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RESEARCH ON FIBER-REINFORCED COMPOSITES

by

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SPACE SCIENCES LABORATORY

MISSILE AND SPACE DIVISION

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MATERIALS SCIENCES SECTION

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*Presented at Refractory Composites Working Group Tenth Meeting, April 12-14, 1965, Georgia Institute of Technology, Atlanta, Georgia.

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MISSILE AND SPACE DIVISION

GENERAL ELECTRIC

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I. INTRODUCTION

The Space Sciences Laboratory of the General Electric Company has been conducting investigations on the preparation and properties of fibers and fibrous composites for more than five years. Much of the original effort was directed towards the growth and properties of whiskers (short, single crystal fibers) and towards the development of high strength metals reinforced with these whiskers. While these investigations are continuing, additional programs have been undertaken which include the preparation of high modulus continuous filaments, a study of the wetting and bonding of metals to (oxide) whiskers, the development of effective composite fabrication procedures, and the evaluation of composite properties in terms of their potential properties.

This report briefly summarizes some of the current results of six programs, sponsored by government agencies, which are being conducted at the Metallurgy and Ceramics Research Operation of the Materials Sciences Section, Space Sciences Laboratory.

II. DEVELOPMENT OF COMPOSITE STRUCTURAL MATERIALS FOR HIGH TEMPERATURE APPLICATIONS (Work performed under U.S. Bureau of Naval Weapons, Contract NOw 64-0540-c)

OBJECTIVE

The goal of the program is the development of composite materials having high strength-to-weight ratios at elevated temperatures.

SIGNIFICANT RESULTS

The feasibility of reinforcing metals with whiskers at both room and elevated temperatures was initially demonstrated with a model system of silver reinforced with Al_2O_3 whiskers[(1)].

The work during the past year has been concerned with translating this whisker reinforcement behavior to higher temperatures with a more refractory metal matrix, so that the program goal of 600,000 inches at $2000^{o}F$ can be demonstrated. Currently, the reinforcement of nickel and nickel alloys with Al_2O_3 whiskers in under investigation. The critical problem of this endeavor has been in the preparation of whisker-reinforced composite test specimens containing appreciable concentrations of reinforcing whiskers which are strongly bonded to the metal matrix. Thus, much of the effort has been devoted to composite fabrication studies. Several techniques have been investigated and some preliminary composite strength data have been obtained.

The results of some of room temperature tensile tests on a nickel alloy whisker-reinforced specimens are summarized in Table I. Tensile specimens of unreinforced control samples were prepared and tested in the the same manner[(2)]. Referring to Table I, it can be seen that all of the specimens exhibited some reinforcement despite the low fiber concentrations.

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(1) W. H. Sutton and J. Chorné, "Potential of Oxide Fiber Reinforced Metals", Presented at the ASM Seminar on Fiber Composite Materials, October 1964, Phila., Penna. To be published in ASM book on conference proceedings.

(2) Sutton, et al, "Development of Composite Structural Materials for High Temperature Applications," Eleventh Quarterly Progress Report, Navy BuWeps Contract NOw 60-0465d, Feb. 1963.

TABLE I

Room Temperature Tensile Data on Ni/Ni Alloy-Al_2O_3 Whisker Composites

Sample No.	Matrix	Whisker Coating	Fabrication Temperature (°C)	v/o Whisker at Fracture Section	Yield Tensile* Strength (psi)
210701-W1	Ni/Pd** (W Saturated)	W	1400	8	63,600
210701-W2	Ni/Pd (W Saturated)	W	1400	7	62,600
25081	Ni/Pd	Re	1400	8.5	75,000
020901	Ni/Pd	Re	1400	9	98,500
Avg. Value	Ni/Pd	--	1350	0	40,000
Avg. Value	Ni/Pd/W	--	1400	0	55,000

*All specimens failed by a "pull-out" of the fibers from the matrix indicating a poor fiber-matrix bond.

** Ni/Pd - Nickel containing 40 w/o Pd.

In many cases, the specimens fractured by having long lengths of whiskers pulling out of the matrix, indicating that the bonds between the fiber and matrix were weak.

The elevated temperature data is summarized in Table II. In many cases, again failure occurred by "pull out" of the whisker from the matrix. The problems encountered in whisker composite fabrication have precluded a valid evaluation of whisker reinforcement at temperatures near 2000°F. Nevertheless, the data obtained are preliminary and encouraging. The results are very significant when compared with the strength-to-weight ratios of commercial alloys at that temperature (~ 2000°F) especially considering the fact that most of the samples tested to date contained very low whisker concentrations and the bonding between fibers and matrix was sometimes poor. Improved fabrication techniques should lead to whisker reinforced composites with even higher strength-to-density ratios.

The progress in terms of composite strength-to-weight ratio for the whisker-reinforced systems investigated to date is summarized in Figure 1.

FUTURE PLANS

The reinforcement of nickel and nickel alloy with sapphire whiskers will continue to be investigated. Lower temperature composite fabrication processes will be investigated, more extensively, since the infiltration techniques appear to be only marginally reliable for the higher melting point (> 2250°F) matrices.

TABLE II

Short Time Elevated Temperature Tensile Data on Ni Alloy - Al_2O_3 (Whisker) Composites

Sample No.	Matrix	Whisker Coating	Fabrication Temp.(^oC)	v/o Whiskers at Fracture Section	Test Temp.	UTS* (psi)	σ/ρ** (inches x 10^{-6})
210703	Ni/Pd W Saturated	W	1350	28	1930°F	22,800	0.103
230702	Ni	W	1500	6	1960°F	9,500	0.043

* All specimens failed by a "pull-out" of the fibers from the matrix indicating a poor fiber-matrix bond.

** σ/ρ = Strength-to-density ratio (inches).

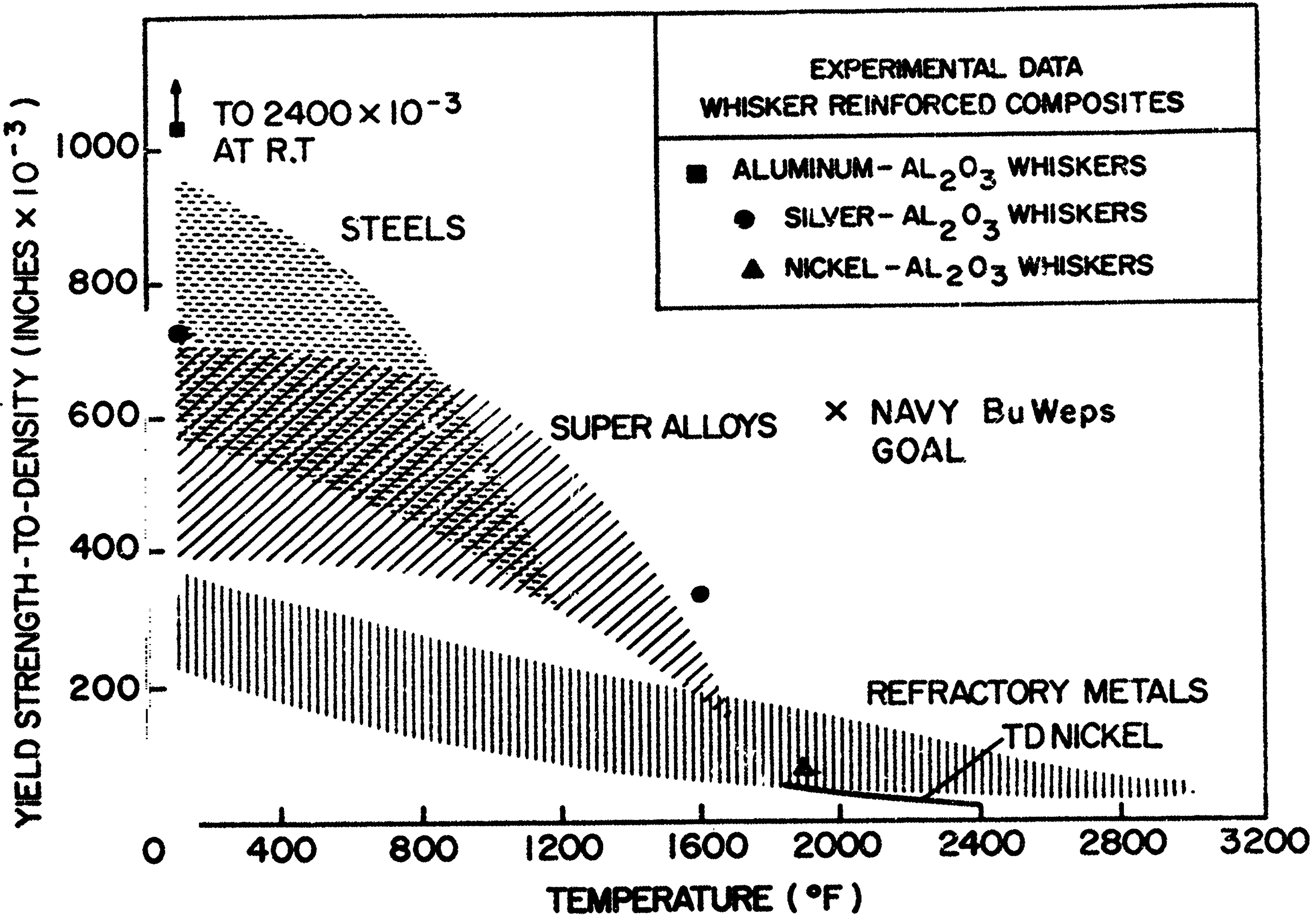

Figure 1. Progress in Composite Strength-to-Weight Ratio for Whisker Reinforced Systems.

III. WETTING AND ADHERENCE OF NICKEL/NICKEL-ALLOYS TO SAPPHIRE (Work performed on Contract No. DA 19-0\60AMC-184(X), AMRA, U.S. Army).

OBJECTIVE

The purpose of this program is the investigation of factors affecting both the wetting and the bonding between metals and oxides. Specifically, the system under investigation is α-Al_2O_3 and Ni. The ultimate objective is the development of high strength fiber (whisker) composite materials by promoting high strength bonding between the metal matrix and the oxide fiber reinforcement.

Current studies are concerned with the effects of certain additives to the nickel, and with optimizing the concentration of these additives which will lead to maximum bond strengths.

SIGNIFICANT RESULTS

Earlier studies have shown that additions of one atomic percent, Cr, Ti, or Zr to nickel were chemically active at the $Ni(\ell)$ - $Al_2O_3(s)$ interface, and thus had profound effects on the wetting and the bonding of Ni to single crystal Al_2O_3. Other additives such as Cu, Al and In affected wetting to a lesser degree. Wetting studies were conducted using the sessile drop technique. The data are summarized in Figure 2. It can be seen in this figure that the contact angle for high purity nickel (HPN) is approximately 100 degrees; equilibrium was reached in less than one minute. One atomic percent additions of Cu or Al to HPN do not significantly alter the equilibrium contact angle. Titanium significantly decreases the contact angle to 95 degrees in about 15 minutes, and to less than 90 degrees in 30 minutes. The greatest change is to be observed in the case of the Zr addition; the resulting contact angle is about 138 degrees.

Detailed examinations have recently been made of the interfaces between sapphire and nickel doped with 1 atomic percent of Cr, Ti or Zr. Bonding in these systems was found to proceed in the following manner: (a) segregation of the active metal, (b) concentration of the active metal at the interface, (c) reaction of the active metal with the sapphire substrate,

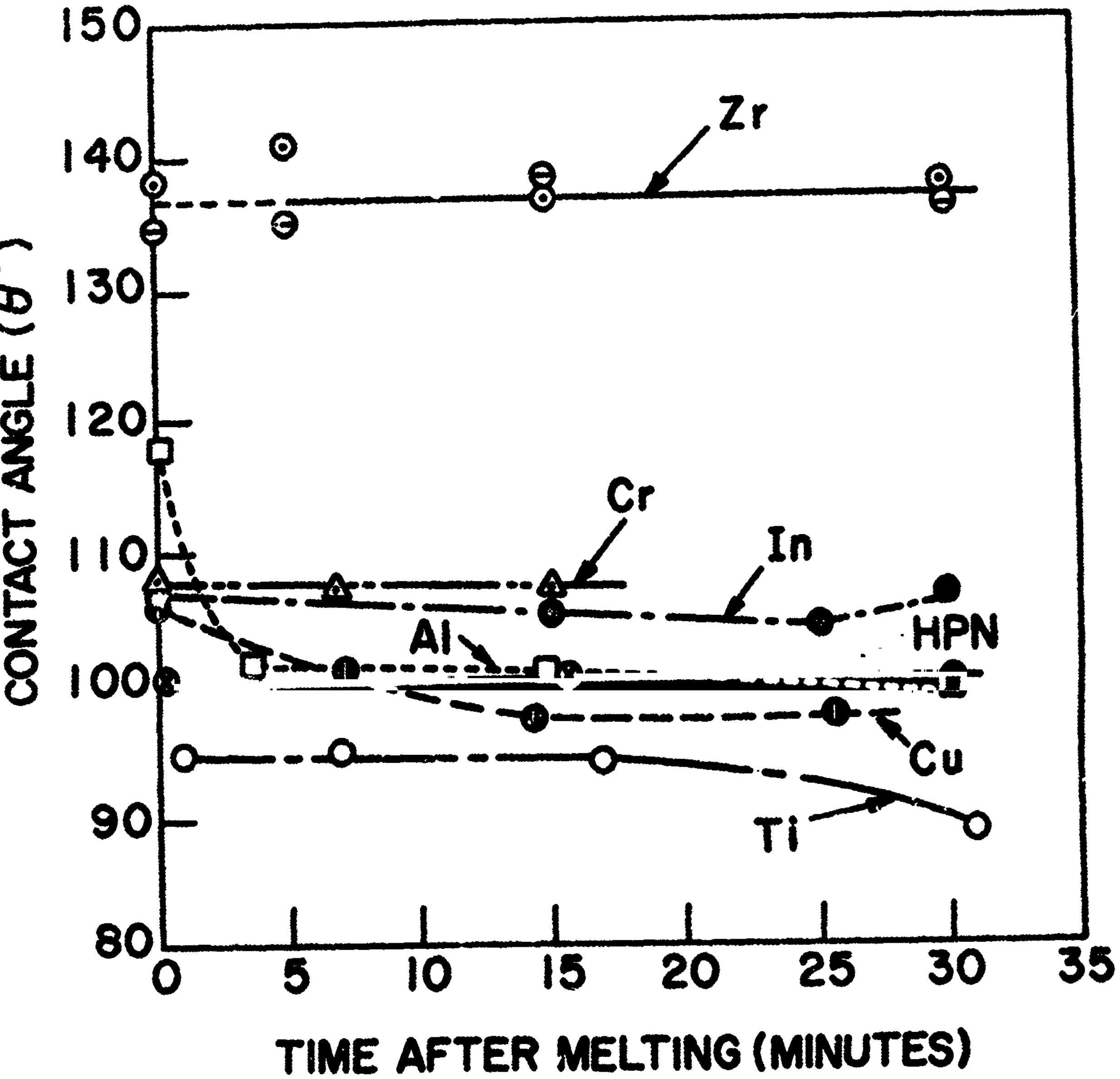

Figure 2. Effect of Additives (1 a/o) to HPN Nickel on Contact Angle Between Ni(ℓ) - Al_2O_3(s) at Various Periods After Melting.

(d) formation of new crystalline phases at the interface, with (e) diffusion of the active metal into the sapphire. The zirconium interface consisted essentially of a zirconium oxide sponge structure. The chromium interface contained primarily β-chromium; and the titanium interface consisted essentially of Ti_3O_5. Only the chromium additive resulted in major bond strengthening between nickel and the sapphire. The reactions of the titanium and zirconium were more severe than the chromium and as a result weakened the sapphire. When a shear load was applied to these samples fracture always occurred in the sapphire. Hence no major strengthening was observed.

FUTURE PLANS

Future studies are being directed toward decreasing the concentration of the active metal additives by 1/10 and 1/100. It is expected that at these lower concentrations the extent of the chemical reaction at the interface will be reduced and that an increase in bond strength will be realized. Also, the effect of ambient atmosphere, (e.g., oxygen pressure, vacuum, hydrogen) on resulting bond strength is being investigated.

IV. EVALUATION OF SAPPHIRE WOOL AND ITS INCORPORATION INTO COMPOSITES OF HIGH STRENGTH (Work performed under Air Force Materials Laboratory, Contract No. AF33(615)-1696).

OBJECTIVE

This program is concerned with the strength evaluation of sapphire (alumina) wool ($d \leq 2.0\mu$) and its incorporation into aluminum composites. Specifically, the following phases are under investigation:

(1) Tensile properties of alumina wool as a function of growth direction, diameter, length, and surface perfection.

(2) Effect of handling severity, surface damage, and surface coatings on strength.

(3) Fabrication and properties of aluminum-Al_2O_3 composites.

SIGNIFICANT RESULTS

About 100 tensile tests on alumina whiskers have been performed, the large portion consisting of wool whiskers ($d \leq 2.0\mu$). The data are shown in Figure 3, together with previous data obtained by other investigators[3, 4, 5, 6]. The closed circles of the present data represent specimens that did not have their cross-sectional area determined, and the stress was computed from the measured strain and an effective modulus (which was a function of gage length).

Some success has been achieved in the fabrication of composites consisting of an aluminum matrix and alumina wool whiskers. A macrophotograph of a composite is shown in Figure 4, and the microstructure in Figure 5. As may be seen, good wetting has been obtained. All the aluminum

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(3) S. S. Brenner, "Mechanical Behavior of Sapphire Whiskers at Elevated Temperatures", J. Appl. Phys. 33, 33-39 (1962).

(4) R. F. Register, "The Strength and Perfection of Aluminum Oxide Whiskers", Master's Thesis, Univ. of Pa., 1963.

(5) P. J. Soltis, "Anisotropic Mechanical Behavior in Sapphire (Al_2O_3) Whiskers", Rpt. NAEC-AML-1831, 1964.

(6) A. L. Cunningham, "Mechanism of Growth and Physical Properties of Refractory Oxide Fibers". Horizons, Inc. Contract Nonr-2619(00), 1960.

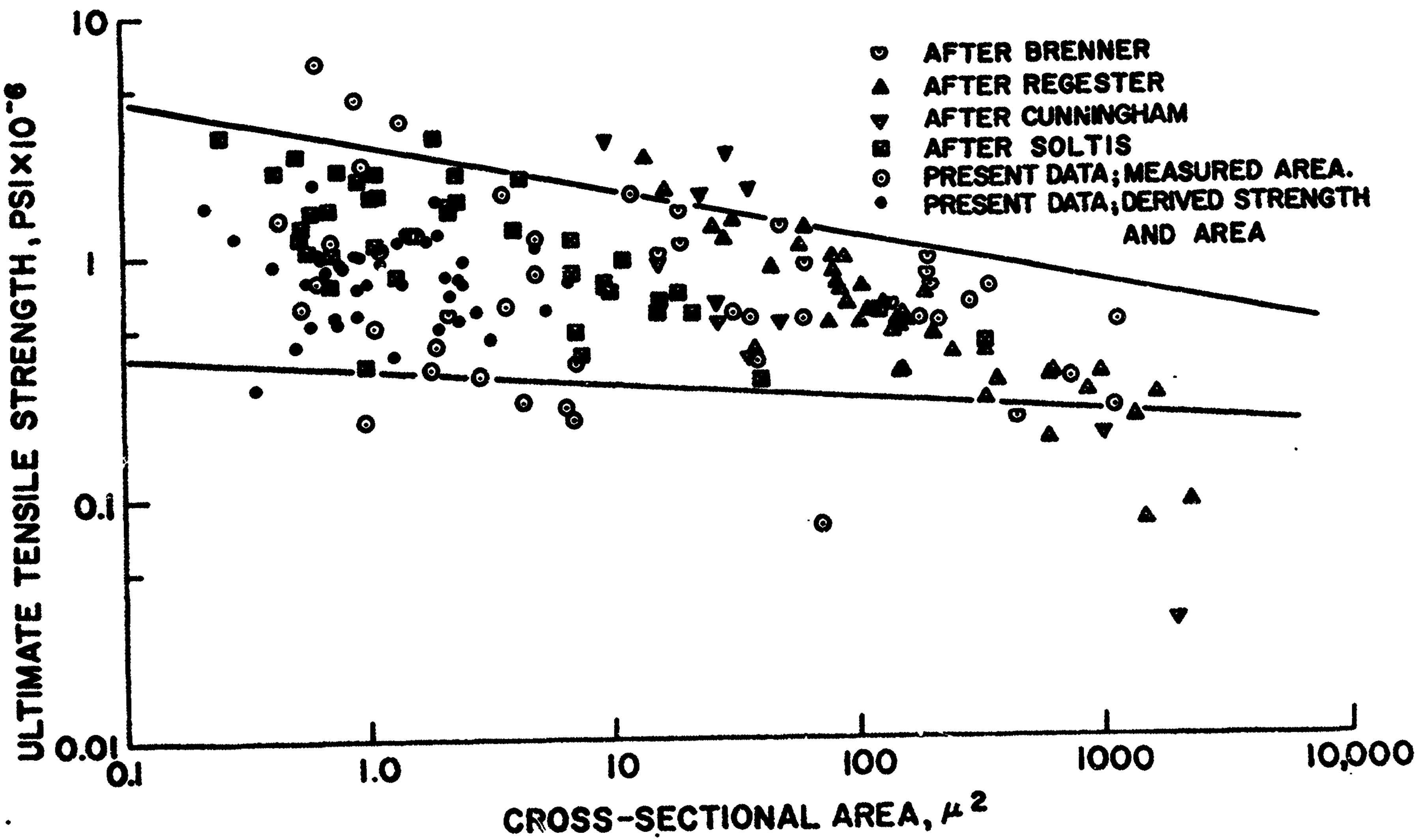


Figure 3. Tensile Strength of Alumina Whiskers as a Function of Area.

was absorbed by the wool, leaving a cavity where the metal was prior to the heat treatment. Two successful composites of this type were made and were prepared for metallographic examination. No mechanical properties on these composites have been obtained as yet.

FUTURE PLANS

It is planned to continue studies on the evaluation of the properties of the (fine) wool Ai_2O_3 whiskers and its reinforcing capabilities in a metal matrix such as aluminum.

Figure 4. Macro[illegible] [illegible]-Al_2O_3 Com[illegible] Using Wool Type Co[illegible] [illegible] Magnification [illegible]

Figure 5. Microstructure of Aluminum-Al_2O_3 Composite Using Wool-Type Whiskers. Magnification: 1280X.

V. STUDY OF THE GROWTH PARAMETERS INVOLVED IN SYNTHESIZING BORON CARBIDE FILAMENTS (Work performed under NAS2-937)

OBJECTIVE

The goal of this program is: (1) the investigation of the synthesis of boron carbide whiskers, (2) the determination of their strength and crystal structure, (3) the incorporation of the whiskers in a metal matrix and (4) subsequent testing and evaluation of the composites thus formed.

SIGNIFICANT RESULTS

A systematic study of the growth of B_4C whiskers has been conducted in order to provide an adequate supply of reproducibly high strength whiskers and also to increase the efficiency of the whisker growth process. Although the original study was concerned with three growth methods, the pure-vapor method, which is based on the vaporization and subsequent recondensation (in whisker form) of bulk B_4C, produced the best whiskers. The other two methods of whisker formation (vapor phase chemical reaction of $BCl_3 + CH_3 + CH_4$, and a modified pure-vapor method) were found to be less effective in producing whiskers of desired quality and thus were discontinued.

Further studies of the pure vapor method have led to an effective catalyst, vanadium, which has resulted in a high productivity per run. Important modifications of the geometry of the deposition area have also led to increased whisker production. Thus, the growth of B_4C whiskers has been increased by more than an order of magnitude over that which was previously possible.

Tensile testing of B_4C whiskers was performed on a Tecam Micro-Tensile Testing machine. Strength data obtained to date as a function of area are shown in Figure 6. The scatter observed is partly due to difficulties associated with area measurements and partly due to batch variations in the batch and in the whisker quality within a particular batch. The dashed line through the data points (Figure 6) must be considered as being very tentative. The Young's modulus of B_4C whiskers has been determined as approximately 65×10^6 psi. The strongest crystal supported a tensile stress of 965,000 psi.

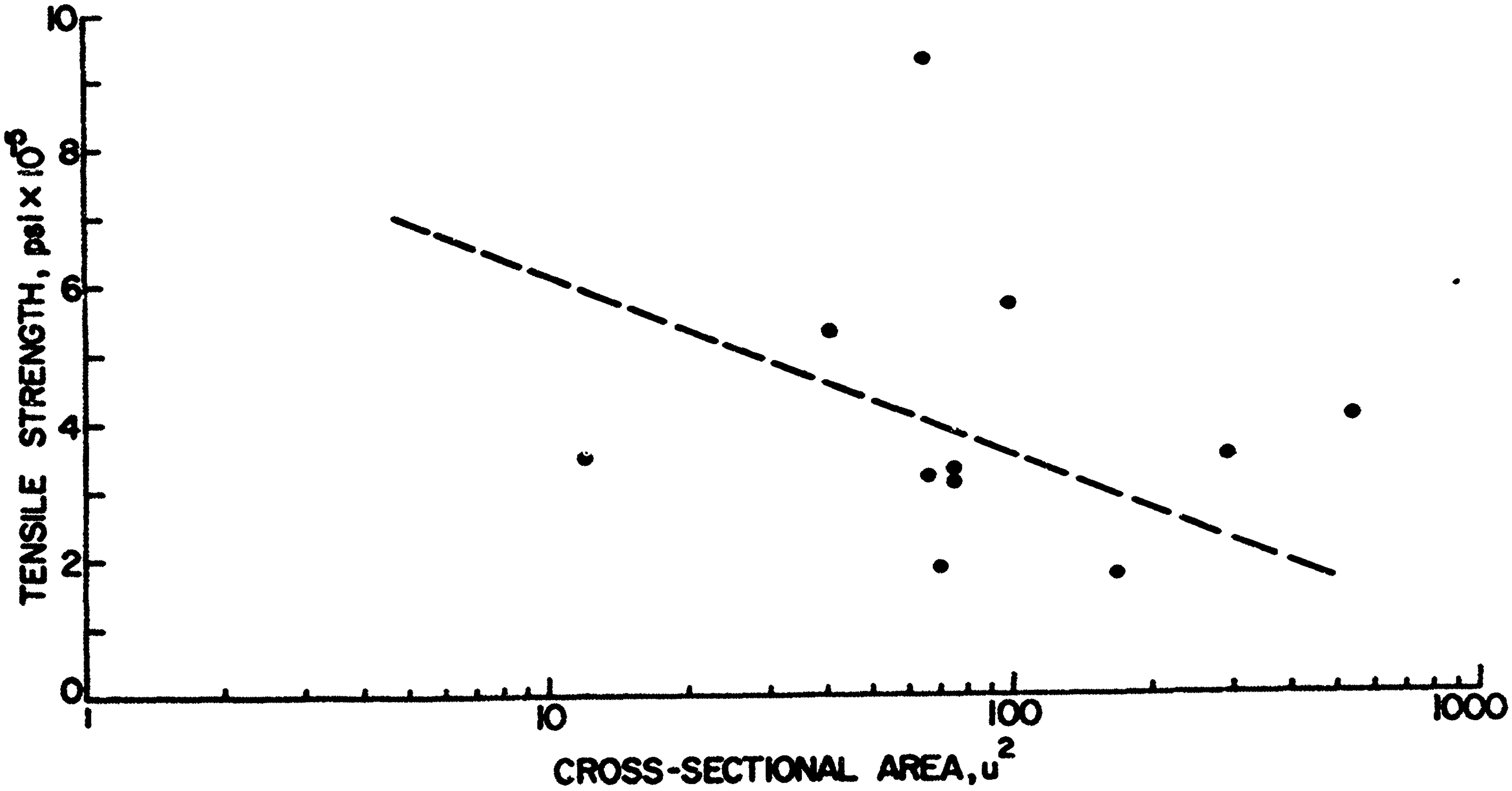


Figure 6. Tensile Strength of B_4C Whiskers as a Function of Area.

The crystal and morphological character of the B_4C filaments were determined by x-ray and electron microscope examination. Except for very preliminary data where odd cell configurations were found, the whiskers studied have all been the 'a' type (major axis parallel to the $\bar{a}$ crystallographic direction).

An extensive study of the state of perfection of B_4C whiskers is progressing. Thus far whiskers which are very perfect and those with varying degrees of imperfection have been examined. No simple method of discriminating between such types on a macroscopic level has been developed as yet.

Small micro-composites containing B_4C whiskers have been made with an epoxy matrix and an aluminum matrix. These composites exhibited tensile strengths of 30,000 psi. The volume fraction of whiskers contained in these composites was of the order of 5 to 10% which is indicative of tensile strengths in the whiskers up to 500,000 psi.

FUTURE PLANS

Extensive studies of the growth of B_4C whiskers will be continued and the effect of various catalytic agents will be investigated.

Additional mechanical testing equipment has been constructed and will be utilized to test B_4C whiskers in bending at elevated temperatures. It is anticipated that the modulus of the whiskers at elevated temperatures will also be determined.

VI. A SURVEY OF THE TECHNOLOGY OF CERAMIC AND GRAPHITE FIBERS AND WHISKERS (sponsored under Air Force Contract AF33(615)-1618)

OBJECTIVE

The purpose of this program was to survey the technology of ceramic and graphite fibers and whiskers and to compile engineering and scientific data into a unified, authoritative source. Except for E-glass, only those filaments useful above 1200°F were considered by this survey. E-glass, because so much information regarding its use is available, was included as a reference point for the other vitreous filaments investigated.

SIGNIFICANT RESULTS

Data was obtained by the following three methods: (1) searching the technical literature including patents, (2) visiting several laboratories and producers where filaments meeting the 1200°F requirement are being produced, and (3) mailing questionnaires to various manufacturers, agencies, laboratories, and universities. The final report includes abstracts of more than 200 patents and a 550 entry bibliography.

Results of the survey can be summarized as follows:

(1) A continuing and expanding effort is underway in the development of high strength, high temperature vitreous filaments.

(2) An increased emphasis on the development of polycrystalline, composites, and single crystal fibers was observed.

(3) A real need exists for the standardization of test procedures and the inclusion of such data as gage length, test method, rate of loading, etc., with reported strength values.

The continuing effort to produce high strength, high temperature vitreous filaments has yielded new glass fibers such as S-994, 29A and 4H-1 having tensile strengths ranging up to 800,000 psi. The reinforced plastics industry has already seen the benefits of these improved filaments in the production of stronger plastic laminates. As soon as resins, having better thermal resistance, are available the strength retention at elevated temperatures of these newer filaments can be more fully exploited.

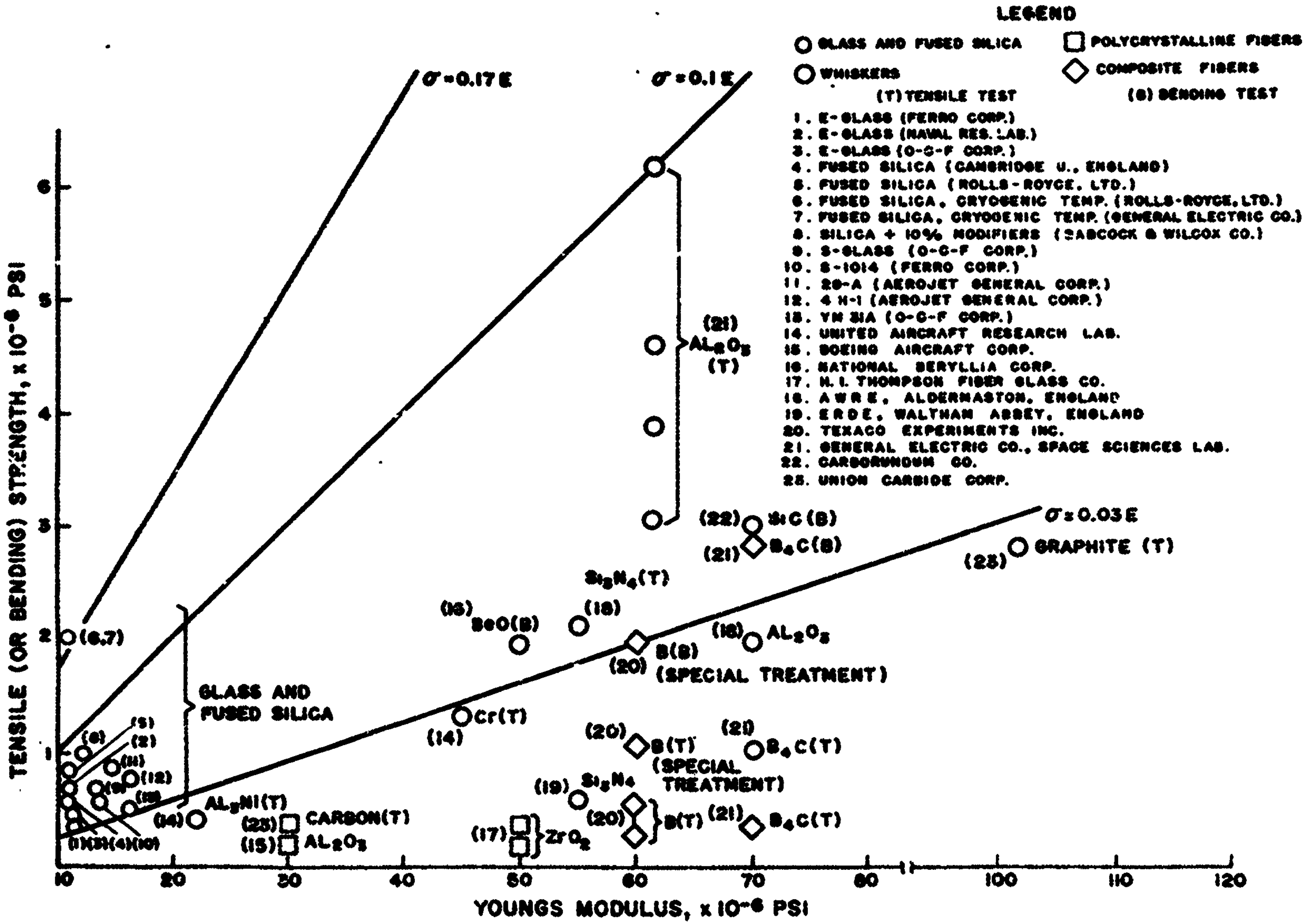
Polycrystalline fibers of alumina, zirconia, zircon and mullite with tensile strengths up to 300,000 psi and Young's modulus of 30×10^6 psi are becoming more available. Their primary use is in applications for ablative thermal protection systems, but their high modulus also makes them likely candidates for improved structural composites.

Carbon, or perhaps more accurately, carbon-graphite filaments are being rapidly improved. One manufacturer reports strength values in the same range as the previously described polycrystalline fibers. Although these materials are being used primarily in ablative thermal protection systems, their relatively low density makes them very attractive materials for structural reinforcements.

Composite fibers include those filaments made by the Taylor wire, the core-sheath or the vapor deposition-on-a-heated-substrate method. Of the three techniques, the production of filaments by vapor deposition appears to be the most promising. Boron carbide filaments having strengths up to 420,000 psi and a Young's modulus of 70×10^6 psi are being produced by this method. A very attractive feature of this method for producing filaments is its ready adaptability to continuous production.

The nearly theoretical strength exhibited by certain single crystal whiskers has given rise to a concentrated effort to use these materials as reinforcing media in the development of structural composites. The refractoriness and chemical inertness of sapphire whiskers has made these materials particularly interesting for high temperature as well as high strength composites. Although various investigators have demonstrated the feasibility of whisker reinforced metals and plastics, many problem areas remain to be solved. Among them are: better control of growth techniques, a more complete understanding of the effects of coatings applied to whiskers, and improved test techniques. Undoubtedly much attention is being given to each of these areas, but the importance of reliable test procedures cannot be too strongly emphasized. The wide range of strength values encountered in the literature suggests that many variations exist in test methods and procedures.

The relationship between tensile strength and Young's modulus for various filamentary materials over a range of theoretical values for E is shown in Figure 7, while the effect of temperature on the strength of various filaments appears in Figure 8.



SELECTED VALUES OF TENSILE AND/OR BENDING STRENGTH AT ACCEPTED VALUES OF YOUNG'S MODULUS FOR VARIOUS FILAMENTS. (ALL DATA OBTAINED AT ROOM TEMPERATURE EXCEPT NOS. 6 & 7)

Figure 7. Relationship Between Tensile Strength and Young's Modulus for Various Filamentary Materials over a Range of Theoretical Values of E

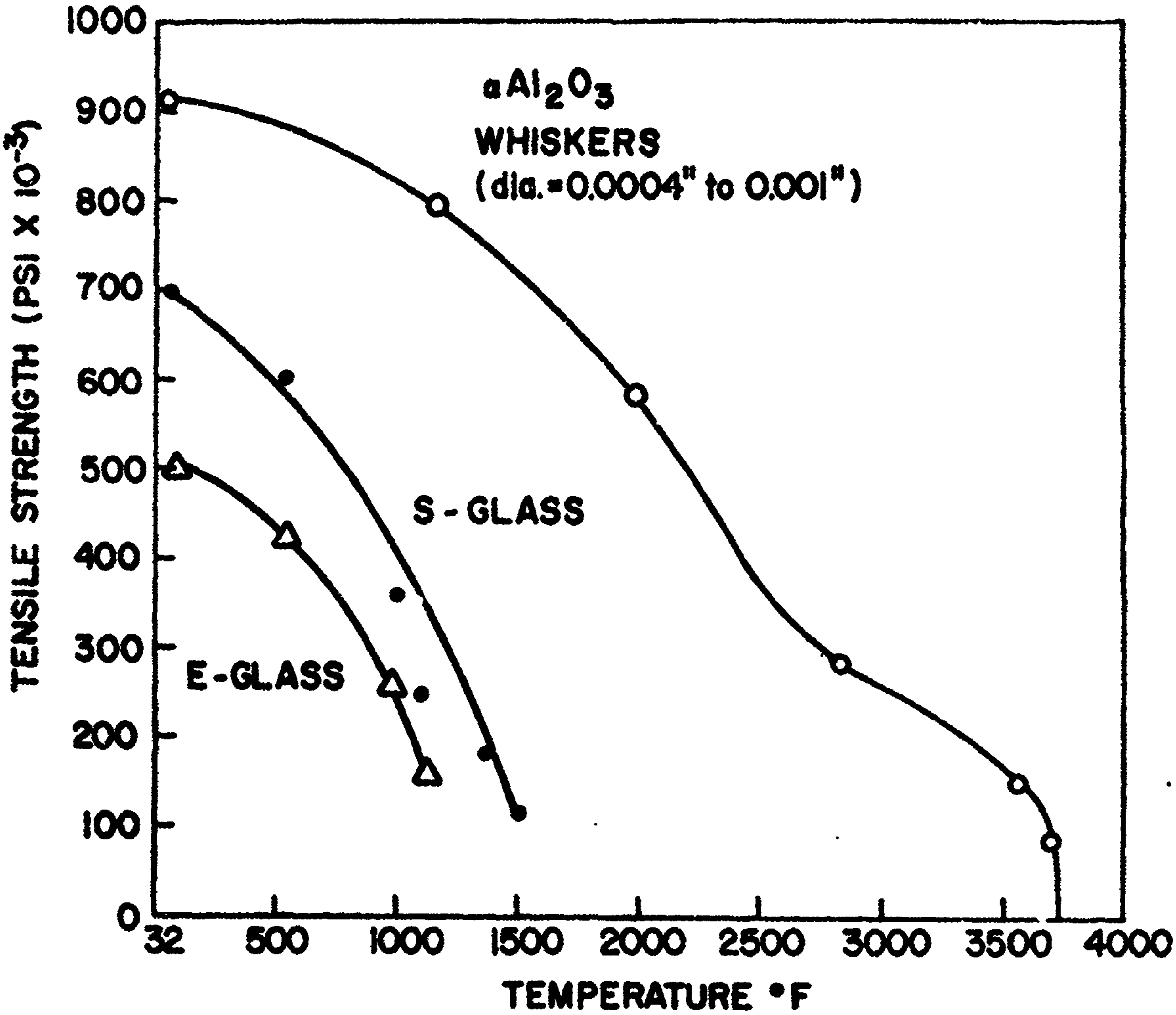


Figure 8. Tensile Strength of αAl_2O_3 Whiskers Compared with E- and S-Glass Filaments at Various Temperatures

VII. RESEARCH ON HIGH STRENGTH, HIGH MODULUS, LOW-DENSITY CONTINUOUS FILAMENTS OF BORON CARBIDE (Work performed under Contract AF33(615)-1644).

OBJECTIVE

The object of the program is to investigate methods which will lead to the production of continuous filaments of B_4C having a fiber strength of 5×10^5 psi and possessing the elastic modulus of bulk boron carbide.

SIGNIFICANT RESULTS

Three methods of forming the fibers have been proposed: (1) the deposition of B_4C from gaseous mixtures of H_2, CH_4 and BCl_3 (dynamic method), (2) the vaporization of B_4C (pure vapor method), and (3) the vaporization of a stoichiometric B_4C compound from HEF-3 (HEF-method) - (All three methods require a substrate material such as tungsten, molybdenum, iron, fused silica, stainless steel, etc.).

The pure vapor method has been discontinued because of several practical limitations. It appears that the HEF method will not be studied due to the unavailability of HEF-3.

B_4C filaments have been produced by the dynamic method varying in both diameter (depending on time of deposition and gas composition) and composition. Figure 9 is a schematic diagram of the apparatus used during deposition. A most favorable operating set of parameters which produces filaments in the .005" to .010" dia. range is 2 minutes at 1200°C. Mole ratios of H_2, CH_4 and BCl_3 can be varied at will, producing similar appearing material but varying greatly in B-C composition and strength properties. Studies are now under way to optimize filaments produced both from the strength measurements and apparent density.

Thus far, filaments of B_4C have been produced utilizing .001 dia. tungsten wire as a substrate. Molybdenum wire was marginal in strength for deposition temperatures now being used. All other substrates failed by plastic flow before deposition could take place. Filament strengths as high as 4.2×10^5 psi in tension have been measured for specimens with 1" gage lengths.

FUTURE PLANS

Further studies will be conducted in order to optimize the filament deposition parameters and thus increase the filament strength. Ultimately a continuous filament apparatus will be developed.