

**AD-753 711**

# **An Investigation of the Mechanical Properties of Silicon Carbide and Sapphire Filaments**

**Air Force Materials Laboratory**

**SEPTEMBER 1972**

Distributed By:

**NTIS**

**National Technical Information Service  
U. S. DEPARTMENT OF COMMERCE**

AFML-TR-72-180

AD753711

**AN INVESTIGATION OF THE MECHANICAL  
PROPERTIES OF SILICON CARBIDE  
AND SAPPHIRE FILAMENTS**

*R. L. CRANE*

TECHNICAL REPORT AFML-TR-72-180

SEPTEMBER 1972

DDDC  
RECEIVED  
DEC 1 1972  
RECEIVED  
E

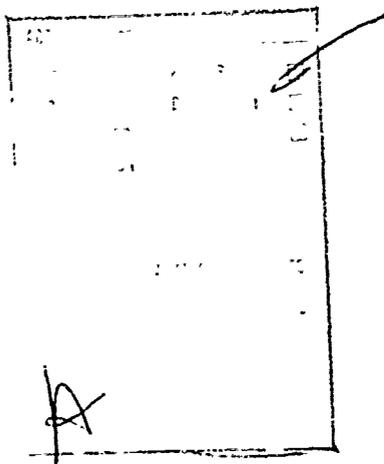
Approved for public release; distribution unlimited.

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U S Department of Commerce  
Springfield VA 22151

AIR FORCE MATERIALS LABORATORY  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.



Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE AN INVESTIGATION OF THE MECHANICAL PROPERTIES OF SILICON CARBIDE AND SAPPHIRE FILAMENTS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) R. L. Crane			
6. REPORT DATE September 1972		7a. TOTAL NO. OF PAGES 28 37	7b. NO. OF REFS 44
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-72-180	
b. PROJECT NO. 7351		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. Task 735107			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson AFB, Ohio	
13. ABSTRACT The mechanical properties of SiC and Al <sub>2</sub> O <sub>3</sub> (sapphire) filaments pertinent to the initial design of a metal matrix composite have been documented. The strength contributions of these filaments to a composite were simulated with tensile tests of self-abraded samples. The strength of virgin SiC filament was found to decrease linearly to about 1100°C (2012°F) and exponentially above this temperature. The abraded strength was found to be constant, as a function of temperature, to about 1100°C (2112°F). The loss of high temperature strength was correlated with the reaction between SiC and the fiber's W core. The strength of single crystal sapphire as a function of temperature was determined for both a- and c-axis filaments. Similar tests were conducted on ruby fiber (Cr <sub>2</sub> O <sub>3</sub> doped sapphire). Ruby fiber was found to be significantly stronger than pure sapphire and insensitive to abrasion above 500°C (932°F). The strength of ruby fiber as a function of Cr <sup>+3</sup> content showed that the optimum dopant level has not yet been reached. A filament strength of 250 ksi at 1100°C (2012°F) was predicted for a c-axis fiber with an optimum Cr <sup>+3</sup> concentration. The use of abraded filament strength to predict the in-situ fiber strength contribution was found to be valid for Al <sub>2</sub> O <sub>3</sub> reinforced Ti.			

DD FORM 1473  
NOV 55

Ia

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Silicon carbide Sapphire Alumina Mechanical Properties Filaments Composites Modulus Tensile Strength						

*I k*

**AN INVESTIGATION OF THE MECHANICAL  
PROPERTIES OF SILICON CARBIDE  
AND SAPPHIRE FILAMENTS**

*BY*  
*R. L. CRANE*

Approved for public release; distribution unlimited.

*IC*

## FOREWORD

This report was prepared by R. L. Crane, Metal Composites Branch, Metals and Ceramics Division, Air Force Materials Laboratory. The work was conducted under Project No. 7351, "Metallic Materials," Task No. 735107, "Metal Matrix Composites."

The research was conducted during the period January 1972 to August 1972. This report was submitted for publication by the author in August 1972.

The author is very much indebted to Mr. D. V. Dempsey of the University of Dayton Research Institute for his assistance in altering many pieces of scientific equipment, which made the timely accomplishment of this task possible.

This technical report has been reviewed and is approved.

*C. D. Stuber*

C. D. STUBER,  
Chief, Metal Composites Branch  
Metals and Ceramics Division  
Air Force Materials Laboratory

TABLE OF CONTENTS

	PAGE
Introduction . . . . .	1
Literature Survey . . . . .	2
Experimental Procedure . . . . .	5
Results and Discussion . . . . .	10
Summary and Conclusions . . . . .	24
References . . . . .	25

## ILLUSTRATIONS

FIGURE		PAGE
1	File card gripping technique for room temperature filament tensile tests.	7
2	Hypodermic needle-pivot bearing gripping technique for elevated temperature filament tensile tests.	7
3	Schematic diagram of the apparatus for filament modulus determinations.	9
4	Strength of Si rich AVCO SiC filament as a function of temperature.	12
5	Tensile strength as a function of temperature for both virgin and abraded, stoichiometric AVCO SiC filament.	12
6	Scanning electron micrograph of the core region of a SiC filament which has been annealed at 1200°C (2192°F) for 128 hours.	14
7	Young's modulus as a function of temperature for AVCO's stoichiometric SiC filament. Data for monolithic, polycrystalline SiC (Reference 26) and boron filament (Reference 41) are included for reference.	16
8	Tensile strength as a function of temperature for both virgin and abraded TYCO c-axis sapphire (Reference 4).	16
9	Tensile strength as a function of temperature for both virgin and abraded TYCO a-axis sapphire.	18
10	Tensile strength as a function of temperature for Cr <sub>2</sub> O <sub>3</sub> coated TYCO c-axis sapphire.	18
11	Tensile strength as a function of temperature for both virgin and abraded ADL Cr <sup>+3</sup> doped, c-axis sapphire. The dotted line shows the strengths of one group.	20

FIGURE		PAGE
12	Tensile strength as a function of temperature for both virgin and abraded ADL Cr <sup>+3</sup> doped, a-axis sapphire.	20
13	Young's modulus of TYCO c-axis sapphire as a function of temperature. The modulus of 30° sapphire rods is included for reference (Reference 26). The dotted line indicates second possible curve connecting the data points.	23

## Introduction

Air Force interest in metal matrix composites has been stimulated by the requirements for materials with high modulus-to-weight and high strength-to-weight ratios for advanced aircraft applications. A great deal of effort in the past few years has been devoted to the identification of new composite systems, their fabrication and their characterization mechanically and chemically. At this time, the number of promising systems has been limited to no more than ten. While there may be a number of variations of each composite system in terms of matrix alloy, the constant denominator in most composites is the reinforcing fiber or filament. There are at present only four basic filaments which are available in sufficient quantity for study: they are graphite, boron or Borsic<sup>(R)</sup>, silicon carbide (SiC), and sapphire (Al<sub>2</sub>O<sub>3</sub>). In the past, it had been the general practice to evaluate each new composite's potential performance by room temperature tests. This practice was also extended to the filaments where a small number was carefully selected and tested under optimum conditions. A high strength value was taken as an indication of the fiber's contribution to the composite strength when fabricated, assuming that the rule-of-mixtures (ROM) is valid. Unfortunately, these predictions were not substantiated by experimentation and composite properties were far below predicted values (1,2). This was not the fault of the mathematical models such as the ROM, but rather was due to the lack of mechanical property data on the filaments. Now that more data are available, the earlier results are explainable and the predictions of the mechanical properties of new composite structures are more in line with observation.

The aim of the present work was to determine the mechanical properties, specifically tensile strength and Young's modulus, of commercially available SiC and Al<sub>2</sub>O<sub>3</sub> filaments. It was noted early in the program that fiber tensile strengths could be degraded by surface damage. Such damage could result from the abrasion involved in the preparation of a composite preform, surface-to-surface contact of the fibers and etching due to the reaction between the fiber and the metal matrix during consolidation and use at elevated temperatures. The loss of filament strength caused by this reaction has been the concern of many investigators and consequently many fiber coating schemes have been devised to preserve fiber integrity (3). Experiments at the AFML with single crystal sapphire filaments indicated that simple fiber-fiber contact could reduce the room temperature strength to a value approximately half that of the pristine strength (4). It was also noted that this loss in room temperature strength did not affect the filament strength at 1100°C (2112°F) - the projected use temperature of a nickel base

alloy/sapphire composite. Thus a coating to protect this filament was unnecessary from a use temperature strength standpoint.

Since the surface damage produced by the reaction between the filament and matrix is no less severe than that produced by fiber self-abrasion, it was believed that the tensile strength of abraded filament could indicate the lower bound of in-situ fiber strength in a well bonded composite. A lower bound strength would be indicated because fibers are broken only once in each test, but in-situ fibers usually fracture a number of times before specimen failure, each time with a higher strength. Likewise, the upper bound in-situ strength is indicated by pristine fiber strengths. By monitoring the filament fracturing process via an acoustic emission technique (5), it was noted that the first sapphire fiber breaks in titanium, nickel, and nichrome composites occurred at stress levels approximating the abraded strengths (4). The effective filament strength was somewhat higher - midway between the abraded and virgin strengths. It is interesting to note that even in a composite where the filament and matrix are thermodynamically stable, i. e., nichrome/ $\text{Al}_2\text{O}_3$ , fibers can be degraded. While the surface sensitivity of SiC and  $\text{Al}_2\text{O}_3$  has been noted, it has not been observed in boron for only mild abrasion. It has been postulated that this is due to the very large compressive stresses in the outer layers of the fiber (6, 7). Other investigators have also noted the surface and in particular the abrasion sensitivity of reinforcing filaments (see Ref 8 for a review). However, the abraded strength as a function of temperature has not been documented for technologically important filaments (except for c-axis sapphire).

Experiments were conducted at the AFML over the past year to determine the mechanical and chemical properties of polycrystalline silicon carbide and single crystal sapphire filaments and are reported herein. Experiments were performed to elucidate the nature of the strength loss in SiC fibers and to assess improvements in the high temperature strength of sapphire. While every effort was made to make this document current, work on improving the strengths of both filaments is still in progress and the reported data may soon be antiquated.

## Literature Survey

### Silicon Carbide

It has long been recognized that silicon carbide (SiC) has many properties that make it very attractive as a composite reinforcement. Silicon carbide is a nearly stoichiometric, thermally stable compound.

It is oxidation resistant, has a low density, a high modulus and can be made in either whisker or filament forms having high strengths. Whiskers of silicon carbide are produced by a vapor growth process which produces a hairlike mass of crystals. Fibers, typically 4.0 to 5.6 mils in diameter, are made by depositing SiC on a hot W substrate. The resultant fiber consists of a polycrystalline sheath on the tungsten core. Unlike boron filaments, there is very little reaction between the reactant gases and the substrate, and very little internal strains due to the growth process. Thus, the SiC fiber does not suffer from a longitudinal splitting problem as does boron. X-Ray diffraction studies of the filament have shown that it consists mainly of  $\beta$ -SiC deposited preferentially so that the (111) planes are parallel to the fiber axis (9).

Since SiC is an important refractory material, its mechanical and chemical properties have been studied for some time. The strength of polycrystalline, bulk silicon carbide has been determined by many investigators. Recent experimentation with high purity, dense material has shown that room temperature strengths up to 120 ksi are possible, and that the strength versus temperature curve is nearly flat to about 1200°C (2192°F) at which point it begins to fall off gradually (10). Room temperature tensile strengths of as high as 1500 ksi have been reported for high purity SiC whiskers (11, 12). The strength of whiskers, as a function of temperature, show the same flat curve as that of the bulk material (13). This characteristic has also been observed in filaments (14). However, in this case, a dramatic loss of strength resulted from exposure to temperatures greater than 1000°C (1832°F). The room temperature strength of an original 320 ksi filament was reduced to about 100 ksi after a ten minute exposure to 1500°C (2732°F) in an argon atmosphere. Strength losses seemed to be nearly independent of time at temperature, but strongly dependent on the maximum temperature of exposure. Strength degradation was attributed to the  $\beta \rightarrow \alpha$  transformation of a small amount of material and to the reaction between W and SiC to form  $\alpha$ -W<sub>2</sub>C. Recent work with the Ti-6Al-4V/SiC composite system has shown that thermal exposure to 871°C (1600°F) for 30 minutes (composite diffusion bonding cycle) does not degrade currently available SiC filament (15).

Since Young's modulus (E) of most composite structures is an important design parameter and since a composite's modulus depends linearly on that of the filament, the modulus of a filament must be known as a function of temperature before a prediction of composite stiffness can be made. The modulus of bulk SiC, measured with an acoustic resonance technique, was reported to decline gradually with increasing temperature to approximately 1000°C (1832°F) and to decrease rapidly above this point (16). However, this loss in modulus above 1000°C (1832°F) has not been

observed with high purity SiC for temperatures up to 1500°C (17). The moduli of some lots of very pure whiskers have been measured at room temperature and reported to be as high as 100-120 million psi (11, 12). The room temperature modulus of early SiC filaments was reported to be in the range 60-70 million psi, but no measurements were made as a function of temperature (14).

Experiments have been conducted to improve the strength of SiC filaments by doping the growing fiber with boron which limits the grain size (9, 14). While strengths of 500 ksi and moduli of 65 million psi were achieved, the average strength and modulus of the doped fiber remained low.

### Sapphire

The potential of single crystal sapphire reinforced metal matrix composite has been the subject of many investigations (2, 3, 18, 19, and 20). Sapphire has the advantages of having a high strength in the temperature range 1000°-1300°C (approximately 2000°-2400°F) and of being either thermodynamically or kinetically stable in both nickel and cobalt alloys which contain minor additions of interfacially active metals (21).

Single crystal sapphire can be produced in either the whisker or filament forms with high strengths. The whiskers are produced by a vapor growth process which produces a hairlike mass of crystals. Oriented single crystal fibers have been produced by both the floating zone and the Edge-Defined Film-Fed (EDFF)<sup>(\*)</sup> growth processes (22, 23). Very long single crystals (typically 4 to 30 mils in diameter) with almost any crystallographic orientation can be grown by either process with high strengths.

Since Al<sub>2</sub>O<sub>3</sub> is a technologically important material, its mechanical and chemical properties have been documented for both the single crystal and bulk forms. Numerous investigations of the tensile strength as a function of temperature have been reported for single crystal sapphire (4, 24, 25, 26 and 27). Most investigators agree that the strength drops to a minimum in the temperature range 250°-600°C (480°-1110°F), increases after this drop and finally decreases after 900°-1000°C (1650°-1840°F). The specific observations depend on crystallographic orientation, strain rate and specimen history. The highest strengths for sapphire single crystals have been reported for

---

\* Patented process for the growth of oriented crystalline compounds by TYCO Labs, Inc., Waltham, Massachusetts.

whiskers. Average room temperature strengths of some lots of whiskers can be as high as 900 ksi (13, 25). Currently, 0° (c-axis parallel to fiber axis) filament is available with average strengths in the range 400-500 ksi (28).<sup>1</sup> It has been the general practice to quote the very high pristine strength of these materials. A number of investigators, however, have noted that the surface of hard, brittle compounds such as Al<sub>2</sub>O<sub>3</sub> is easily damaged via handling and chemical reaction, as in the case of metal matrix composites, and that this can lead to substantial strength losses (3, 4, 8, 29, and 30). In one study (29), it was noted that the extent of mechanical damage was very much a function of orientation with the c-axis direction being the most sensitive.

Similarly, there have been a number of investigations of Young's modulus (E) of both single and polycrystalline Al<sub>2</sub>O<sub>3</sub>. An investigation of the modulus of a 30° sapphire rod as a function of temperature, via an acoustic resonance technique, showed that the material has a modulus of approximately 52 million psi at room temperature and decreases linearly to 42 million psi at 1200°C. The modulus of 30° ruby rods (a solid solution of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>) also decreases linearly from 54 million psi at room temperature to 44 million psi at 1200°C (16).

It has long been known that the strength, Young's modulus and creep resistance of 30° sapphire rods could be substantially improved by doping with selective cations, such as Cr<sup>+3</sup>, Ti<sup>+3</sup>, and Mg<sup>+2</sup> (31, 32, 33, and 34). Recent work has also shown that the strength and thermal shock resistance of polycrystalline Al<sub>2</sub>O<sub>3</sub> can be increased by surface doping (35). In a manner analogous to most metal systems 30° sapphire rods may also be strengthened by doping with Ti<sup>+3</sup> ions and then annealing in an oxygen atmosphere to precipitate an as yet unknown phase (36, 37). In this comparatively new area of research only the surface has been scratched and the strength potential of sapphire has not yet been realized.

### Experimental Procedure

The SiC filament used in this study was obtained from both AVCO, Lowell, Mass. and Service Des Poudres, Paris, France. The filament was wrapped on large plastic spools after growth for storage before use. These fibers have a composite structure comprised of a polycrystalline SiC sheath on a W substrate, consist mainly of β-SiC and have a nominal diameter of 0.004 in. Both silicon rich and stoichiometric (determined by X-ray diffraction) AVCO filaments were tested.

Sapphire filament was obtained from TYCO, Waltham, Mass. and Arthur D. Little (ADL), Cambridge, Mass. TYCO fiber (Sapphicon<sup>(R)</sup>),

---

(R) Registered trademark for single crystal sapphire products grown by the Sapphicon Div. of TYCO Labs, Inc., Waltham, Mass.

grown by the EDFF process, was coated with an acryloid after growth to protect it from self-abrasion, and stored on spools before use. The filament had a nominal diameter of 0.010 inch. To obtain uncoated specimens, the acryloid was removed by placing the specimens on a Pt rack and heating to 1000°C (1832°F) in air for approximately two hours. Spools were sampled in a random manner such that any specimen had an equal probability of being used in any series of tests. ADL fiber was grown by a floating zone technique from feed rods which had a nominal dopant level of 2.0 weight percent (w/o) Cr. Specimens approximately eight inches long were individually packaged in polyethylene tubes to protect them from self-abrasion. The filament was essentially pore free and had a nominal diameter of 0.011 inch. Since ADL c-axis samples were grown under atmospheres containing two different amounts of oxygen, care was taken to ensure that both types of filament were included in each series of tests. The a-axis ADL filament was grown from 6 different feed rods, each having a somewhat different composition, therefore a fiber grown from each feed rod was included in the tests at each temperature. Both a- and c-axis filament grown by TYCO (pure) and ADL (Cr<sup>+3</sup> doped) were tested. In each case, the crystallographic axis was within 5° of the fiber axis.

The room temperature tensile strengths of both SiC and Al<sub>2</sub>O<sub>3</sub> filament were determined using a tabletop Instron testing machine and the file card specimen holder shown in Figure 1. In the case of the sapphire, the filament was beaded on each end using a gas-oxygen torch before being cemented in place along the center line of the card. The file card was cut precisely to the dimensions of the grips to keep bending moments to a minimum. The gauge length of the specimens was approximately 6 inches. Elevated temperature tests were performed with the hypodermic needle-pivot bearing arrangement shown in Figure 2. The filaments were cemented into the needles with epoxy. This scheme allowed the needle to rotate in the bearing, thus reducing off-axis bending moments. Tensile tests were performed on the tabletop Instron machine using a 50 lb load cell and a crosshead speed of 0.02 inches/min. For high temperature testing a Pt-Pt, 50% Rh wound tube furnace was attached to the Instron machine in such a way that it could be swung out away from the grips to facilitate loading of the specimens. The hot zone of the furnace was approximately one inch long. Therefore, the fiber gauge length of elevated temperature tests was assumed to be about one inch. The furnace was controlled to ±2°C with a Pt-Pt, 10% Rh thermocouple cemented to the inside of the tube. The thermocouple was approximately 3/16 inch from the

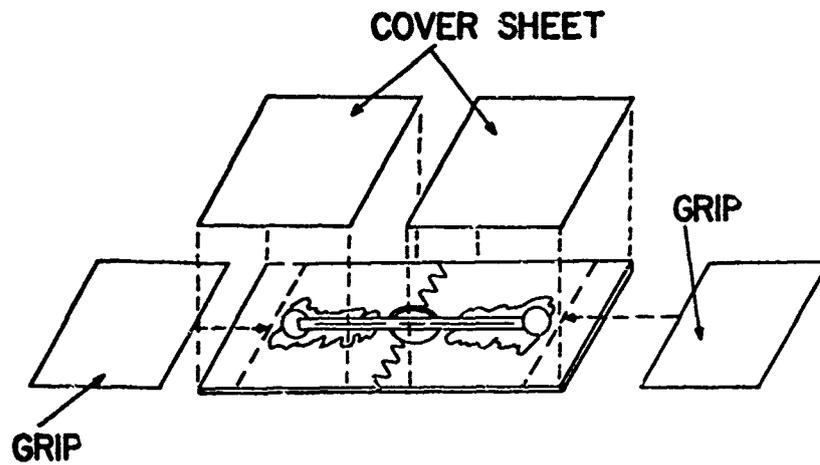


Figure 1. File Card Gripping Technique for Room Temperature Filament Tensile Tests

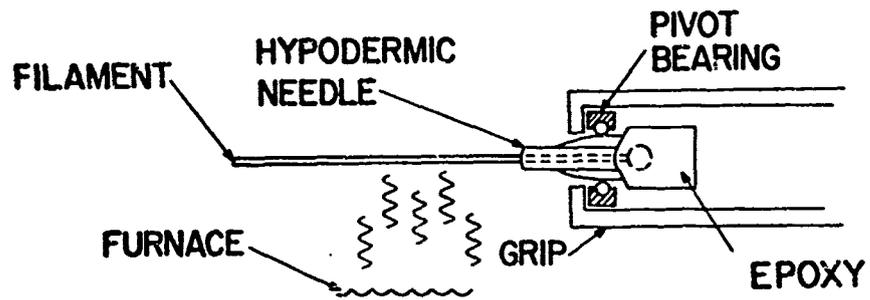


Figure 2. Hypodermic Needle-Pivot Bearing Gripping Technique for Elevated Temperature Filament Tensile Tests

specimen. Once a specimen was threaded through the furnace and positioned in the grips, the furnace was maintained at temperature for ten minutes to allow the filament and furnace to come to equilibrium. Self-abrasion was accomplished by tumbling the filaments in batches of thirty in a tube mill for approximately four hours. Since the SiC filaments tended to stick to the side of the tube mill, presumably due to a static charge, sapphire filaments were added to these batches to mechanically dislodge adhering fibers. Ten specimens were tested at each temperature, except in the case of the a-axis filaments where the amount of material available limited the number of tests to five at each temperature.

Since it is possible to achieve strength increases and a decreased sensitivity to abrasion by surface doping, the following experiment was performed. Twenty-five c-axis TYCO filaments were coated with  $\text{Cr}_2\text{O}_3$  by r-f sputtering. These were then annealed in an Ir enclosure for 48 hours at  $1700^\circ\text{C}$  ( $3092^\circ\text{F}$ ). The filaments were arranged in such a way that they did not touch and the enclosure sealed to prevent the loss of the volatile  $\text{Cr}_2\text{O}_3$ . Tensile tests were performed on these filaments in the usual manner. One batch of five coated filaments was abraded with 20 regular fibers to duplicate the usual treatment. These five specimens were tested at  $500^\circ\text{C}$  ( $932^\circ\text{F}$ ) in the usual manner.

The Young's moduli of both SiC and c-axis sapphire filaments were determined by optically monitoring specimen strain as a function of load. The apparatus used in these experiments was built by the Southern Research Institute and is shown schematically in Figure 3. Load was monitored with the load cell. Total elongation was monitored on a one inch gauge section by tracking the shadows of the flags with the photo cell-servo mechanism shown in Figure 3. The imaging system provided a  $\times 10$  to  $\times 1$  magnification of the gauge section. The separation of the photo cells was measured electrically and recorded as elongation on an x-y recorder. Since load and elongation were recorded, only cross-sectional area of the filament and gauge length needed to be known to calculate Young's modulus. The gauge length was measured with a cathetometer and the diameter of the filament was measured with a micrometer; both to an accuracy of 1 part in 10,000. A comparison of the methods of calculating the cross-sectional area with a photograph of a sectioned filament and a planimeter showed the calculated area to be within 3% of the measured area. A 17 inch fiber was mounted in a hypodermic needle-pivot bearing arrangement shown in Figure 2. A 50 lb load cell and strain rate of approximately 0.002 inches/minute were used for all experiments. The load cell was calibrated with dead weight loading. The strain rate was determined by first calibrating strain read out with

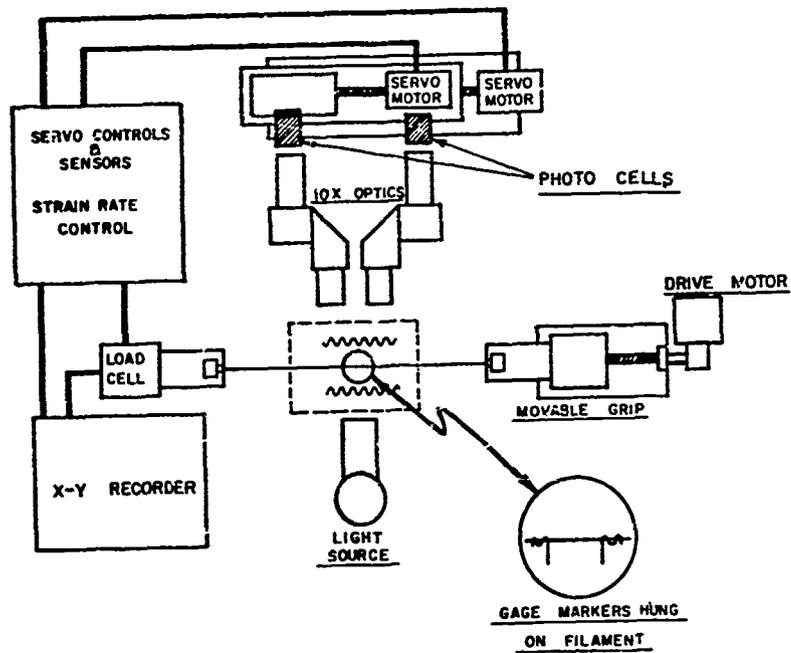


Figure 3. Schematic Diagram of the Apparatus for Filament Modulus Determinations

a dilatometer, which was accurate to 1 part in 10,000, and second by using a stopwatch to determine the time to reach a definite strain at a fixed loading rate for each fiber. For high temperature tests, a split graphite resistance furnace was placed around the fiber. This furnace was equipped with graphite baffles to give it a 1-1/2 inch hot zone with a temperature variation of  $\pm 5^{\circ}\text{C}$ . Temperature was controlled with a Pt-Pt, 10% Rh thermocouple to within  $\pm 10^{\circ}\text{C}$ . The thermocouple was approximately 1/4 inch from the filament. A constant flow of purified argon was necessary for all high temperature tests. Once the fiber was in place, the furnace was maintained at the desired temperature for 10 minutes to allow the furnace and filament to come to equilibrium. Most specimens were used at three different temperatures. However, separate filaments were used in experiments which included a room temperature and then a test at one of the five high temperature points, to minimize any strain hardening effects. At least seven separate determinations were made at each temperature.

## Results and Discussion

### Silicon Carbide

The results of the investigation of the tensile strengths of both Si rich and stoichiometric SiC filament (AVCO) are shown in Figures 4 and 5. The range of strengths at each temperature represent two standard deviations. The tensile strength of virgin, Si rich SiC filament is nearly constant to about  $750^{\circ}\text{C}$  ( $1382^{\circ}\text{F}$ ), but drops off rapidly at higher temperatures. Since the testing in this study was performed in air, some oxidation of the fibers did occur which may have contributed to the strength loss, but this effect was assumed to be small and was not investigated. The strength of stoichiometric filament is much improved over the Si rich material as shown by Figure 5. Using the usual techniques, an average virgin room temperature strength of 465 ksi was obtained. However, when the abrasion sensitivity of the filament was discovered and care was taken to minimize surface damage during mounting procedures, an average strength of 523 ksi was obtained. This point and the  $500^{\circ}\text{C}$  ( $932^{\circ}\text{F}$ ) point are connected by a dotted line in Figure 5, revealing a linear strength versus temperature relationship between room temperature and  $1100^{\circ}\text{C}$  ( $2012^{\circ}\text{F}$ ). The strength of abraded, stoichiometric filament is also higher than Si rich material. The strength versus temperature curve is constant to  $800^{\circ}\text{C}$  ( $1472^{\circ}\text{F}$ ), which is very similar to that of monolithic SiC indicating that similar surface defects limit the strengths in both cases. An examination of the fracture surfaces of abraded filament from room temperature tests indicated that a much higher percentage of failures

were initiated at the surface than for virgin filaments, where most failures seem to be initiated at the W core SiC interface. Filaments with strengths greater than 250 ksi usually failed by shattering. Only rarely does a filament break into two pieces so that the fracture surface may be examined. Therefore, any conclusions drawn from fractography must be viewed with caution.

Room temperature tensile strengths of both virgin and abraded French SiC filament are shown in Table I. Even though self abrasion reduced the average strength, this can be accounted for by the significant loss in only three filaments. This is indicated by the increase in the standard deviation of the abraded filament over the virgin material. In all other cases, the standard deviation of abraded filament is smaller than virgin. Examination of the few fracture surfaces of abraded fibers that were available indicated that most failures were initiated at the core. Chemical analyses of both types of filament showed little differences (38). So at this time, the reason for its apparent abrasion resistance is unknown and it appears that the French filament would have a higher in-situ strength.

The strength of monolithic SiC decreases only slightly up to 1300°C (2372°F), but filament strength drops off rapidly at temperatures above 1000°C (1832°F). Several experiments were performed to elucidate the nature of this loss in strength. Filaments were annealed for various times in air by hanging a long fiber through a furnace, then sectioned perpendicular to the fiber axis and examined optically, by X-ray diffraction and in the SEM. Filaments were examined to determine if there had been any oxidation of the W core - none was detected. Previous work with a Ti/SiC composite had shown that a reaction between the core and SiC was easily observable after a 20 hour anneal at 1050°C (1922°F) (39). Since this is insufficient time for Ti to diffuse to the core for reaction, the reaction product must consist of a combination of W, Si and C. This reaction layer could not be duplicated with anneals of single filaments. The reaction between the core and SiC to form  $\alpha$ -W<sub>2</sub>C and W<sub>5</sub>Si<sub>3</sub> and the transformation of some  $\beta$ -SiC to  $\alpha$ -SiC was detected by X-ray diffraction after 1200°C (2192°F) in 20 hours. However, the reaction product could not be seen either optically or with the SEM until a fiber had been annealed at 1200°C (2192°F) for 128 hours. The extent of this reaction at the core is shown in Figure 6. Not only had the core reacted completely, but numerous pores formed at the W/SiC interface. A previous investigator (14) concluded that the  $\beta \rightarrow \alpha$  transformation was the primary cause of the strength loss. However, another investigator (38) concluded that the formation of a tungsten silicide (W<sub>2</sub>Si) during growth

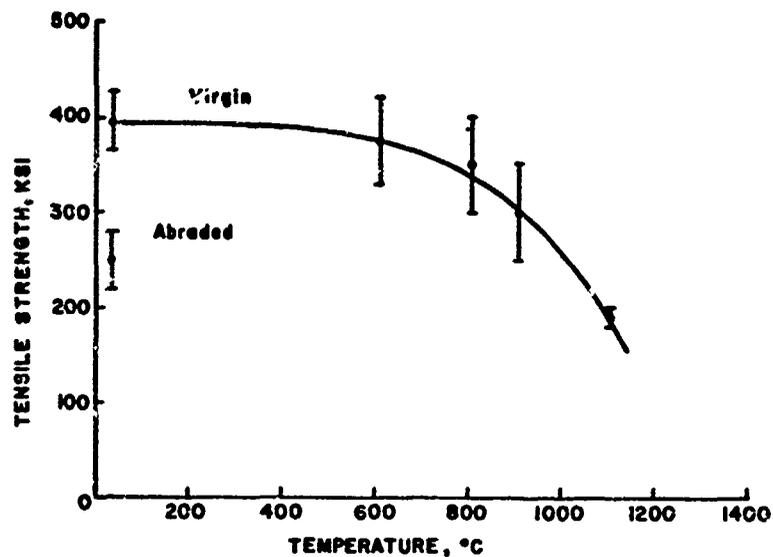


Figure 4. Strength of Si Rich AVCO SiC Filament as a Function of Temperature

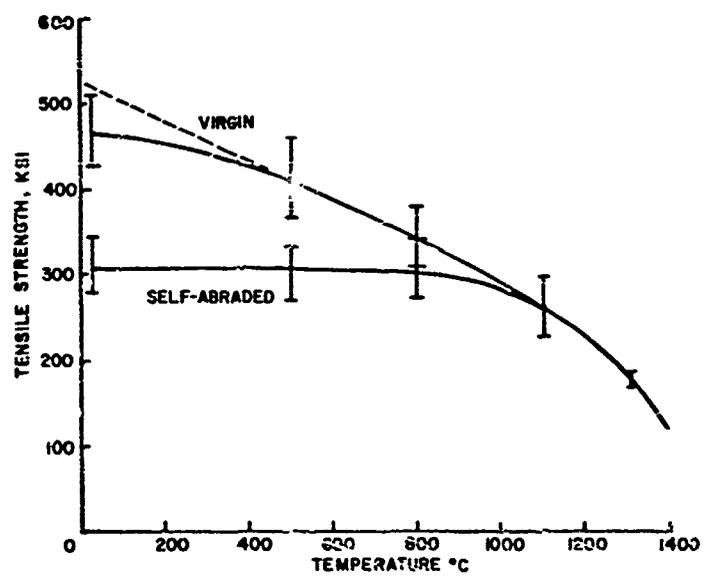


Figure 5. Tensile Strength as a Function of Temperature for Both Virgin and Abraded, Stoichiometric AVCO SiC Filament

TABLE I

A comparison of the room temperature  
tensile strengths of virgin and abraded  
French SiC filament

<u>Virgin</u>		<u>Self-Abraded</u>	
No.	UTS (ksi)	No.	UTS (ksi)
1	379.16	1	317.43
2	445.28	2	405.61
3	352.70	3	321.84
4	321.84	4	220.44*
5	326.25	5	379.16
6	308.62	6	414.43
7	316.22	7	440.88
8	372.02	8	361.52
9	316.22	9	229.26*
10	399.93	10	260.12*

Average UTS = 353.82 ksi  
Standard Deviation = 44.77 ksi

Average UTS = 335.07 ksi  
Standard Deviation = 78.57 ksi

\*If these low strength values are eliminated from consideration, the average strength = 377.12 ksi with a standard deviation = 48.15 ksi (very similar to the virgin strength level). A much more significant fact is that three filaments had strengths over 400 ksi. Such high values for abraded filament were not observed in this investigation for other SiC filaments.

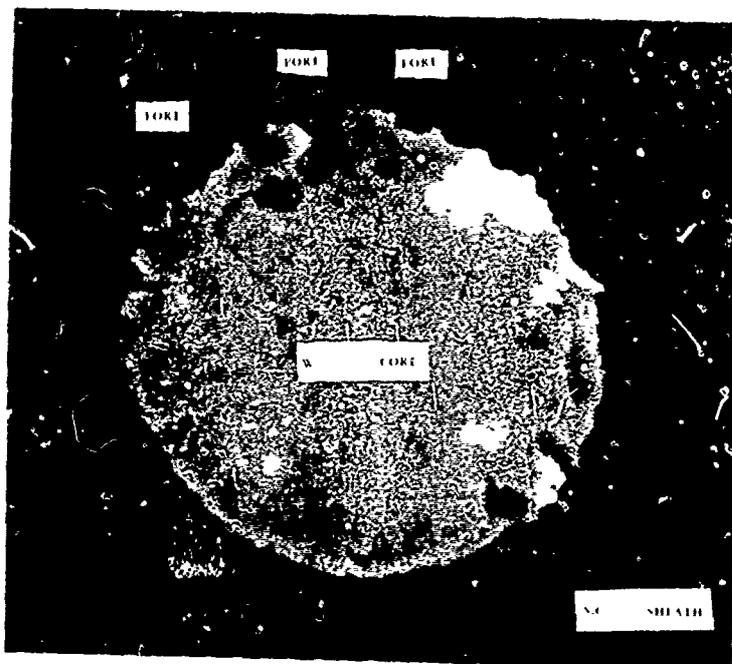


Figure 6. Scanning Electron Micrograph of the Core Region of a SiC Filament Which Has Been Annealed at 1200°C (2192°F) for 128 Hours

would seriously degrade filament strength, presumably due to its higher coefficient of expansion relative to  $\beta$ -SiC, and W, and  $\alpha$ -W<sub>2</sub>C. In the present investigation W<sub>5</sub>Si<sub>3</sub> and  $\alpha$ -W<sub>2</sub>C were identified as reaction products between the core and sheath in SiC filament. These are the most reasonable reaction products in light of the W-Si-C phase diagram data (40). The formation of WSi<sub>2</sub> would seem unlikely from its position in the diagram. Whether the transformation or reaction was the primary cause of strength loss was not determined. However, it can be concluded that the strength degradation, caused by either or both processes, limits the long time use temperature to less than 700°C (1292°F) and the short time exposures to temperatures less than 1000°C (1832°F) (as might occur in a metal matrix composite fabrication cycle).

Recent experiments with Ti(6-4)/SiC composites yielded strengths of 147 ksi (15). Calculated filament strength based on a composite failure strain of 5000 micro inches and the ROM was about 230 ksi (15). This is below the 300 ksi that might be predicted from abraded filament strengths. However, optimum bonding parameters for this composite system have not yet been completely defined. An in-situ strength of approximately 300 ksi is a more realistic prediction when the abrasion due to handling and etching (due to the chemical reaction between the reinforcement and matrix) are taken into account than the virgin strength of 500 ksi.

Young's modulus (E) of stoichiometric filament (AVCO) as a function of temperature is shown in Figure 7. The modulus of bulk SiC is included for reference (16, 17). The range of moduli at each temperature represent the range of values obtained in this investigation. These data fall between commercially available KT grade and very dense monolithic SiC to 600°C (1112°F) (17). Above this temperature the modulus of the filament falls off rapidly, presumably as a result of the core-sheath reaction. The modulus of boron filament is also included for comparison (41). SiC filament has a higher modulus advantage at elevated temperatures, an important consideration in the design of modulus critical jet engine fan blades.

### Sapphire

The strengths of both virgin and abraded c-axis TYCO sapphire as a function of temperature have been reported elsewhere (4), but are reproduced here for purposes of discussion (Figure 3). The range of strengths at each temperature represent two standard deviations. The strength maximum at approximately 800°C (1472°F) was not observed since the specimen did not have a reduced gauge section. However,

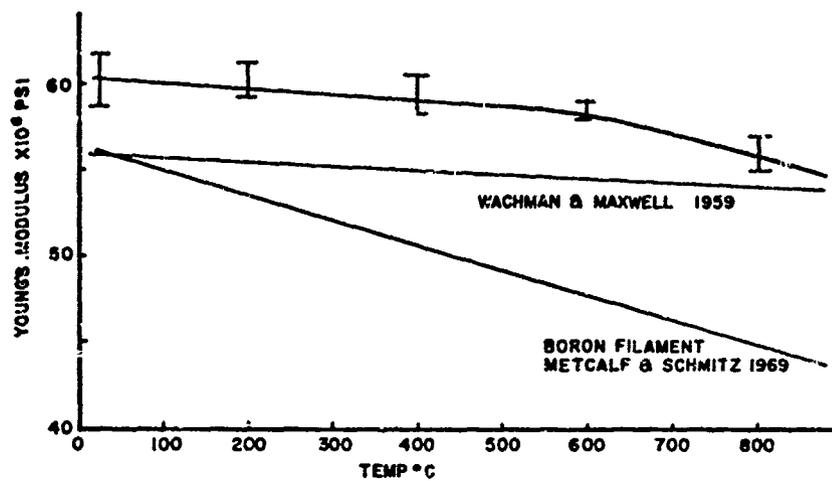


Figure 7. Young's Modulus as a Function of Temperature for AVCO's Stoichiometric SiC Filament. (Data for monolithic, polycrystalline SiC, Reference 26, and boron filament, Reference 41, are included for reference.)

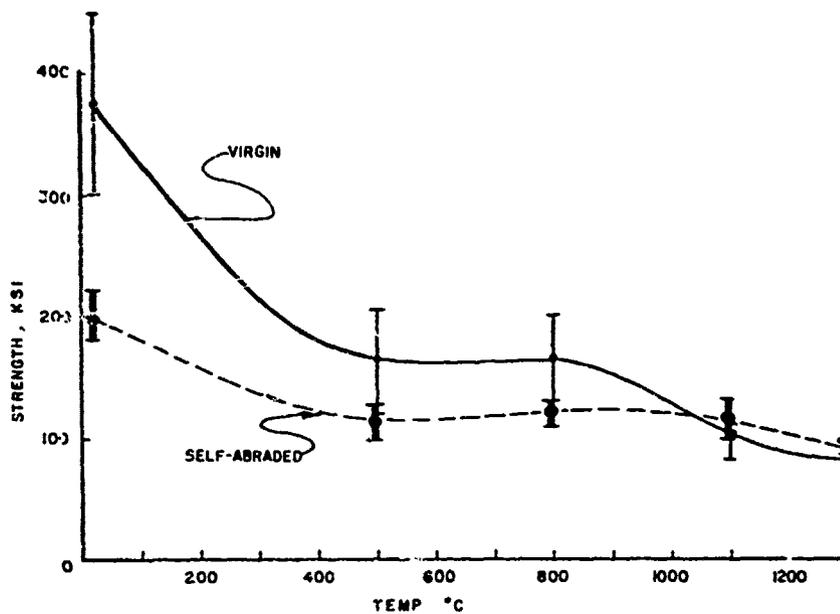


Figure 8. Tensile Strength as a Function of Temperature for Both Virgin and Abraded TYCO c-Axis Sapphire, Reference 4

there is a slight but definite increase in the 800°C (1292°F) strength which probably occurs for the following combination of reasons. The strength of sapphire is a function of both temperature and the distribution of strength limiting flaws. For this experimental setup the strength minimum in the temperature range 250°-600°C (482°-1112°F) would normally limit higher temperature strengths. However, this temperature range exists over two short sections of a sample due to the steep thermal gradients of the furnace. Since the probability of a strength limiting flaw occurring in these low temperature zones is less than the probability of the same size flaw occurring in the hot zone, the average 800°C (1292°F) strength should be somewhat higher than the average 500°C (932°F) strength.

Little is known about the strength of sapphire as a function of crystallographic orientation. The orientation of a high temperature filament is limited to either an a- or a c-axis direction because of the ease of slip on the basal plane (0001) and the necessity of maintaining a zero resolved shear stress on that plane. For these reasons the strength of a-axis TYCO sapphire was investigated as a function of temperature. The a-axis filament is somewhat different than c-axis material. The fiber grows in such a manner that its cross section is not round, but has flats in the direction of the c-axis. Also a slight misorientation (as small as 3°) of the growing filament will produce surface steps which act as stress risers. The specimens were examined but no steps were noted. Optical examination also revealed that the filament contained many more pores than the c-axis fiber. The results of the strength study are shown in Figure 9. The a-axis material shows a definite improvement in strength in the temperature range 500°C to 1000°C (932°F to 1832°F). This is most interesting in light of the fact that little work has been done to optimize the growth parameters of this fiber. These data would suggest that the potential intermediate temperature tensile strength of a-axis sapphire is greater than that of c-axis sapphire; however, more will be said of this point later. The use of these fibers would be limited to temperatures less than 1100°C (2112°F), since recent work has shown that a prismatic slip system ( $\{11\bar{2}0\} \langle 1\bar{1}00 \rangle$ ) is operative at temperatures of 1150°C (2102°F) and above (42). It was expected that the a-axis filament would be very sensitive to abrasion, in light of previous work with sapphire. However, this does not seem to be the case. The abraded strength was not significantly lower than virgin strength when compared with c-axis data.

Previous work has shown that doping the surface of polycrystalline alumina with  $\text{Cr}^{+3}$  could substantially increase its tensile strength. To determine if a similar effect could be achieved with single crystal

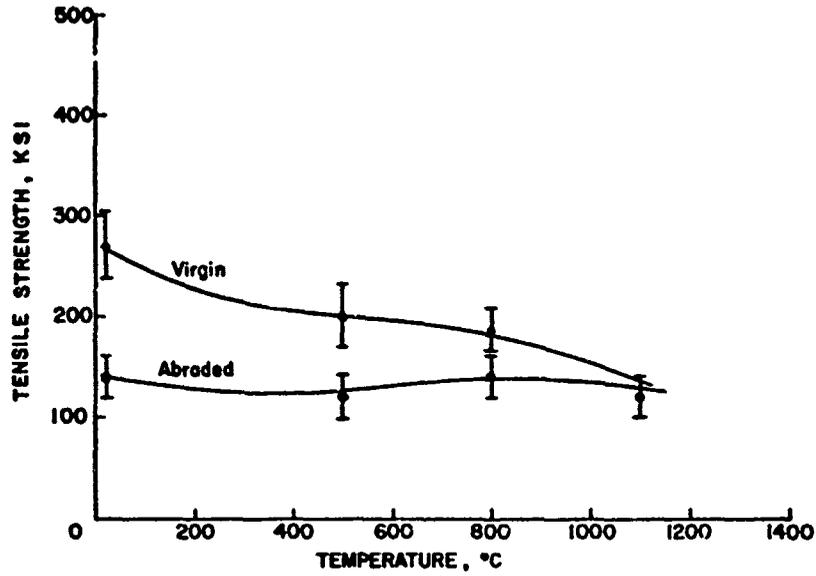


Figure 9. Tensile Strength as a Function of Temperature for Both Virgin and Abraded TYCO a-Axis Sapphire

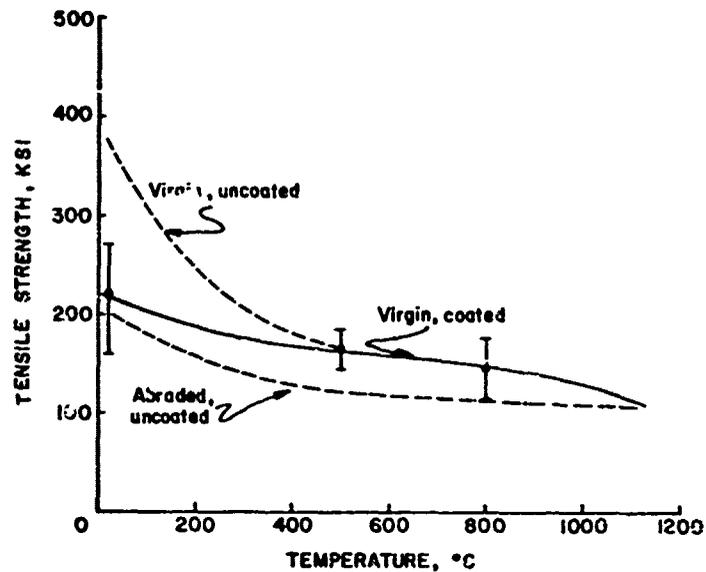


Figure 10. Tensile Strength as a Function of Temperature for Cr<sub>2</sub>O<sub>3</sub> Coated TYCO c-Axis Sapphire

filament the following experiment was performed. C-axis TYCO fibers which had been coated with  $\text{Cr}_2\text{O}_3$  and annealed were tested in the usual manner. The results are shown in Figure 10. Not only was there no improvement, but the virgin room temperature strength was degraded to abraded strength levels. The reason for this loss of strength may be explained as follows. It has been suggested that a layer of  $\text{Cr}_2\text{O}_3$  deposited by r-f sputtering is usually polycrystalline and does not necessarily assume the same crystallographic orientation as that of the substrate (43). If this occurred in the above experiment, the grain boundary grooving that occurs during annealing would create stress concentrations in the filament surface which would limit strength.

Doping alumina to increase strength, creep resistance, etc., has been in use for some time. Therefore, a study was undertaken to document the strength of doped sapphire filament. The results of this study using  $\text{Cr}^{+3}$  doped, c-axis ADL fiber are shown in Figure 11. There was essentially no difference between the abraded and virgin strengths at temperatures above  $500^\circ\text{C}$  ( $932^\circ\text{F}$ ). During the testing it was noted that one lot of fibers had strengths superior to the average. The strengths of these fibers are shown with a dotted line in Figure 11. Spark source mass spectrometric analyses of one of these fibers and one with an average strength, are shown in Table II. The higher strength filament had 5 times the amount of Cr, 2 times the amount of Fe (both strengthening elements) and  $1/2$  the amount of Si (a strength degrading element), as did the average strength filament. The magnitude of the increased tensile strength, with small increases in strengthening element concentration, parallels the increased compressive yield strengths of similarly doped sapphire specimens (oriented for yield on the basal plane) in the temperature range  $1100^\circ\text{-}1600^\circ\text{C}$  ( $2012^\circ\text{-}2912^\circ\text{F}$ ) (31).

Since an increased strength was noted for pure a-axis sapphire filament in the temperature range  $500^\circ\text{-}1000^\circ\text{C}$  ( $932^\circ\text{-}1852^\circ\text{F}$ ), experiments were conducted to document the strength of  $\text{Cr}^{+3}$  doped ADL a-axis filament. The abraded strength of a-axis material was measured only at  $500^\circ\text{C}$  ( $932^\circ\text{F}$ ) because there was no difference in abraded and virgin strengths of c-axis doped fiber. The results of these experiments are shown in Figure 12. The abraded and virgin filaments again have the same strengths. The expected increase in strength over c-axis fiber was not observed. The reason for the apparent higher strength of pure a-axis sapphire and the absence of this effect in doped material is not apparent. It may possibly be due to the different microstructure of the ADL and TYCO fibers.

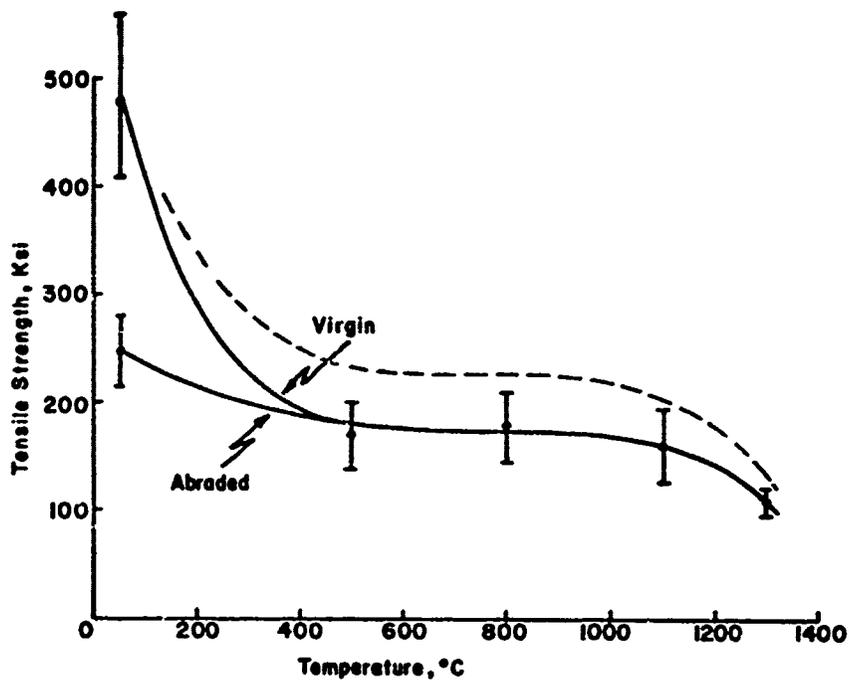


Figure 11. Tensile Strength as a Function of Temperature for Both Virgin and Abraded ADL Cr<sup>+3</sup> Doped, c-Axis Sapphire. (The dotted line shows the strengths of one group.)

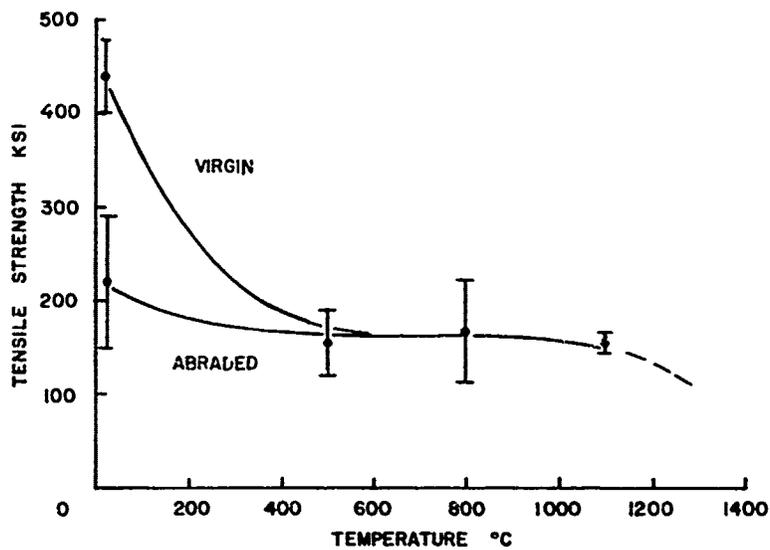


Figure 12. Tensile Strength as a Function of Temperature for Both Virgin and Abraded ADL Cr<sup>+3</sup> Doped, a-Axis Sapphire

TABLE II

The spark-source mass spectrometric  
chemical analyses of an exceptionally  
strong and an average strength ADL  
Cr<sup>+3</sup> doped c-axis filament

<u>Element</u>	<u>ppm (wt) average</u>	<u>ppm (wt) strong</u>
Na	2.0	2.0
Mg	10.0	10.0
Si	100.0	50.0
P	2.0	-
S	20.0	20.0
Cl	5.0	5.0
K	5.0	5.0
Ce	20.0	20.0
Ti	5.0	2.0
V	5.0	1.0
Cr	1000.00	5000.0
Mn	1.0	1.0
Fe	100.00	200.0
Ni	2.0	2.0
Cu	5.0	5.0
As	2.0	1.0
Se	20.0	2.0
Rb	5.0	1.0
Sn	< 2.0	10.0
Ba	5.0	< 2.0
Hf	10.0	5.0
Pb	10.0	2.0

All other elements were present in amounts less than 0.5 ppm (wt)

The elastic modulus of c-axis sapphire was determined as a function of temperature as shown in Figure 13. The modulus of 30° sapphire is included for comparison (15). The range of values at each temperature represent the range in values determined during this investigation. While the data points may be connected by a straight line, there was a reproducible minimum in the modulus of all specimens tested in the temperature range 200°-600°C (392°-1112°F). This minimum has not been reported by previous investigators. The modulus of Cr<sup>+3</sup> doped sapphire was not determined for lack of a suitable specimen. It has been shown to be slightly higher than pure 30° sapphire, by about 4% (15).

During this investigation care was taken to determine both virgin and abraded filament strengths. This was done because it was felt that in-situ filament strengths would be somewhere between these two strength levels. Indeed, it has been noted by early workers that whisker reinforced composites did not yield strengths in line with predictions made from whisker strength data. Both whiskers and filaments can be and probably are degraded by most composite consolidation operations. It is known that both contact with substances of equal or greater hardnesses and chemical reactions with the matrix reduce reinforcement strengths. Unfortunately, little data exist with which to compare the abraded strength levels with in-situ strength levels. If, however, the data from a study on the Ti-6Al-4V/Al<sub>2</sub>O<sub>3</sub> composite system (20) are used, along with the model for composite strength proposed by Rosen (44), a comparison can be made. Using the ROM, Tressler and Moore (20) calculated an in-situ filament strength contribution of 270 ksi for a well bonded Ti-6Al-4V/Al<sub>2</sub>O<sub>3</sub> composite. With Rosen's model and the following assumptions an in-situ filament strength contribution of 260 ksi would be predicted. The accuracy of the prediction is surprising.

(1) Assume that the ineffective length ( $\delta$ ) of Al<sub>2</sub>O<sub>3</sub> fibers may be calculated using the Ti-6Al-4V shear modulus of 6.1 million psi, Young's modulus of c-axis sapphire of 70 million psi and Rosen's model. A  $\delta$  of approximately 0.003 inches was calculated.

(2) Assume that the TYCO fibers have a Weibull strength distribution (this has been verified for most brittle materials).

(3) Assume that the in-situ fibers have been degraded to abraded strength levels with an average strength = 200ksi and a standard deviation = 20 ksi.

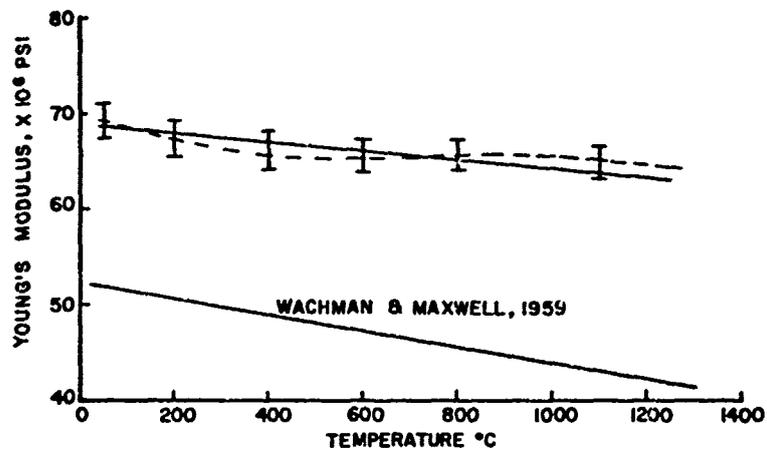


Figure 13. Young's Modulus of TYCO c-Axis Sapphire as a Function of Temperature. (The modulus of 30° sapphire rods is included for reference, Reference 26. The dotted line indicates a second possible curve connecting the data points.)

The above model simply put is a method of quantitatively accounting for the fact that an in-situ fiber breaks many times during the composite fracture process, and therefore, the filament strength contribution is above that measured in single filament tests. Observations of fracture surfaces by Tressler and Moore indicate that filaments were fragmented into small lengths supports the first assumption made above. Unfortunately, no appropriate data exist for similar comparisons of other  $\text{Al}_2\text{O}_3$  reinforced metal matrix composite systems.

### Summary and Conclusions

The tensile strength and Young's modulus of both SiC and  $\text{Al}_2\text{O}_3$  filaments have been documented as a function of temperature. The properties of currently available SiC filament clearly indicate that its use is limited to the lower temperature matrices such as Al and Ti. While it has a modulus advantage over B filaments, the same cannot be said of its strength. The abrasion sensitivity of SiC filament should be examined closely to point out methods of limiting the severity of the degradation. If this problem can be overcome or at least mollified, the strength contribution of this filament to a metal matrix could be increased and its other desirable properties (oxidation resistance, modulus, etc.) may be taken advantage of.

It has been shown that strength of  $\text{Cr}^{+3}$  doped sapphire is superior to undoped material. While a-axis, pure filament has higher intermediate temperature strength, doped c-axis sapphire clearly is stronger and has the greatest strength potential. Unfortunately, only two dopant levels were investigated but the increased strength as a function of concentration showed that the optimum has not yet been reached. A strength of 250 ksi at  $1100^\circ\text{C}$  ( $2012^\circ\text{F}$ ) should be easily attainable with ruby fiber. It is significant that this fiber is also insensitive to abrasion and presumably also insensitive to matrix-fiber chemical reactions. This should allow a full utilization of the fiber's strength in high temperature matrices (Ni and Co) where it has a clear advantage over other currently available filaments. Sapphire has the highest modulus as a function of temperature of all the fibers. This property alone could be significant in the design of modulus critical structures.

The sensitivity of hard, brittle materials to surface damage has been the concern of many investigators. In the past the development of adequate composite models has been hampered by the lack of a description of the strength of in-situ fibers. Rosen (44) was concerned about this unknown quantity in his modeling of a composite's failure processes.

The use of the abraded filament strength to predict in-situ strength contributions has been shown to be valid for one composite system. More importantly the abraded strength should be included as a standard data item for reinforcing filaments because it indicates a lower bound fiber strength and allows a much more accurate prediction of initial composite strengths.

#### References

1. Harold N. Barr: Air Force Materials Laboratory Report, AFML-TR-67-296, 1967.
2. R. L. Mehan: Metal Matrix Composites, p. 29, American Society for Testing and Materials Special Technical Publication No. 438, 1968.
3. M. L. Noone, R. L. Mehan, and W. H. Sutton: Naval Air Systems Command Final Report on Contract N00019-68-C-0304, Jan 1969.
4. R. L. Crane and R. E. Tressler: Journal Composite Materials, 1971, Vol. 5, p. 537.
5. R. L. Mehan and J. V. Mullin: Journal of Composite Materials, 1971, Vol. 5, p. 266.
6. Robert M. Witucki: Air Force Materials Laboratory Report AFML-TR-66-187, 1967.
7. K. G. Kreider and K. W. Prewo: American Society for Testing and Materials Special Technical Publication No. 497, 1972, p. 539.
8. B. A. Proctor: Composites, 1971, Vol. 2, p. 85.
9. Francis S. Glasso: High Modulus Fibers and Composites, Chap. 4, Gordon and Breach, Science Publishers, New York, 1969.
10. M. L. Torti: Materials Development -  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ ,  $\text{ZrB}_2$  -  $\text{SiC}$  -  $\text{C}$ , presented at the Nineteenth Meeting of the Refractory Composites Working Group, Houston, Texas, February 1972.
11. J. A. Herzog: Air Force Materials Laboratory Report AFML-TR-67-244, October 1967.

12. J. A. Herzog: Air Force Materials Laboratory Report AFML-TR-66-417, February 1966.
13. J. A. Herzog: Air Force Materials Laboratory Report AFML-TR-67-326, December 1967.
14. R. P. I. Adler, et al.: Air Force Materials Laboratory Report AFML-TR-67-290, September 1967.
15. W. D. Brentnall and I. J. Toth: Interim Technical Report on Air Force Contract No. F33615-71-C-1873, January 1972.
16. J. B. Wachman, Jr., and D. G. Lam, Jr.: Journal of the American Ceramic Society, 1959, Vol. 42, p. 254.
17. Peter T. B. Shaffer and Choll K. Jun: Materials Research Bulletin, 1972, Vol. 7, p. 63.
18. W. H. Sutton and J. Chorner: Fiber Composite Materials, Chap. 9, American Society for Metals, Metals Park, Ohio, 1965.
19. R. L. Mehan and T. A. Harris: Air Force Materials Laboratory Report, AFML-TR-71-150, August 1971.
20. R. E. Tressler and T. L. Moore: Metals Engineering Quarterly, 1971, Vol. 2, p. 161.
21. W. H. Sutton and Earl Feingold: Materials Science Research, Vol. III, Chap. 31, Eds. W. W. Kriegel and Hayne Palmour III, Plenum Press, New York, 1966.
22. J. S. Haggerty and W. P. Menashi: National Aeronautics and Space Administration Report NASA CR-72811 on Contract NAS 3-13479, February 1971.
23. Bruce Chalmers, H. E. LaBelle and A. I. Mlauskys: Journal of Crystal Growth, 1972, Vols. 13 and 14, p. 84.
24. E. Stofel and H. Conrad: Trans. AIME, 1963, Vol. 227, p. 1053.
25. S. S. Brenner: Journal of Applied Physics, 1962, Vol. 33, p. 33.
26. J. B. Wachman, Jr. and L. H. Maxwell: Journal of the American Ceramic Society, 1959, Vol. 42, p. 432.

27. P. Shahinian: *Journal of the American Ceramic Society*, 1971, Vol. 54, p. 67.
28. G. F. Hurley and J. T. A. Pollock: *Met. Trans.*, 1972, Vol. 3, p. 397.
29. F. P. Mellinder and B. A. Proctor: *Phil. Mag.*, 1966, Vol. 13, p. 197.
30. S. S. Brenner: Fiber Composite Materials, Chap. 2, American Society for Metals, Metals Park, Ohio, 1965.
31. K. C. Radford and P. L. Pratt: *Proc. British Ceramic Society*, 1970, p. 185.
32. J. B. Wachman, Jr. and L. H. Maxwell: *Journal of the American Ceramic Society*, 1957, Vol. 40, p. 377.
33. J. B. Wachman, Jr. and L. H. Maxwell: *ibid*, 1959, Vol. 42, p. 432.
34. Roger Chang: *Journal of Applied Physics*, 1960, Vol. 31, p. 484.
35. H. P. Kirchner, R. M. Gruver, and R. E. Walker: *Journal of Applied Physics*, 1969, Vol. 40, p. 3445.
36. R. J. Bratton: *Journal of Applied Physics*, 1971, Vol. 42, p. 211.
37. S. E. Hsu, W. Kobbs and M. E. Fine: *Journal of the American Ceramic Society*, 1967, Vol. 50, p. 149.
38. Val Krukonis: AVCO Systems Division, Lowell, Mass., private communication.
39. Floyd A. Ashdown, Thesis, Air Force Institute of Technology, 1968, GSF/MC/68-1.
40. C. E. Brukl: Air Force Materials Laboratory Report, AFML-TR-65-2, Part II, Vol. VII, May 1966.
41. A. E. Metcalfe and G. K. Schmitz: Paper No. 69-GT-1, presented at Gas Turbine Conference and Products Show, Cleveland, Ohio, March 1969.

42. D. J. Gooch and G. W. Groves: *Journal of the American Ceramic Society*, 1972, Vol. 55, p. 105.
43. John Haggarty: Arthur D. Little, Inc., Cambridge, Mass., private communication.
44. B. Walter Rosen: Fiber Composite Materials, Chap. 3, American Society for Metals, Metal Park, Ohio, 1965.