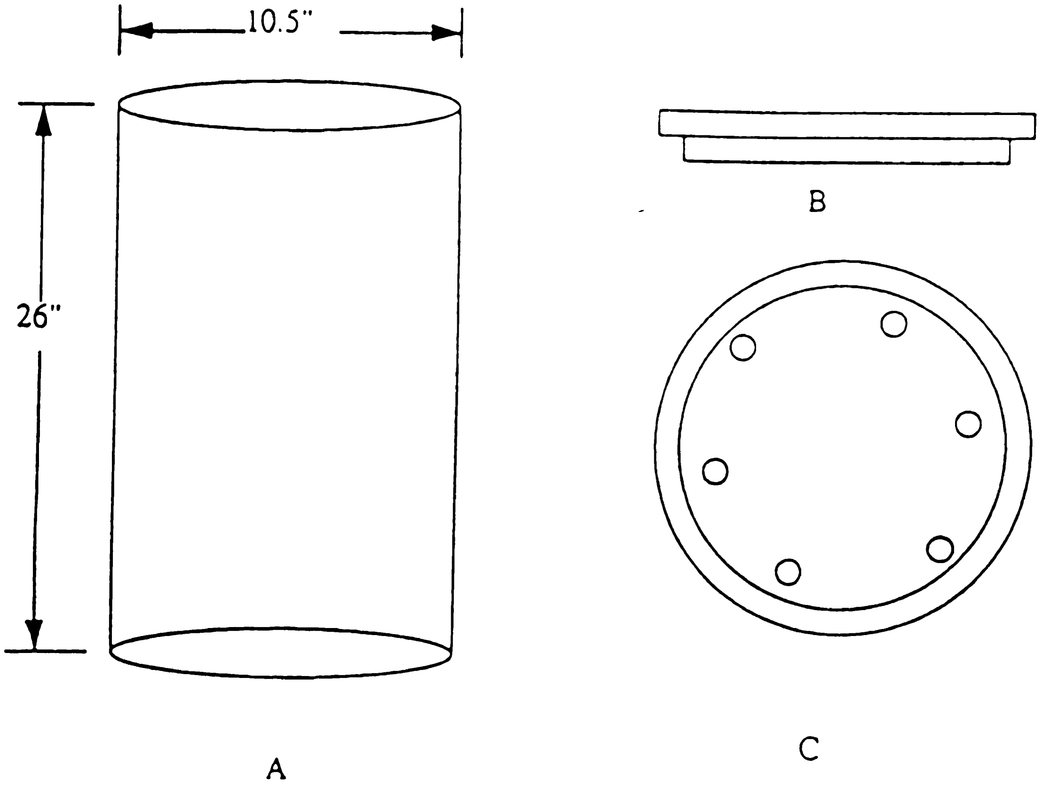


Figure 5.1 The experimental chamber [4].

and the bottom (Figure 5.2). The lids have an o-ring around the inside to assure sealing for vacuum purpose. The calculations show that the plexiglas tube and the aluminum lids are strong enough to withstand an external pressure of atmosphere [4]. During experiment, the two lids are held onto the chamber by three stretch cords for safety.

The inside tube is a hollow glass tube where the actual coating occurs (Figure 5.3). Half an inch from the top, a small indentation in the outside is for an o-ring to hold the top membrane. At three inch from the top, six tungsten pins are mounted around the circumference to serve as electrical feedthroughs for the heating system. Two gas ports on the glass tube open to the outside tube through air filters. The inside tube is set on the aluminum flange which is fixed by the woodbox above the speaker. There is a membrane between the glass tube and the aluminum flange, which serves as the fluidization bed.

The heating system, which is a flexible heater wound around a metal tube, is hung on two of the tungsten pins in the inside glass tube. The prepreg tapes are fixed by spring clips inside the tin tube where the temperature is almost uniform. Figure 5.4 shows the location of the heating system and the prepreg tapes. Tables 5.1 and 5.2 gives the distribution of the temperature inside the metal tube. Electrical feedthroughs are needed to pass a signal from the



A: Plexiglas tube.

B: Design of the top and bottom lid.

C: Bottom view of the top lid.

Figure 5.2 Outside tube [4].

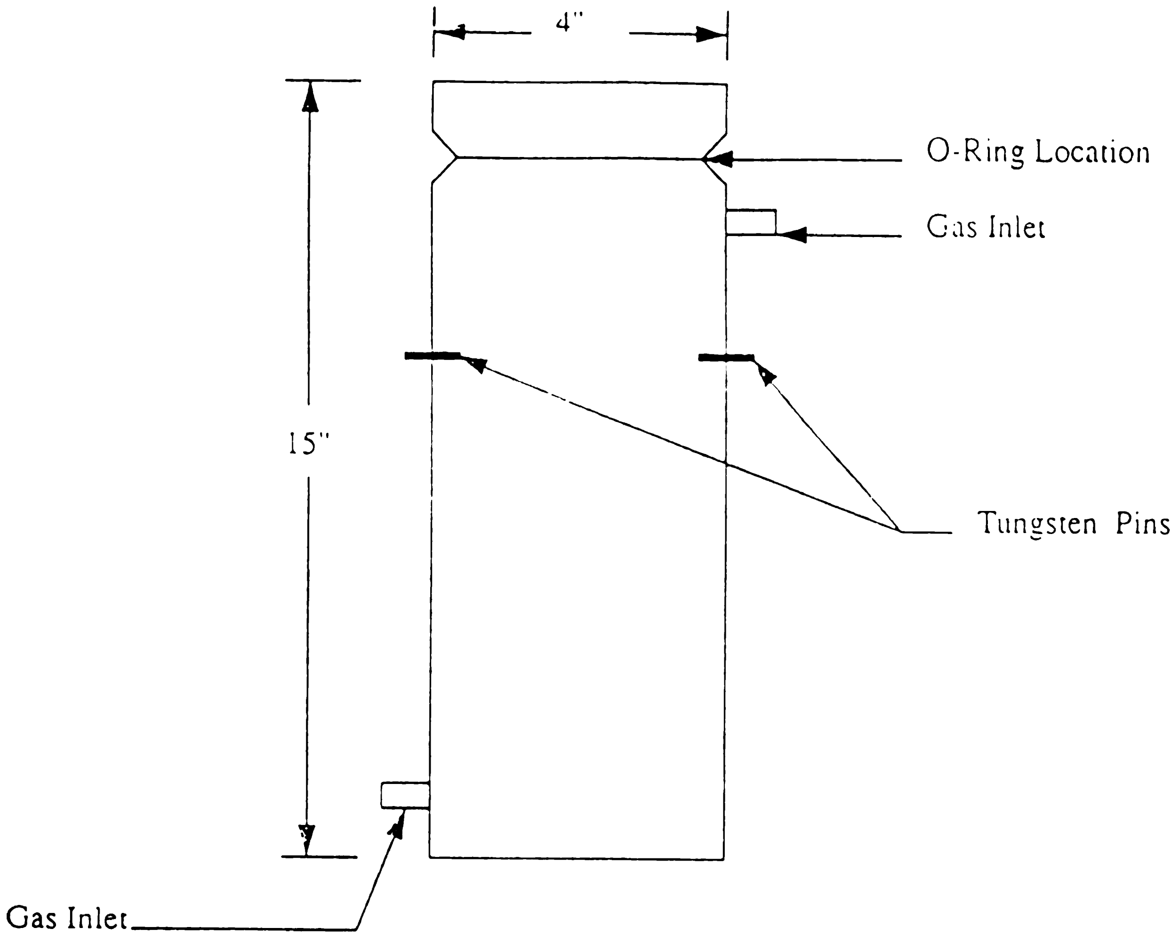


Figure 5.3 Inside tube [4].

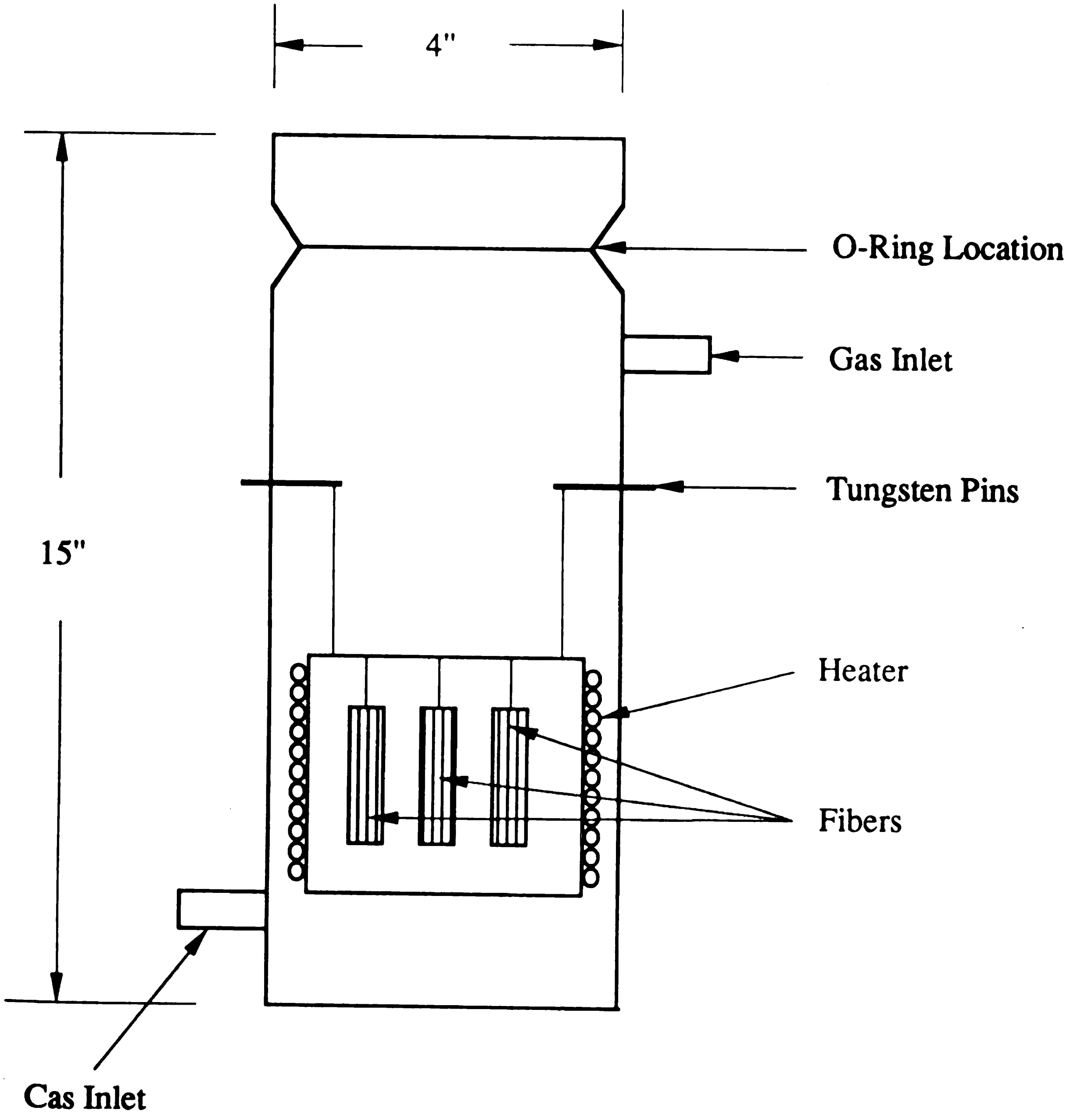


Figure 5.4 Heater inside glass tube.

Table 5.1 The distribution of the temperature inside the metal **tube.**

Time (min.)	Temperature at Bottom (°C)	Temperature at middle (°C)	Temperature at top (°C)
5	165	156	167
6	177	168	176
7	181	178	186
8	189	186	192
9	197	192	197
10	198	198	201

Table 5.2 The temperature as a function of heating time

Time (min.)	Temperature at middle (°C)
0	27
1	78
2	120
3	140
4	156
5	160
6	172
7	183
8	187
9	191
10	197

outside to the inside of the chamber without interfering with the vacuum level. The feedthroughs are made of bulk head unions that fit the holes of the top lid. O-rings are used for a complete sealing.

The speaker is mounted inside a wood box which has a circular opening on top to allow the upward propagation of the sound waves. The wood box is painted with epoxy glue to avoid the release of volatile that could interfere with the vacuum level. The speaker box is connected to the inside tube through an aluminum flange whose circular base covers the opening of the wood box. The aluminum lip also has an outside indentation for an o-ring to hold the bottom rubber membrane where the inside tube is fitted. The speaker is controlled by a frequency generator and a power amplifier located near the experimental chamber.

The vacuum system is best understood by referring to Figure 5.5. The vacuum pump is connected to the chamber by thick wall flexible vacuum hoses. Ball valves are used to control the gas flow in and out of the experimental chamber. Vacuum feedthroughs are made in a similar way to the electric feedthroughs.

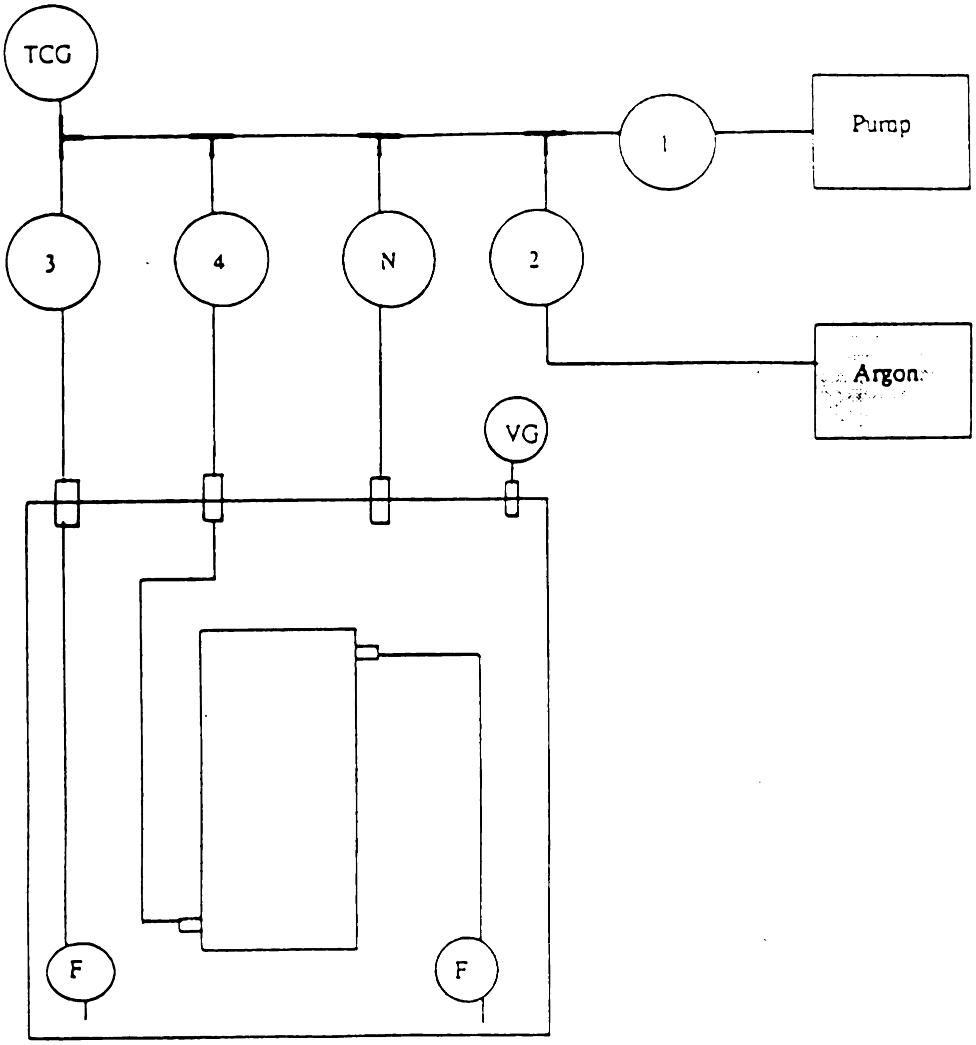


Figure 5.5 Vacuum system [4].

5.2 Safety Concerns

5.2.1 Risk Factor: Explosions

Safe handling of aluminum powder is necessary because of the potential risk of an explosion. Aluminum reacts instantaneously with oxygen to form a thin film of aluminum oxide on the surface of the aluminum when exposed to the atmosphere. The oxide layer is stable in air and prevents further oxidation of underlying aluminum. However, if fine aluminum powder, usually less than 44 microns (325 mesh), are suspended in air and are heated by one source of ignition to reach the ignition point, then the burning extends from one particle to another with such rapidity (rate of pressure rise in excess of 20,000 PSi/Sec) that a violent explosion results [83]. It has reported that the proportion of aluminum powder required for an explosion is very little (45 g/m^3). Aluminum dust will ignite with as little as 9% oxygen present (the balance being nitrogen; or 10% oxygen with the balance helium; or 3% oxygen with the remainder carbon dioxide) [83]. Very small amount of energy are required to ignite certain mixtures of aluminum powder and air. In some case energy as low as 25 millijoules may cause ignition.

5.2.2 Safety Precautions

Some basic safety principles of handling aluminum powder which are recommended by the Aluminum Association [83] will be reviewed in this section.

Rule 1: Avoid any condition that will suspend or float powder particles in the air creating a dust cloud. The less dust suspended in the air, the better.

1) Keep all containers closed and sealed. When a drum of aluminum powder is opened for loading or inspection, it should be closed and resealed as quickly as possible.

2) in transferring aluminum powder, dust clouds should be kept at an absolute minimum. Powder should be transferred from one container to another using a non-sparking, conductive metal scoop with as little agitation as possible. Handling should be slow and deliberate to hold dusting to a minimum. Both containers should be bonded together and provided with a grounding strap.

3) In mixing aluminum powder with other dry ingredients, frictional heat should be avoided. The best type of mixer for a dry mixing operation is one that contains no moving parting, but rather affects a tumbling action such as a conical blender. Introduction of an inert atmosphere in the blender is

highly recommended since dust clouds are generated. All equipment must be well-grounded.

Rule 2: When possible, avoid actions that generate static electricity, create a spark or otherwise result in reaching the ignition energy or temperature.

1) Locate electric motors and as much electrical equipment as possible outside processing rooms. Only lighting and control circuits should be in operating rooms. All electrical equipment must meet National Electrical Codes for hazardous in installations. This includes flash lights, hazardous portable power tools, and other devices.

2) Use only conductive material for handling or containing aluminum powders.

3) No smoking, open flames, fire, or sparks should be allowed at operation and storage areas or dusty areas.

4) No matches, lighters, or any spark-producing equipment can be carried by an employee.

5) During transfer, powder should not be poured or slid on non-conductive surfaces. Such actions build up static electricity.

6) Powder should always be handled gently and never allowed to fall any distance because all movement of powder over powder tends to build up static charges.

7) Work clothing should be made of smooth, hard-finished, closely woven fire resistant/fire retardant fabrics which tend not to accumulate static electric charges. Trousers should have no cuffs where dust might accumulate.

8) Bonding and grounding machinery to remove static electricity produced in powder operations are vital for safety.

9) All movable equipment, such as drums, containers, and scoops, must be bonded and grounded during powder transfer by use of clips and flexible ground leads.

Rule 3: Consider the use of an inert gas which can be valuable in minimizing the hazard of handling powder in air.

However, in the three general rules, rule 3 is the most important safety precaution method for the process of aluminum powder coating on fibers, which is the key step in the new fabrication technique of CFMMC, because the coating operation will be performed in aluminum cloud at 170°C. By pumping vacuum and introducing argon repeatedly, oxygen can be reduced to the safe volume fraction.

The amount of oxygen left inside the chamber can be determined by the ideal gas law:

$$PV = nRT \tag{5-1}$$

First, assume that after pulling a vacuum on the chamber of volume V at temperature T to decrease the pressure from one atmosphere to a pressure P_o, only n_o moles of O_2 and $4n_o$ of N_2 are left in the chamber. Applying the equation (5-1) gives:

$$5n_o = P_o(V/RT) \tag{5-2}$$

Second, assume that n_1 moles of Ar are introduced to the chamber to go back to atmospheric pressure. The total number of gas moles n is given by $n = 5n_o + n_1$. Applying the equation (5-1) again to get:

$$5n_o + n_1 = (1\ \text{atm})(V/RT) \tag{5-3}$$

Combining equation (5-2) and (5-3), and rearranging it gives the Ar/O_2 ratio as:

$$n_1/n_o = 5[(1/P_o) - 1] \tag{5-4}$$

Table 5.3 gives the Ar/O_2 ratio and oxygen volume percentage for different vacuum levels.

As a conclusion, the oxygen amount present can be controlled by the vacuum level reached in the chamber before introducing argon and to prevent the explosion of aluminum powder. On the positive side, argon adsorption to surface of aluminum powder is beneficial for a limited time following re-entry to air [4].

In addition, health protection must be concerned for

Table 5.3 Oxygen volume percentage as a function of different vacuum levels

Vacuum level (torr)	Ar/O_2 ratio	Number of O_2 moles	Oxygen volume percentage
76.3*	49	28.02×10^{-3}	2.0%
36.5	99	14.55×10^{-3}	0.96%
24.0	150	9.76×10^{-3}	0.65%
11.5	328	4.54×10^{-3}	0.30%
0.76	4995	0.30×10^{-3}	0.02%

* If pump twice to reach the vacuum level 76.3 torr again,

then:

Ar/O_2 ratio: 499

Number of O_2 moles: 3.03×10^{-3}

Oxygen volume percentage: 0.20%

handling aluminum powder. Goggles and mask are strongly recommended to be used.

5.3 Materials

The matrix material used in this experiment is pure aluminum metallic powder (atomized) manufactured by Valimet Inc. The powder has spherical shape with average 5.5 microns in diameter. The reinforced fiber is a continuous high-strength, PAN-based carbon fiber manufactured by Hercules Inc. The filament has a size of 8 microns in diameter with round shape. There are 3000 filaments per tow which has 3587 MPa in terms of tensile strength. However, the reinforced components used directly were prepreg tapes of nylon-coated carbon fibers produced by the powder prepregging system at the Composite Materials and Structures Center (CMSC), rather than the original tow fibers. Type A prepreg is the regular product of CMSC for the production polymer matrix composite, which was processed at 170°C. Type B prepreg is the special product for the production of C/Al composite using the new fabrication method investigated in this thesis, which is processed at 165°C. More information about the properties of each material is shown in Table 5.4.

Table 5.4 Properties of materials used in the experiment

Material/Property	Value
Hercules as-4 Carbon Fibers	
Diameter (microns)	8.0
Specific gravity (g/cm^3)	1.80
Tensile strength (MPa)	3,587
Tensile modulus (GPa)	235
Polyamide	
Average particle size (um)	10.0
Specific gravity (g/cm^3)	1.02
Melting point (°C)	175
Surface tension (mJ/m^2)	30.0
Aluminum Powders	
Average particle size (um)	5.5
Density (g/cm^3)	2.69
Apparent density (g/cm^3)	0.6
Chemical composition:	
Aluminum	99.7%
Iron	0.18%
Silicon	0.2%
Type A Prepregs	
Processing temperature (°C)	170
Type B Prepregs	
Processing temperature (°C)	165

5.4 Production of precursors

The procedures involved in production of precursors will be given in detail in this section.

1) Cut polymer prepreg tapes into 5 cm pieces.

2) Fix the prepreg tapes inside the heating tube with spring clips.

3) Hang the heating tube on the pins inside the glass tube.

4) Deposit 3-5 g aluminum powder on the bottom membrane.

5) Fit the glass tube on the top of the aluminum lip.

6) Place the top membrane in position with the help of the O-ring.

7) Connect all the electric wires and vacuum hoses properly.

8) Put aluminum lid on the outside tube.

9) Pump vacuum until the pressure inside the chamber is reduced to below 3 in Hg.

10) Introduce argon slowly to one atmosphere.

11) Redo 9 and 10.

12) Turn on the heater, heat 6 for minutes for type A prepreg and 3 minutes for type B prepreg.

13) Turn on the frequency generator and the power amplifier to fluidize the aluminum powder for 3 minutes for type A prepreg and 4 minutes for type B prepreg.

14) Turn off the heater after heating 8 minutes.

15) Extract the precursors in reversed order of 1-8 after the powder settled down and the temperature cooled down.

5.5 Consolidation by Vacuum Hot Pressing

The aluminum-coated carbon fiber precursors then were consolidated by vacuum hot pressing using a MTS-810 Material Test System. The procedures and processing parameters used were:

1) Align dozens of precursor layers in mats.

2) Cut the aligned precursors into 2 cm long and 1 cm wide.

3) Wrap the aligned and trimmed precursors with two pieces of aluminum foils in transverse direction.

4) Put a layer of boron nitride paster evenly on the outside of the aluminum foils.

5) Place the wrapped and pasted precursors between two pieces of thin alumina plates.

6) Place the sample in the fixture.

7) Put the fixture on the bottom platen inside the pressing furnace.

8) Press the top platen on the sample with pressure of a little more than zero.

9) Close the furnace and pump vacuum to less than 2×10^{-5} Torr.

10) Ramp the temperature to 420°C in 15 minutes.

11) Keep the temperature at 420°C for one hour to evaporate the binder material, nylon.

12) Increase the temperature to 570°C in 5 minutes.

13) Keep the temperature at 570°C for 5 minutes.

14) Press the sample under 30 MPa at 570°C for 30 minutes.

15) Release the pressure and decrease the temperature to 400°C in 5 minutes.

16) Cool the sample naturally to room temperature.

17) Extract the sample after the furnace cooled.

5.6 Mechanical Test and Microscopy Examination

The mechanical properties of the composite were measured using United Testing System SFM-20. A three-point bending test was performed. The original composite is approximately a 1 mm thick x 12 mm wide x 21 mm long plate for sample A which was made from type A prepreg, and a 2 mm thick x 12 mm wide x 21 mm long plate for sample B which was made from type B prepreg. The plates were cut into 1.65 mm wide specimens by a low speed diamond saw after the composite plate was trimmed to eliminate unconsolidated materials at the edges, and cleaned to remove the stop-off materials. The flexural strength and modulus of the composite was evaluated by following equations (refer to Figure 5.6):

$$S_{Fc} = 3PL / 2bd^3 \qquad (5\text{-}5)$$

$$E_{Fc} = Pl^3 / 4\delta bd^3 \qquad (5\text{-}6)$$

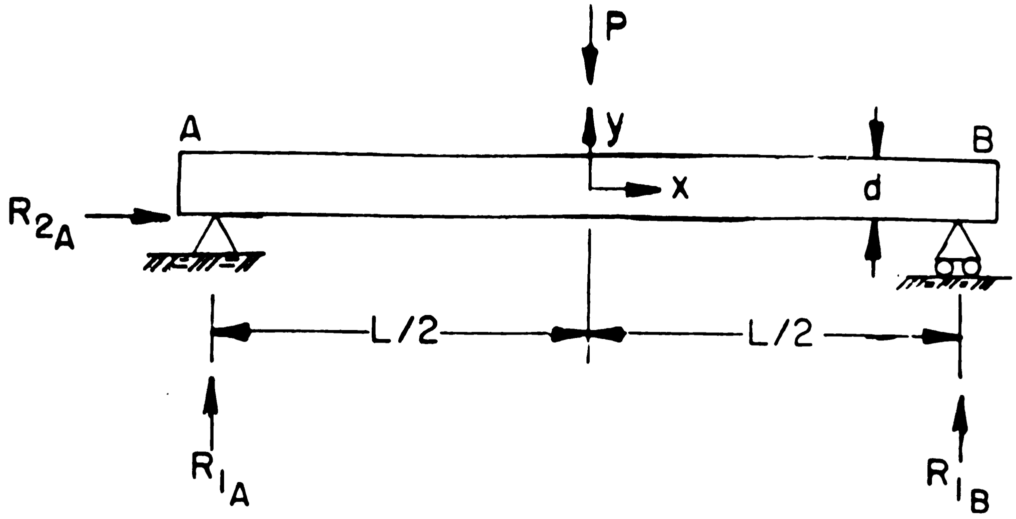


Figure 5.6 Simple beam subjected to three-point bending.

Where S_{Fc} = the flexural strength of the composite

P = the loading

L = the span

b = width of the specimen

d = thickness of the specimen

E_{Fc} = the flexural modulus of the composite

δ = deflection increment at midspan

The flexural strength of the composite from the three point bending test can be compared with the theoretical value calculated from equations (3-3) and (5-7) [84] which is derived from the rule of mixtures and the contribution of the matrix is neglected.

$$S_{Fc} = 3V_f S_{Tf} / (1 + S_{Tf} / S_{Cf}) \qquad (5\text{-}7)$$

Where S_{Fc} = the flexural strength of the composite

S_{Tf} = the tensile strength of the fiber

S_{Cf} = the compression strength of the fiber

V_f = the fiber volume fraction

If S_{Cf} is not known, $S_{Cf} = 0.9\ S_{Tf}$ is a good approximation for graphite fiber/matrix composites.

The broken specimens from the mechanical test then were mounted, polished and examining by Olympus PME 3 Metallograph. The fracture surfaces of the specimens were examined using Hitachi S-2500C scanning Electron Microscope (SEM).

The fiber volume fraction was determined by counting the fibers observed on a composite cross section and using the relation:

$$V_f = (N \times A_f)/A_t \tag{5-8}$$

Where V_f = the fiber volume fraction

N = the number of fibers

A_f = the average cross sectional area of a single fiber

A_t = the total cross sectional area

This work was done by Optical Numeric Volume Fraction Analysis Software.

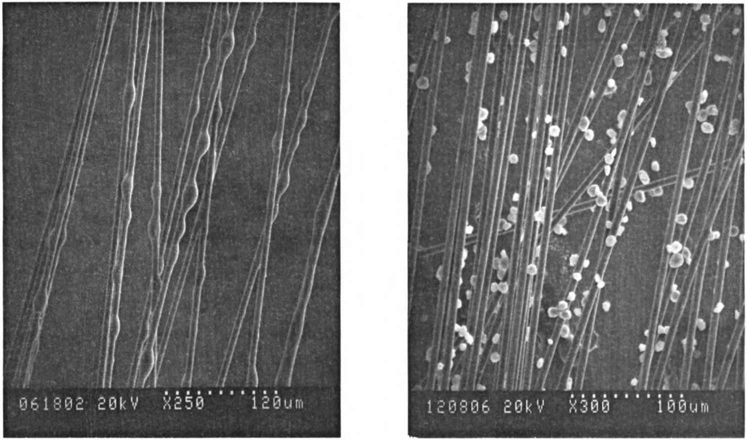
Chapter 6

Results

6.1 Prepreg Tapes and Composite Precursors

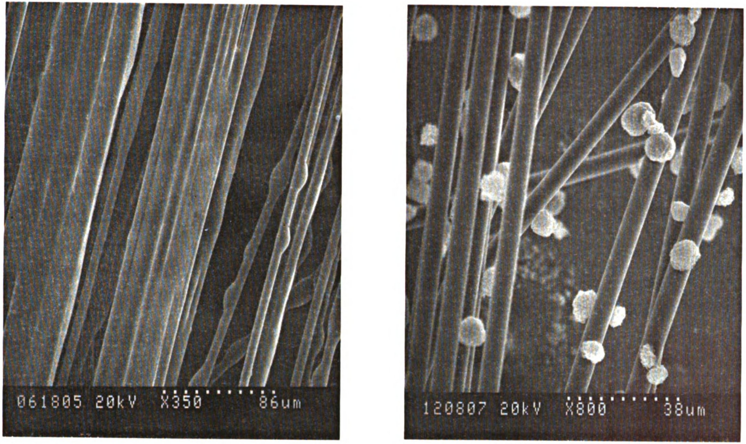
Figures 6.1 and 6.2 show scanning electron microscope (SEM) images of type A prepreg and type B prepreg at different magnifications. The prepregs, which were produced by the Composite Materials and Structures Center at Michigan State University, were used to make the precursors of aluminum matrix composites. For type A prepreg, It is apparent from these micrographs that there is satisfactory coating with nylon on the carbon fibers in the prepreg although there are some droplets formed on the fibers. The fibers were almost spreaded uniformly while some fibers contacted together and some fibers crossed. For type B prepreg, the nylon particles just begin sintering or even the sintering has not occurred. So some nylon particles were lost during handling and the fibers were not held together by nylon to form tape.

Figures 6.3 and 6.4 show two types of SEM images of C/Al composite precursors at different magnifications. The precursor has a satisfactory aluminum powder pick-up. The successes include: 1) the amount of aluminum powder is large enough; 2) the adhesion between the fiber and the powder is



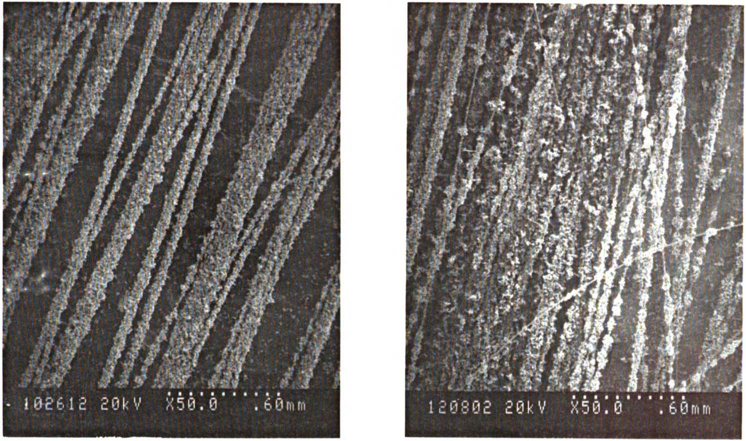
(a) (b)

Figure 6.1 SEM micrograph of type A prepreg (250x)(a) and type B prepreg (300x) (b).



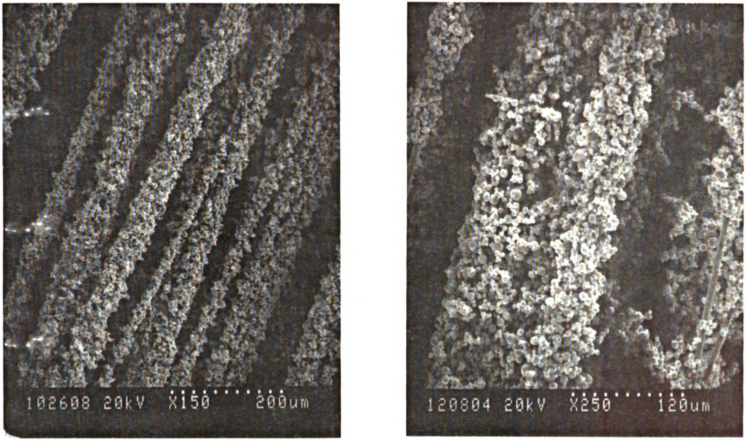
(a) (b)

Figure 6.2 SEM micrograph of type A prepreg (350x) (a) and type B prepreg (800x) (b).



(a) (b)

Figure 6.3 SEM image of type A precursor (50x) (a) and Type B precursor (50x) (b).



(a) (b)

Figure 6.4 SEM image of type A precursor (150x) (a) and type B precursor (250x) (b).

strong enough to survive handling; 3) the distribution of the aluminum powder is uniform for type A precursors. For type B precursors, fiber coating is uneven because of the existence of some uncoated fibers. The disadvantage is that the fiber contacting and crossing can still be found, which is due to the fabrication of nylon coated fiber prepregs.

6.2 Mechanical Properties of The Composite

The results of the mechanical test for the continuous high strength carbon fiber reinforced aluminum matrix composite materials are shown in Table 6.1 and Figures 6.5 and 6.6. The flexural strength of the composite is 335 MPa for sample A (343 MPa for sample A1 and 328 MPa sample A2) and 285 MPa for sample B as compared to 82.8 MPa for the unreinforced pure aluminum matrix. The flexural modulus of the composite is 108 GPa for sample A (122 GPa for sample A1 and 94 GPa for sample A2) and 74 GPa for sample B as compared to 69 GPa for the unreinforced pure aluminum matrix.

Figure 6.7 and 6.8 show the typical optical micrographs of the cross section of the C/Al composites, which were used to determined the fiber volume fraction. It was found that the fiber volume fraction is 50% for sample A and 20% for sample B. Using the above value of fiber volume fraction and the tensile strength and modulus value of carbon fibers and aluminum matrix from Tables 3.2 and 5.4, the flexural strength

Table 6.1 Mechanical properties of the composites at room temperature

Specimens	A1	A2	B1
Span, mm (in.)	18.0 (0.71)	18.0 (0.71)	18.0 (0.71)
Width, mm (in.)	1.65 (0.065)	1.65 (0.065)	1.65 (0.065)
Thickness, mm (in.)	1.07 (0.042)	1.13 (0.0445)	1.93 (0.076)
Yield load, N (lbs)	0.08 (0.0183)	0.54 (0.122)	0.11 (0.0244)
Peak load, N (lbs)	23.84 (5.359)	25.61 (5.756)	64.90 (14.587)
Yield STR MPa (Psi)	1.2 (170.1)	0.7 (101.1)	0.5 (69.25)
Flexural STR MPa (Psi)	343 (49775)	328 (47622)	285 (41380)
Fiber Fraction (%)	50	50	20
% ROM Strength	13	13	28
Flexural Modulus, GPa (Ksi)	122 (17625)	94 (13554)	74 (10754)
% ROM Modulus	80	62	66
Strain fail (%)	0.6543	0.5548	1.044

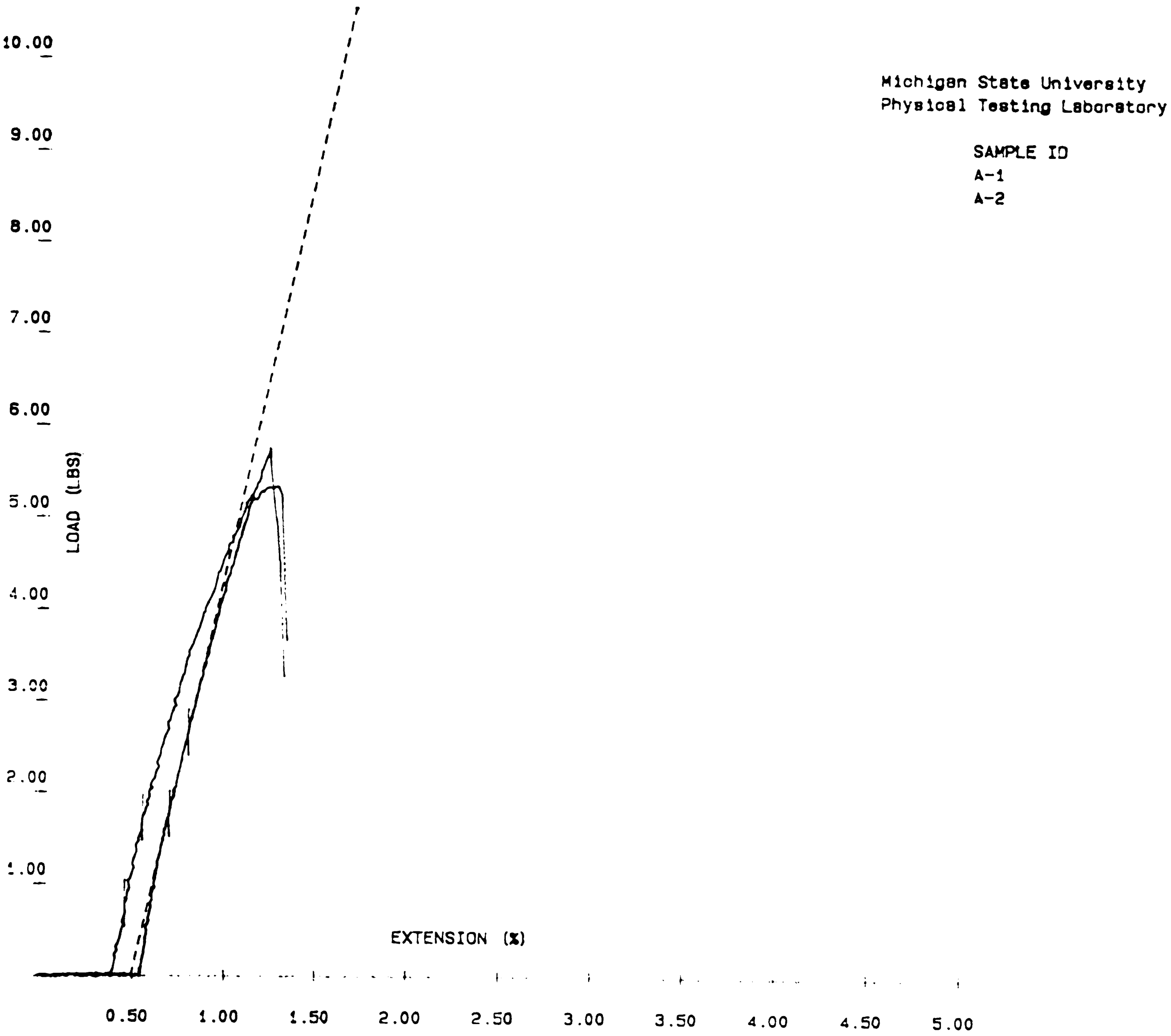


Figure 6.5 Load-Extension curve of sample A.

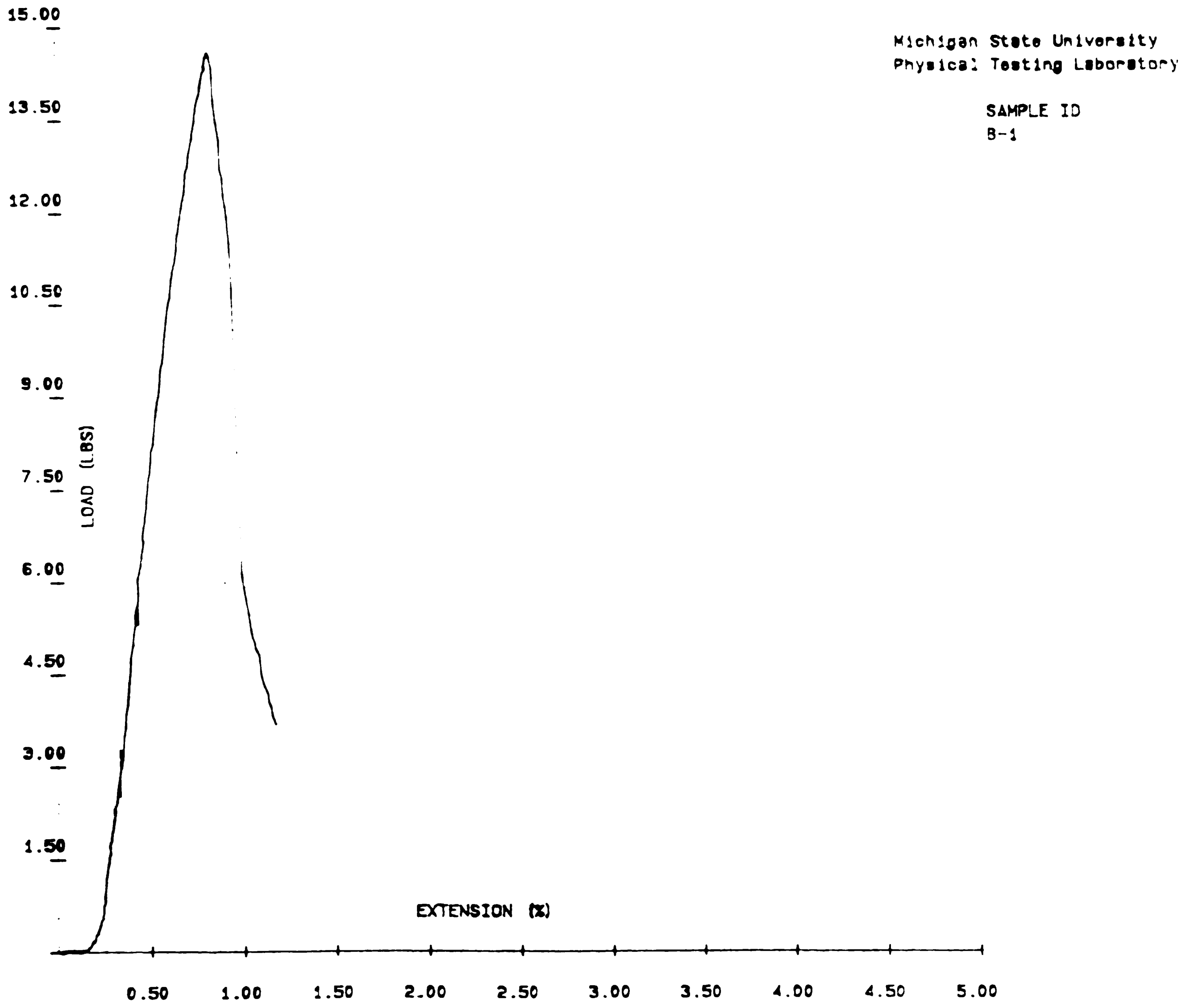
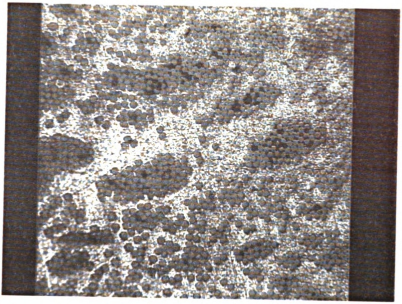
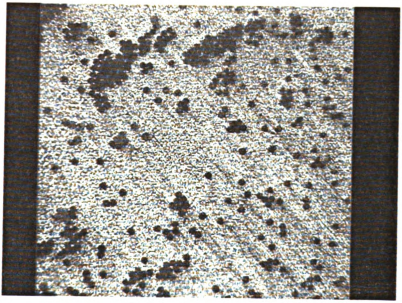


Figure 6.6 Load-Extension curve of sample B1.

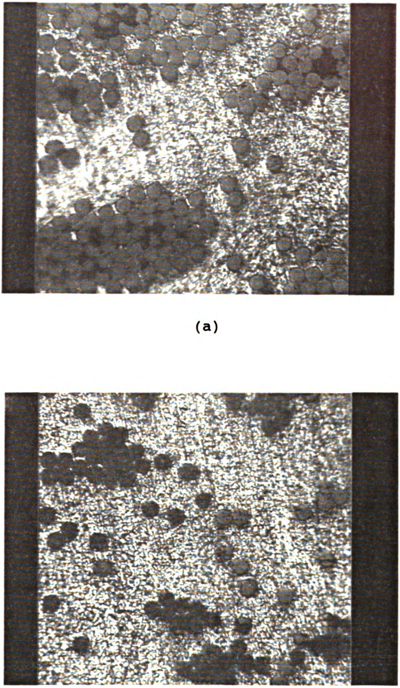


(a)



(b)

Figure 6.7 Typical optical micrograph of cross section of sample A (200x) (a) and sample B (200x) (b).



(a)

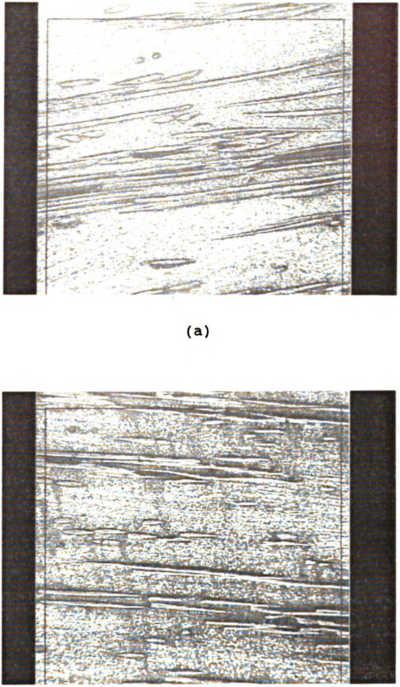
(b)

Figure 6.8 Optical micrograph of the transverse section of sample A (500x) (a) and sample B (500x) (b).

of the rule of mixtures at these fiber volume fractions were calculated to be 2549 MPa for sample A and 1019 MPa for sample B. the flexural strength of the composite is 13% of the rule of mixtures for sample A and 28% for sample B. The modulus of the rule of mixtures at these fiber volume fractions was determined to be 151 GPa for sample A and 112 GPa for sample B. The modulus of the composite is 71% of the rule of mixtures for sample A and 66% for sample B.

6.3 Optical Microscope and SEM Examination

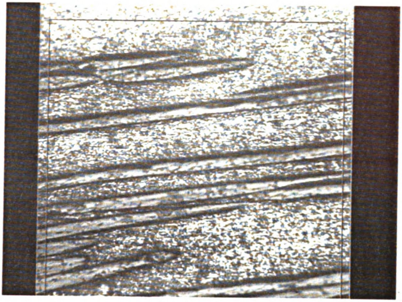
Figures 6.7 and 6.8 show the optical micrographs of the transverse section of sample A and sample B. Figure 6.9 and 6.10 show the optical micrographs of the longitudinal section of Sample A and sample B. From these figures, it is obvious that the fiber-matrix interface is smooth with no discontinuities observed even at higher magnification. This implied that the fiber-matrix bonding is good with no excessive interface reaction and no fiber damage. However, these micrographs show that some carbon fibers contact together to form the fiber clusters, especially for sample A. Figures 6.11 and 6.12 show the SEM fractographs of sample A and sample B. It can been seen that the dispersed fibers were not pulled out while the clustered fibers were pulled out. The fractographs show that the aluminum powders were sintered well generally while a few of unsintered aluminum powders can be found in sample B in Figure 6.12 at arrow. This could be due to these powders were located in a local void where the pressure could not reach them.



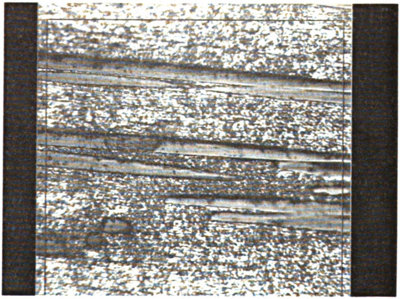
(a)

(b)

Figure 6.9 Optical micrograph of the longitudinal section of sample A (200x) (a) and sample B (200x) (b).

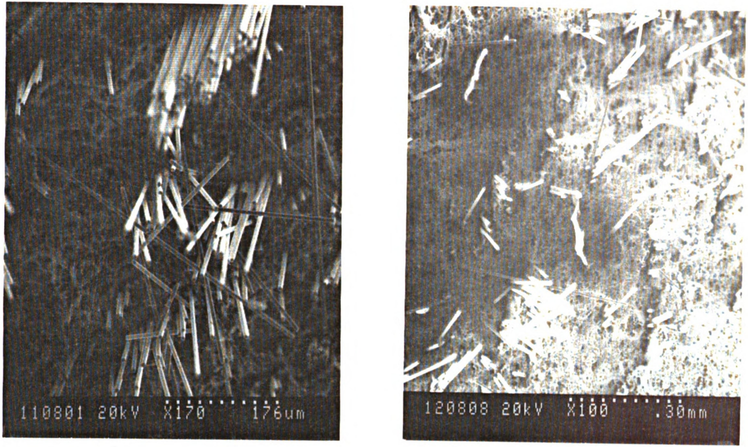


(a)



(b)

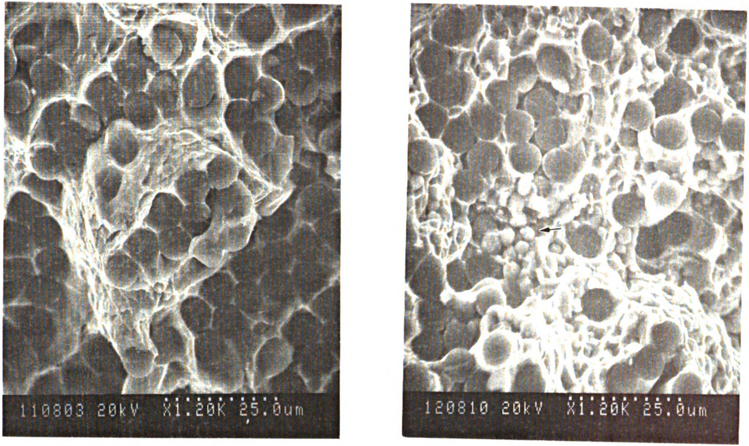
Figure 6.10 Optical micrograph of the longitudinal section of sample A (500x) (a) and sample B (500) (b).



(a)

(b)

Figure 6.11 SEM fractograph of sample A (170x) (a) and sample B (100x) (b).



(a) (b)

Figure 6.12 SEM fractograph of sample A (1.20kx) (a) and sample B (120kx) (b).

Chapter 7

Discussions

7.1 The Spreading and The Prepregs

The new fabrication process of composite precursors is capable of picking up desired volume fraction of matrix. The distribution of fine metal powder around the reinforcing fibers is uniform. The precursor tapes are almost as flexible as the reinforcing fiber tow with good handling properties. The polymer works well as the binder and hence no significant powder loss was found during the layup procedure prior to consolidation. This suggests that the adhesion of the aluminum powder to the carbon fibers is strong enough. For sample A, the formation of the fiber clusters plays two roles. First, the precursors are easy to handle during the layup procedure because the fibers do not move relative to one another. Second, it makes the fibers distribute unevenly.

There are four key factors which result in success of composite precursor production.

1) The spreader which works on the principle of acoustic energy is able to spread collimated fiber tows into their individual filaments. It works best at the natural frequency

of the reinforcing fibers.

2) The aerosolizer which utilizes acoustics to provide a buoyant force to the powder is a stable entrainment system which can provide an aerosol of constant powder concentration for extended periods of time. It operates best at its natural frequency.

3) The use of fine powder roughly of the order of dimensions of the reinforcing fibers makes the distribution of the matrix around each fiber be uniform.

4) Polyamide works very well as a binder to adhere aluminum powder on carbon fibers at proper temperature.

However, the presence of fiber clusters in the prepreg tape is a remaining problem for the quality of the precursors. Iyer [82] studied this phenomena and pointed that the impregnated fibers show a tendency to cluster in bundles in the heater. The preferred configuration of the prepreg tapes is the array of fiber-matrix cluster, each cluster diameter ranging from that of a single fiber to multiple fibers (most cluster diameters are between 10-50 microns). In the heater, the coalescence of the polymer on the fibers goes through three steps: the heating up of fibers and the particles; interparticle sintering between adjacent particles until a film forms on the fiber surface; and, finally, the formation of a stable configuration of axisymmetric or non-symmetric droplets. The physical situation has been shown in Figure 4.7. In the first step, the temperature of the powder-impregnated fiber tow is raised by convection and radiation to a value greater than the melting or softening point of the polymer particles. Then, interparticle sintering begins with a neck formation between adjacent particles. The neck grows till the particles coalesce into one. Interparticle sintering time (defined to be the time when the interparticle bridge is equal to the particle diameter) are primarily influenced by the temperature, the polymer viscosity and the particle size. The work required for a shape change is equal to a decrease in surface energy. Interparticle sintering leads to the formation of a film which breaks up to form droplets on the fiber. The transition from a polymer film on the fiber surface to droplets is driven by the finite wetting abilities of most thermoplastics. These droplets are of varying shape and symmetry with respect to the fiber axis. The shape of these droplets changes with time to equilibrium configuration which can be axisymmetric or non-symmetric depending on droplet volume and the influence of gravitational forces. If in the case of a spread fiber tow in which the impregnated fibers are in intermittent contact with each other, capillary forces between adjacent fibers may make film formation thermodynamically favorable. The final configuration depends on interfiber distances and droplet sizes in addition to surface tension forces. Therefore, there three ways to improve the quality of prepreg tapes.

1) Improve the spreader operation. Interfiber distances have to be larger to avoid the bonding of adjacent fibers by the droplets. It is advantageous to have good spreading so that individual fibers are exposed thereby reducing the average cluster diameter.

2) Find proper polymer as the binder for a given fiber. Interparticle sintering and film formation are influenced by viscosity, surface tension and particle size of the polymer. Surface tension of most polymers lies between 20-50 dynes/cm whereas viscosity can vary by orders of magnitude. Hence there should be an optimum polymer for a given fiber.

3) Control the temperature of the heater and the speed of the fiber motion. For a given fiber-polymer system and a given speed of the fiber motion, interparticle sintering and the film formation are influenced only by the temperature of the heater. If the temperature is too low, interparticle sintering will not occur and the prepreg tape can not be formed. On the other hand, if the temperature is too high, the droplets and fiber clusters will form, which is not desired for the production of the precursors. However, there should be a proper temperature at which the interparticle sintering has occurred but the film has not formed completely. In this case, it is possible to get high quality of prepreg tapes because

the particle sintering can hold fibers as prepreg tape by periodic fiber-to-fiber contact. In the next chamber, the new added metal powder coating chamber, a greater fraction of the fiber surface is exposed to the cloud of the fine metal powder before the sintering is completely finished.

Type B prepreg is an attempt of this idea. It is obvious that 165°C is too low to be the best processing temperature because the sintering have not occurred for some nylon particles which will be lost during handling and the prepreg tape can not be formed. However, the mechanical property has showed the distinct improvement for sample B.

7.2 The Processing Parameters and The Mechanical Properties

Flexural strength and modulus of 335 MPa and 108 GPa for sample A, 285 MPa and 74 GPa for sample B were obtained when the precursors were vacuum hot pressed at 570°C for 30 minutes under 30 MPa pressure. It corresponds to a value of 13% and 28% of the rule of mixtures strength, 71% and 66% of the rule of mixtures modulus respectively. The lower measured strength and modulus may be due to several factors.

1) The distribution of the fibers in the composite was not always uniform, and this affected the maximum fracture load. Some areas had a high density of fibers and others had a low density. There are some fiber clusters (fiber-to-fiber

contact) in the composite although sample B is better than sample A. Fiber clusters in sample B were smaller than in sample A. Thus a larger fraction of the fibers in sample B were completed surrounded by matrix. The micrographs of the fracture surface showed fiber pullout in the fiber cluster areas, which suggested that tow of fibers did not fully work as a reinforcement. The high magnification fractographs (Figure 6.12) showed that where fibers were in direct contact with each other, the fracture in fibers started at the fiber-fiber interface. This suggests that fibers in direct contact lead to premature fracture. This can explain why the strength of sample A is less than the strength of sample B in terms of the percentage of the rule of mixtures. So it is the poor distribution of the fibers that mainly cause the lower strength.

2) The fiber coating with aluminum powders is uneven for type B precursors, and this may affect the load transfer efficiency at the interface. As mentioned before, type B prepregs were processed at 165°C and some nylon powder particles were not as evenly distributed due to inadequate sintering at the lower processing temperature. This resulted in the existence of portions of the fibers without any coating. These uncoated regions resulted in some voids in the fiber-matrix interface, where the powder particles were not completely consolidated due to the fact that the pressure could not reach these regions during consolidation. The

bonding in these regions is very poor because some unsintered aluminum powders can be found (Refer to Figure 6.12 at arrow). Therefore, since some portions of the fibers can not transfer elastic loading to the matrix, the stiffness of the composite is reduced. It is the uneven fiber coating that may cause the lower modulus of sample B than that of sample A in terms of the percentage of the rule of mixtures. However, since the modulus values are close, they may also represent experimental variation.

3) The best consolidation parameters have not been found due to limited experimental results. Higher temperatures and longer times give lower strength because of brittle carbide formation at the interface of the aluminum and the carbon fibers. Lower temperatures and shorter times give lower strength due to poor bonding strength at the inter-aluminum matrix. The occurrence of low strength may be due to poor bonding strength of the aluminum matrix under higher pressures or damage of the reinforced fibers under high pressures. Therefore, the optional processing parameters must be selected from a series of trials to get the maximum in strength of composite.

4) The matrix material and the characteristics of the reinforcing component have important influence to the strength of the composite. As mentioned earlier, most aluminum matrix composites were produced by aluminum alloy. So the use of pure

aluminum could be a factor because pure aluminum has lower strength and is more reactive than aluminum alloys. Regarding the reinforcing component, high modulus carbon fibers have a high content of crystallized carbon and good chemical stability but high cost because they were carbonized at 2000-3000°C. In contrast, high strength carbon fibers were carbonized at 1000-1500°C, so these fibers are cheaper but more reactive with aluminum than high modules carbon fibers. Although some successful results have been reported on composites using high modulus carbon fibers, composites with high strength carbon fibers have been reported very few [27]. In view of the lower costs, the use of high strength carbon fibers, as described in this investigation, should be significant in the productions of C/Al composites although it's strength is lower.

5) Increasing fiber volume fraction in the composite is a way to increase the strength of the composite. It is well established that the strength of composite is a function of fiber volume fraction in direct proportion. Hence reducing the time of aluminum powder fluidizing can increase the fiber volume fraction and the strength of composite.

6) Selecting a more proper polymer as the binder is another way to increase the strength of composite, and it will be discussed in detail at next section.

7.3 The Binder

The binder plays a very important role in the new fabrication method of CFMMC. A good binder should improve the distribution of the fibers and the matrix powder during the production of the precursors. It is more important that the binder should not promote the interfacial reactions. Therefore, the polymeric binder must fulfill a succession of requirements as it proceeds through the operation.

1) It must be thermoplastic to be a binder at high temperature [85].

2) The binder must provide suitable viscosity and surface tension and flow properties [85,86].

3) It must be capable of being removed in vacuum furnace by controlled pyrolysis without disrupting the particle arrangement [87].

4) It must have a suitable melting point temperature and be stable around the melting point temperature [88].

5) It does not react with aluminum and carbon fibers at high temperature, so polymers without oxygen could be the best choice.

The mechanisms of the pyrolytic removal of binder must be understood in order to understand the last requirement. There are three mechanisms for the pyrolytic removal of binder, which are evaporation, thermal degradation and oxidative degradation [87,89]. Evaporation is the dominant mechanism when low molecular weight waxes are used as the binder. Here the organic species do not undergo chain scission and are independent of the atmosphere used. Thermal degradation of the binder is carried out in an inert atmosphere where oxygen is absent. The decomposition of the polymer takes place entirely by thermal degradation processes by a free-radical reaction. The predominant process is the formation of lower-molecular-weight substances by intramolecular transfer of radicals, resulting in random chain scission and a reduction in molecular weight. Molecular fragments less than a critical size are lost by evaporation. The presence of oxygen during binder removal superimpose on thermal degradation an additional reaction with polymer and metal powder. The reaction products may or may not be volatile substances [90].

Polyamide was used as the binder in present study, and it was supposed to be removed completely by thermal degradation in the vacuum furnace. In fact, polyamide is not the best choice as the binder for the C/Al system because it contains oxygen. It was mentioned earlier that the presence of oxygen will catalyze the formation of aluminum carbide at carbon/aluminum interfaces. Comparing with polyamide, thermoplastic polymers such as polystyrene, polyethylene, polypropylene are more suitable to be the binder because they fill the demand: thermoplastic, proper melting point, removable, without oxygen. Although the thermal decomposition products of polymers are difficult to be detected exactly because the several investigations report different results [91,92], Polymers without oxygen are desired for preventing the interfacial reactions. Therefore, selecting a more suitable binder can be a effective method to improve the quality of composite.

However, the binder may be not play a important role by checking the micrographs of the prepregs and precursors. This implies that the binder is not necessary since the electrostatic forces can make the aluminum powder stick to the carbon fibers. Without the binder, the fiber cluster will not form and the quality of composite can be improved greatly.

Chapter 8

Conclusions and Future Work

The new fabrication method of continuous fiber reinforced metal matrix composite materials was investigated and the following conclusions were obtained.

1) The fiber spreading method is a new technique and works well for the production of CFMMC. The spreading width is limited only by the length of the spreader over which the fiber tow passes and the spreader width under a set of optimum conditions. However, the fibers tend to collapse to a narrow width after passing through the spreader, which need to be improved in the future.

2) The fluidization of fine aluminum powder was successful by using the acoustic energy coming off a speaker through a rubber membrane. The aerosolizer is efficient with the uniform distribution of aluminum powder around the fibers.

3) Heating nylon-coated carbon fiber prepreg tapes to a temperature above the softening point of nylon created a sticky polymer host for fine aluminum powder. The perfect adhesion of aluminum powder to carbon fibers was achieved by making nylon serve as the binder. However, other polymers such

as polystyrene, polyethylene, polypropylene should be more suitable binder for C/Al system because these polymers do not contain oxygen.

4) The new fabrication method of CFMMC combining fiber spreading, powder coating and vacuum hot pressing was successful. The strength of the C/Al composite fabricated by this new method was lower than that expected from the rule of mixtures. It may be mainly attributed to the presence of fiber clusters due to imperfect fiber spreading.

The following recommendations for future work are make as a result of this investigation:

- Improve the quality of prepreg tapes by improving the fiber spreading operation and controlling the speed of the fiber motion and the temperature in the heater.

- Select the best consolidation conditions by empirical fashion.

- Investigate more suitable polymer binder.

- Find a proper way to coat aluminum powders first, then the original polymer prepregging system van be directly used to produce the precursors of CFMMCs.

- Use spread carbon fibers without nylon to see if the electrostatic forces can make the aluminum powder stick to the carbon fibers. This can prevent the formation of fiber clusters to improve greatly the quality of composite.

- Investigate other metal matrix materials and reinforcing fibers.

- Built the whole system together by adding the new metal powder coating chamber to the original polymer powder prepregging system and investigate the new process further.

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