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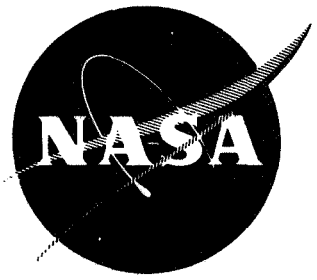

INVESTIGATION TO DEVELOP A CORE SHEATH PROCESS FOR PRODUCTION OF OXIDE FIBERS

by

Stanley Freske

WHITTAKER CORPORATION

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-12434
Project Managers
Albert Anglin
Leonard Westfall

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FINAL REPORT

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ABSTRACT

Under this program, the feasibility of manufacturing an oxide fiber with a core-sheath configuration was investigated. Both large and small diameter fibers possessing high strength and outstanding creep resistance at 2000°F (1100°C) were produced. To manufacture these high performance fibers required the addition of alumina to the glass sheath composition to prevent formation of mullite in the core. The metal used in the fiber forming equipment was critical. Chemical composition and crystalline structure of the ceramic core were determined and the tensile strength of the fiber as affected by test temperature and previous heat treatment was evaluated.

I. SUMMARY

The primary objective of this program was to develop a core-sheath process for the production of high strength oxide fibers showing negligible creep at 2000°F (1100°C) and above. Large diameter core-sheath fibers showing little or no creep at 2000°F were produced. Properties of these fibers varied but were found to have tensile strengths approaching 50,000 psi (34,500 N/cm^2) at room temperature. Tensile properties of these fibers were not measured at 2000°F because of testing difficulties and dimensional irregularities in the core portion of the fiber caused by mullite formation. Smaller diameter core-sheath fibers were also produced and tested at room temperature and 2000°F with core tensile strengths ranging as high as 76,000 psi at 2000°F. It was concluded that high temperature strengths in the 100,000 psi range could be attained provided the formation of mullite in the core could be prevented.

Fibers composed of an alumina core and Vycor* glass sheath were found to creep excessively at 2000°F because of mullite formation in the core resulting from diffusion of silica into the alumina core. Mullite formation was essentially eliminated and the highest strength fibers were attained by incorporating 5% Al_2O_3 in the SiO_2 glass sheath composition. Larger quantities of alumina in the glass sheath reduced the glass viscosity too much and made processing more difficult. By modification of the sheath bushing orifice it is felt that greater quantities of alumina can be utilized in the glass formulation and stronger core-sheath fibers can be produced.

Compatibility of glass compositions with bushing alloys proved to be critical. The 5% alumina modified glass composition could not be used in the tungsten bushing because of tungsten contamination and it was necessary to procure an all-iridium bushing.

*Corning Glass Works

II. INTRODUCTION

The development of high-temperature resistant structural composites is contingent upon the development of high-temperature resistant fibers. The purpose of this program was to develop a process for the continuous production of an oxide fiber exhibiting high strength and negligible creep at a temperature of at least 2000°F (1100°C). The continuity of the forming process is highly desirable from the point of view of both manufacture and application.

The process of drawing continuous glass fibers from a melt contained in a bushing is very efficient and economical, but requires the long viscosity range typical of glass. Unfortunately, another consequence of the long viscosity range is that even at a temperature as modest as 2000°F (1100°C), the glass is subject to creep. This includes pure silica, the most refractory of the glasses. On the other hand, many oxides which are not glass formers and which therefore cannot be drawn into fibers, are mechanically stable at or above 2000°F. One particularly attractive candidate, considering all pertinent properties, is alumina.

The approach in this program was to utilize a dual-melt bushing to draw a glass fiber with a core of a material such as alumina. The intent was to produce an alumina fiber with a thin glass sheath. The purpose of the glass sheath was to stabilize the flow of the liquid alumina. The possibility of creep in the sheath is of no consequence since the sheath is extremely thin, although the ability of the glass to deform may actually prove beneficial by providing stress relief. Due to the high melting point of materials such as alumina, only high-silica glasses with forming temperatures considerably above those of conventional glasses can be used. This calls for unconventional equipment and techniques developed specifically for the purpose.

III. EQUIPMENT

A. Fiber Manufacturing Equipment

The basic fiber-forming equipment was already on hand when the work on the contract commenced. Figure 1 shows the power supply, furnace chamber, and gloved box system, and accessory equipment, e.g., pyrometer, dew-point meter, etc. Expendable items naturally had to be purchased. Figure 2 shows the heat insulation, heating element, and bushing inside the furnace chamber.

The design of the tungsten-iridium, dual-melt bushing used initially and during the greater portion of this program is shown in Figure 3. The outer bushing contains a glass melt from which the fiber is actually drawn, while the inner bushing contains the core material which gives the fiber its desirable high-temperature properties. The core material used almost exclusively in this program because of its superior properties was alumina. Earlier work had revealed that alumina and tungsten are not completely compatible. No violent reaction occurs, but the alumina melt becomes contaminated when in contact with tungsten. For this reason, the core melt was contained in iridium.

The glass used originally was Vycor* glass which is perfectly compatible with tungsten. Later on, a glass containing alumina was substituted. This glass was found to be incompatible with tungsten. The decision was therefore made to procure a bushing made entirely from iridium. The design is shown in Figure 4. The changes in the design were made to save material and to simplify the manufacturing process, thus reducing cost. The narrow core bushing is quite adequate, and is actually an improvement since it leaves more room for the glass, which is depleted rather quickly in normal drawing. In the new design, the bushing rests on a support made of Zircoa-Cast;** the same material used for heat insulation in the furnace.

The suitability of graphite as a material from which to manufacture either bushings or heating elements was investigated. It was found to react with glass even before the forming temperature had been reached, thus precluding its use as a bushing material. Furthermore, it was found to react with all the refractory metals W, Mo, Ta, and Ir at or below the forming temperature. The conclusion was reached that it would be too risky to use it even as a heating element. In our experimentation, only one other material has been found to react with iridium, namely boron. In fact, only a minute amount of boron is needed to destroy a part made from solid iridium. An indication is given in the literature[1] of a boron-iridium eutectic at only 1046 °C in the very high iridium region.

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* Corning Glass Works

** Zirconium Corporation of America

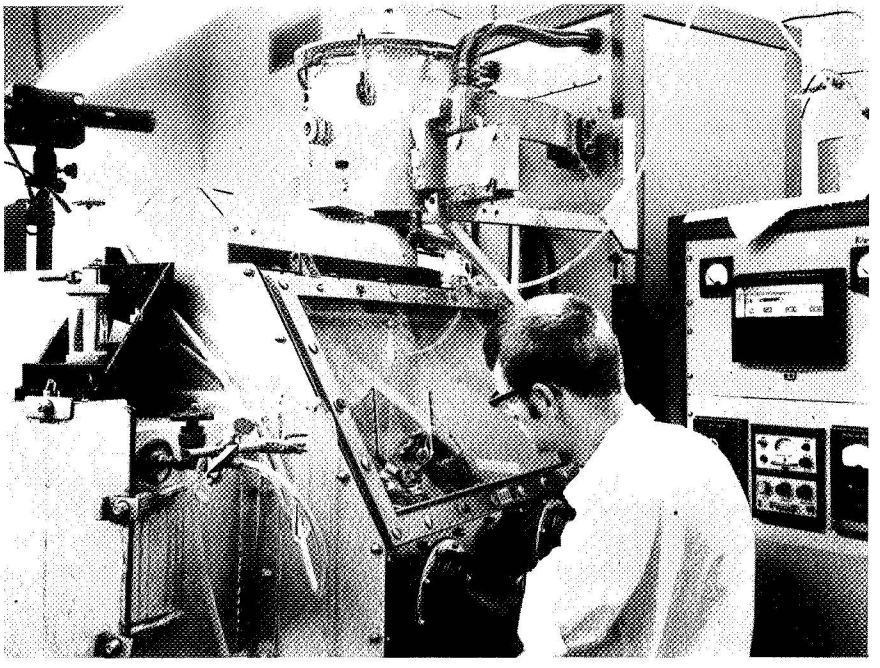


Figure 1. Fiber Forming Equipment

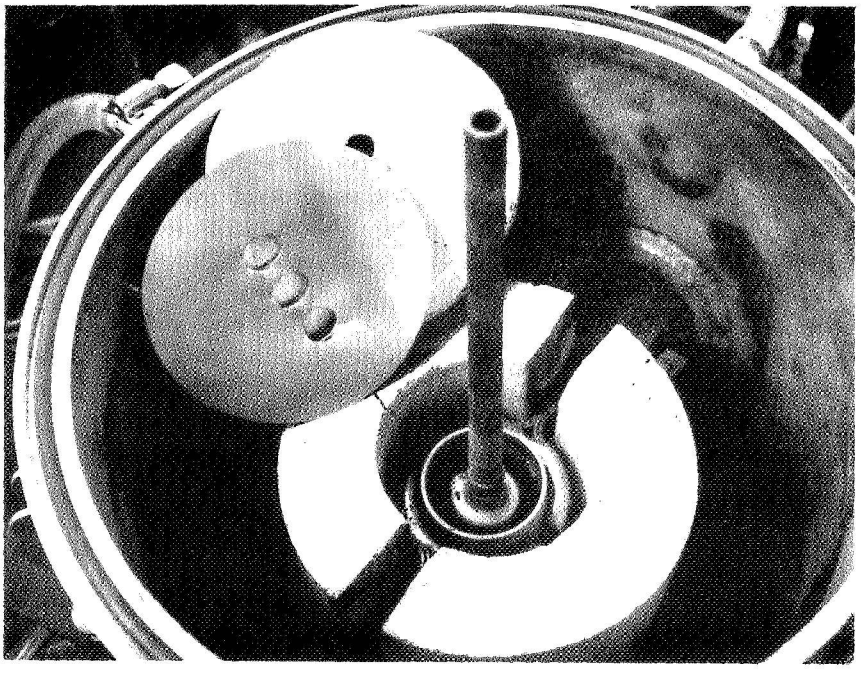


Figure 2. Furnace, Interior View

Material: Tungsten, except as noted

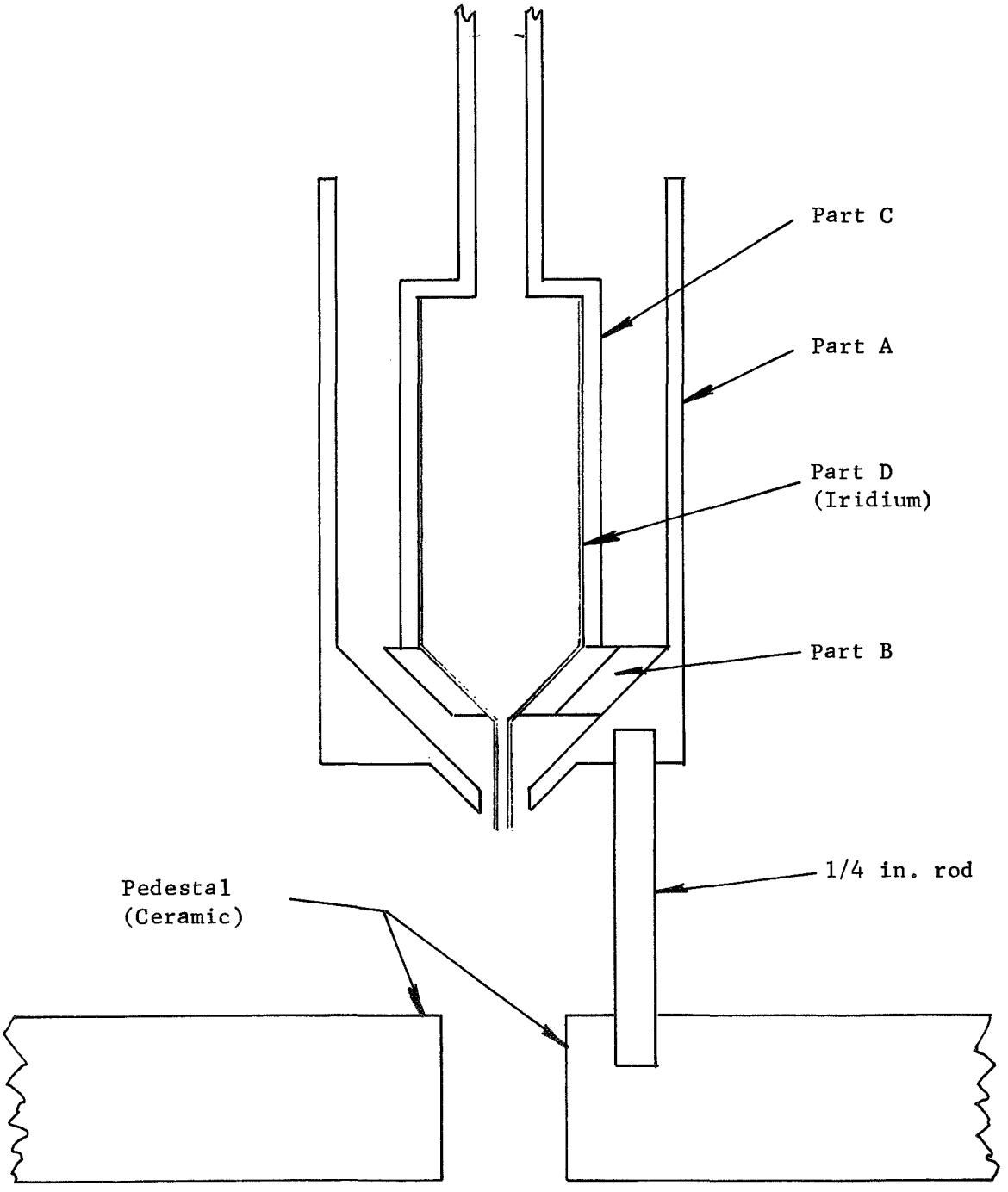


Figure 3. Tungsten-Iridium Dual-Melt Bushing

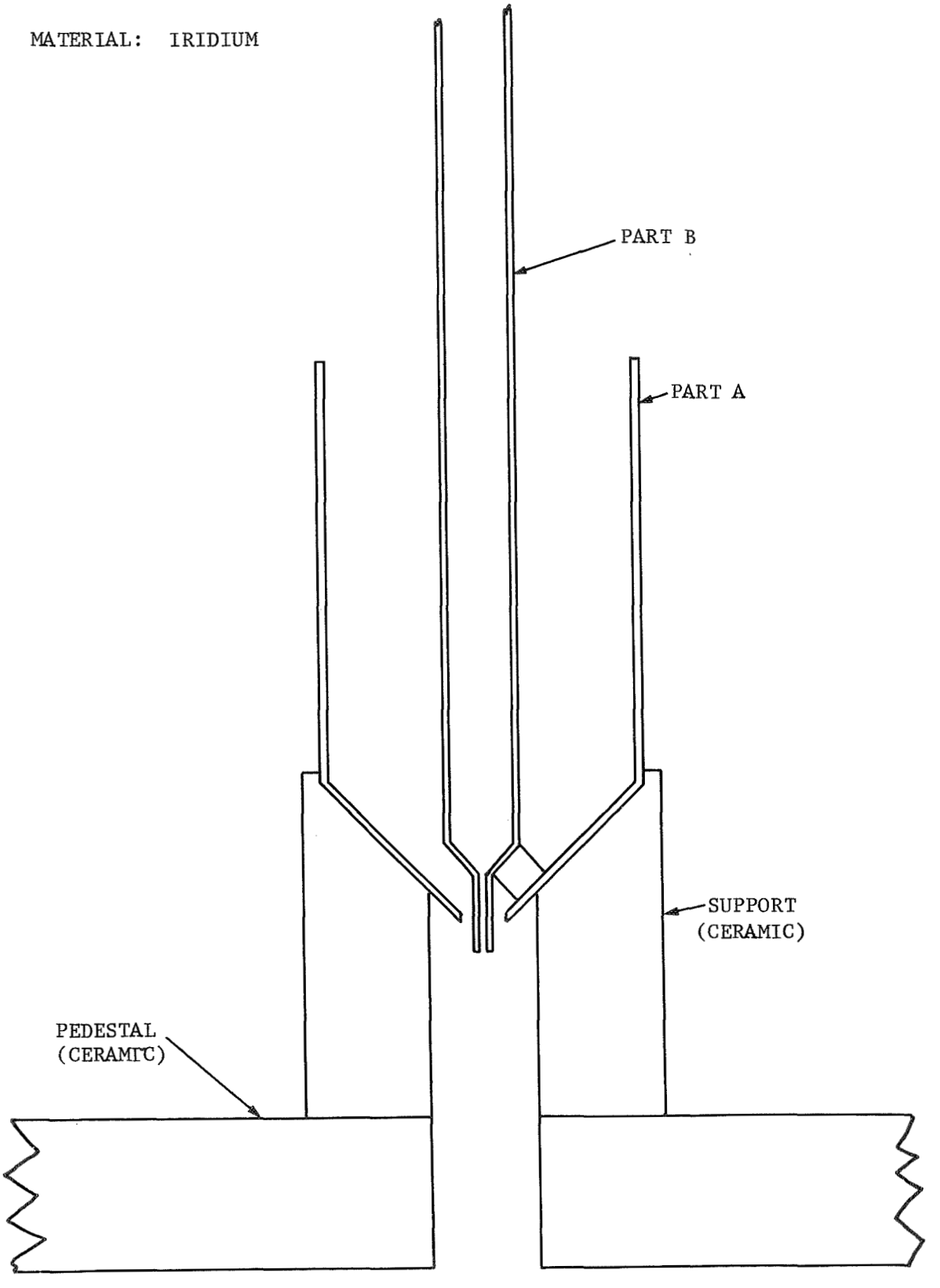


Figure 4. All-Iridium Dual-Melt Bushing

During most of this program, a winder with a drum diameter of six inches (15 cm) was used. It had a drawing speed ranging from about 100 ft/min to several thousand (0.5 to over 10 m/sec). Toward the end of the program it was decided that a larger fiber was more desirable. A winder with a 12-inch (30 cm) diameter drum and a maximum speed of 69 ft/min (0.35 m/sec) was put into service. However, on occasion it was desirable to exceed this speed. Therefore, the 12-inch drum was incorporated in a winder with a speed ranging from 31 ft/min to several hundred (0.16 to over 1.0 m/sec).

Successful core-sheath fiber forming requires control of the flow of core material. This is accomplished by means of a variable pressure system, shown in Figure 5, which controls the pressure above the core melt and therefore the flow through the orifice. The system permits negative as well as positive pressure of more than 12 inches (30 cm) of water equivalent.

B. Fiber Evaluation Equipment

One of two single fiber tensile testers is shown in Figure 6. Calibration is accomplished simply and accurately by suspending a standard weight from a light string which runs over a pulley and is attached to the load cell jaw. Included in the picture is a platinum furnace which permits testing at temperatures up to about 2200°F (1200°C). When higher values became essential, two coil furnaces were made. The first, using a platinum coil, extended the range to approximately 3000°F (1650°C), while the second, with an iridium coil, could be used at temperatures considerably in excess of this value. A difficulty was encountered in that many fibers which had to be tested were so short that they did not extend outside the furnace, and could not be attached directly to the tester jaws. This was overcome by attaching thin alumina tubes to the jaws, inserting the ends of the fiber into the tubes, and bonding with Ceramabond 503*. Unfortunately, with large fibers, i.e., about 10 mil (254 micron) diameter, no bonding agent could be found which had both the cohesive and adhesive strength required.

The stress-rupture apparatus shown in Figure 7 was modified to extend its temperature range to above 2000°F (1100°C). Three quartz lamps were placed below the fibers in addition to the three already situated above. With this equipment six fibers can be tested simultaneously.

Figure 8 shows the microscope used to measure and examine the fibers. Measurements were made using a Filar eyepiece. Calibration was performed for each magnification used by means of a Bausch and Lomb calibration scale having 100 and 10 micron divisions. When a core-sheath fiber is viewed from the side, the core is optically magnified by the sheath.

*Aremco Products Inc.

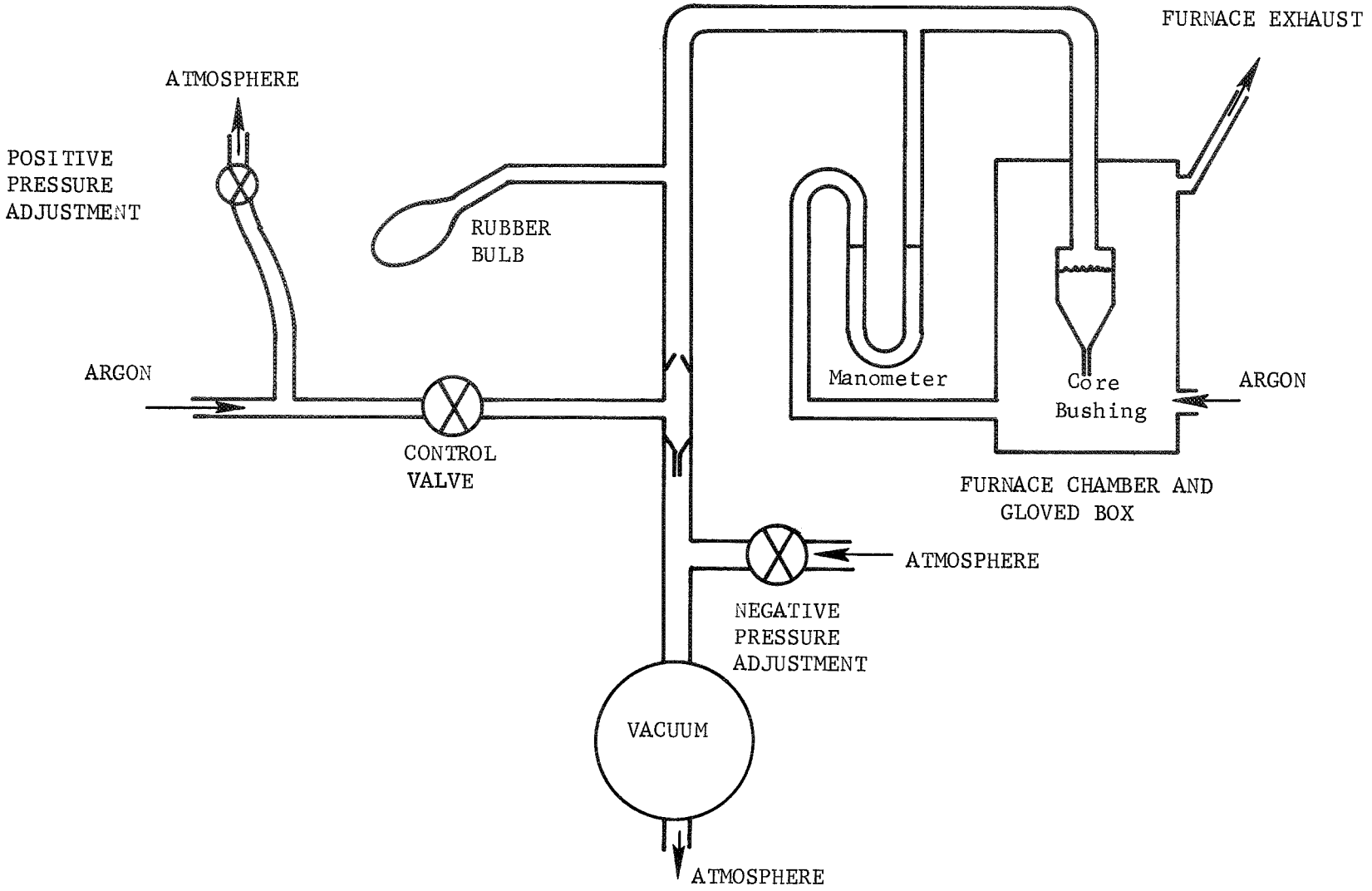


Figure 5. Variable Pressure System

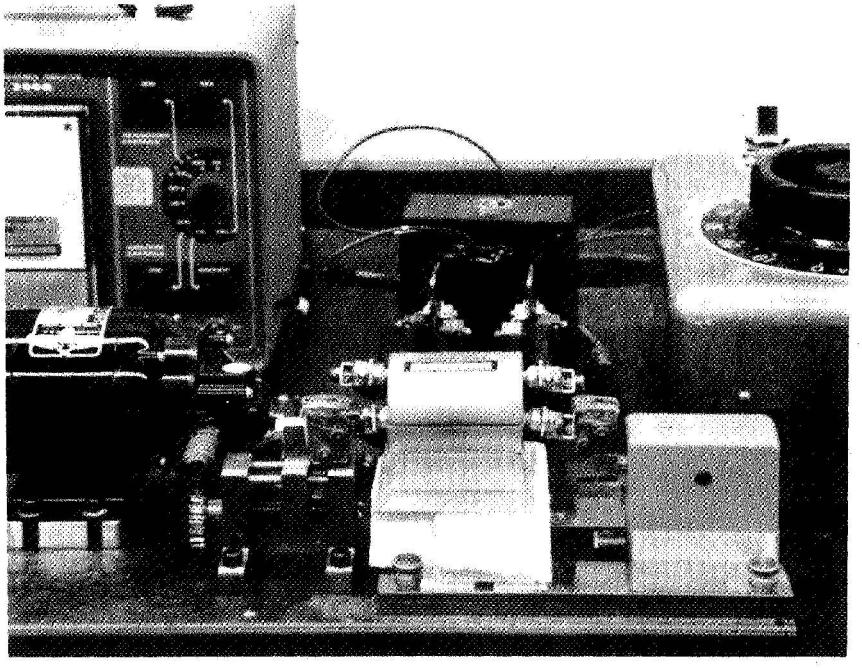


Figure 6. High Temperature Tension Tester

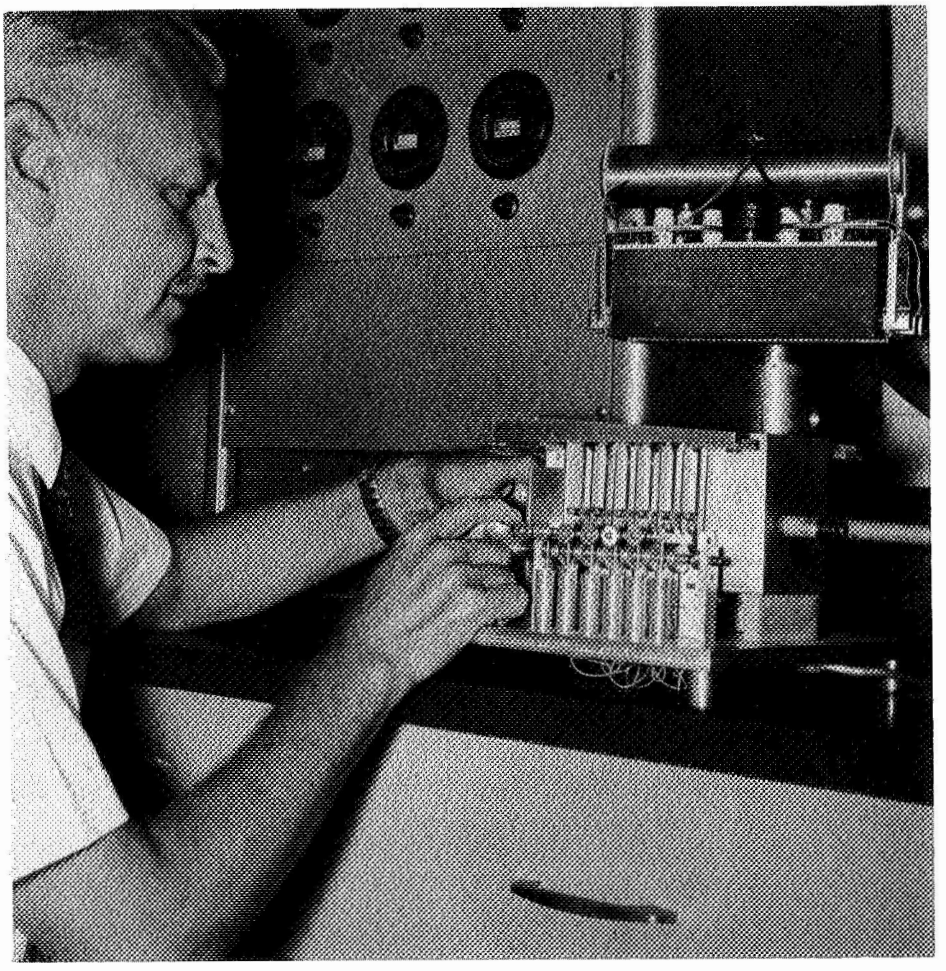


Figure 7. Stress-Rupture Apparatus

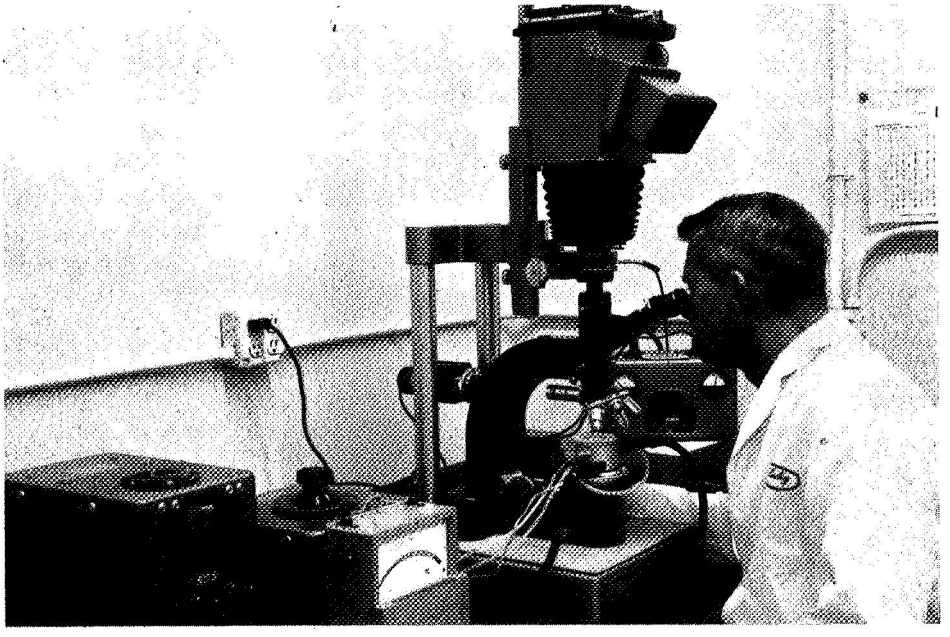


Figure 8. Microscope

The magnification, and thus the correct core diameter, can be calculated using the equation:

$$M = \frac{1 + \left[(p^2 - 1) \quad (n^2 p^2 - 1)\right]^{\frac{1}{2}}}{p^2}$$

Where (p) is the ratio of fiber diameter to apparent core diameter, (n) is the index of refraction of the sheath glass, usually taken to be $n = 1.5$, and (M) is the magnification. Also shown in Figure 8 is the hot stage furnace which made it possible to study microscopically observable changes in the fiber at elevated temperatures as they occurred.

The Norelco X-ray diffraction unit used to identify the various crystalline materials obtained in the core-sheath fiber is shown in Figure 9. Since the fiber configuration is ideal for use in the powder camera, only this unit, seen at the left, was utilized.

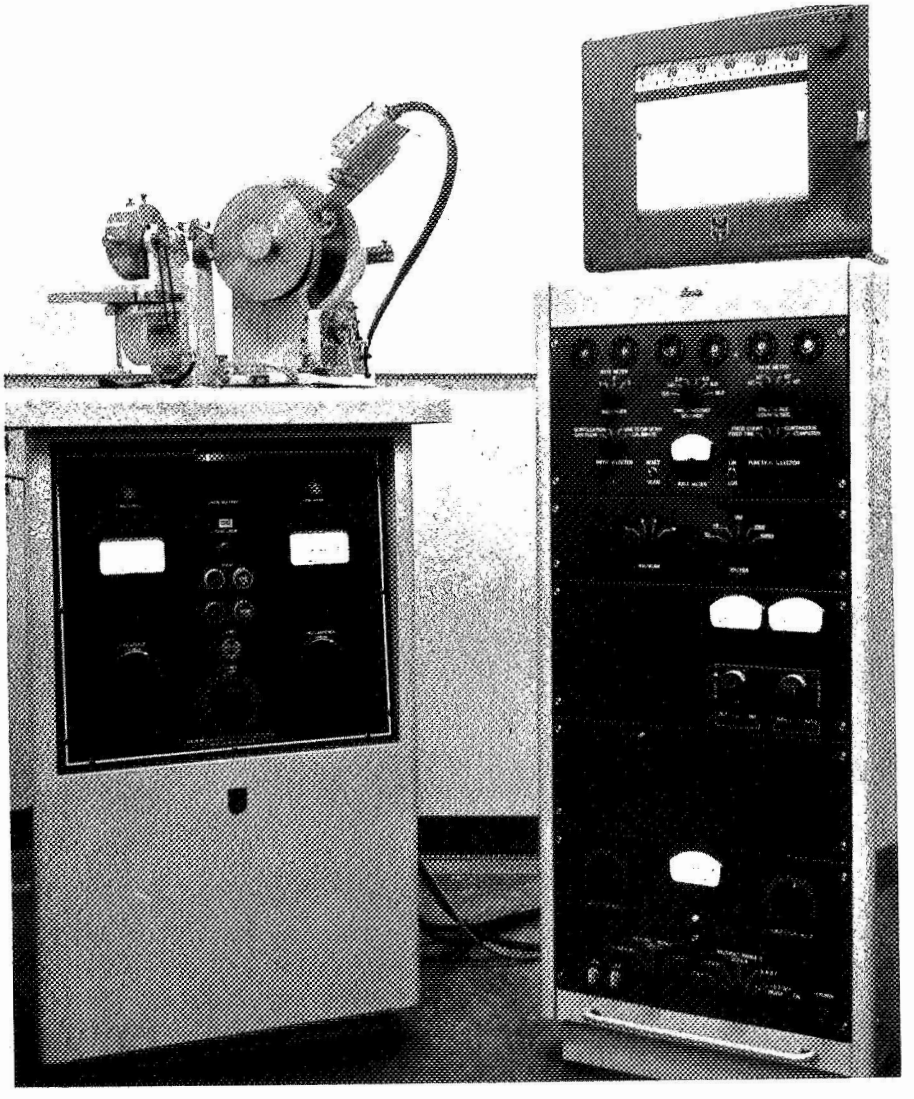


Figure 9. X-Ray Diffraction Unit

IV. FIBER DEVELOPMENT

A. Titania Core Fibers

While awaiting the arrival of the first dual-melt bushing, the furnace was tested successfully to a temperature of 2100°C after a long period of inactivity. Upon arrival, the sheath bushing was charged with Vycor glass, and the core bushing with TiO_2. Judging from the literature, this material looked rather promising and the fiber is easy to form. When the 1.5 - 2.0 mil (38-51 micron) diameter fibers were tested at room temperature, however, an average strength value of only 15,000 psi (10,300 N/cm^2) was obtained. Moreover, when tested at an elevated temperature, breaks were observed to occur in the core, permitting creep in the glass, and elongation of the fiber. The use of TiO_2 was discontinued, and this material will not be discussed further.

B. Vycor-Alumina Fibers

During the remainder of the program, the core material used was Lucalox* alumina. Diameters of the first fibers formed, using Vycor glass in the sheath, ranged from 1.9 to 2.5 mils (48-63 microns). The average strength value obtained at room temperature was 72,000 psi (49,600 N/cm^2), which is quite satisfactory for completely unprotected fibers taken from a bundle. One fiber was tested at 1800°F (980°C) and a value of 144,000 psi (99,300 N/cm^2) was obtained. Unfortunately, a considerable amount of creep was also observed at this temperature. X-ray analysis revealed that mullite ($3Al_2O_3 \cdot 2SiO_2$) had been formed in the core and apparently was the cause of the excessive amount of creep. Methods to reduce the migration of the SiO_2 into the alumina were then investigated and it was decided to reduce the SiO_2 migration rate by incorporating Al_2O_3 in the composition of the glass sheath.

C. Alumina-Silica Sheath Compositions

Mixtures of alumina and silica containing 0, 9.1, 15, 20, 25, 30, 40, 45, and 50% alumina by weight were melted in the hydrogen flame. In the flame, long fibers could be drawn from all of these except the last one. On the other hand, when a single melt bushing was filled with a mixture containing 45% alumina, and an attempt at fiber forming was made, it was completely unsuccessful. When the material was allowed to drip out of the bushing and solidify, a white, opaque mass was obtained which was probably silica mixed with devitrified mullite.(2)

The mixture containing 25% alumina was then tried. Fibers could be drawn in the temperature range between 1650°C and 1700°C although great care was required to avoid devitrification. For greater ease of processing and to increase the glass viscosity the Al_2O_3 content was reduced to 10%. With this mixture the glass moved easily out of the

*General Electric Co.

orifice at 1790°C. Fibers were being formed at temperatures around 2000°C, but the viscosity was too low making fiber drawing difficult. Need for further decrease in alumina content of the glass sheath composition was indicated. A description of the other compositions investigated follows.

D. Miscellaneous Sheath Glass Compositions

As the alumina content in the sheath glass is reduced, one would expect the advantages of adding it in the first place to gradually disappear. It was hoped that in addition to reducing the silica diffusion rate, it would be possible to increase the thermal expansion coefficient of the sheath glass so that it would match more closely that of the alumina in the core. Several compositions were made with these objectives in mind.

Three compositions from the MgO-Al_2O_3-SiO_2 system were made. The first contained 50 wt % spinel (MgO-Al_2O_3), and 50 wt % silica. This composition formed a glass and fibers were drawn in the flame, but the viscosity was much too low to make it compatible with either an alumina or a spinel core. The phase diagram was consulted to find compositions with a melting point in the region of 2050°C. Two were made: one containing five parts spinel and one part silica (by weight), and one containing 70 wt % MgO and 30 wt % SiO_2. Neither one formed a glass.

It has been reported that fibers can be drawn from mixtures of alumina and silica containing as much as 70% alumina when the proper amount of P_2O_5 is added. A composition was made containing 2.5 grams each of alumina and silica, and 1.75 grams of P_2O_5. Fibers were drawn in the flame without difficulty, which, as mentioned earlier, was not possible when the mixture contained equal amounts of alumina and silica, but without the P_2O_5 addition. The proper amount of P_2O_5 was then added to an alumina-silica mixture containing 70% alumina. This time the mixture was kept molten in the flame for an extended period of time to simulate conditions in the bushing. Subsequently, the material proved completely incapable of being drawn into a fiber. Apparently, during the prolonged heating, all the P_2O_5 was driven off.

A peculiar glass composition, containing very little silica, was found in the literature.[3] Theory predicts that the compound $12CaO \cdot 7Al_2O_3$ will form a glass. This turns out to be true in practice, but with great difficulty. However, a very small addition of silica, i.e., 5% or even less, greatly enhances the glass-forming capability and two compositions of this type were made. One given in the reference just quoted, contained 49.4% CaO, 39.8% Al_2O_3, 5.8% SiO_2 and 5.0% MgO by weight. The second was made by mixing 20 parts $12CaO \cdot 7Al_2O_3$, and 1 part SiO_2 (i.e., 4.76 wt % SiO_2). The very low silica content would eliminate any significant amount of silica migration into the core, if this type glass were used in the sheath. Fibers were drawn in the flame from both compositions, but, unfortunately, the viscosity of each was too low to be compatible with the melting point of an alumina core melt.

E. 5A Sheath - Alumina Core Fibers

An alumina-silica sheath composition containing 5 wt % alumina was made and was found to have a suitable viscosity in the region of 2050°C, the melting point of alumina. This composition was designated 5A glass. The viscosity was actually somewhat lower than that of Vycor glass, which proved to have a beneficial effect on the forming characteristics. It also aided in fining the glass. The glass was loaded into the bushing in powder form, and initially the melt was filled with bubbles. One hour at 2050°C with the orifice plugged was sufficient to remove all the bubbles except just under the top surface where they are harmless. The thermal expansion coefficient of this glass did not seem to be any higher than that of Vycor glass, but the large difference between it and the coefficient for alumina did not appear to create any serious problems.

Core-sheath fibers were formed using 5A glass in the sheath and Lucalox alumina in the core. It was immediately apparent that the core in these fibers, being for the most part white and opaque, was different from the transparent core in the Vycor-alumina fibers. Unfortunately, the white core was not continuous, but was interrupted by short transparent sections. In a typical fiber, the length of these sections averaged about 1/32 inch (0.8 mm), while their frequency varied to a considerable extent. The spacing between them, i.e. the length of continuous white core, varied between about 1/16 of an inch (1.6 mm) in very poor samples, up to approximately one foot in the best sample produced.

Most of the 5A sheath-alumina core fibers produced during this program may be referred to as small-diameter fibers, having diameters between 3 and 4 mils (76 and 102 microns). These were drawn on a 6-inch (15 cm) drum at speeds in the vicinity of 100 ft/min (0.5 m/sec) and at a forming temperature of about 2050°C. Core-to-sheath diameter ratios were generally considerably larger than those obtained with Vycor glass in the sheath.

The last portion of the program was spent producing large-diameter fiber. This fiber required a reduction in the drawing speed, and a large (12-inch) winding drum to prevent it from breaking. At a speed of 25 ft/min (0.127 m/sec) and a temperature of about 2030°C, fiber forming was quite difficult. Breaks occurred frequently, and numerous globs of glass were pulled down with the fiber. Apparently the pull was too slow to prevent the glass from accumulating at the orifice. Core-sheath fibers were drawn at 49 ft/min (0.25 m/sec). Fiber diameters averaged, and were all close to, 8.7 mil (221 microns). Core diameters varied from 72% of the fiber diameter up to a diameter so large that, under the microscope, the core seemed to fill the entire fiber.

At this point in the program the all-iridium bushing was put into use. Since the core material could now be watched as it entered the forming cone, it was possible to pull a continuous fiber for a period

extending over several minutes. It was found that once the pressure had been adjusted to give a desirable flow rate of core material, constant attention was no longer necessary. A large fiber bundle was produced, but the fiber was poor with a high frequency of core discontinuities. The drawing speed was 69 ft/min (0.35 m/sec), and the temperature 2010°C, which is comparatively low. The fiber diameter was 6.7 mil (170 micron), which is somewhat smaller than ideal.

A fiber was also pulled at 115 ft/min (0.58 m/sec) and 2030°C. Only a few turns on the drum were obtained and the diameter was only 5.9 mil (150 micron); however, the core had few and very small discontinuities. The distance between two adjacent discontinuities was approximately one foot (30 cm).

V. FIBER EVALUATION

Except for the few instances reported earlier, evaluation and testing was confined to the 5A sheath-alumina core fiber.

The nature and composition of the core was studied by means of X-ray diffraction analysis. In a spectrum obtained on a white core section, 14 lines were analyzed. All, except two weak ones, belong to the spectrum for θ-alumina. The two exceptions can be accounted for by traces of other forms of alumina. Furthermore, there are no important lines in the θ-alumina spectrum which cannot be found in the spectrum obtained. Thus, the white sections of the core in these fibers are θ-alumina as opposed to mullite which was obtained when Vycor glass was used in the sheath. θ-alumina is closely related to α-alumina, into which it is supposed to convert completely in about an hour at 1200°C.(4) When this heat treatment was tried, however, conversion did not take place. Instead, the spectrum for θ-alumina became more intense, indicating that this phase became more firmly established.

Spectra have also been obtained for the transparent sections, one before and one after heat treatment. The first showed few lines; only five were analyzed, all of which can be found in the mullite spectrum. Heat treatment in the propane torch brough out several additional lines. Sixteen were analyzed, and all of these can be accounted for by the presence of mullite. The treatment also changed the mullite sections from transparent to opaque. In every respect, these sections behaved exactly like the core in the fiber using Vycor glass in the sheath.

The closeness of the discontinuities in the core would suggest that, if indeed caused by variations in the flow, these variations would be too rapid to be followed by the eye. They might conceivably be produced by rapid changes in the pressure above the core melt, such as might be generated by the mechanical vacuum pump used in the variable pressure system. To investigate this possibility three empty argon cylinders were connected to the system and evacuated. In subsequent runs, these were used to obtain any negative pressure required, with the pump turned off during forming. Unfortunately, the formation of core discontinuities persisted.

When the alumina core was examined under the microscope, the polycrystalline structure was clearly evidenced by the grainy appearance. When the fiber with the sheath removed was placed between two microsccpe slides which were then rubbed together, the grains were separated. Heat treatment for one hour at 3000°F (1650°C) preceding this test did not affect the results. Small balls obtained by melting the fiber, and small pieces of Lucalox, could also be crushed in this manner, although they seemed somewhat stronger than the as-drawn fiber core.

The alumina fiber was heated slowly toward its melting point in the hot stage-furnace. As red heat was reached, it showed a tendency to bend, and at temperatures approaching the melting point it started to break up, this process continuing until melting occurred. Apparently, grain growth

became so rapid and extensive that the structural integrity of the fiber was destroyed. When a fiber treated in this manner, but without being melted, was ground between two glass slides, the average particle size, and the size of the marks made in the glass, were considerably larger than in the case of an untreated fiber.

The mechanical performance of the fiber, especially at elevated temperatures, is of course of primary interest. The 5A sheath-alumina core fiber was found to possess the essential quality of being creep resistant at 2000°F (1100°C). In one particular experiment, although the load was only 1500 psi (1030 N/cm^2), it is significant that no creep was observed at a temperature as high as 2200°F (1200°C).

Tensile strength values obtained under various conditions are shown in Table I. In the case of the room temperature tests, only the fiber as a whole has been considered. Since the individual Young's moduli of the sheath and core are not known, the load carried by each cannot be specified. On the other hand, tests carried out on 5A glass fibers at 2000°F (1100°C) have shown that the glass deforms very rapidly under load at this temperature. Thus, although the breaking loads for core-sheath fibers tested at 2000°F have been calculated using both the fiber diameter and the core diameter, it is probably safe to assume that the load is carried by the core alone. The table then shows that the core is stronger at 2000°F than the fiber as a whole at room temperature. Attempts were made to capitalize on this condition by removing the sheath using 52% hydrofluoric acid. Immersion for a period of 15 minutes removed the entire sheath and most of the mullite sections in the core. An additional 15 minutes was sufficient to remove the remainder of the mullite, but did not change the diameter of the alumina core. It is seen that the strength values obtained on this all-alumina fiber were disappointingly low (No. 5 and 6). It appears that the HF has a detrimental effect on the alumina fiber. In one case where the sheath was removed mechanically, a method which might have been expected to cause considerable damage, the strength value obtained was considerably higher (No. 12).

In addition to being tested at an elevated temperature, fibers were also subjected to heat treatment. Three fibers (Nos. 7, 8, 9) which had had their sheaths removed by means of HF were treated at temperatures well above 2000°F (1100°C): one at 2200°F (1200°C) and two at 2700°F (1480°C), each for a period of one hour. In each case the strength was reduced to such an extent that a reliable value could not be obtained. A fiber with the sheath retained was also treated for one hour at 2700°F and then tested at 2000°F. Although the loss in this case too was considerable, it retained a significant amount of strength (No. 10).

The effect of heat treatment at the test temperature for periods longer than one hour was also investigated. The value for the core strength obtained after five hours (No. 11) is the second highest of any shown in the table, but it is significantly below the value obtained when the fiber was tested immediately upon attaining 2000°F (1100°C) (No. 4). The two values obtained after 50 hours represent a further considerable reduction

TABLE I
PROPERTIES OF SMALL-DIAMETER CORE-SHEATH FIBERS

Sample No.	Test Temp. °F	Test Temp. °C	Sheath Retained	Sheath Removed	Treatment Temp. °F	Treatment Temp. °C	Treatment Time Hrs.	Diameter Fiber Mil	Diameter Fiber Micron	Diameter Core Mil	Diameter Core Micron	Tensile Strength Fiber psi	Tensile Strength Fiber N/cm^2	Tensile Strength Core psi	Tensile Strength Core N/cm^2
1	Room		X		NA		0	3.91	99.3	2.65	67.3	28,000	19,300	NA	
2	Room		X		NA		0	3.91	99.3	2.65	67.3	33,000	22,800	NA	
3	Room		X		NA		0	3.91	99.3	2.65	67.3	44,000	30,300	NA	
4	2000	1100	X		NA		0	3.59	91.1	2.25	57.1	30,000	20,700	76,000	52,400
5	2000	1100		X	NA		0	NA		2.08	52.8	NA		24,000	16,500
6	2000	1100		X	NA		0	NA		2.47	62.7	NA		31,000	21,400
7	2060	1130		X	2200	1200	1	NA				NA		Low	
8	2000	1100		X	2700	1480	1	NA				NA		Low	
9	2000	1100		X	2700	1480	1	NA		1.25	31.8	NA		Low	
10	2000	1100	X		2700	1480	1	3.74	95.0	2.13	54.1	7,000	4,800	22,000	15,200
11	2000	1100	X		2000	1100	5	3.32	84.3	2.09	53.1	21,000	14,500	53,500	36,900
12	2000	1100		X*	2000	1100	5	NA		2.22	56.4	NA		42,000	29,000
13	2000	1100	X		2000	1100	50	3.36	85.4	1.91	48.5	9,100	6,300	28,000	19,300
14	2000	1100	X		2000	1100	50	3.78	96.0	2.20	55.9	12,000	8,300	35,000	24,100

* Sheath removed mechanically rather than by using HF.

in the strength (Nos. 13 and 14). In the course of this heat treatment, the sheath changed from transparent to translucent. X-ray diffraction analysis showed that mullite had formed, probably as inclusions in the glassy matrix. Immersion in HF brought about dissolution of the sheath while the core remained intact, indicating that mullite formation did not extend into the core.

The large-diameter fiber could not be successfully tested in tension at 2000°F (1100°C) before funds were depleted. As mentioned earlier, no bonding agent with sufficient strength could be found. The highest load applied to a fiber before bond failure occurred was 29,000 psi (20,000 N/cm^2); not sufficient to break the fiber. If a long fiber without core discontinuities had been produced, the fiber would have been attached directly to the tester jaws outside the furnace, eliminating the need for a bond sufficiently strong at 2000°F.

Core-sheath fiber samples were sent to NASA for examination and testing.* Values obtained are shown in Table II. These were not virgin fibers, and the samples were slightly bent, both of which are factors contributing to a reduction in the strength.

TABLE II

PROPERTIES OF NASA-TESTED CORE-SHEATH FIBERS

No.	Diameter		Tensile Strength	
	Mil	Micron	psi	N/cm^2
1	6.0	152	40,700	28,100
2a	8.2	208	32,200	22,200
2b	8.2	208	34,500	23,800
3	7.65	194	32,000	22,100
4#	-	-	-	-
5	3.8	96.5	46,000	31,700
6	4.4	112	37,500	25,800

Photomicrographs were also made of some of these samples. Figure 10 shows a fairly small fiber with a fairly thick sheath. The fiber shown in Figure 11 has a diameter of 8.2 mil (208 micron), and the sheath is extremely thin. In fact, on one side, the sheath is virtually nonexistent. This is the same fiber as Sample No. 2 in Table II. The magnification in both figures is 91.5.

Figure 12 shows longitudinal cross-sections of the fiber in Figure 11. An impressive amount of structural detail is displayed in these photographs. The magnification is 200 in Figure 12a, and 500 in Figure 12b.

* The work was conducted by Mr. Leonard J. Westfall, NASA-Lewis Research Center

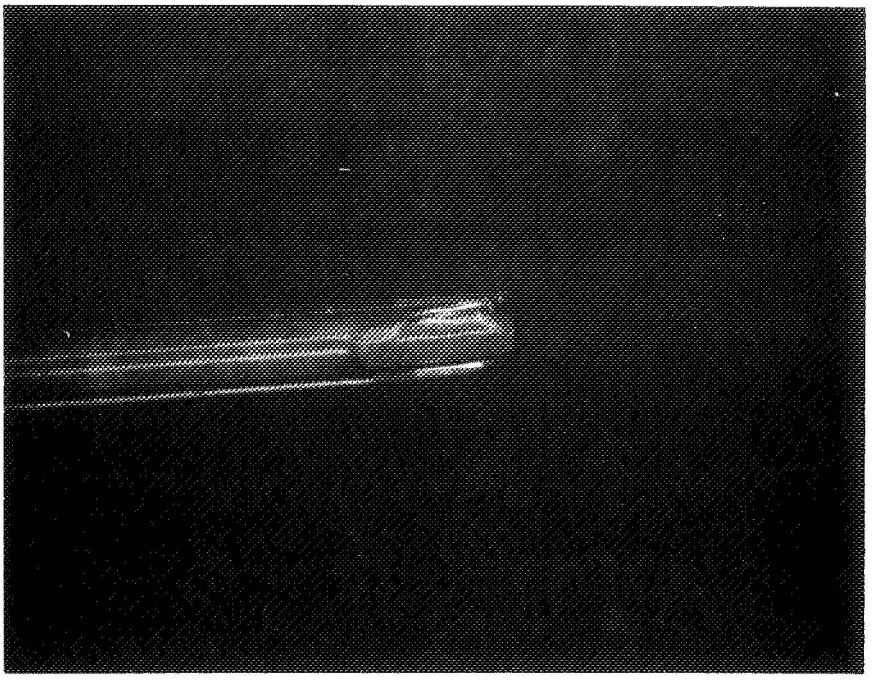


Figure 10. Small Core-Sheath Fiber
Magnification 91.5

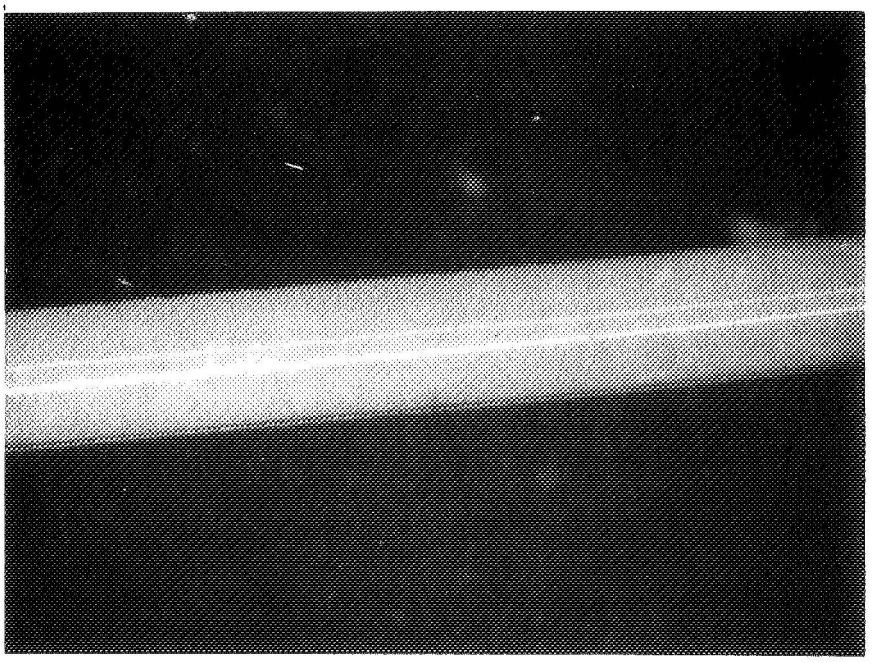
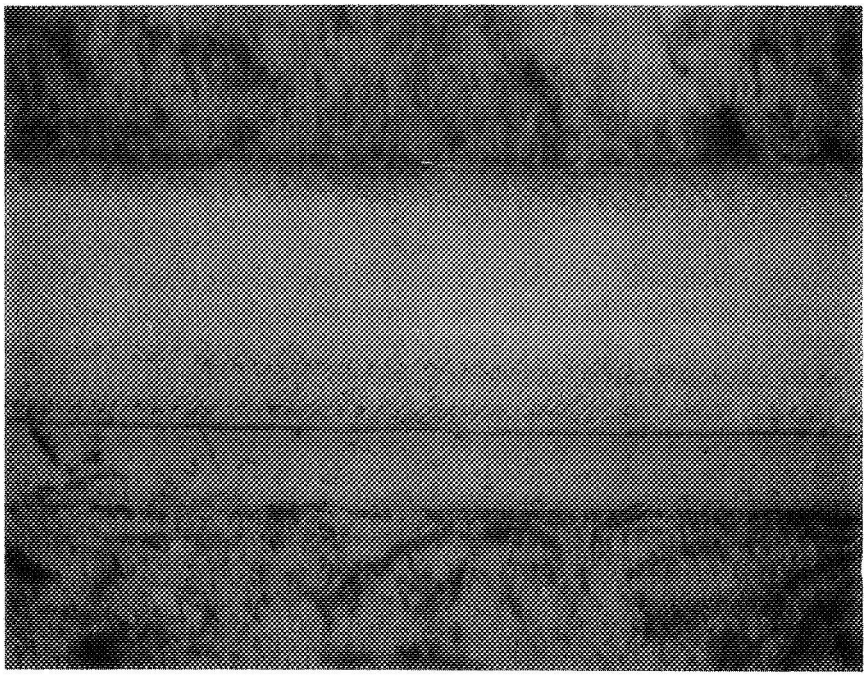
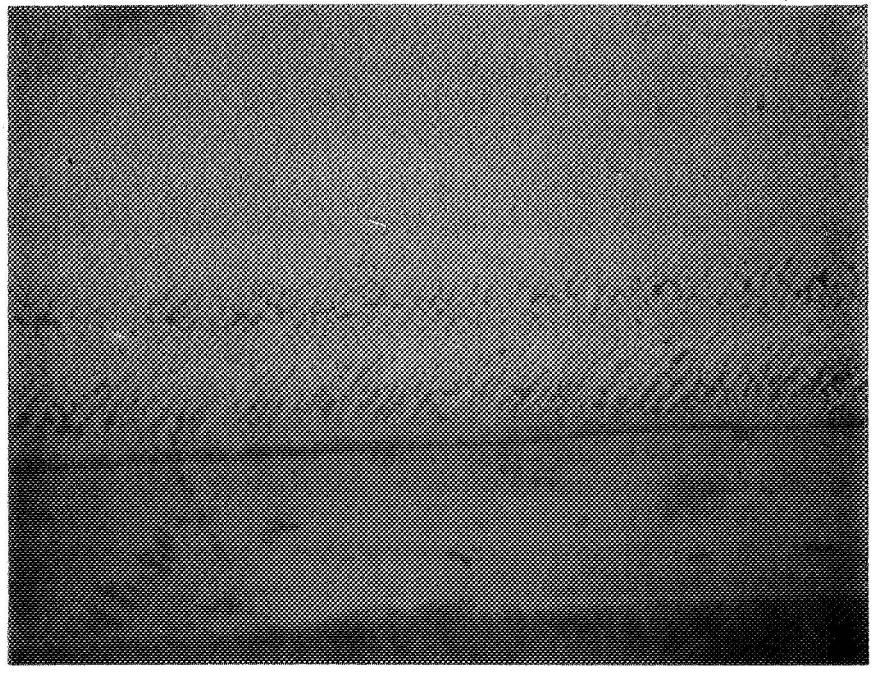


Figure 11. Large Core-Sheath Fiber
Magnification 91.5



(a) Magnification 200



(b) Magnification 500

Figure 12. Cross-Section of Large Core-Sheath Fiber

VI. DISCUSSION OF RESULTS

The substantial increase in strength of the Vycor sheath-alumina core fiber which was obtained when the test temperature was increased was not unexpected. In the region of 1800°F (980°C) stress concentrations produced by imperfections in the glass surface are rapidly relieved.

The creep observed at this temperature constituted a rather severe setback at this early stage of the program. Creep in Vycor at 1800°F (980°C) is not surprising; in fact, a fused silica fiber was tested and found to creep at this temperature. However, some creep in the sheath would be harmless due to the small thickness of the sheath. On the other hand, the creep actually observed in the core-sheath fiber indicated creep in the core, and this is completely unacceptable. X-ray diffraction analysis of this type of fiber had already revealed that the core is not alumina, but mullite ($3Al_2O_3 \cdot 2SiO_2$). This material is obtained because during fiber forming a substantial amount of silica migrates from the sheath into the core, where it combines with the alumina. It was now evident that the mullite did not have satisfactory mechanical properties at the crucial temperature of 2000°F(1100°C), and that a drastic change in fiber composition was required. Since alumina appears to be superior to all other ceramic materials with the possible exception of some containing beryllia, it was decided to concentrate on modifying the sheath composition so as to prevent silica migration. The diffusion rate is governed by the equation[5]: $Q = -DA(dc/dx)$, where (Q) is the rate of material transfer in the x-direction through the area (A), (D) is the diffusion coefficient, and (c) is the concentration of diffusing material. One method of reducing the diffusion rate consists of adding alumina to the sheath glass. Vycor glass, consisting of approximately 96% silica and 4% boric oxide (B_2O_3), is virtually devoid of alumina.

In the case of the alumina-silica sheath composition containing 45% alumina, it appears that the proper viscosity for fiber forming occurs at a temperature considerably below the liquidus. When the fiber is drawn in the hydrogen flame, the material is first heated above its liquidus, the torch is then withdrawn, and the fiber drawn when the viscosity has increased sufficiently, but before devitrification has occurred to a significant extent. (The fiber iteself is quenched rapidly enough to remain in a glassy state.) The technique of drawing while the melt is cooling is of course not applicable to continuous fiber forming from a bushing, and the experiment shows that the ability to draw a fiber from a material in the flame is no guarantee that it can be drawn from the same material in the bushing.

In the case of the mixture containing 25% alumina, the obvious problem was that proper forming viscosity was attained at a temperature approximately 350°C below the melting point of alumina. If the temperature were raised by this amount, the viscosity of the glass would be much too low for fiber forming.

The production of the creep resistant 5A-fiber containing for the most part alumina in the core as opposed to mullite, naturally constituted the most important development during this program. The improved forming characteristics which may eventually eliminate the need for constant regulation of the flow of core material will be important if large scale production is ever contemplated. The appearance of θ-alumina rather than α-alumina in the core is not necessarily undesirable, although the possibility of bringing about improvement in the mechanical properties of the fiber through conversion into the α-phase certainly exists.

No explanation for the formation of the mullite sections has yet been found. Irregularities in the flow of alumina causing momentary shortages of this material in the core would seem like a plausible explanation. A tendency of the alumina to drip rather than flow evenly out of the core orifice was observed during earlier work. When the 5A glass was first put into use it was impossible to observe the behavior of the alumina as it left the core orifice. This was due to the fact that the alumina-containing glass, when in contact with the tungsten bushing at forming temperature, turned very dark and virtually opaque. The alumina could not be seen through the glass in the forming cone. Toward the end of the program, this problem was eliminated by substituting an all-iridium bushing, described earlier. With the glass now being perfectly clear, the flow of alumina could be observed closely, and was found to be perfectly even. It should be noted here that checking the evenness of the flow was not the only purpose of introducing the iridium bushing. The ability to observe the flow of core material is absolutely essential to the production of continuous core-sheath fibers with a large and uniform core diameter.

From the results of the tensile strength tests it is evident that immersion in hydrofluoric acid has a detrimental effect on the strength of the alumina core. This is true under any circumstances, but the effect is greatly emphasized when the fiber is also heat treated at a very high temperature, e.g. 2700°F (1480°C), before testing.

The reduction in strength produced by the 50-hour treatment at 2000°F (1100°C) naturally creates concern regarding the fiber's ability to retain strength when exposed to temperatures in this region for extended periods of time. However, considering the scarcity of data, any definite conclusions at this point would certainly be premature. More samples are needed to establish the points examined, and furthermore, the period of heat treatment should be extended to determine if the apparent trend continues. Since the basic material is alumina, which would not normally be expected to deteriorate at 2000°F (1100°C) other possible causes should be investigated. The origin of the weakening of the fiber may lie in the sheath rather than the core, as indicated by the noted change in appearance of the sheath.

VII. CONCLUSIONS AND RECOMMENDATIONS

A fiber consisting of an alumina core within a glass sheath has been produced using a continuous fiber-drawing process, and samples have been delivered to NASA-Lewis Research Center. The fiber is creep-resistant at 2000°F (1100°C), a characteristic not shared by any glass fiber, including a pure silica fiber. The room temperature tensile strength approached 50,000 psi (34,500 N/cm^2) for large diameter fibers containing a large amount of alumina. An increase by a factor of two in the tensile strength values obtained would be desirable, and does not appear entirely beyond reach. Factors which may have contributed to a reduction in the measured strength are mechanical abrasion of the glass surface, curvature of the fiber, and a high frequency of jaw-breaks. On the other hand, no reduction in the strength of the core was observed when the test temperature was increased from ambient to 2000°F. Fibers tested at 2000°F showed a core strength as high as 76,000 psi (52,400 N/cm^2). Prolonged heat treatment at 2000°F appears to produce a loss in strength, however, the data is inconclusive. Heat treatment should be carried out for periods longer than 50 hours, the longest period used in this program.

The occurrence of discontinuities in the alumina core in the form of short mullite sections remains an unsolved problem, even though occasional fibers with hardly any discontinuities have been produced. Considering the drastic improvement in core composition when the glass containing 5% alumina was introduced, it is reasonable to expect that a sheath glass containing, say, 10% alumina would completely eliminate any mullite formation. The low viscosity of such a glass makes it inconvenient, but not impossible to use at the temperature where alumina melts. The inconvenience could be greatly reduced, if not eliminated, by decreasing the size of the sheath orifice. An incidental advantage of increasing the alumina content of the sheath glass would be an increase in the thermal expansion coefficient, thus bringing it closer to that of the alumina core. It may also be noted that the decrease in the viscosity attending the introduction of the 5A glass made it possible to increase the core-to-sheath ratio. A further decrease in the viscosity may produce a further improvement in this respect.

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