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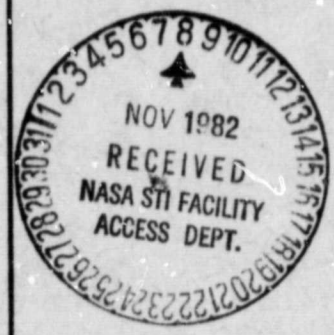
ALUMINA FIBER STRENGTH IMPROVEMENT

R.T. Pepper And D.C. Nelson

Contract No. NAS3-22154

FINAL REPORT



Prepared For:

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Cleveland, Ohio 44135

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September, 1982

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16. Abstract

The effective fiber strength of alumina fibers in an aluminum composite was increased to 173 x 10^3 psi. A high temperature heat treatment, combined with a glassy carbon surface coating, was used to prevent degradation and improve fiber tensile strength. Attempts to achieve chemical strengthening of the alumina fiber by chromium oxide and boron oxide coatings proved unsuccessful. A major problem encountered on the program was the low and inconsistent strength of the DuPont Fiber FP used for the investigation.

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ABSTRACT

The effective fiber strength of alumina fibers in an aluminum composite was increased to 173 x 10^3 psi. A high temperature heat treatment, combined with a glassy carbon surface coating, was used to prevent degradation and improve fiber tensile strength. Attempts to achieve chemical strengthening of the alumina fiber by chromium oxide and boron oxide coatings proved unsuccessful. A major problem encountered on the program was the low and inconsistent strength of the DuPont Fiber FP used for the investigation.

FOREWORD

This work was performed by the Advanced Materials Development Laboratory of Fiber Materials, Inc., Biddeford, Maine for NASA-Lewis Research Center, Cleveland, Ohio under Contract No. NAS3-22154 from September 21, 1979 to December 21, 1980. The NASA Technical Monitor was Mr. David McDanels. The FMI Program Manager was Dr. Roger T. Pepper, with Mr. Daniel C. Nelson assisting as Project Engineer.

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1.0 INTRODUCTION

The ability to fabricate alumina/aluminum composites has been well demonstrated in recent work by Fiber Materials, Inc.,[1,2] E.I. DuPont de Nemours and Co.,[3] and United Technologies Research Center.[4] Outstanding features of this composite are good high temperature strength, high specific modulus, high compressive strength and a projected low-cost ($20/lb). The tensile strength of the composite is satisfactory for many applications, however, increasing it would greatly extend the usefulness of the system. Higher tensile strengths in the composite can only be obtained by increasing the effective tensile strength of the reinforcing fiber.

The fiber, currently available, that has the best combination of properties for fabrication of alumina/aluminum is Dupont's Fiber FP. It has high specific properties, environmental stability and compatability with aluminum alloys. This fiber is continuous, polycrystalline α - Al_2O_3 yarn containing 210 filaments. Each filament has a round cross section with an average diameter of 20 microns. The purity is greater than 99% alumina and the density is 98% of theoretical. The surface has the typical "cobblestone" appearance of glass-free polycrystalline alumina. The average particle grain size in the fiber is 0.5 microns.

The typical filament strengths of Fiber FP measured in single fiber tests at 0.25" gage length are 200-220 x 10^3 psi. Previous work on aluminum matrix composites demonstrated maximum effective fiber strengths of 122 x 10^3 psi based on Rule of Mixtures extrapolation.[1,2] At present, DuPont can raise the strength level by 40-45 x 10^3 psi by coating the fiber with silica. However, the silica coating generally reacts with molten metal and in particular, with lithium-containing aluminum alloys, so the coated fiber has not demonstrated significantly increased aluminum composite strength.

The objective of this program was to strengthen DuPont's Fiber FP to a minimum level of 250 x 10^3 psi as demonstrated in an aluminum matrix composite. Investigations were directed in two areas for possible strengthening techniques. Plastic deformation of the fiber tows at elevated temperatures was investigated to straighten kinked fibers and heal grain boundary cracks and voids to improve fiber tow tensile strength. Chemical strengthening techniques were also explored to alter the fiber surface and increase

fiber strength. A combination of the two techniques proved the most effective for increasing fiber strength.

Tensile strength measurements were performed on alumina/aluminum composite wire prepared using the Ti/B flux infiltration process developed on previous programs.[1,2] The Effective Fiber Strength was then calculated using the Rule of Mixtures formula on the composite wire property. Evaluation of Baseline Fiber FP strengths were performed with considerable variation in fiber quality observed.

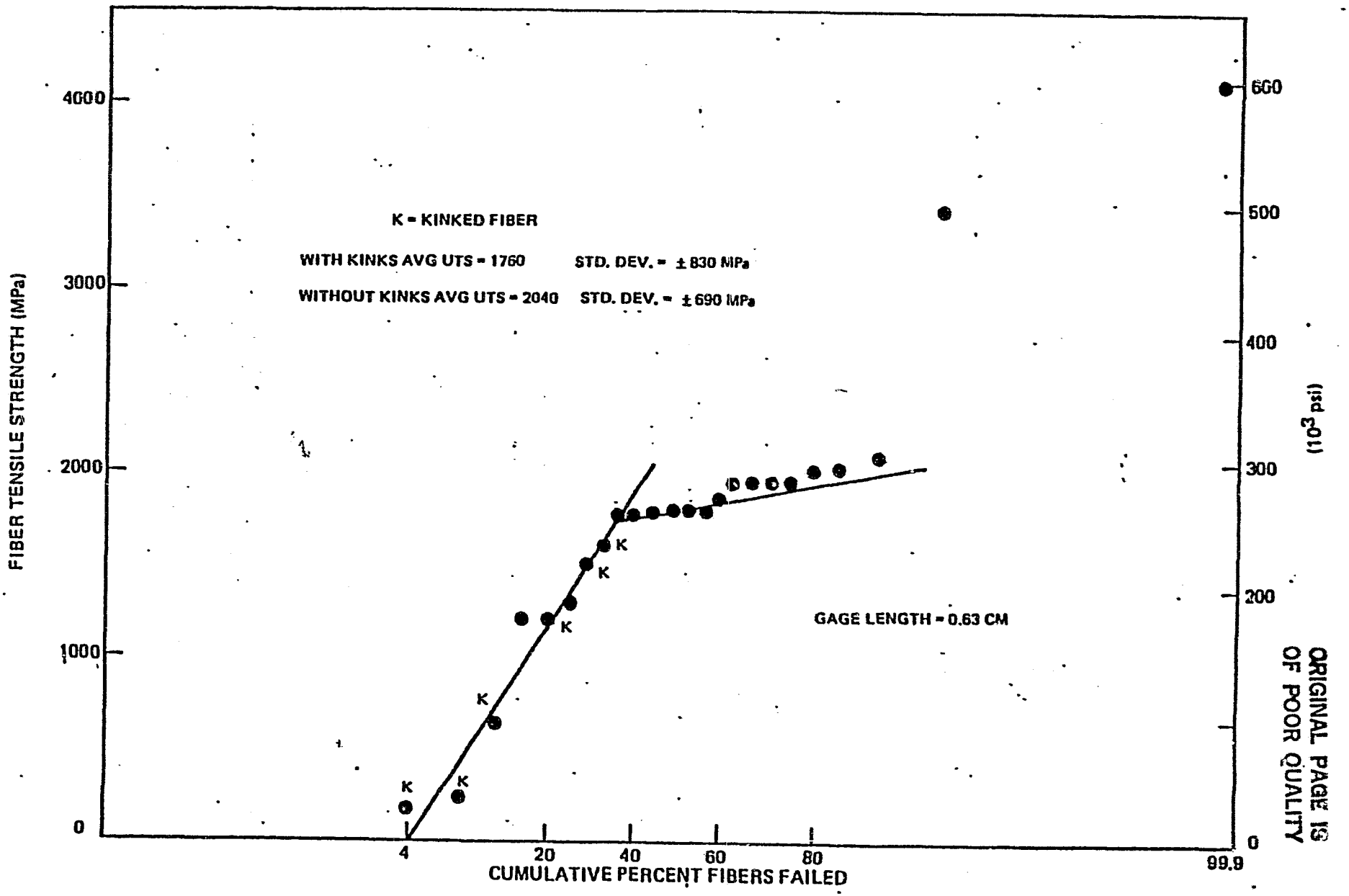


Figure 1. FP FIBER STRENGTH DISTRIBUTION (Reference 4)

2.0 TASK I - METHODS FOR IMPROVING GRAPHITE FIBERS

2.1 SUMMARY OF LITERATURE SEARCH

During Task I of the program, a literature search was conducted into past research and development of strengthening of aluminum oxide. Information gained through the search suggested several possible methods for the improvement in strength of FP alumina fiber.

In work for the Office of Naval Research, Prewo investigated the properties of "as received" FP alumina fibers (See Figure 1)[4]. His analysis of tensile test data obtained by testing individual filaments of FP-IV divides the filaments into three distinct strength populations: low, medium and high strength. The low strength fibers were all found to be somewhat kinked or curved prior to testing. Based on the radii of curvature of the kinks that were observed, stresses of 300 ksi may have been superimposed onto the applied tensile stresses during fiber tensile tests. This would lead to the premature failure of fiber bundles. The low values within this group are not characteristic of the FP material itself, but instead are due to the kinked condition.

The filaments in the medium strength range did not have the visual kinks observed in the low group. Fracture in this group is related to the material structure and defects. Causes of early fracture could have been surface cracks, internal microcracks and voids, weak grain boundaries, local stress concentrations induced by crystal anisotropy, and weak second phases. Prewo was not able to locate the fracture origin due to the granular nature of the fracture surface.

The highest levels of strength (600 ksi) indicate the strength potential of the AL_2O_3 fiber.

A vast amount of work has been performed to investigate the properties of polycrystalline alumina. Two of the most interesting areas of investigation are plastic deformation and chemical strengthening. Knowledge and techniques developed in these areas have provided the basis for improving the properties of alumina fibers.

2.1.1 Plastic Deformation in Fine-Grain Alumina

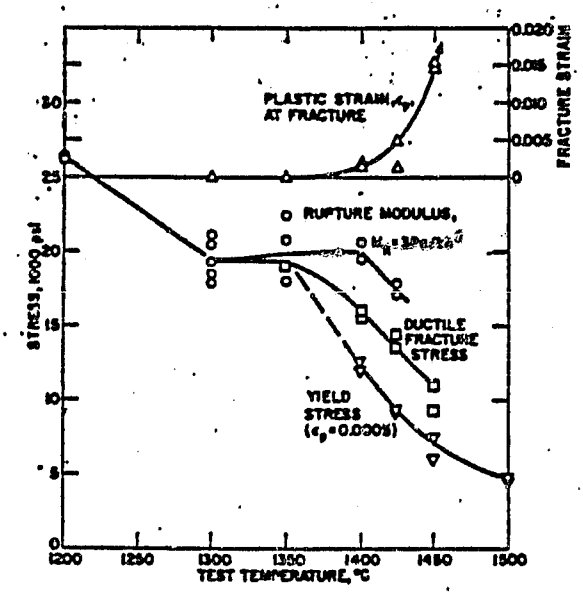
One method commonly used for strengthening fibrous material is stretching. Straightening of kinked fibers and the healing of grain boundary cracks and voids are the major structural changes that occur in polycrystalline fibers to improve tensile strength. Plastic deformation must occur during stretching for these changes to take place.

Recently, a number of studies have demonstrated that, under certain conditions, fine grained polycrystalline aluminum oxide deforms plastically at relatively high strain rates. During work to determine the effect of microstructure on the room and elevated temperature mechanical properties of Al_2O_3 Spriggs, Mitchell and Vasilos[5] found that fine grained alumina (1 to 2μ grain size) exhibited ductile behavior at 1000°C and above. At 1500°C, fine grained alumina specimens bent to the limit of the mechanical testing apparatus without fracturing. The outer fiber strain was approximately 7% at an estimated strain rate of 3×10^{-6} inches per second. Only after increasing the strain rate nearly seven times did the specimen fracture with 1% outer-fiber strain. The strained specimens did not exhibit grain boundary parting and cracks, which suggested to Spriggs, Mitchell and Vasilos that the homogeneous deformation of the alumina grains could have contributed to the plastic behavior.

Larger grained alumina (10-15μ) also exhibited similar plastic behavior; however, the nonlinear deflection before fracture was greatly reduced. The high temperature ductile behavior of alumina has been further substantiated by Passmore, Moschetti and Vasilos[6]. They determined that a brittle-to-ductile transition occurs in a 2-3μ grain size alumina at 1350°C. Above 1350°C the yield stress of polycrystalline alumina decreased following an exponential relationship. Also, the plastic strain at fracture increases rapidly above 1350°C to where, at 1500°C, the specimens were bent to testing limits without fracture. Figures 2 and 3 show these relationships. The low stress and high strain at failure indicate considerable plastic deformation may be easily accomplished at elevated temperatures.

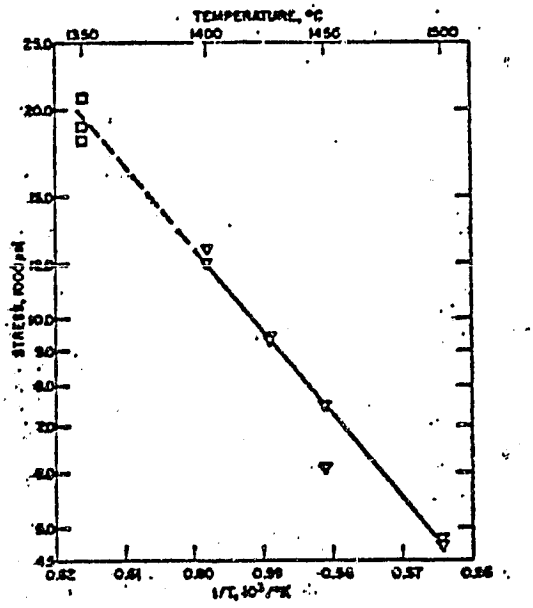
Heuer, Cannon, and Tighe[7] furthered the investigations of plastic deformation in fine-grain alumina. They studied the influence of grain size (1-10μ), strain-rate (2×10^{-6}" - 3×10^{-4}"/sec) and temperature (1100°-1700°C), and attempted to determine the deformation mechanisms. The results

FIGURE 2



Effect of Test Temperature Strength and Ductility of Aluminum Oxide in Bending (Reference 6)

FIGURE 3



Exponential yield stress-temperature relationship with fracture stress (rupture modulus) plotted at 1350°C (Reference 6)

of their work are consistent with the previous work. In Figure 4, the load deflection curve shows the change from brittle to ductile behavior in 1-2μ grain size alumina specimens. At 1350°C the specimens deformed to an outer fiber plastic strain of 1.3 percent at a true strain rate of 6.7×10^{-5} inches/sec without fracturing. With larger grain size materials, higher temperatures were required to obtain equivalent deformation rates. Transmission electron microscopy of the strained specimens disclosed extensive evidence of grain boundary sliding and some rhombohedral twinning. The study indicated that a transition occurs from a diffusional deformation process to a grain boundary sliding process as the grain size decreases.

2.1.2 Chemical Strengthening of Alumina

Surface flaws lead to premature fracture in well-made polycrystalline oxide bodies. This statement is supported by alteration in strength properties from experiments in which the surface perfection of alumina is changed. FP alumina fibers contain many surface flaws such as voids, cracks and inclusions. These flaws undoubtedly contribute to premature failure of the fibers. The use of compressive layers to prestress ceramic bodies has been employed by the glass industry for many years.

Some of the more common methods for creating compressive surface layers are surface crystallization, chill tempering and ion exchange at low temperature. A high temperature chemical reaction, such as the inward diffusion of Cr_2O_3[8] may create a compressive stress on the surface during cooling. Kirchener[9] showed that it is possible to obtain a considerable increase in strength of polycrystalline alumina by chemically treating the surface. Inward diffusion of Cr_2O_3 and Co_xO_y into alumina surfaces at 1500-1800°C was found to give a substantial increase in modulus of rupture value in polycrystalline alumina and sapphire rods[8]. The compressive surface stresses so formed are thought to prevent propagation of cracks from the surface defects thus leading to higher strengths on the application of tensile stress. Experimental techniques, such as the packing of alumina specimens in the reactive oxides prior to firing, were used by these workers. Such techniques could be readily adapted to the low cost processing of alumina fibers.

FIGURE 4

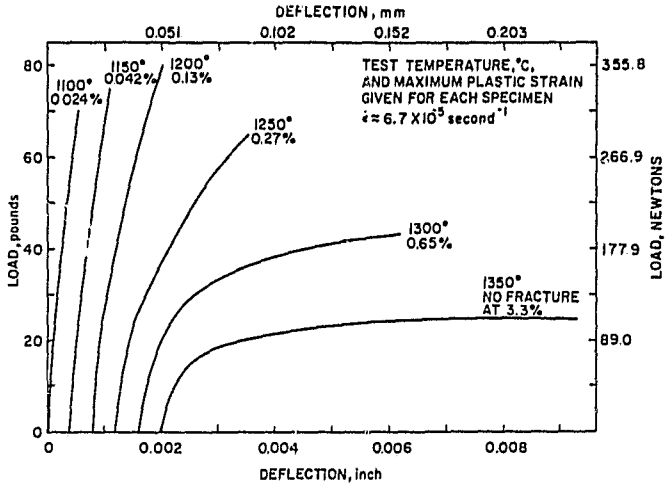


Figure 2 Load-deflection curves for a number of dense, fine-grain ($\sim 1\ \mu$) hot pressed alumina specimens as a function of temperature, indicating a brittle-ductile transition.

(Reference 7)

2.2 PRELIMINARY HOT STRETCHING EXPERIMENTS

Based on the available information, preliminary research was conducted in Task I to evaluate hot stretching. A system was set up where the DuPont Fiber FP could be stretched at temperatures above 1350°C. Figure 5 shows a schematic diagram of the system. The Al_2O_3 fiber was processed under constant strain through the system. It was noted that above 1350°C the fiber showed ductility. At 1650°C the strain to failure was between 20 and 30% as the fiber was continuously processed. At a temperature of 1800°C the tow sintered together and would not negotiate the take-up devices. The load on the fiber tow during the stretching runs was very low and not measurable.

The experimental effort discussed above demonstrated that stretching of the fibers is feasible. The sintering of the tow at the higher temperatures indicates that healing of defects, such as voids, may be achieved by this process, as diffusion bonding between individual fibers is possible under these conditions. Process conditions of temperature, residence time and draw ratio were evaluated to determine their effect on fiber properties in Task II. The simplicity of this system would make this a very cost-effective technique for improving fiber strength.

2.3 PRELIMINARY CHEMICAL TREATMENTS OF Al_2O_3 FIBER TO IMPROVE STRENGTH

The second method evident from the literature for improvement of the strength of Al_2O_3 is chemical strengthening. Surface diffusion of oxides, such as Cr_2O_3 in the Al_2O_3 fiber should establish a compressive layer on the surface of the fibers. It is well known that compressive surface layers help to prevent premature failure due to surface flaws in polycrystalline bodies. FP alumina fibers contain many surface flaws and the chemical strengthening method may significantly improve the strength of the material.

A preliminary experiment was conducted in Task I to evaluate a technique for application of Cr_2O_3 to the surface of Al_2O_3 fibers. The equipment shown in Figure 5 was modified with a dip tank for the application of chromic acid to the fiber surface. A 10% weight solution of chromium trioxide was used; this was reduced at 1000°C in air to Cr_2O_3 on the fiber surface. The tow was then processed at 1650°C where the coating was diffused into Al_2O_3 fiber. Color changes clearly showed the state of the coating at each step

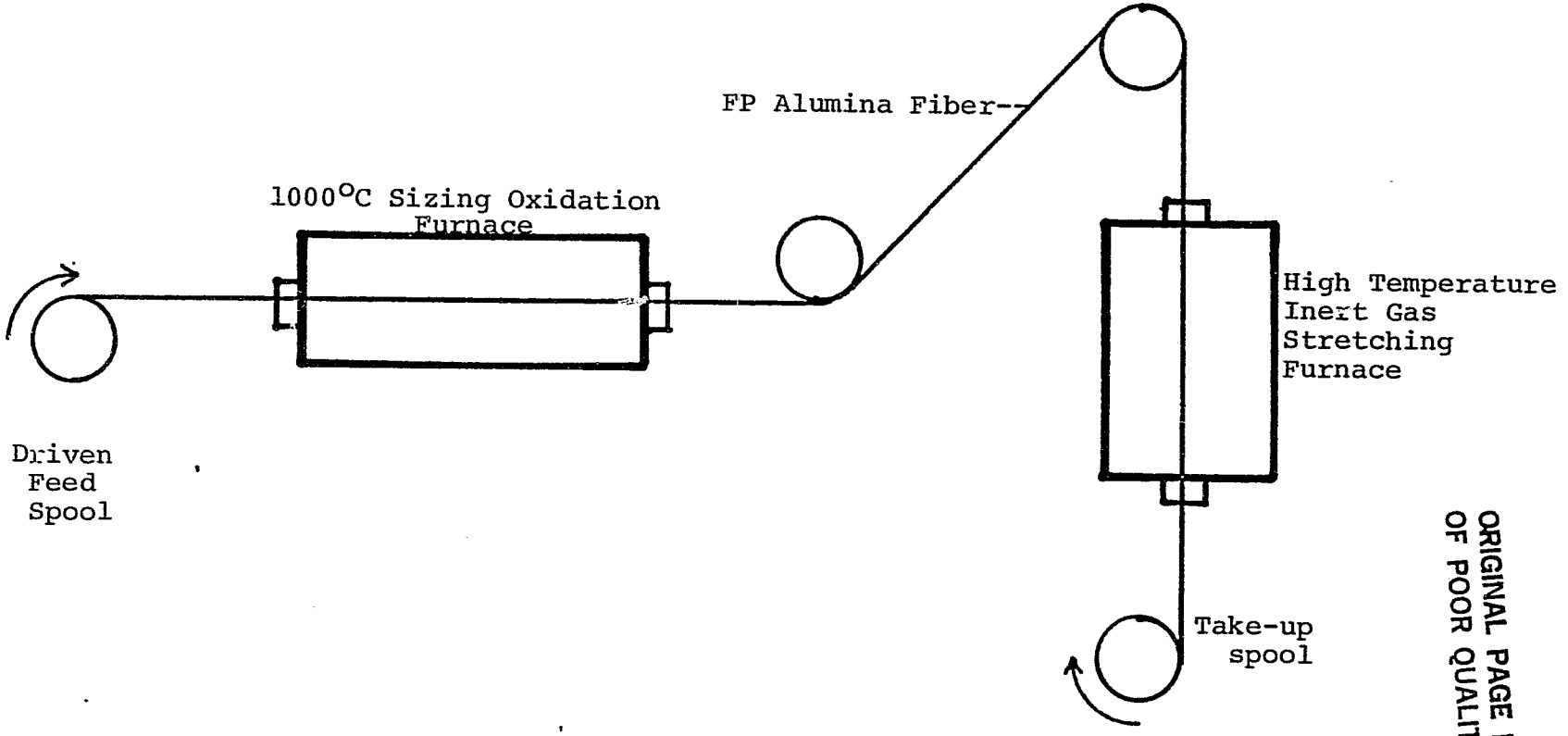


Figure 5

Al_2O_3 Fiber Hot Stretching System

of the process. The red-orange chromic acid solution was converted to a green solid during the reduction at 1000°C. Upon firing to 1650°C, the color of the fiber changed to a light pink, indicating that the Cr_2O_3 had diffused into Al_2O_3. This simple experiment demonstrated that such techniques are feasible and at a very low cost on a large scale. Further evaluation of this process was conducted in Task II.

2.4 BASELINE EFFECTIVE FIBER STRENGTH

To accurately measure any improvements in fiber strengths, a baseline fiber strength was determined on Fiber FP as received from the manufacturer. Samples of alumina fiber were infiltrated with aluminum by the process described below. Tensile properties of the composite wire were determined using standard test methods (See Appendix I). Calculations of the effective fiber strength from the composite wire was done to evaluate baseline fiber performance.

2.4.1 Test Specimen Fabrication

The Ti/B infiltration process developed for the fabrication of metal composite material was used to fabricate tensile test specimens. Modification of the process for alumina fibers was accomplished on NASA Contract No's. NAS3-21013 and NAS3-21371.

The coating process involves the chemical vapor deposition of a titanium/boron layer on the alumina fibers by the reduction of titanium tetrachloride ($TiCl_4$) and boron trichloride (BCl_3) with zinc vapor. The Ti/B coated yarn is then pulled through an in-line aluminum alloy melt to yield a composite wire. The infiltration process is shown schematically in Figure 6. Aluminum alloy A201 was used as the matrix material for all composite prepared on this program.

2.4.2 Effective Fiber Strength Determination

The alumina/aluminum composite wire properties are shown in Table 1 for the as received Fiber FP. From this data the effective fiber strength (EFS) can be determined from the Rule of Mixtures as follows:

$$EFS = \frac{\text{Composite Strength} - (\text{Matrix volume fraction}) \times (\text{Matrix Strength})}{\text{Fiber Volume Fraction}}$$

Figure 6. CONTINUOUS PROCESS FOR ALUMINA/ALUMINUM COMPOSITE WIRE

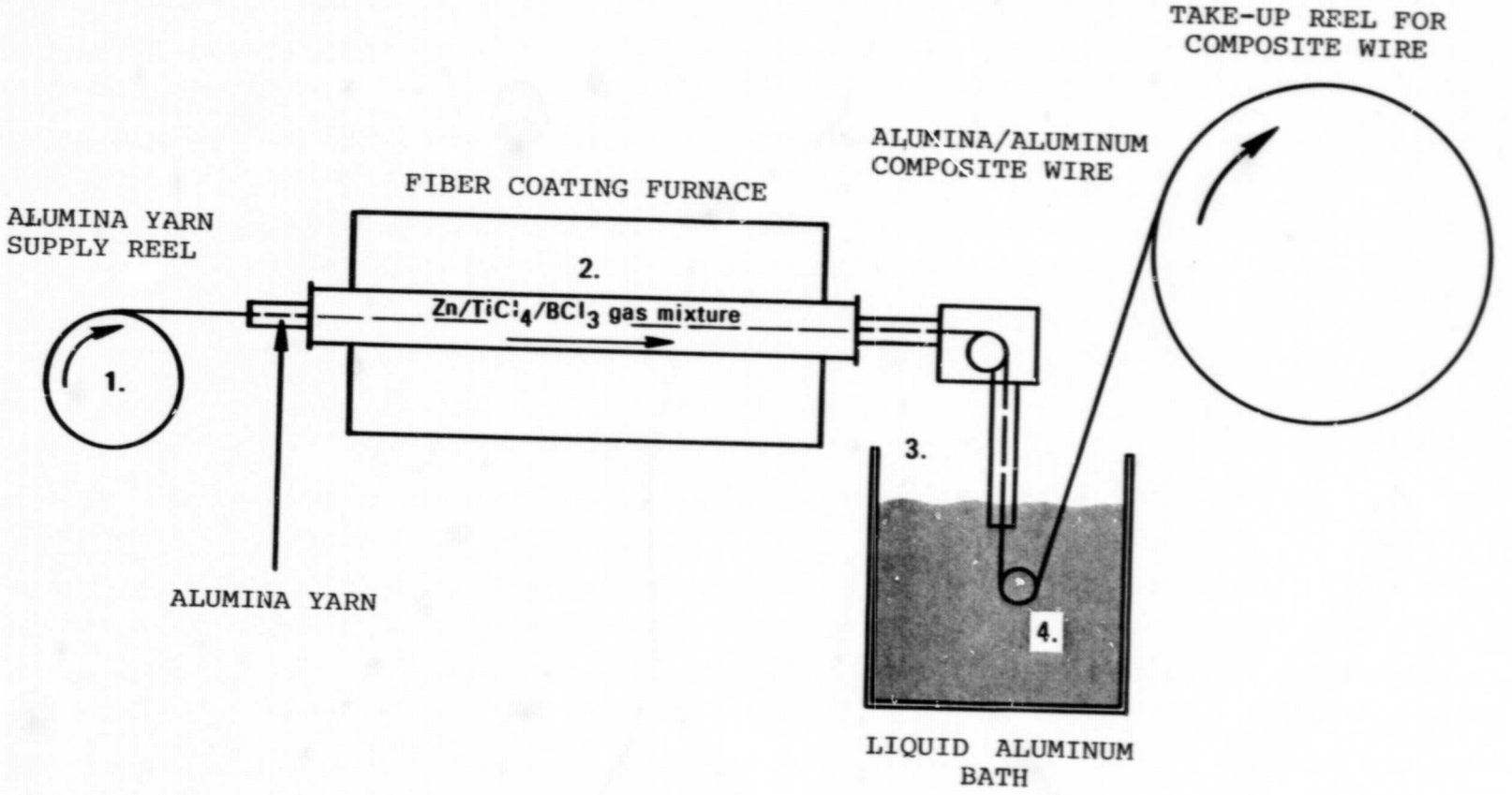


TABLE I. FIBER FP/A201 - BASELINE COMPOSITE PROPERTIES

Ultimate Tensile Strength	30.9×10^3 psi
Tensile Modulus	17.4×10^6 psi
Strain to Failure	0.21%
Composite Wire Cross-Sectional Area	2.91×10^{-4} in^2
Fiber FP Cross-Sectional Area	8.79×10^{-5} in^2
Volume of Fiber	22.5%

A201 aluminum is generally assumed to have a strength of 10×10^3 psi as a matrix in composites. Using this value, with the properties in Table I, the effective fiber strength is calculated as follows:

$$EFS = \frac{30.9 \times 10^3 - (0.775) \times (10 \times 10^3)}{0.225} = 103 \times 10^3 \text{ psi}$$

The actual contribution of the matrix to the composite strength is difficult to evaluate adding some uncertainty to the Rule of Mixtures calculations. A useful property to evaluate is the effective fiber strength, assuming the matrix does not contribute at all to the strength of the composite. The value thus determined is the maximum contribution of the fiber possible in the composite. It can be calculated as follows:

$$(EFS)\ \text{maximum} = \frac{\text{composite strength}}{\text{volume fraction fiber}}$$

$$= \frac{30.9 \times 10^3}{.225}$$

$$= 137 \times 10^3 \text{ psi}$$

From these values it is apparent that the baseline aluminum oxide fiber is degraded when infiltrated with aluminum, since the same baseline fiber tested in an epoxy matrix demonstrated a tensile strength of 176×10^3 psi. Typical Fiber FP/aluminum composite wire, as produced on a previous program, had an average tensile strength of 39.7×10^3 psi. The effective fiber strength calculated from the ROM of that fiber is 122×10^3 psi.

To isolate the cause of strength degradation between the Ti/B flux and the aluminum alloys, fiber was tested after the flux application and prior to infiltration. Alumina fiber, so treated and tested in an epoxy matrix, had a tensile strength of 170.5 ksi. This slight reduction in tensile strength is not indicative of chemical attack but only that due to the handling of the fiber tow or due to fiber variation. It is therefore concluded that the major cause of fiber degradation is the attack of the aluminum alloy on the fiber, which has also been reported earlier by other workers.[4]

2.4.3 Evaluation of Fiber FP Consistency

During preliminary experimental trials, considerable variation in properties was observed on fiber samples. Therefore, an evaluation of the consistency of the "as-received" Fiber FP was conducted. A one-pound spool of Fiber FP was sampled at 1000 foot intervals for mechanical property testing in epoxy matrix. Also, samples from all spools of fiber on hand were tested for mechanical properties. The results of these tests are shown in Tables 2 and 3.

The average tensile strength of spool P284-14 varied from 125.6×10^3 psi to 181.0×10^3 psi when sampled at eight points on the roll. Most of the samples demonstrated tensile strengths well below the manufacturer's specifications. The highest strength observed on any single 10" test sample from spool P284-14 was 193.0×10^3 psi. No significant difference in strength was observed on samples taken from different spools of Fiber FP. This indicates that the properties, as measured on spool P284-14, are probably typical of all spools.

A further study was conducted to try to determine if the inconsistencies of the fibers were controlled by the length of sample or by variation of fibers within the tow. A sample of fiber was tested at various gage lengths from 10" to ¼". The results of these tests are shown in Table 4. It is important to note that the sample used to generate the data in Table 4 was taken immediately before sample P284-14H in Table 2. The latter sample demonstrated a strength of 181×10^3 psi while the former 143.2×10^3 psi and both were tested on a 10" gage length. These samples were less than 100 feet apart on the same spool. The properties shown in Table 4 show scatter in the variation of strength with gage length similar to that observed on the 10" gage length samples in Table 2. The average strengths do appear to be higher with shorter gage lengths and the variation within the samples generally decreased with shorter gage lengths. In no case do the average values reach the 200×10^3 psi minimum strength advertised by the manufacturer. This indicates that there is considerable inconsistency in the 200 fibers of the tow and along the length within the spool. It should be pointed out, however, that the manufacturer values for fiber strength were determined by single fiber testing, whereas bundle tests were conducted on the present program.

TABLE 2

TENSILE STRENGTH OF FIBER FP

(Samples at 1000' intervals on spool P284-14)

Sample	AVERAGE U.T.S	σ_{n-1}	C.V.
P284-14A	175.5×10^3 psi	16.3×10^3 psi	0.093
P284-14C	125.6×10^3 psi	20.8×10^3 psi	0.166
P284-14F	134.0×10^3 psi	26.2×10^3 psi	0.195
P284-14H	181.0×10^3 psi	11.3×10^3 psi	0.063
P284-14J	141.0×10^3 psi	29.0×10^3 psi	0.205
P284-14L	134.3×10^3 psi	7.8×10^3 psi	0.058
P284-14N	129.5×10^3 psi	17.1×10^3 psi	0.132
P284-14P	128.3×10^3 psi	17.2×10^3 psi	0.134

Test Conditions: Epoxy impregnated tow, 10" gage length

TABLE 3

TENSILE STRENGTH OF FIBER FP

(Samples from beginning of spools)

SPOOL #	AVERAGE U.T.S.	σ_{n-1}	C.V.
P284-13	176.0×10^3 psi	6.23×10^3 psi	0.036
P284-14	175.5×10^3 psi	16.3×10^3 psi	0.093
P284-15	153.8×10^3 psi	26.9×10^3 psi	0.175
P284-19	171.0×10^3 psi	14.0×10^3 psi	0.082
P284-21	153.5×10^3 psi	27.3×10^3 psi	0.178
P284-22	159.3×10^3 psi	23.4×10^3 psi	0.147

Test Conditions: Epoxy impregnated tow, 10" gage length

TABLE 4

TENSILE STRENGTH OF FIBER FP

(Variation with gage length)

Sample P284-14-G

Gage Length	UTS	σ_{n-1}	C. V.
10"	143.2×10^3 psi	42.9×10^3 psi	0.339
6"	165.8×10^3 psi	29.6×10^3 psi	0.179
3"	193.2×10^3 psi	21.4×10^3 psi	0.111
1"	150.6×10^3 psi	52.2×10^3 psi	0.347
¼"	187.0×10^3 psi	5.6×10^3 psi	0.03

A spool of fiber was chosen from the results in Table 3 to be used on the final optimization runs of this program. Spool P284-13 was consumed in the preliminary experiments and spool P284-14 showed excessive variation when tested (See Table 2). Spool P284-19 was chosen as one of the strongest and also tested along its length at 500 feet intervals. The fiber between the test samples was used in the strength improvement studies. The tensile strength of these test samples are shown in Table 5. There is significant scatter throughout the roll, however the latter part of the roll (Samples P284-19 E-L) has the most consistenly high strengths found. Fiber from this portion of the roll was used for experiments 035-43B through 035-43 E.

TABLE 5

TENSILE STRENGTH OF FIBER FP

Samples at 500' Intervals on Spool #P284-19

SAMPLE	AVERAGE U.T.S.	σ_{N-1}	C.V.
P284-19A	146.2×10^3 psi	24.7×10^3 psi	0.17
P284-19C	137.2×10^3 psi	19.5×10^3 psi	0.14
P284-19E	190.6×10^3 psi	23.5×10^3 psi	0.12
P284-19G	182.6×10^3 psi	17.8×10^3 psi	0.10
P284-19J	195×10^3 psi	32×10^3 psi	0.16
P284-19L	180×10^3 psi	35×10^3 psi	0.20

Test Conditions: Epoxy Impregnated Tow, 1" Gage Length

3.0 TASK II - ALUMINUM FIBER STRENGTH IMPROVEMENT STUDIES

3.1 HOT STRETCHING OF ALUMINA FIBERS

The hot stretching process, described in Section 2.2 was optimized for temperature, residence time, and amount of stretching. Preliminary fiber samples were tested in an epoxy matrix for determination of mechanical properties. A summary of these experimental results is presented in Table 6.

It was noted that above 1350°C the fiber showed ductility. At 1650°C the strain to failure was between 20 and 30% as the fiber was continuously processed. At a temperature of 1800°C the tow sintered together and would not negotiate the take-up devices. The load on the fiber tow during the stretching runs was very low and not measurable.

The decrease in U.T.S. of samples processed at 1650°C, with long residence times (Sample 035-11#9, 10) may have been caused by excessive grain growth in the Al_2O_3. This is supported by evidence that at shorter residence time the properties of the material improve above those of the as-received fiber. Also, a significant increase in the modulus (+12%) was observed on these samples.

Attempts were made to aluminum infiltrate fiber prepared under conditions similar to sample 035-18#3. The fiber exhibited high tensile strength (203×10^3 psi) when tested on a 10-inch gage length but the dry fiber tow would not support its own weight over the five foot length required in the infiltration process. This indicates that some fiber breakage occured during the stretching operation; probably at points where defects already existed in the individual filaments.

Even though the average filament strength was increased by stretching, filament breakage prevented using such stretched fiber for continuous aluminum infiltration. Further experimentation showed that high temperature heat treatment with minimum applied load and no stretching was possible without significant filament breakage. Fiber so prepared (Sample 035-34-B, Table 6) still demonstrated high tensile strength on 10-inch gage length and would tolerate the handling of long sections of yarn required for infiltration process.

TABLE 6

HOT STRETCHED Al_2O_3 FIBER DATA (EPOXY MATRIX)

SAMPLE	RESIDENCE TIME SEC.	TEMP ^oC	CROSS-SECTIONAL AREA $x10^{-5}$ in^2	% STRETCH	UTS $x10^3$ psi	MODULUS $x10^6$ psi	TOTAL STRAIN %
As Received	-	-	8.79	-	176	53.0	0.33
035-11 #5	48	1325	8.57	3	180.7	54.3	0.316
035-11 #9	48	1650	7.57	16	133	54.0	0.278
035-11 #10	48	1650	7.08	24	99.5	48.8	0.205
035-11 #12*	48	1650	7.15	23	105.5	54.7	0.205
035-11 #14	1.8	1650	7.78	13	206	58.2	0.34
035-18 #3	0.36	1650	7.80	13	203	59.3	0.33
035-34-B	0.36	1650	8.63	0	204	63.2	0.32

* Cr_2O_3 Coated

It was at this point in the experimental investigation that the problem of consistency in the original Fiber FP became apparent. A second sample of fiber, prepared under identical conditions to sample 035-34-B (U.T.S. -204 x 10^3 psi) had a tensile strength of only 150 x 10^3 psi in epoxy. The two fiber samples were prepared from different spools of Fiber FP. Spool P284-17 was consumed in the preliminary investigation of hot stretching (including sample 035-34-B) and was not available for the evaluation of fiber consistency (See Section 2.4.3). It appears that this spool had relatively high tensile strengths compared with Spool P284-15, which was used to produce sample 035-40-B.

Fiber prepared by the high temperature heat treatment did show excellent retention of strength when infiltrated with aluminum. Sample 035-40-B demonstrated an effective fiber strength (EFS) of 144 x 10^3 psi in the aluminum composite. This fiber, when tested in an epoxy matrix, had a strength of 150 x 10^3 psi. This represents a 96% retention of epoxy strand test strength into the aluminum matrix.

3.2 CHEMICAL STRENGTHENING STUDIES

3.2.1 Chromium Oxide Coatings

The process developed in Task I (See Section 2.3) was evaluated for fiber strength improvement in Task II. Alumina fiber was coated with a chromic acid solution and heat treated at 1000°C to produce a Cr_2O_3 coating on the fiber surface. Further heat treatment of the fiber was carried out at 1420°C and 1550°C to allow for diffusion of the coating into the fiber. Fiber samples were generated for infiltration with aluminum and determination of effective fiber strength.

Considerable difficulty was experienced in the aluminum infiltration of the samples prepared with the Cr_2O_3 coatings. Handling characteristics of the fiber were very poor and accumulation of broken filaments, "fuzz", caused tow breakage during the infiltration process on several of the samples. The infiltration chemistry was also altered by the fiber treatments, requiring adjustments to infiltration conditions to achieve wetting. Continuous infiltration was not achieved on any sample. Treatment conditions for the samples are listed in Table 7 with results of the aluminum infiltration trials.

TABLE 7

ALUMINA FIBER SAMPLE PREPARATION CONDITIONS (Cr_2O_3 coated)

Sample	Residence time at 1000°C	Secondary Heat Treatment Temperature	Heat Treatment Residence Time	Aluminum Infiltration Characteristics
035-22-B	30 sec.	-	-	Poor infiltration, excessive fuzz no samples obtained
035-22-D	8.6 sec.	-	-	Poor infiltration, excessive fuzz no samples obtained
035-24-B	8.6 sec.	1420°C	3 sec.	Infiltration Obtained tensile samples prepared
035-24-C	8.6 sec.	1550°C	3 sec.	Infiltration Obtained tensile samples prepared
035-24-D	8.6 sec.	1550°C	8.5 sec.	Poor infiltration, excessive fuzz no samples obtained

Table 8 lists the properties of the small amount FP/Aluminum composite wire, that was obtained from the Cr_2O_3 coated fiber. The sample labelled 'Baseline" gives the data determined on the initial runs of this program. A sample of untreated Fiber FP (fiber from the spool used in the Cr_2O_3 coating studies) was infiltrated immediately prior to the Cr_2O_3 coated samples and is labelled "Control" in Table 8. Variation in the calculated EFS between the "Baseline" and "Control" samples (103 x 10^3 psi vs. 90.5 x 10^3 psi) can be accounted for by variation of as-received Fiber FP properties, variation in interface reactions between fiber and matrix due to infiltration conditions, and statistical sampling errors in the two batches of composite wire.

Improvements in the EFS were observed for the Cr_2O_3 coated fiber samples. Fiber heat treated at 1420°C shows a 10% improvement over the EFS of the "Control" sample. At 1550°C, a 25% improvement in EFS was observed over the "Control" sample. The higher temperature sample shows a 10% increase in EFS above the "Baseline" fiber property. No further evaluation of this process was conducted due to the small strength improvement and the poor infiltration characteristics.

3.2.2 Boron Oxide Coatings

Evaluation of low temperature glassy surface coatings for improving fiber strengths was conducted during Task II. Low temperature glasses were evaluated to heal surface defects in Al_2O_3 fiber while avoiding undesirable grain growth that occurred at high temperatures. Compatibility with aluminum was also a consideration in the choice of coating materials.

Coatings were applied to Fiber FP from a boric acid solution and reduced at 1000°C under N_2 to form B_2O_3 glass. Results of fiber tested in an epoxy matrix showed severe fiber degradation by this process. Excessive reactions between the Al_2O_3 and B_2O_3 may be the cause of the reduction in tensile strength observed. Baseline Fiber FP tensile strength, in epoxy, measured 176 x 10^3 psi; B_2O_3 coated fiber FP had a tensile strength of 107 x 10^3 psi. Aluminum composite samples were not prepared with this fiber.

TABLE 8

TENSILE PROPERTIES OF ALUMINA/ALUMINUM COMPOSITE WIRES

Sample	Heat Treatment Temperature	Average Composite U.T.S. $x10^3$ psi	Volume Fraction Fiber	Effective Fiber Strength $x10^3$ psi
Baseline		30.9	0.225	103
Control		26.9	0.210	90.5
035-24-B *	1420°C	42.1	0.360	99.2
035-24-C *	1550°C	57.0	0.450	114

*Samples coated with Cr_2O_3 prior to heat treatment.

3.2.3 Glassy Carbon Coatings

Another low temperature glass evaluated as a coating material was glassy carbon. Coatings were applied to Fiber FP with good success by decomposition of acetylene at 1000°C under nitrogen. The glassy nature of the coating material was evident by deposits within the coating chamber and the improved texture of the fiber. Figure 7 shows a schematic of the coating process.

Initial fiber samples coated with glassy carbon demonstrated an epoxy tensile strength of 250 x 10^3 psi (Sample 035-32-J). A second batch of fiber was prepared under similar conditions for infiltration with aluminum (Sample 035-38-C). The fiber used for the second batch was from a different spool and demonstrated a tensile strength of 212 x 10^3 psi in epoxy. The effective fiber strength of this fiber in aluminum was 155 x 10^3 psi.

Glassy carbon was also evaluated as a coating in conjunction with high temperature heat treatment at 1650°C. The uncoated heat treated samples, when infiltrated with aluminum, yielded an effective fiber strength of 144 x 10^3 psi.

A batch of heat treated fiber from sample 035-40-B was further processed by applying a glassy carbon coating from acetylene at 1000°C. This sample (035-40-D) demonstrated an effective fiber strength of 173 x 10^3 psi in an aluminum composite, a significant improvement over the 103 x 10^3 psi baseline effective fiber strength. A summary of these experiments is listed in Table 9.

It is important to note that the high effective fiber strengths were achieved from a spool of fiber that demonstrated relatively low strength in epoxy tests. Samples 035-40-B and 035-40-D showed greater than 90% retention of fiber strength in the aluminum composite.

From the data shown in Table 9 the combination of high temperature heat treatment with glassy carbon coating provided the best effective fiber strength. Further optimization of the glassy carbon coating temperature was performed both on the as-received Fiber FP and on the high temperature heat treated fiber. Results from these trials are shown in Table 10. The optimum temperature for coating fibers was found to be 1000°C, this applied to both the heat treated and as-received fiber samples.

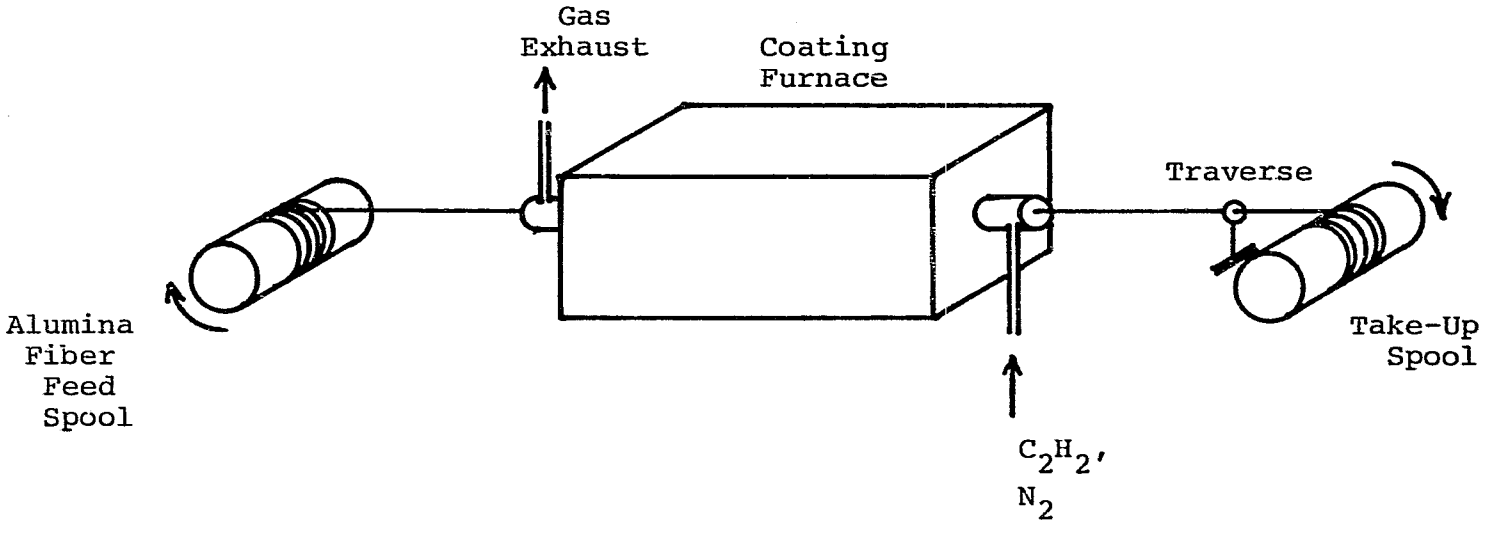


FIGURE 7. Glassy Carbon Coating System

TABLE 9

GLASSY CARBON COATED ALUMINA FIBER DATA

Sample	Treatment	Fiber Tow Strength In Epoxy x 10^3 psi	Aluminum Composite Strength x 10^3 psi	Volume Fraction Fiber	Effective Fiber Strength x 10^3 psi
Baseline Spool #P284-13	as received	176	30.9	0.225	103
035-32-J Spool #P284-17	glassy carbon coated at 1000°C	250	-	-	-
035-38-C Spool #P284-15	glassy carbon coated at 1000°C	212	45.4	0.24	155
035-34-B Spool #P284-17	heat treated at 1620°C	204	-	-	-
035-40-B Spool #P284-15	heat treated at 1620°C	150	43.5	0.25	144
035-40-D Spool #P284-15	heat treated at 1620°C and glassy carbon coated at 1000°C	185	58.8	0.30	173

TABLE 10

GLASSY CARBON COATED ALUMINA FIBER DATA

SAMPLE	TREATMENT	ALUMINUM COMPOSITE STRENGTH x 10^3 psi	VOLUME FRACTION FIBER	EFFECTIVE FIBER STRENGTH x 10^3 psi
035-43-B Spool P284-19F	Heat treated at 1650°C Glassy Carbon coated at 900°C	48.8	0.255	162
035-43-C Spool P284-19F	Heat treated at 1650°C Glassy Carbon coated at 1100°C	46.5	0.246	158
035-43-D Spool P284-19H	Glassy carbon coated at 1100°C	40.6	0.219	150
035-43-E	Glassy carbon coated at 900°C	40.8	0.235	141

3.3 OPTIMUM TREATMENT CONDITIONS

The optimum conditions found on this program for the treatment of alumina fibers are listed in Table 11. A high temperature heat treatment, followed by an application of glassy carbon to the fiber surface, was found to be the most effective for improving the effective fiber strength.

Composite properties from fiber produced by this process are also listed in Table 11. The effective fiber strength of 173×10^3 psi is a significant improvement above the baseline effective fiber strength of 103×10^3 psi. Correspondingly, the tensile strength of 58.8×10^3 psi is a significant improvement for a 30 volume % alumina/aluminum composite over previous work.[1,2]

These conditions were chosen for the treatment of a one-pound lot of Fiber FP. The improved alumina fiber was delivered to NASA per contract requirements.

TABLE 11

OPTIMUM ALUMINA FIBER TREATMENT

High Temperature Heat Treatment Conditions

Temperature:	1650°C
Residence Time:	0.9 sec
Atmosphere:	Argon

Glassy Carbon Coating Conditions

Temperature:	1000°C
Residence Time:	60 sec
Atmosphere:	N_2/C_2H_2

Aluminum Composite Properties (Sample 035-40-D)

Ultimate Tensile Strength	58.8×10^3 psi
Tensile Modulus	13.8×10^6 psi
Strain to Failure	0.53%
Composite Wire Cross-Sectional Area	2.98×10^{-4} in^2
Fiber Cross-Sectional Area	8.83×10^{-5} in^2
Volume Fraction Fiber	0.30
Effective Fiber strength	173×10^3 psi

4.0 DISCUSSION OF TECHNICAL RESULTS

One of the major problems encountered on this program was the consistency of the as-received Fiber FP. Variations of over 50% in tensile strength of the fiber was observed. Fiber samples less than 100 feet apart had a strength variation of over 25%. This variation prevented an accurate determination of the actual strength improvements due to the treatment processes.

Evaluation of the strengthening process was done by maximizing the effective fiber strength with a careful eye toward the properties of the starting fiber. The optimum conditions chosen in Table 11 were picked for the exceedingly high effective fiber strength (173×10^3 psi) produced from fiber so treated. This strength level is a considerable improvement over the baseline EFS of 103×10^3 psi and is greater than can be accounted for by fiber variation alone. Previous work has shown maximum effective fiber strengths of 122×10^3 psi.[1,2]

Observations made during the treatment processes demonstrated that the high temperature heat treatment was effective in improving fiber quality if the residence time was minimized. Long residence time probably allowed excessive gain growth to occur, causing a reduction in tensile strength. The improvement in effective fiber strength by heat treatment may be due to a reduction in surface flaws which can act as points of attack by molten aluminum.

The chromium oxide coating studies were effective in producing small strength improvements but they may have been due to the heat treatment process. Significant strength improvement was not observed for samples where the coating was allowed to diffuse into the fiber. It was hoped that this would establish a surface compressive layer strengthening the filaments, however, the time and temperature required for significant diffusion were similar to those that caused strength loss upon heat treatments alone. The attainment of the desired chromium oxide containing surface layer may have been offset by the undesired grain growth. The adverse effect of the chromium oxide on the infiltration characteristics also limited the usefulness of this process.

The glassy carbon coating was applied to the fiber at temperatures below those at which significant grain growth occurred, and demonstrated an improvement in tensile strength. One possible mechanism for this improvement is the healing of surface flaws by the glassy nature of the coating. The carbon coating also improved the stability of the fibers in aluminum and improved the wetting characteristics of the fibers in the aluminum infiltration process.

5.0 CONCLUSIONS

1. One of the major problems limiting the utilization of DuPont's Fiber FP in alumina/aluminum composites is the low and inconsistent Fiber Strength.

2. High temperature heat treatment at 1650^{o}C significantly reduced the degradation of alumina fibers during infiltration with aluminum.

3. Glassy carbon coatings, applied to the surface of alumina fibers, can increase their tensile strength.

4. A combination of high temperature heat treatment and glassy carbon surface coating of alumina fiber significantly improves the effective fiber strength of alumina/aluminum composites.

5. The glassy carbon surface coating developed for strength improvement also improves fiber handling and aluminum wetting characteristics.

6. Attempts to achieve chemical strengthening by the use of Chromium oxide and Boron oxide coatings were unsuccessful.

6.0 RECOMMENDATIONS

1. Before further work is conducted in strengthening Fiber FP, a detailed evaluation of fiber characteristics should be performed. This investigation is required to obtain a firm data base as to the true properties of Fiber FP and to determine the primary cause of fiber failure.

2. Once detailed evaluation of Fiber FP is completed, further investigations are recommended to enhance fiber strength by the heat treatment and glassy carbon coating techniques developed on this program. Processing conditions need to be further optimized.

3. A more detailed study of composite fabrication techniques should be conducted. Direct infiltration by casting of shaped fiber preforms using the strengthened glassy carbon coated FP fibers should be investigated. The improved wettability observed in the Ti/B flux process indicates that direct casting may be feasible with these fibers.

4. Aluminum composite properties should be more completely evaluated for a fuller understanding of material characteristics. A quantity of treated fiber should be prepared at various conditions to produce sufficient composite wire for fabrication of bulk composite shapes of bars and panels. Mechanical testing is recommended to determine the off-axis properties of the composite system.

7.0 REFERENCES

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8.0 APPENDIX

STANDARD TEST METHOD

FOR

DETERMINING TENSILE PROPERTIES

OF

ALUMINA/ALUMINUM COMPOSITES

8.1 SCOPE

This method has been developed to insure acquisition of accurate repeatable tensile properties of fiber reinforced materials when tested under well-defined conditions of pretreatment, temperature, humidity, and testing rates. This method complies in substance with ASTM Test Method D638.

8.2 DEFINITION OF TERMS

Definition of terms applying to this method are listed in the following paragraphs.

Tensile Strength (nominal) is the maximum tensile load per unit area of the minimum original cross-section within the gage length, carried by the test specimen at any time during the test sequence. It is expressed in force per unit area, usually pounds per square inch.

Gage Length is the original length of the portion of the specimen over which strain is determined.

Strain is the ratio of the change in length of the gage section to the original gage length and is usually expressed in inches per inch.

Percent Total Strain is the total change in length produced in the gage section of the test specimen by the tensile load applied during the test sequence divided by the initial gage length and multiplied by 100.

Strain at Maximum Stress is the strain seen by the gage length of the test specimen at the highest value of load achieved.

Tensile Stress-Strain Curve is a diagram in which the values of tensile stress are plotted as ordinates and corresponding values of tensile strain as abscissas.

Offset Yield Stress is the stress at which the strain exceeds by a specified amount (the offset) an extension of the initial proportional portion of the stress-strain diagram. It is expressed in force per unit area, usually pounds per square inch.

Proportional Limit is the point on the stress-strain diagram at which the stress-strain ratio ceases to maintain a linear relationship.

Modulus of Elasticity is the ratio of stress (nominal) to corresponding strain below the proportional limit of the material. It is expressed in force per unit area, usually pounds per square inch.

Stress Rate is the change in tensile stress per unit time. It is expressed in force per unit area per unit time, usually pounds per square inch per minute.

Strain Rate is the change in tensile strain per unit time. It is usually expressed as inches per minute.

8.3 SIGNIFICANCE

This method is designed to produce tensile properties data with the accuracy and detail required to characterize the material and permit sound engineering decisions concerning its applications. Tensile properties may vary with specimen geometry, preparation, area from which test specimen is taken, changes in the testing environments, and changes in testing rates.

8.4 APPARATUS

Testing Machine - A testing machine with precisely controlled constant crosshead velocity. The crosshead drive system shall be insensitive to loading and shall be capable of maintaining a constant velocity throughout the entire test sequence.

Grips - Grips used for restraining the test specimen during the test sequence shall be self aligning as the specimen is stressed to insure axial alignment of the specimen and loading axis of the testing machine. Finely serrated grips (25 teeth/inch) should be used on flat surface tensile specimens with highly polished shoulder bearing grips being used on cylindrical samples.

Load Weighing System - The load weighing system shall be capable of indicating the total tensile load carried by the specimen during the test sequence. The system shall be free from inertial lag at the specified rate

of testing and shall indicate the load with an accuracy of ± 0.5% of the indicated load or better. The accuracy of the load weighing system shall be verified in accordance with ASTM Methods E4, "Verification of Testing Machines".

Strain Sensor - A suitable strain sensor shall be used on all test specimens to continuously determine the change in length of the gage section during the entire test sequence. The instrument shall be capable of transmitting a signal for autographic recording of strain during the test sequence. The instrument shall be free from inertial lag at the specified testing rate and be accurate to ± 0.25% of its calibrated range or better.

Recorder - A recording system shall be used that can record stress (load) and strain simultaneously during the test sequence in either a stress vs. time or in a stress-strain-time format, and is capable of maintaining the same level of accuracy as the source signals.

Environmental Enclosure - The environmental enclosure shall be able to provide the capabilities required in the materials test specifications without interfering with the operation of the testing machine or diagnostic equipment.

Micrometers - Micrometers reading to at least 0.001" ± 000 shall be used to measure width, thickness, diameter, and length of test specimen before testing.

8.5 TEST SPECIMENS

Test specimens shall be designed to insure plane strain in the cross-section of the gage length. Specimens requiring machining shall be prepared machining (surface grinding primarily) with the depth of cut being such that surface heating of the material is held to an absolute minimum. All surfaces of the test specimen shall be free from visible flaws and there shall be no undercutting at the transition from gage section to blend radius. Composite yarn or wire specimens shall have fiberglass loading spreading tabs bonded to each end at the desired test length.

8.6 NUMBER OF TEST SPECIMENS

At least three specimens shall be tested in each direction of interest.

8.7 SPEED OF TESTING

Speed of testing shall be specified as either a constant stress rate of a constant strain rate during the elastic portion of the stress-strain curve,

8.8 PROCEDURE

Measure the width and thickness of specimens with rectangular cross-sections or the diameter of cylindrical specimens to the nearest .001" at several points along the gage length. Install test specimen in the grips taking care to align the specimen and grip assembly on the central axis of the machine. Maximum strain gradient across the specimen shall be less than 5% of the total strain at failure. Install the strain sensor on specimen (unless bonded strain gages are used). Set crosshead velocity to give the specified stress or strain rate. Prepare recorder for recording test sequence. Start testing machine and record test data.

8.9 CALCULATIONS

Tensile Strength - Calculate the tensile strength by dividing the maximum load in pounds by the original minimum cross-sectional area of the test specimen. Express the results in pounds per square inch (psi) and report the result to three significant figures.

Percent Total Strain - Calculate the percent total strain by counting the number of blocks of chart displacement and multiplying by the block value in inches per inch times 100.

Modulus of Elasticity - Calculate the modulus of elasticity by extending the initial linear portion of the stress-strain (load-strain) curve and dividing the change in stress by the corresponding change in strain between two points on the extended line (preferably zero and full scale). The modulus values shall be calculated using the initial cross-sectional area and expressed in pounds per square inch (three significant figures).

Average (Mean) Value ($\overline{X}$)- Calculate the average value of each parameter by summing all value of that parameter and dividing by the number of values.

Estimate of the Standard Deviation(s) - Calculate the estimate of the standard deviation of each parameter using the following formula:

$$S = \frac{NEX^2 - (EX)^2}{N(N-1)}$$

where:

S = Estimate of the standard deviation
X = Value of a single observation
N = Number of observations

Coefficient of Variance (CV) - Calculate the coefficient of variance by dividing the estimated standard deviation(s) by the mean $\bar{x}$ and multiplying by 100. Express value as a percentage.

Range (R) - The range in the spread of the data used in a statistical calculation.

8.10 REPORT

The report should include the following:

Complete identification of the material tested, including type, sources serial number, form, principal dimensions, and prior history;
Method of preparing test specimen;
Type of test specimen and dimensions;
Orientation of test specimen;
Conditioning procedure followed;
Testing environment;
Laboratory environment;
Number of specimens tested;
Speed of testing;
Ultimate tensile stress and yield stress (if applicable);
Modulus of elasticity;
Percent total strain to failure;
Proportional limit;
Statistics outlined in Section 9;
Test date; and
Operator's name.