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**A REVIEW OF CARBON FIBER REINFORCED METAL MATRIX COMPOSITES -
THE POTENTIAL OF LARGE-DIAMETER CARBON-BASE MONOFILAMENTS**

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ABSTRACT

While currently available carbon-base yarns are being used to effectively reinforce resin matrices, their small diameter and multifiber form makes metal matrix composite fabrication difficult. NASA-Lewis has awarded two contracts to develop large-diameter carbon-base monofilaments specifically designed for reinforcement of metal matrix composites. The two methods, pyrolytic deposition on a carbon substrate and resin impregnation followed by pyrolysis are described. Both methods show promise for producing large-diameter monofilaments which may help reduce the problems of fabrication and compatibility encountered in previous carbon-reinforced metal matrix composites.

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SUMMARY

This paper reviews the properties of currently available small-diameter carbon-base multifiber yarns and discusses some of the problems involved in using these yarns to reinforce metal matrix composites.

The small diameter, twist, and multifiber form of these yarns, makes composite fabrication difficult. A review of the literature showed that a limited amount of work has been reported on the reinforcement of metal matrix composites with carbon multifiber yarns. Most of these efforts showed some strength degradation due to fiber breakage and fiber-matrix reactivity.

Two contracts were awarded by NASA-Lewis to develop large-diameter carbon-base monofilaments to try to minimize some of these problems. These monofilaments are specifically designed for use with metal matrix composites. The two methods, pyrolytic deposition on a carbon substrate and resin impregnation followed by pyrolysis, both show promise. Tensile strengths of 300,000 psi for 3.5 mil diameter monofilaments are regularly being obtained in the first method, while strengths of 150,000 psi for 8 mil diameters were obtained using the second.

It is hoped that these large-diameter monofilaments will allow additional fabrication methods to be used that will eliminate fiber breakage and also allow the use of coatings that will reduce problems of compatibility and thermal expansion mismatch. If these problems are overcome, the high

specific strength and modulus properties of carbon-base monofilaments may be utilized to make metal matrix composites with properties superior to those available today.

INTRODUCTION

The high strength/weight and modulus/weight properties of filaments have been used to create superior structural materials by the use of these filaments to reinforce composites. The greatest amount of developmental effort in composite materials has been devoted to resin-matrix composites, reinforced with either boron or graphite fibers. Currently, boron-epoxy composites are being flight tested by the Air Force on such components as flaps, doors, panels and stabilizers.

One of the areas of greatest advantage for the use of fiber reinforced composites is in the turbojet engine. Figure 1 shows a sketch of a turbojet engine. The temperature ranges shown are for an advanced supersonic engine. For current engines, the temperatures are lower. Work done at NACA in 1953 (ref. 1) was among the first devoted to the application of fiber reinforced composites to turbojet engines. In this work, fiber glass reinforced phenolic matrix composite compressor blades were fabricated and tested in an engine for over 100 hours with no damage. With the development of better filaments and matrix materials, the emphasis has now been placed on boron-epoxy and carbon-epoxy composites for these applications. Currently, resin matrix composites are being designed for use as air flow ducting and fan and compressor blading for engine applications at temperatures up to about 300°F.

At higher temperatures (300 to 500°F), however, the resins weaken and composites with metal matrices become more attractive. Metal matrix composites

such as aluminum-boron are currently being developed, although their stage of growth is considerably less advanced than that of the resin matrix composites. Structures made of aluminum-boron composites have been designed and tested for missiles and aircraft and are being developed for compressor blade applications.

A variety of filaments have been developed to reinforce composites. Boron filaments, in which boron is vapor deposited upon a tungsten wire substrate, has received the greatest developmental effort. The boron filaments also have been coated with silicon carbide to reduce reactivity with metal matrices and allow higher fabrication temperatures to be used. Other programs are in progress to replace the tungsten substrate with a carbon or silica substrate to reduce the cost with no accompanying loss in properties.

While the development of boron filaments has proceeded rapidly, research has continued on other filamentary materials for use as composite reinforcement. One of the most promising of these is the carbon-base filament. These filaments have very high strengths and moduli and are about a third lighter than boron. The filaments come in a yarn containing many small filaments with a nominal diameter of about 8 microns. These filaments have been shown to be very effective in reinforcing resin matrices (ref. 2). Figure 2 shows that development of graphite-epoxy composites has proceeded to the point where they are being used to make doors, flaps and stabilizers for the F-5 (ref. 3). They are also being used to make fan blades for turbojet engines (ref. 4) which have already undergone flight testing.

The 8-micron diameter of these fibers, however, makes them difficult to use for metal matrix composites due to problems of fabrication and fiber-matrix reaction. It was felt that many of the problems encountered using

these currently available 8-micron diameter fibers could be reduced through the use of larger diameter monofilaments, but unfortunately, such fibers were not available. Consequently, a decision was reached at the NASA-Lewis Research Center to stimulate development of large diameter carbon-base monofilaments intended for the reinforcement of metal matrix composites.

It is the purpose of this paper to discuss the development of these large diameter carbon-base monofilaments, to review some of the results reported in the literature using existing carbon-base fibers in metal matrix composites and to discuss some of the problems which may be encountered in metal matrix composites reinforced with carbon-base filaments.

NOMENCLATURE

Before entering a discussion of carbon-base filaments, either currently available or under development, it would be worthwhile to consider the nomenclature used for these materials. This is necessary because carbon occurs in various forms, which differ from each other in crystal structure, appearance, and properties. For example, lampblack and charcoal are amorphous and graphite is crystalline and soft, while diamond is crystalline and hard.

The processing history of carbon-base fibers determines the form in which carbon will exist in the material. Reference 5 states that all carbon fibers of commercial importance are manufactured from organic precursor fibers by a series of heating steps which may include chemical treatments. "Carbon fibers" were defined as a general term to cover all fibers that have been heat treated to temperatures substantially above the decomposition temperature of the precursor polymer, usually to an intermediate temperature

from 1000 to 1500°C (1832 - 2732°F). "Graphite fibers" were defined as those that have been heated to higher temperatures, usually above 2500°C (4532°F).

Commercially available carbon-base fibers have been further classified by ref. 6 into three categories depending upon the extent of their processing history. The characteristics of each of these three types of carbon fibers are shown in Table I. "Carbon" fibers are those in which the polymer precursor has been heated to approximately 1832°F (1000°C). "Graphite" fibers are those in which the carbonized fibers have been heated to approximately 5432°F (3000°C) and have crystal structure which has an orientation similar to that of the precursor material (ref. 7). The "Structural Carbon" or "Structural Graphite" fibers undergo a combination of thermal-mechanical processing which is believed to orient the crystallites with simultaneous grain growth leading to increased mechanical properties (ref. 8). Those carbon-base fibers that have been given special processing are termed "structural" fibers because of the large increase in strength and modulus achieved by these treatments and to differentiate them from other forms of carbon fibers. These structural carbon fibers are the ones generally used to reinforce composites and are usually called simply carbon or graphite fibers.

Reference 9 presents a review of carbon fiber processing and points out some of the controversial areas such as fiber structure and processing kinetics. It also points out that there are two basic types of carbon - that which can be graphitized and that which cannot. The ideal fiber, however, falls in between these two. A graphitizable polymer can be made into a structural fiber by the use of treatments such as oxidation that retard low temperature fusion and subsequently reduce the grain size of the crystallites during graphitization. A non-graphitizable polymer precursor can be

made into a structural carbon fiber through the use of a carbon-molecular-chain intensifier such as mechanical stretching which causes preferred orientation and limited graphite formation during subsequent heating. Density measurements reported in ref. 10 indicated that both of the precursor polymers (rayon and PAN) used for commercial fibers are classed as non-graphitic under normal processing conditions.

It is generally thought that structural carbon fibers have a "turbostratic" structure. This means that the graphite crystallites present have a preferred orientation parallel to the fiber axis and occur in layers which are surrounded by amorphous carbon. There is a great deal of controversy as to the exact structure and strengthening mechanisms of these fibers and much research is currently being directed towards answering these questions. These structural carbon fibers could be considered a composite consisting of short-length, discontinuous graphite "mini-fibers" in a matrix of amorphous carbon.

In addition several other definition of terms to be used in this paper should be considered. A yarn is a bundle of many fibers. Rayon precursor yarns come in plies of 720 fibers, and two plies are twisted together to form the yarn. PAN precursor yarns come in tows, which are relatively twist-free bundles, of 10,000 fibers per tow. A large-diameter, carbon-base single filament, for purposes of this paper, will be called a monofilament, while a continuous, small-diameter filament will be called a fiber and an array of these will be called a multifiber yarn.

HISTORICAL DEVELOPMENT OF CARBON-BASE FILAMENTS

Research on the development of processes to manufacture carbon-base filaments has been underway for many years. Reference 11 presents a

comprehensive review of much of this work.

Fibrous carbons were first produced by Edison (ref. 12) in 1880 in his search for filament materials for incandescent lamps. This initial work was done by carbonizing naturally occurring cellulosic materials, such as cotton and linen threads. These filaments were in the 1 to 5 mil diameter range and it was reported by ref. 13 that filaments made by the same process had a strength of 18,000 to 33,000 psi. These filaments were quite fragile, non-uniform and subject to hot spots during resistance heating. To correct these problems, a number of improvements on these materials by pyrolytic deposition of carbon onto defect areas were patented by Edison and others.

Intensive work continued to improve carbon fibrous conductors until the early 1900's, when metal filaments supplanted carbon. Osmium and tantalum were first substituted (ref. 14) until finally with the development of the Coolidge process (ref. 15) tungsten filaments were used almost exclusively as lamp filaments since 1909. The development of these more efficient, more durable metal filaments caused interest in carbon filaments to wane.

During the 1950's, however, the need for ablative materials caused a resurgence in the interest in carbon-base filaments. Woven precursor fabrics, such as rayon, were pyrolyzed and carbon and graphite yarns and fabrics were made and marketed in quantity. These yarns and fabrics were used to strengthen and control ablative materials such as carbon or resins for very high temperature applications such as re-entry nose cones and rocket nozzles.

During the early 1960's the desire to find a higher modulus replacement for fiberglass caused renewed interest in low density monofilaments. The majority of this work was sponsored by the Air Force Materials Laboratory. Initially the competition for a large diameter monofilament was between pyrolytically deposited boron (ref. 16) and pyrolytically deposited graphite (ref. 17). Thornel 25 multifiber yarns were also available. The properties of boron were superior to the other materials and the development of boron filaments was emphasized. Subsequently the properties of the carbon multifiber yarns were also improved.

Various processes were patented to make carbonized yarns, the most important of which was probably that of ref. 13, in which a process was patented for making graphitic yarns from rayon precursors. These yarns were about 6 microns in diameter and had tensile strengths of about 120,000 psi. These filaments showed a highly graphitic structure with a large amount of preferred orientation. With further development, these graphitic yarns were replaced by structural carbon fibers with significantly higher properties.

CURRENTLY AVAILABLE STRUCTURAL CARBON FIBERS

The properties of various carbon-base multifibers are tabulated in Table II. The final properties of each carbon-base fiber are a function of its precursor, spinning technique, and thermomechanical history. The table is divided into the two main categories of currently available fibers: rayon-base precursor and polyacrylonitrile (PAN)-base precursor.

The first high-strength, high-modulus carbon-base fiber to be commercially available was Thornel 25. It was introduced in 1959 by the Union Carbide Corporation. Since that time, rayon-precursor fibers have also been

brought out by Hitco. Also since the time of the first introduction, the modulus of the fibers has been increased to 40 and 50×10^6 psi with experimental quantities at 75 to 100×10^6 psi ready to come onto the market soon.

Reference 18 describes the process by which the rayon precursor is converted into structural fibers. As shown, schematically in fig. 3, the rayon precursor is slowly heated from room temperature to 752°F (400°C) so that the cellulose may pass through a complex series of pyrolysis reactions. These reactions have been described in detail in ref. 19. Carbonization may then be completed more rapidly at a temperature of about 1832°F (1000°C). The material is then graphitized by rapid heating to above 4532°F (2500°C). The fiber at this stage has a strength of about 100,000 psi and a modulus of about 6×10^6 psi. The fiber is stretched while in the graphitization temperature range. This stretching (up to 30 percent elongation) causes a high degree of preferred orientation of the graphite crystallites parallel to the fiber axis and forms a turbostratic structure. This stretching and alinement of the layers raises the strength and modulus to very high values. There is a trend for these rayon-precursor fibers to have the strength increase along with the modulus. The final properties are dependent upon the amount of stretch and the stretching temperature.

The other structural carbon fibers shown in Table II are made using polyacrylonitrile (PAN) precursors. The original work on PAN-base fibers was done at the Royal Aircraft Establishment in England. Reference 20 describes the process by which these fibers are made. The process is shown schematically in fig. 4. The PAN precursor is oxidized in air at $392 - 572^\circ\text{F}$ ($200 - 300^\circ\text{C}$). This oxidation treatment is conducted with the fibers wound around restraining bobbins. The longitudinal and diametric shrinkage

accompanying the oxidation process puts the fiber under tension and causes a preferential alinement of the PAN molecular chains. The oxidized precursor is then heated to 1832°F (1000°C) and converted to carbon. The carbonized material is then heat treated to give it its final properties. As shown by the insert in fig. 4, there are two types of fibers available. There is a strength peak occurring at heat treatments of about 2732°F (1500°C). At treatment temperatures above this, the strength drops off, but the modulus continues to increase (ref. 21). If a high strength material is desired, it is heat treated to this temperature. If a high modulus material is desired, it is heat treated to 4532°F (2500°C). The properties of these fibers come from the orientation of carbon crystallites for strength and of the graphite crystallites for modulus. The Morganite and Courtaulds PAN-precursor fibers are in continuous lengths, while the Fortafil 5Y is a staple yarn composed of discontinuous 8 μ diameter individual fibers.

Summarizing the currently available carbon-base structural fibers, either rayon- or PAN-precursor, they all draw their properties primarily from their thermo-mechanical history and they all come in a multifiber (1440 to 10,000 individual fibers) form and they have a nominal diameter of 8 microns (0.0003 inch).

FABRICATION OF COMPOSITES

We have described the types of carbon-base fibers that are commercially available. Before these fibers can be utilized in a structure, however, they must be combined with a resin or metal matrix to form a composite.

Before discussing the fabrication of metal matrix composites, let us first consider the fabrication of resin matrix composites. Carbon-base fibers, commercially available in small-diameter multifiber yarns, are currently being used in resin matrix composites. Normally these composites are fabricated from prepregs, which are tapes made from bundles of fibers that have been preimpregnated with resin. The prepreg tapes may then be laid up in any desired orientation or cut to any shape. The tapes are then adhesively bonded together to form the desired structure. Sometimes resin matrix composites are also made by filament winding in which the yarns are wound over a mandrel after passing through a resin bath. The resin allows the yarns to adhere to each other. Additional resin is added and compacted and cured in an autoclave or press. Bonding may also be accomplished using atmospheric pressure in an evacuated bag.

For metal matrix composites, the fabrication of composites is more complicated and difficult. In resin matrix composites, most of the resins have a low enough viscosity to flow in between the fibers in the yarn. Metals, however, usually must be forced in between these fibers.

Methods of fabricating metal matrix composites can be divided into four general categories. The advantages and disadvantages of some of these methods are shown in Table III.

The first category is liquid metal fabrication. This includes techniques such as casting, and gravity or vacuum infiltration. These methods offer the advantages of low operating cost, short processing times and high fiber contents. They have the disadvantages of high fabrication temperatures which causes greater fiber-matrix interfacial reaction. Also the

strength of the interfacial bond is influenced by the wetting characteristics at the interface.

The second general fabrication category is transport fabrication. This is a group of fabrication methods in which the matrix material is transported to the filament which acts as a substrate. This category includes methods such as electro- or electroless plating, plasma spraying and vacuum or vapor deposition. These methods offer the advantage of being a fairly low temperature, relatively non-reactive operation. However, these methods do not produce a composite with uniform distribution of the matrix material throughout the entire cross section of the yarn. It is particularly difficult to cause matrix penetration into shadow or impinged areas. Composites made using these methods may be used in the as-fabricated condition, but usually they undergo an additional treatment.

The third general category is powder metallurgy fabrication. This category covers methods that take metal powders and distribute them in the proper position and consolidate them. Gravity, vibration, or slip casting may be used to fill the matrix areas. The powders may be cold compacted. Final consolidation occurs through sintering, which is a static heating to allow diffusion to occur to cause grain coalescence. Sintering may also be accompanied by static deformation (hot pressing) or dynamic deformation (roll pressing, co-extrusion, etc.) in which the material is reduced in thickness to accelerate compaction. These methods have the advantage of being relatively low temperature operations (relative to the melting point), thus giving somewhat reduced reactivity, and being able to undergo forming to shape during processing. Composites can also be made with a wide range

of fiber contents. They have the disadvantage of requiring cleaning of the powders to remove surface oxides because of the large surface area of the powders and of requiring fairly extensive sintering schedules. In addition, the hot pressing, either static or dynamic, of elastic filaments can cause breakage of the filaments, unless considerable care is exercised during processing.

The fourth general category is foil metallurgy fabrication. This method is sometimes called diffusion bonding, pressure bonding or hot pressing of foils. In this method, illustrated in fig. 5, the filaments are wound on a mandrel with foil sheets above and below the filament layer. The filament may be held in place with a styrene adhesive. Additional layers can be built up by alternately laying layers of filaments and foil sheets on top of each other. Tapes, similar to prepregs, may also be used. These tapes consist of a single layer of filament bonded to foil sheets and laid up in the proper order. The lay-up is sealed in an evacuated retort. The retort is placed in a heated platen press, for static bonding, or in a rolling mill, for roll bonding. During the heating and pressing cycle, the foil sheets deform and flow around the filaments by creep. When the two foil surfaces meet, diffusion across the boundary occurs and eventually they are well bonded and no bonding line is left between the two former surfaces. This method has the advantages of being able to conveniently make sheet and plate products directly and to allow controlled orientation of the filaments in the final product. The method has the disadvantages of requiring fairly long processing times and being limited to fiber contents of about 50 volume percent. Most work done on aluminum-boron composites has been done using diffusion bonding techniques.

All four of the categories of metal matrix composite fabrication have two problems inherent in them: matrix distribution and fiber-matrix reaction. Both of these problems are magnified by the use of small-diameter multifiber yarns and are reduced by the use of large diameter monofilaments.

CARBON FIBER REINFORCED METAL MATRIX COMPOSITES

Now that we have discussed the general methods that can be used to fabricate metal matrix composites, let us examine some of the methods of fabrication of carbon fiber reinforced metal matrix composites and the properties that were reported in the literature. The types of tests and their purposes are tabulated in Table IV and described in the ensuing discussion.

In 1966, it was reported in ref. 22 that Thornel 25 yarns were hot pressed between sheets of 2024 aluminum. The assembly was heated between the solidus and liquidus temperature of the aluminum alloy and incipient melting occurred. The combination of pressure and melting caused the aluminum to penetrate into the yarn and formed a sound composite. There did not appear to be any fiber-matrix reaction and the interfacial bond appeared to be good. There did, however, appear to be a great deal of fragmentation of the fibers during processing. This was probably due to the twisting and overlapping of individual fibers in the yarn. The tensile strength of the composites was about 50 percent of the rule-of-mixtures predicted strength, while the modulus was unaffected by the processing.

In 1967, results were reported in ref. 23 on a program designed to determine the friction and wear characteristics of metals reinforced with Modmor I fibers. The fibers were chopped to 1/8 inch lengths and the composites were made in one of two ways. Mixtures of chopped fibers and powders

of lead or copper were blended and hot pressed, while chopped fibers were also electroless plated with nickel, cobalt or silver. No interfacial reactions were observed for these composites, although there was some phosphide formation with the nickel and cobalt composites. No tensile tests were performed on the composites. Wear and friction tests were conducted in which the composite was held under load against a rotating tool steel cylinder. The results obtained indicated that the coefficient of friction of the composites was unchanged compared to the unreinforced material, however the wear rate during sliding was reduced appreciably. This enhanced resistance to wear was attributed to surface strengthening in which the carbon fibers impeded the flow of the metal in the surface layers.

In 1968, results were reported for Thornel 25 yarns in nickel (ref. 24) and nickel and cobalt (ref. 25). In each case the matrix was applied by electroless plating of the fiber yarns. After plating the composites were consolidated by hot pressing. Composites tested in each of the programs showed about 60 percent of the predicted rule-of-mixtures strength up to about 55 volume percent fibers. Above that fiber content, the strength dropped off rapidly. The strength degradation at the lower volume percents could be attributed to fiber fragmentation due to the hot pressing and to phosphide formation in the matrix due to the plating process. Although no reaction was observed at the interface between the fiber and the matrix some reaction may have occurred and could have contributed to the strength degradation. At higher volume percents, fiber breakage probably became more severe and greater strength degradation occurred.

In 1969, ref. 26 reported data on composites of 1/32 inch chopped Courtaulds Type B carbon fibers in aluminum. About 0.1 volume percent fibers

was incorporated onto aluminum preforms by electrophoretic co-deposition. The strength of the composite was increased by a factor of 3 over the electrodeposited 1100 aluminum. The modulus was also increased from 8.2 to 13.2×10^6 psi. These increases in strength and modulus are much more than would be expected from composite theory, so the reason for these increases are not known.

Also in 1969, ref. 27 reported the results of a detailed study of the effect of high-temperature exposure on the compatibility and strength of coated fiber "microcomposites". Individual fibers were mounted on frames and coated with metal by vacuum evaporation (aluminum), or electrodeposition (nickel, cobalt, chromium, platinum and copper). The coated fibers were then heat treated in vacuum for one day at temperatures up to 2192°F (1200°C). After heat treatment, bundles of about 15 coated fibers were bonded together on the frame by running epoxy between them followed by curing. This was done to facilitate handling and to reduce scatter. These microcomposites were tested in tension at room temperature. Tensile strength and interfacial reaction were correlated against time and temperature of the heat treatment exposure. The properties were compared to those of uncoated carbon fibers, which were unaffected in this temperature range.

All the composites tested in this study showed the same type of behavior. The strength held constant up to some temperature and then fell off. The temperature varied with different matrices. For aluminum matrices, the drop-off temperature was about 1022°F (550°C), with a reaction layer of Al_4C_3 being observed to coincide with the degradation. Nickel

caused degradation at 1832°F (1000°C) which appeared to be caused by a recrystallization of the Modmor structure to a random graphitic structure. Cobalt acted in a similar manner to nickel, however the degradation temperature was lowered to about 1292°F (700°C). Nickel-chromium coated Modmor I degraded at about 932°F (500°C) and showed that a very thin reaction zone layer of Cr₃C₂ caused the strength to drop catastrophically. Platinum coatings caused degradation at about 1652°F (900°C), but no evidence of reaction or structural change was observed. Likewise copper coated fibers showed degradation at about 1472°F (800°C), but with no apparent microstructural or X-ray changes.

Further work was reported on nickel and cobalt coating on Modmor I fibers using the same techniques in ref. 28 in 1970. This work showed the same results, but added additional X-ray work that indicated that the structural recrystallization that the fiber undergoes when in contact with nickel is similar to that encountered with nickel and tungsten wire in composites reported in ref. 29. In this work, there was a diffusion and reprecipitation in the graphite to form a more fully graphitic, but weaker, form of carbon. It was also found that graphitized fibers withstood recrystallization better than carbonized fibers.

Also in 1970, work was reported in refs. 30 and 31 on Thornel 50 composites with an aluminum-silicon eutectic alloy matrix. The composites were made by liquid infiltration following a special treatment on the surface of the fibers to enhance wetting by the molten aluminum alloy. The composites retained about 80 percent of their rule-of-mixtures strength prediction. They did not appear to have any interfacial reaction between the molten alloy and the fibers. In addition the composites were subjected

to a thermal cycling consisting of 20 cycles between -315 to 932°F (-193 to 500°C) and exhibited no drop in tensile strength after cyclic exposure.

Summarizing the results reported, it appears that carbon-base filament reinforced metal matrix composites appear very promising. However, all the results reported to date show some strength degradation below that expected from rule-of-mixtures prediction. The modulus did not appear to be affected and maintains its full contribution to the properties of the composites.

The strength degradations observed are probably attributable to two basic factors - fabrication problems and compatibility.

The first problem encountered during fabrication is how to get the matrix around all the fibers. Most reinforcing filaments, such as boron, silicon carbide, tungsten, etc., used for metal matrix composites are in the form of large-diameter (.003 to .010 inch) monofilaments. The use of commercial multifiber yarns presents a different set of fabrication conditions. A monofilament and a multifiber yarn are shown in figure 6. In a monofilament, the matrix has to cover one surface. In a commercial carbon multifiber yarn, there are 1440 to 10,000 fibers in the yarn, and there are many of these yarns across the cross section of the composite. Thus the matrix metal must be able to penetrate into all of these inter-fiber spaces.

The method most successful to date of doing this is liquid metal fabrication. Since these inter-fiber spaces are small, capillarity must be relied on to carry the molten metal into all these spaces. This means that there must be sufficient wetting of the fiber surfaces to allow capillarity to occur. Carbon is not readily wetted by most molten metals. Thus in

order to avoid non-infiltrated "pipes" some type of surface treatment would probably be needed to allow wetting. The other fabrication methods offer even more difficulties in matrix penetration of multifiber yarns. Electroforming can allow deposition on most of the fibers, but the plating bath can become depleted by the interior fibers and the plating rate reduces relative to the exterior fibers. In plasma spraying and the deposition methods, the interior fibers may be masked and the matrix material cannot penetrate. With powder metallurgy methods, it is difficult to get the metal powders into these interfiber spaces, while with the diffusion bonding processes, the matrix cannot creep around and into these spaces.

The other major problem encountered with metal matrix composite fabrication is fiber-matrix reaction. Interfacial reaction is important because it can change the failure behavior of the filaments and thus cause strength degradation of the composite. Unfortunately, there is little data in the literature on reaction with carbon fibers or the effect of reaction on strength. Data has been presented in refs. 27 and 28 that showed that the strength of carbon-base fibers can be reduced by reaction with various potential matrix materials, however with shorter exposure times or at lower temperatures, reaction has little effect. Most of the reaction data reported in the literature was obtained on composites reinforced with boron or tungsten filaments. Let us look at some of the results to gain insight into the possible effects of fiber-matrix reaction on carbon fiber reinforced metal matrix composites. Filaments such as boron and carbon fail in the elastic region and are more prone to degradation than are metal fibers that fail after elastic and plastic deformation.

Tungsten wire, in the as-drawn condition, is relatively ductile and exhibits about 3 percent strain at failure (Ref. 32). In composites with

mutually insoluble matrices, like copper, the plastic properties of the filament were unaffected and the full strength of the filament may be utilized. In matrices where the matrix is soluble (ref. 29) reaction may occur between the filament and the matrix (fig 7-a). If a slight reaction occurred at the interface, there may be a slight reduction in strength of the composite. This is a notch effect that reduced the ductility of the filament somewhat. Plastic flow alleviated the major effect of the notch, but the plastic flow was somewhat restricted, thus a slight property degradation occurred. Some alloying additions, however, diffused into the wire and caused the heavily cold-worked structure to recrystallize into a brittle, weaker structure. In this condition, the wire could not alleviate the effects of notches since the brittle structure did not allow plastic flow. The brittle fracture caused the composite to fail at a catastrophically reduced strength.

In contrast, elastic filaments, such as boron and carbon, do not exhibit plastic flow and thus are more susceptible to notch embrittling effects. A slight surface reaction can cause severe strength degradation. Figure 7-b (ref. 33), shows a slight reaction zone around the boron filament. This reaction zone was enough to cause the filament to lose almost half of its strength. Reference 34 has shown that with titanium-boron composites, reaction zone thicknesses of as small as 5000 \AA could cause explosive cracks to propagate through the filaments and degrade the strength of the composite. Coatings have been applied to brittle, elastic fibers to reduce reactivity and its accompanying property degradations. Boron filaments coated with SiC (refs. 35 and 36) and with BN (ref. 37) have shown that the fiber-matrix interface can be made more stable and the reactivity and property loss can be significantly reduced.

Carbon filaments would be expected to have similar problems. The results reported in ref. 27 showed that every one of the potential matrix materials tested caused a degradation to the strength of the carbon fibers after exposure to elevated temperatures. Although some of the degradation temperatures were rather high, most metal matrix composite are designed for long-time applications. The test data cited was for exposure times of one day. For longer time applications, the degradation temperature would probably be considerably lower.

Unfortunately, the nominal 8-micron diameter of the fibers in the multifiber yarns are not amenable to coating in that a coating thickness of only 2 microns would occupy an area greater than that of the original 8-micron fiber. Thus the use of coatings would significantly reduce the effective fiber content of carbon in the composite so that even though a greater portion of the strength of the fibers could be maintained, the total strength of the composite would be less, because low fiber contents would have to be used.

DEVELOPMENT OF LARGE-DIAMETER CARBON-BASE MONOFILAMENTS

Because of the difficulties of fabrication and compatibility encountered with commercially available small-diameter carbon multifiber yarns, it was decided at NASA-Lewis that in order to fully exploit the potential of carbon-base filaments in metal matrix composites, it was necessary to develop a large-diameter carbon-base monofilament. Such a monofilament would eliminate many of the problems of matrix penetration and consolidation, and allow the use of coating for reactive matrix systems and for higher-temperature, longer-time applications.

In order to try to overcome these problems, NASA-Lewis decided to award two contracts to stimulate the development of large-diameter carbon-base monofilaments, designed specifically for use as a reinforcement for metal matrix composites.

The first of these contracts was awarded to Philco-Ford Corporation under NASA Contract NAS3-13204. The results of this contract are reported in ref. 38. This program was a feasibility study on the fabrication of large-diameter carbon-base monofilaments by impregnating bundles of commercially-available small-diameter multifiber yarns with organic resins. The resin surrounding the fibers was subsequently converted to carbon by pyrolysis.

The results of this contract were encouraging in that a high percentage of the strength of the small-diameter multi-fibers was retained in the final pyrolyzed composite monofilament. However, problems were encountered in the fabrication of these composite monofilaments and resultant porosity and non-uniform distribution of the yarn probably kept the composite from reaching its maximum strength. The modulus of the multifibers was unaffected during processing and contributed their full modulus to the composite monofilaments.

Several resins were impregnated into Thornel 50 and Modmor I and II yarns. Furfuryl alcohol was chosen as the major resin to be studied because of its low viscosity and fast curing characteristics. In some runs epoxy novolac was added to increase surface tension in order to draw the yarn into a denser compact. Phosphoric acid was also added to the furfuryl alcohol to promote faster curing. A polyimide resin (P-13-N) and a polyquinoxaline resin (NAV-P-10) were also used, but the higher viscosity of these resin made impregnation difficult.

Figure 8 shows a schematic diagram of the fabrication methods used. First, the yarns were impregnated with resin allowing capillarity to carry the

resin throughout the entire length. It was found that this method did not give full impregnation and several other methods were tried to remove voids, and force tighter and more uniform packing of the fibers. Other methods of consolidation, such as rolling and drawing through an orifice were tried, but problems were encountered in resin adhesion and fiber fraying. The above methods used an unrestrained, free standing bundle of fibers for initial impregnation. Closed die pressure molding was used in an attempt to reduce porosity and increase the fiber content and decrease the resin content in the composite monofilament. The composite was then cured and pyrolyzed. The monofilament was subsequently reimpregnated under vacuum and repyrolyzed.

Figure 9 shows a photograph of these monofilaments.

Because of the problems of resin impregnation, there was a tendency for the carbon from the converted resin to be porous after pyrolyzation. Some of this porosity was removed during the subsequent reimpregnation and pyrolysis, but it was never fully removed. The effect on resin pyrolysis of phosphoric acid activator and the speed of the curing and pyrolysis steps of the process may have contributed to the porosity. Also, it was difficult to get a uniform distribution of the yarn throughout the monofilament. There was a tendency for the yarn to gather in resin-starved areas with resin-rich areas surrounding them.

The results obtained are shown in fig. 10. For purposes of comparison, the strengths shown are normalized by determining the breaking load of the pyrolyzed bundle, ignoring the strength contribution of the carbon matrix and assuming that all the load was carried by the fibers. This breaking load at each step of the fabrication process is compared to the breaking load of a bundle of the same fibers, impregnated by epoxy as the starting value.

The figure shows that the best strength retention was in the furfuryl alcohol-Modmor I composite monofilaments, with a strength retention of 86 percent after pyrolysis.

Summarizing the results of this contract, the feasibility of the resin impregnation and pyrolysis method for making large-diameter monofilaments was shown. The full modulus and as high as about 85% of the strength of the original small-diameter multi-fibers were retained in the final monofilament. However, fabrication problems were encountered in the impregnation, curing and pyrolyzing stages. Porosity and non-uniform distribution of the fibers within the monofilament probably prevented the composite from attaining its maximum strength. It is felt that additional effort is warranted for developing better fabrication techniques to gain the full potential of this method.

The second contract to develop a large-diameter carbon-base monofilament was awarded to Hough Laboratory under NASA Contract NAS3-12429. This program was a feasibility study of the pyrolytic deposition method.

The feasibility of the chemical vapor pyrolytic deposition method was demonstrated. Carbon-base monofilaments were produced with diameters of 3.5 mils and tensile strengths up to 546,000 psi. The results of this program are reported in ref. 39.

Figure 11 shows a schematic diagram of the fabrication method used. The substrate filament was passed through a mercury standpipe electrode into a reaction chamber containing reactive gases. The self-resistance heated wire substrate caused the gases to decompose and carbon is deposited on the substrate surface. The substrate passes through another electrode and is collected on a take-up reel.

During the course of this contract, it was found that a redesign of the mercury standpipe electrodes was needed to eliminate soot formation and improve the surface of the deposit. It was also found that hot spots in the substrate, caused by diameter increases due to deposition, could be controlled better with a multiple chamber, multiple electrode apparatus. The final configuration showed two reaction chambers with each chamber containing five electrodes.

The final properties of the monofilament were found to be dependent upon the substrate, atmospheric gas combinations, voltage, current, gas flow rate and substrate velocity.

Initial studies were performed using a 0.5 mil tungsten substrate. The substrate was heated to the 2192 to 2912°F (1200 to 1600°C) temperature range while passing through the reaction chamber. The highest tensile strength observed was 180,000 psi and was processed in an atmosphere of propane, hydrogen and ethyl iodide.

Early in the program, it was found that a glassy carbon substrate yielded monofilaments of higher strength than with tungsten substrates. Monofilaments made using 1.3 mil carbon substrates were heated in a two-stage apparatus. The first stage was an etching treatment at 2382 to 2552°F (1300 to 1400°C). The second stage was the deposition stage and was in the 3002 to 3182°F (1650 to 1750°C) temperature range.

As the deposition parameters were optimized, the strength of the monofilament was increased. The best results have been obtained using various ratios of borane and ethylene gases. The initial 1.3 mil diameter glassy carbon substrate had a strength of 100,000 psi and a modulus of 4.8×10^6 . After processing, monofilaments of about 3.5 mil diameter are being made

consistently in the 250,000 to 300,000 psi strength range. The modulus is in the 25 to 30×10^6 psi range. Tensile strength up to 546,000 psi have been obtained on these monofilaments. Currently development is continuing on this program to optimize the processing parameters and to increase the properties of the monofilament. Figure 12 shows a photograph of a typical monofilament made by this process.

Figure 13 shows a plot of the specific modulus and specific strength of the monofilaments made under these contracts compared with other filaments and matrix materials. As can be seen from the figure, the specific strength of the pyrolytically deposited monofilament is greater than that of boron and to the other carbon fibers shown. In fact, it is second in strength only to S glass. The monofilament made by the resin conversion method has a specific modulus equal to that of boron although its strength is still low. It is felt that this lower strength is caused by the porosity of the converted-resin carbon matrix. Better starting multifibers and better fabrication techniques should improve the properties of these monofilaments to even higher values.

ADVANTAGES AND PROBLEMS OF METAL MATRIX COMPOSITES REINFORCED WITH LARGE-DIAMETER CARBON-BASE MONOFILAMENTS

The results reported in the literature on metal matrix composites reinforced with commercially available, small-diameter carbon-base multifiber yarns indicate that some degradation of properties occurred with each composite system. This degradation was caused either by damage during fabrication or by reaction with the matrix.

The use of large-diameter carbon-base monofilaments will allow the use of less severe fabrication conditions, which will make the reinforcement more applicable to a larger range of matrix materials. It will also allow the

monofilament to be coated with a protective barrier to reduce the effects of reaction with the matrix during fabrication and during usage.

Using large-diameter monofilaments, there would be sufficient surface area to allow the coating to be applied easily. The coatings could be applied as an extension of the initial fabrication process (as an additional pyrolytic deposition step) or as a separate step applied prior to incorporation into the composite. The larger diameter allows a thin coating to be applied, which would be a small fraction of the total monofilament area, whereas with a small-diameter multifiber, the coating area may be as great as the fiber area itself.

Perhaps one of the most interesting findings in refs. 30 and 31 was that an aluminum-Thornel 50 composite had withstood 20 thermal cycles of about 932°F (500°C). In an application such as a turbojet engine compressor or turbine, or in a leading edge of a nosecone or wing, thermal cycling will occur during operation. A thermal stress accompanies this thermal cycling. Ref. 40 states that the thermal expansion of Thornel 50 is $15.6 \times 10^{-6} \text{ } ^\circ\text{F}^{-1}$ ($8.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) perpendicular to the fiber axis and 0 (from room temperature to 750°F) parallel to the fiber axis. Matrix materials under consideration for use with these composites have considerable greater thermal expansion coefficients as shown in Table V (ref. 41).

In the direction parallel to the fiber axis, a high residual stress will be on the matrix and a residual compressive stress in the fiber due to cooling from the fabrication or application temperature. These stresses will be somewhat compensated for by the fact that the metal matrix yield strength drops with increasing temperature and thus plastic flow may alleviate some of the residual stresses. Furthermore the thermal expansion of the coating

applied to the filaments will have to be considered so that thermal spalling will not occur during operation and cycling. Thus the thermal mismatch of the filament, the matrix and the coating all must be optimized for optimum performance of the composites.

CONCLUDING REMARKS

The survey of the results reported in the literature have shown that the currently available small-diameter carbon-base multifiber yarns have high specific strength and modulus properties. These multifiber yarns have been used to reinforce resin matrix composites and yield high strength materials.

Some carbon-base fiber reinforced metal matrix work has been reported. The results obtained show that the composites are promising, however there are problems inherent in the fabrication of these composites using the currently available small-diameter fibers. It was felt that many of the problems encountered using these small diameter multifibers could be reduced through the use of larger diameter monofilaments, but unfortunately, such fibers were not available. Consequently, a decision was reached at NASA-Lewis to stimulate development of large diameter carbon-base monofilaments intended for the reinforcement of metal matrix composites.

The feasibility of two methods of manufacturing large diameter carbon-base monofilaments has been demonstrated. The pyrolytic deposition method on a carbon substrate has yielded monofilaments of 3.5 mils diameter with production strength regularly in excess of 300,000 psi. The resin conversion method has yielded monofilaments of about 150,000 psi of 8 mil diameter. Development of these processes is continuing.

It appears, however, that before these carbon-base monofilaments can be fully exploited as reinforcement for metal matrix composites, additional

work investigating the problems of reducing fiber-matrix reactivity and thermal mismatch must be done.

From these considerations, it appears that the use of large-diameter carbon-base monofilaments may eliminate some of the problems that have been present in previous carbon fiber-metal matrix composites. The monofilaments will allow easier fabrication, better compatibility, and better coatings, however possible problems from thermal expansion mismatches must still be considered. In general, however, the future of large-diameter, carbon-base monofilaments appears very promising and the properties of some of the large-diameter monofilaments already developed show great potential towards their use as reinforcement for metal matrix composites.

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TABLE I

Classification of Carbon-Base Fibers

Classification	Carbon Content	Maximum Processing Temperature	X-Ray Diffraction Crystal Structure	Crystallite Orientation	Treatment	Approx. Modulus of Elast. x 10 ⁶ psi	Approx. Tensile Strength x 10 ⁵ psi
Carbon	>80%	<1832°F (1000°C)	Crystallites too small to be detected	"amorphous"	Carbonization	5	100
Graphite	>99%	>4532°F (2500°C)	Crystallites large enough to be detected	Similar to precursor "random"	Graphitization	14	150
Structural Carbon or Structural Graphite	>99%	>4532°F (2500°C)	Crystallite number and size greater than in graphite fiber	Preferred orientation of graphite crystallites in a carbon matrix ("Turbostratic")	Combination thermal-mechanical treatments	>25	>180

TABLE II

Properties of Commercially-Available Structural Carbon-Fibers

Fiber	Supplier	Precursor	Density pci	Ultimate Tensile Strength $\times 10^3$ psi	Modulus of Elasticity $\times 10^6$ psi
Thornel 25	Union Carbide	Rayon	.052	180	25
Thornel 40	Union Carbide	Rayon	.056	250	40
Thornel 50	Union Carbide	Rayon	.059	285	50
HMG-50	Hitco	Rayon	.062	287	50
Modmor I	Morganite	PAN	.072	250	60
Modmor II	Morganite	PAN	.063	400	40
HM	Hercules (Courtaulds)	PAN	.069	300	55
HT	Hercules (Courtaulds)	PAN	.064	350	36
A	Hercules (Courtaulds)	PAN	.063	275	29
Fortafil 5Y	Great Lakes Carbon	PAN	.069	250	50

TABLE III

Fabrication Processes for Metal Matrix Composites

<u>Fabrication Category</u>	<u>Processes</u>
Liquid Metal	Casting, gravity of vacuum infiltration
Transport	Electroforming, plasma spraying, vapor or vacuum deposition
Powder Metallurgy	Powder metallurgy, slip casting, co-extrusion
Foil Metallurgy	Diffusion bonding, brase bonding, roll bonding, gas- pressure bonding

TABLE IV

Carbon-Fiber/Metal-Matrix Composites Reported in Literature

Year	Composite Fiber	Matrix	Investigators	Ref. No.	Affiliation	Fabrication Process	Fiber Content	Purpose
1966	Thornel 25	Aluminum 2024	Place & Gage	22	Philco-Ford	Hot pressing- incipient melting	16-49	Tensile
1967	Modmor I	Pb, Ag, Cu, Ni, Co	Giltrow & Lancaster	23	RAE	Chopped fibers blended with metal powders and hot pressed	12-25	Friction
1968	Thornel 40	Ni	Sara	24	Union Carbide	Electroplated and hot pressed	28-62	Tensile
1968	Thornel 25	Co, Ni	Niesz et al	25	Battelle	Electroless plating and hot pressing	48-62	Tensile
1969	Courtaulds B	Al	Buschow et al	26	General Electric	Electro- phoresis	0.1	Tensile
1969	Modmor I	Al Cr, Ni, Co, Cu, Pt	Jackson	27	Rolls Royce	Vac. Dep. Electroplate	- -	Tensile and Compatibility
1970	Modmor I	Ni, Co	Jackson	28	Rolls Royce	Electroplate	-	Reaction Phenomenon
1970	Thornel 50	Al	Pepper et al	30-31	Aerospace Corp	Liquid infiltration	28-34	Tensile

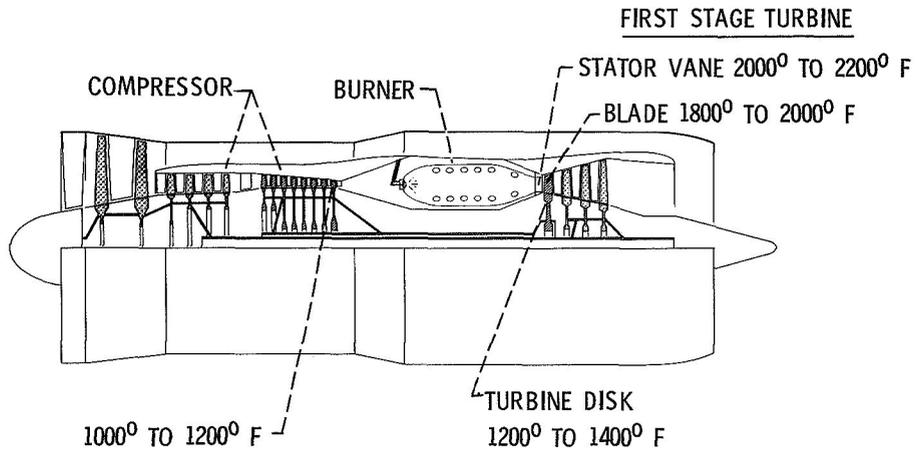
TABLE V

Thermal Expansion Coefficients of Selected Materials

Material	α	
	cm/cm/ $^{\circ}$ C	in/in/ $^{\circ}$ F
Thornel 25		
\perp to Fiber Axis	8.7×10^{-6}	15.6×10^{-6}
\parallel to Fiber Axis	0	0
Boron		
\parallel to Fiber Axis	4.9	2.7
Epoxy	48.6	27.0
Magnesium	27.1	15.1
Aluminum	23.6	13.1
Copper	16.5	9.2
Cobalt	13.8	7.7
Nickel	13.3	7.4
Iron	11.8	6.5
Titanium	8.4	4.7
Columbium	7.3	4.1
Tantalum	6.5	3.6
Molybdenum	4.9	2.7
Tungsten	4.6	2.6

Thermal expansion data for room temperature

JET ENGINE



CD-10586
CS-52152

Figure 1

SKETCH OF F-5 AIRCRAFT

SHADED AREAS SHOW COMPONENTS WHERE CARBON-FIBER
REINFORCED RESIN COMPOSITES ARE TO BE USED

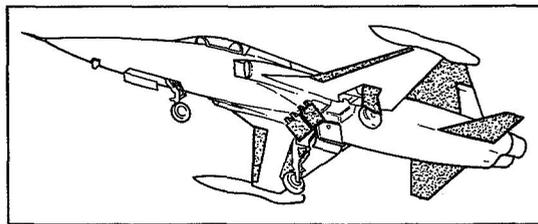


Figure 2

CS-56480

FABRICATION OF RAYON-PRECURSOR CARBON-BASE FIBERS

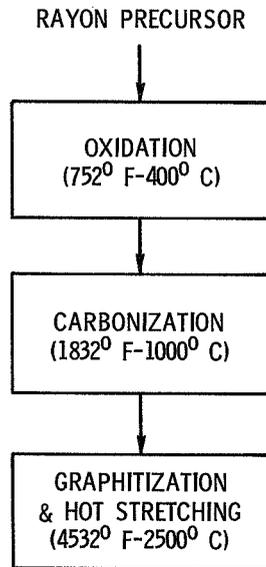


Figure 3

CS-56479

FABRICATION OF PAN-PRECURSOR CARBON-BASE FIBERS

POLYACRYLONITRILE (PAN) PRECURSOR

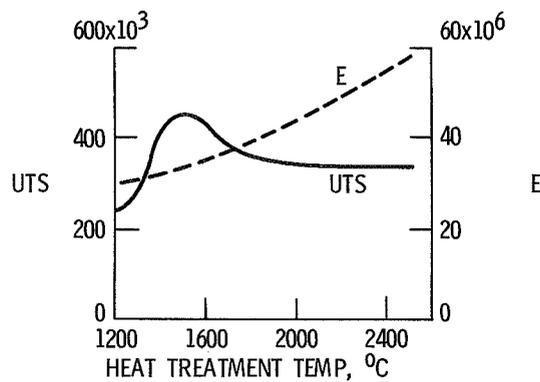
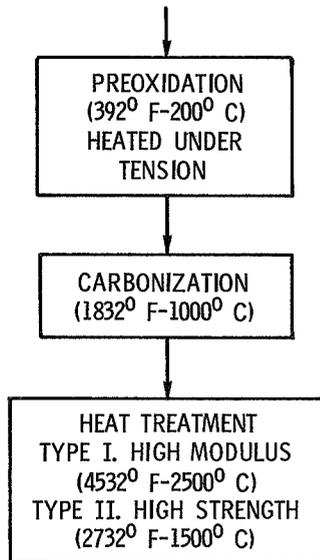
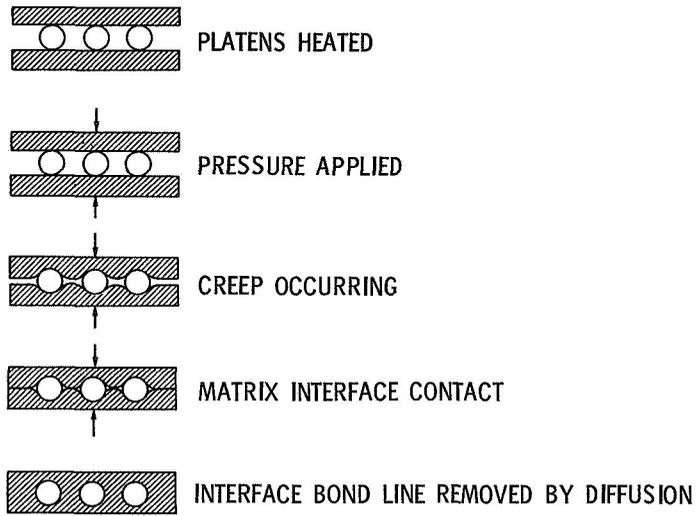


Figure 4

CS-56485

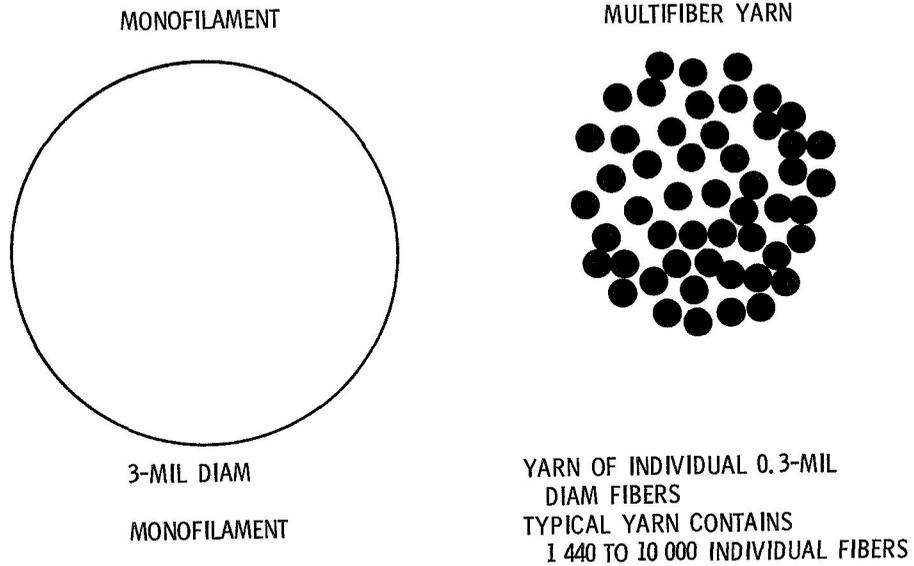
DIFFUSION BONDING PROCESS



CS-56484

Figure 5

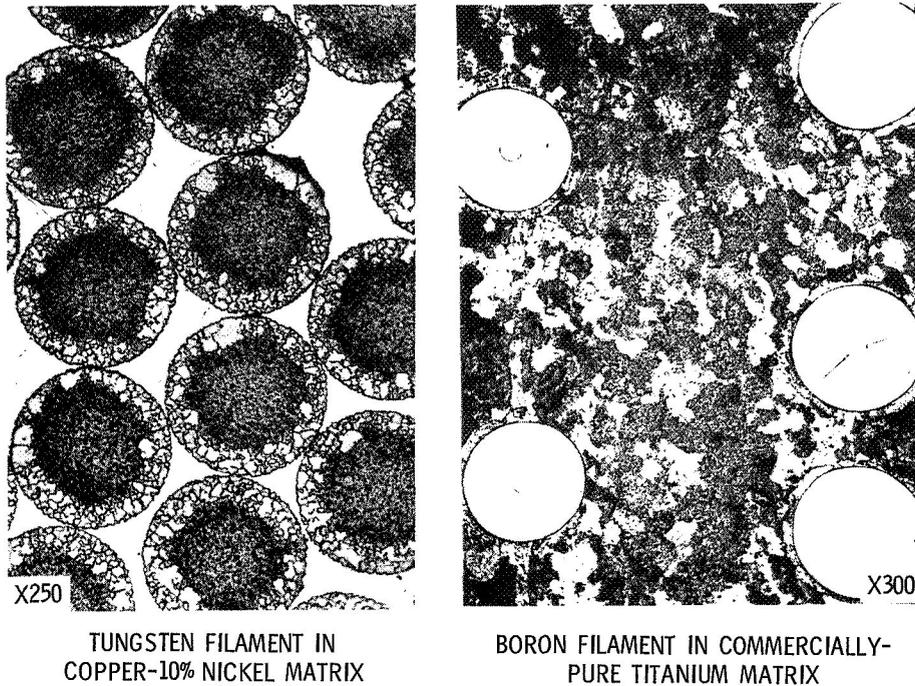
TYPES OF FIBERS



CS-56488

Figure 6

EXAMPLES OF FILAMENT-MATRIX INTERFACIAL REACTIONS



TUNGSTEN FILAMENT IN
COPPER-10% NICKEL MATRIX

BORON FILAMENT IN COMMERCIAL-
PURE TITANIUM MATRIX

Figure 7

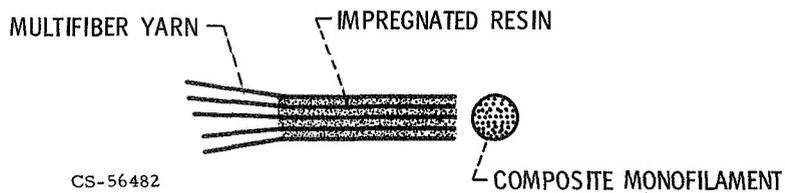
CS-56492

LARGE-DIAMETER CARBON-BASE MONOFILAMENT

RESIN CONVERSION METHOD

FABRICATION STEPS

1. RESIN IMPREGNATION INTO MULTIFIBER BUNDLES
2. CONSOLIDATION OF RESIN SURROUNDING FIBERS
3. CURING OF CONSOLIDATED COMPOSITE MONOFILAMENT
4. CARBONIZATION OF CURED COMPOSITE MONOFILAMENT



CS-56482

Figure 8

LARGE-DIAMETER CARBON-BASE MONOFILAMENTS

RESIN CONVERSION METHOD

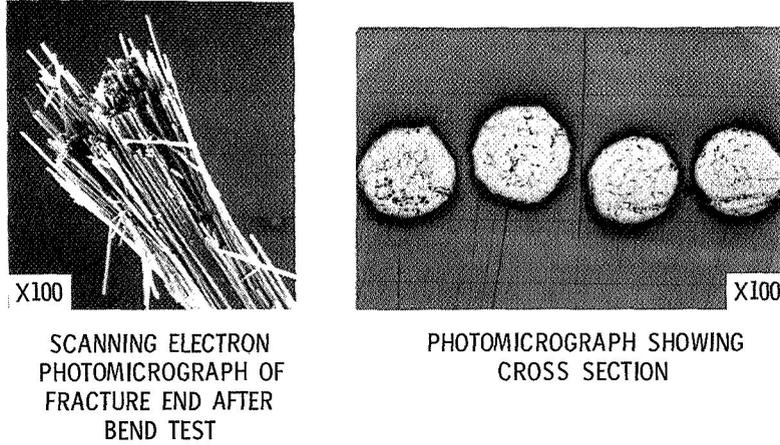


Figure 9

CS-56490

TENSILE STRENGTH RETENTION

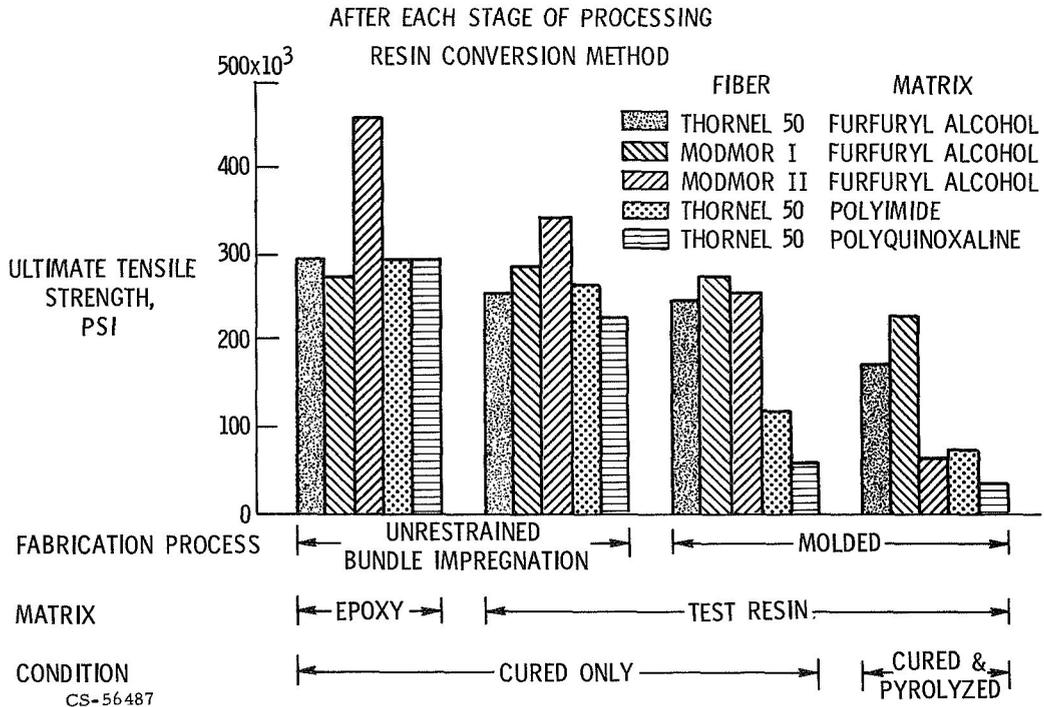


Figure 10

LARGE-DIAMETER CARBON-BASE MONOFILAMENT

PYROLYTIC DEPOSITION

SUBSTRATE: TUNGSTEN OR CARBON

REACTIVE GAS ATMOSPHERE: VARIOUS RATIOS OF HYDROGEN,
HYDROCARBONS, & BORANE GASES

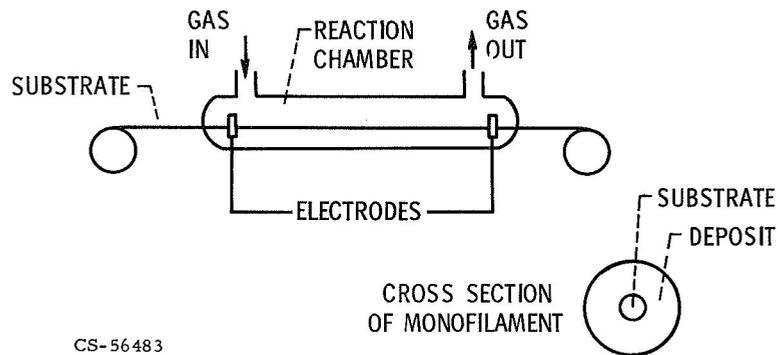


Figure 11

LARGE-DIAMETER CARBON-BASE MONOFILAMENT

PYROLYTIC DEPOSITION METHOD



SCANNING ELECTRON PHOTOMICROGRAPH
OF FRACTURE END AFTER BEND TEST

CS-56491

Figure 12

SPECIFIC STRENGTH AND SPECIFIC MODULUS

COMPARISON OF CARBON-BASE MONOFILAMENTS WITH OTHER FILAMENTS & CONVENTIONAL MATERIALS

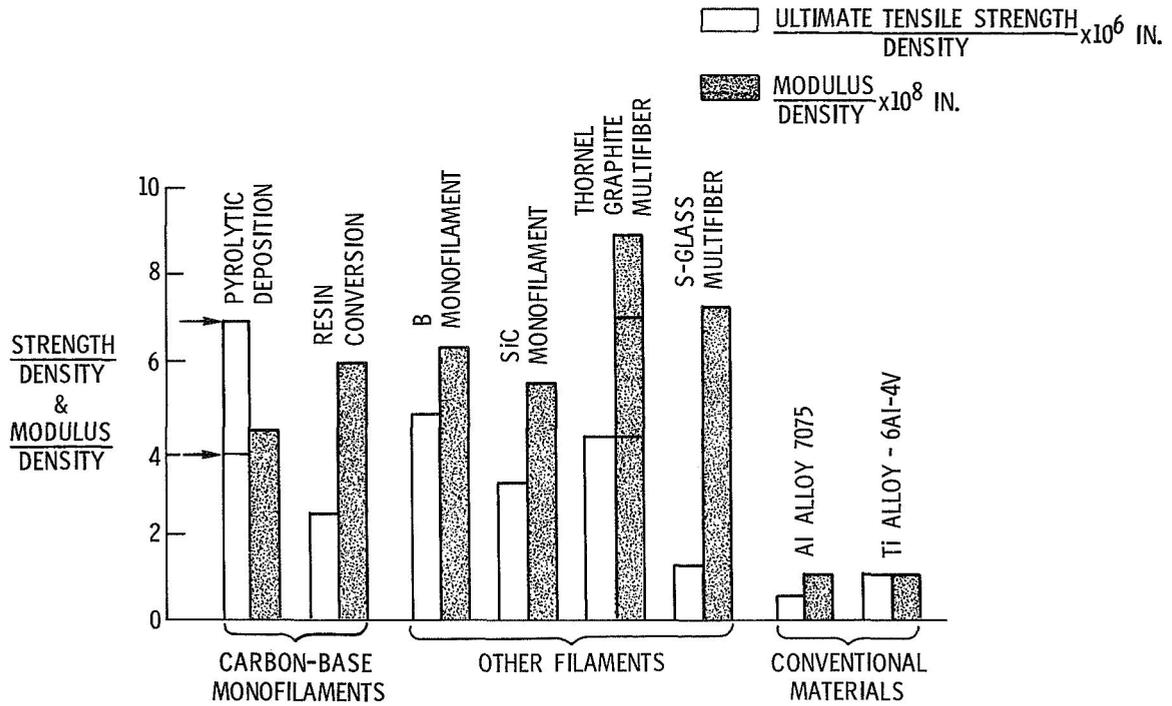


Figure 13

CS-56486