N74-10548
NASA CR-132319

DEVELOPMENT OF A PROCESS FOR PRODUCING RIBBON SHAPED FILAMENTS

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Prepared under Contract NAS1-12103

October 15, 1973

By

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For

U. S. Army Air Mobility R&D Laboratory (Langley Directorate) and
National Aeronautics and Space Administration
Langley Research Center
Langley Station
Hampton, Virginia 23365

FOREWORD

This report was prepared by Avco Systems Division of Avco Corporation, under NASA contract NAS1-12103 and covers the work performed during the period of February, 1973 through September, 1973. This program was jointly funded by the Materials Division of NASA-Langley Research Center and the U.S. Army Air Mobility Research and Development Laboratory (Langley Directorate). The contract was monitored by R.L. Foye of the Composites Section.

The authors wish to acknowledge the following Avco and General Electric Company personnel: The assistance of T. Henze of Avco in the construction and operation of the deposition reactor and evaluation of the material is gratefully acknowledged. The carbon ribbon substrate was provided with assistance of D. Flom and B. Horowitz of General Electric Research and Development Center.

UNITS

Dimensional information is presented, in general, in the International System of Units (SI) with the equivalent values in the FPS system following in parenthesis.

All calculations were performed in SI units.

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SUMMARY

Silicon carbide (SiC) ribbon filaments were produced on a carbon ribbon substrate, about 1500 microns (60 mils) wide and 100 microns (4 mils) thick in lengths up to 2 meters (6 ft), and with tensile strengths up to 142 KN/cm^2 (206 Ksi). During the course of the program, ribbon filaments of boron were also produced on the carbon ribbon substrate; the boron ribbon produced was extremely fragile.

The tensile strength of the SiC ribbon was limited by large growths or flaws caused by anomalies at the substrate surface; these anomalies were either foreign dirt or substrate imperfections or both. Related work which is currently being carried out on round 100 micron (4 mil) diameter SiC filaments on a 33 micron (1.3 mil) diameter, very smooth carbon monofilament substrate has showed that tensile strengths as high as 551 KN/cm^2 (800 Ksi) are obtainable with the SiC-carbon round substrate combination, and indicates that if the ribbon substrate surface and ribbon deposition process can be improved similar strengths can be realizable. Cost analysis shows that 100 micron x 5-10 micron SiC ribbon can be a very low cost reinforcement material.

INTRODUCTION

To date most of the high strength, high modulus reinforcements such as boron or silicon carbide (SiC) have consisted primarily of round filaments each 100, 140, or 200 microns in diameter. Besides the inorganic fibers, graphite yarns, consisting of a large number of individual round filaments each about 8 micron diameter, have also found wide utilization in advanced composite applications. These round filaments provide high composite strengths in a direction parallel with the axis of the monofilaments, but they have produced much lower strengths perpendicular to the filament axis. Several theoretical investigations have pointed out that a ribbon-shaped reinforcing filament offers the potential of substantially higher shear and transverse properties. Besides the potential technical advantage of increased transverse strength, ribbon shaped filaments offer a substantial potential cost reduction which results from the substantially higher production rate of a ribbon filament reactor. For example, one deposition reactor producing 2500 x 100 micron (100 x 4 mil) ribbon is equivalent to the production rate of 30 reactors producing 100 micron (4 mil) round filament. The ribbon concept, despite the potential advantages, has remained a laboratory curiosity.

The objective of the program reported herein was to develop and demonstrate a viable process for producing ribbon filament. The target dimensions were 125-250 microns thick (5-10 mils), by 2500 microns wide (100 mils) by 0.25 meters or more long (1 ft), with 10% or less of the cross-sectional area used for the substrate. The target strength of these ribbon filaments was 140 KN/cm^2 (200 Ksi).

TECHNICAL DISCUSSION

The original material investigated for deposition on this program was boron. Preliminary studies prior to and during this program showed that boron ribbon was very fragile because of the growth strain characteristics of boron deposition. To avoid this problem the program was broadened to include SiC as a reinforcing material in addition to boron. The substitution of SiC deposition in place of boron made it possible to meet the program objective of 140 KN/cm^2 tensile strength (200 Ksi). The modulus of SiC is 44 MN/cm^2 (63 MSi), about 10% higher than boron, and its density is 3.17 g/cm^3, compared with 2.33 g/cm^3 for boron.

The substrate used for most of the deposition studies was a glassy carbon ribbon about 1500 microns wide (58 mils), by 17 microns thick (0.66 mils), produced by the General Electric Research Center. The supporting graphite ribbon technology was previously developed under GE and other sponsorship[1].

The sections below will describe first the studies conducted with a static reactor in which the substrate was held fixed during deposition in a 38 cm (15 inch) long reactor tube. Next, the studies conducted in a continuous deposition reactor process will be described. The Appendix will describe some related studies which include the very successful deposition of SiC on a round carbon monofilament substrate, carbonization of DuPont Kapton^R film, resin coating of the GE ribbon to improve its surface smoothness, deposition on Union Carbide Graphoil^R, and deposition attempts on carbon yarn and nickel and nichrome ribbon.

Preliminary Static Reactor Deposition Studies

At the beginning of the program, the deposition studies were conducted on a static reactor, wherein the substrate was held fixed in a 38 cm (15 inch) long reactor tube while the gases and filament heating power were held on for approximately 40 seconds duration of the deposition. Figure 1 shows the schematic of the system that was used for these preliminary deposition studies. Before a deposition test, the carbon ribbon substrate was first lowered through the reactor tube, affixed at the top, and weighted at the bottom. A slotted metal

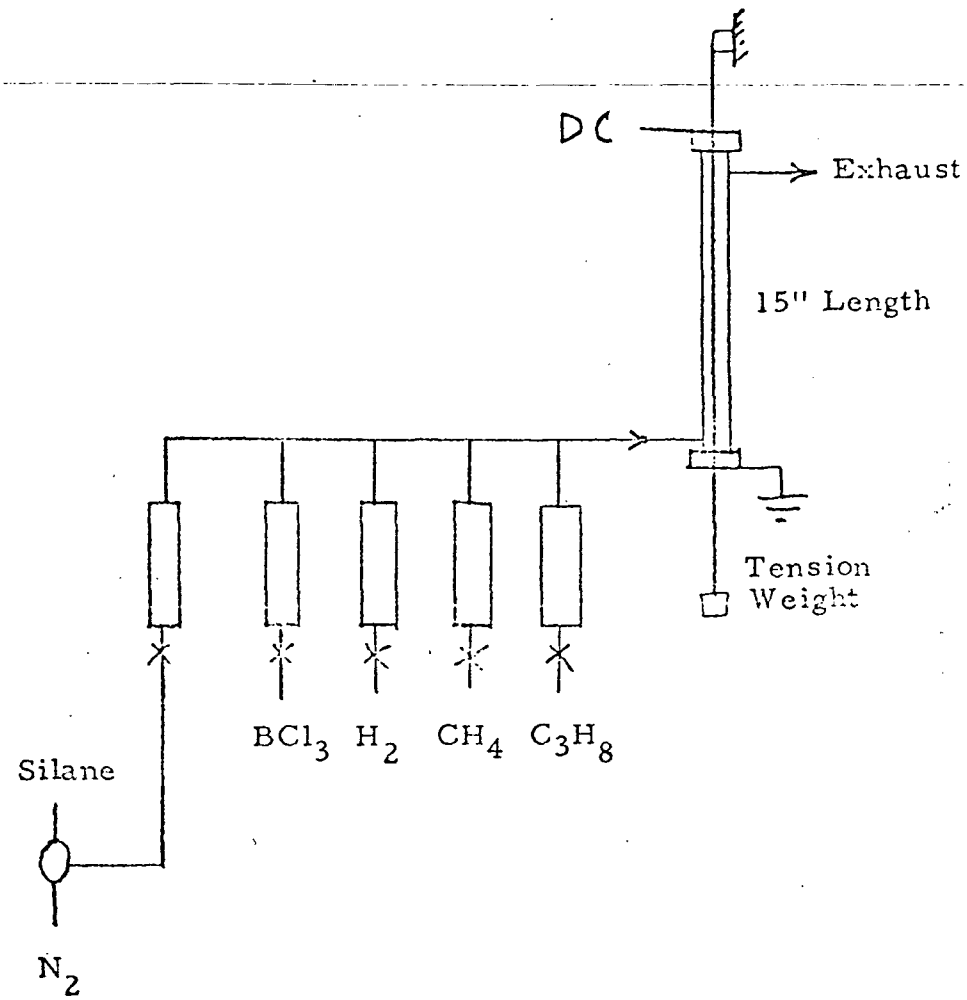

Figure 1. Schematic of Static Reactor for Making Ribbon Filament.

disc was then slipped over the ribbon and inserted into the electrodes at both ends, and the electrode cavities filled with mercury. The deposition gases were then turned on and the filament heated electrically, using DC current at about 1 ampere. For some of the tests the filament was first heated in N_2 or H_2 to about 1500°C to clean the substrate. The reactive gas was a 50/50 mixture of H_2 and BCl_3 or subsequently in the program a 70/30 mixture of H_2 and organo-silanes. The filament was heated to the deposition temperature of 1350°C, (measured with a 2-color optical pyrometer, a Milletron Thermoscope), for 20 to 40 seconds. When SiC was deposited some propane was added during the first or last two seconds, or both, to provide a modified surface layer. The propane was found beneficial during an earlier AFML program[2] which was directed to the establishment of an improved process to produce SiC filament. Some of the tests included deposition of a layer of pyrolytic graphite (PG) on the substrate before deposition of the boron or SiC layer. This was achieved by heating the substrate to temperatures of 1500-2500°C in a gaseous mixture of CH_4 and either H_2 or N_2.

After deposition, the coated filament was removed through the slotted electrodes and tensile tested. When 10 to 100 ft lengths of carbon substrate became available from GE, a new substrate section was drawn into the reactor as the coated section was extracted.

Boron was deposited on the ribbon during the initial tests, and the resulting ribbon was fragile. These boron ribbons were studied exhaustively to determine the cause of low strength and to determine means to improve it. The most difficult problem was caused by the internal stresses due to the expansion of boron after it was deposited. This expansion phenomenon, still not fully understood, was investigated in detail during an earlier Avco IRAD program to develop a process to deposit boron on a carbon monofilament substrate. The expansion of boron had been observed by measuring the increase in filament length in a static reactor during boron deposition on the substrate. The length increase observed at constant deposition temperature as a function of thickness of boron deposited is shown in Figure 2. The end result of boron expansion, as it effects round filaments, is a residual stress distribution which manifests itself as compressive stresses in the outer layers and tensile stresses in the inner layers. The expansion resulted in the fracture of the carbon substrate when its ultimate

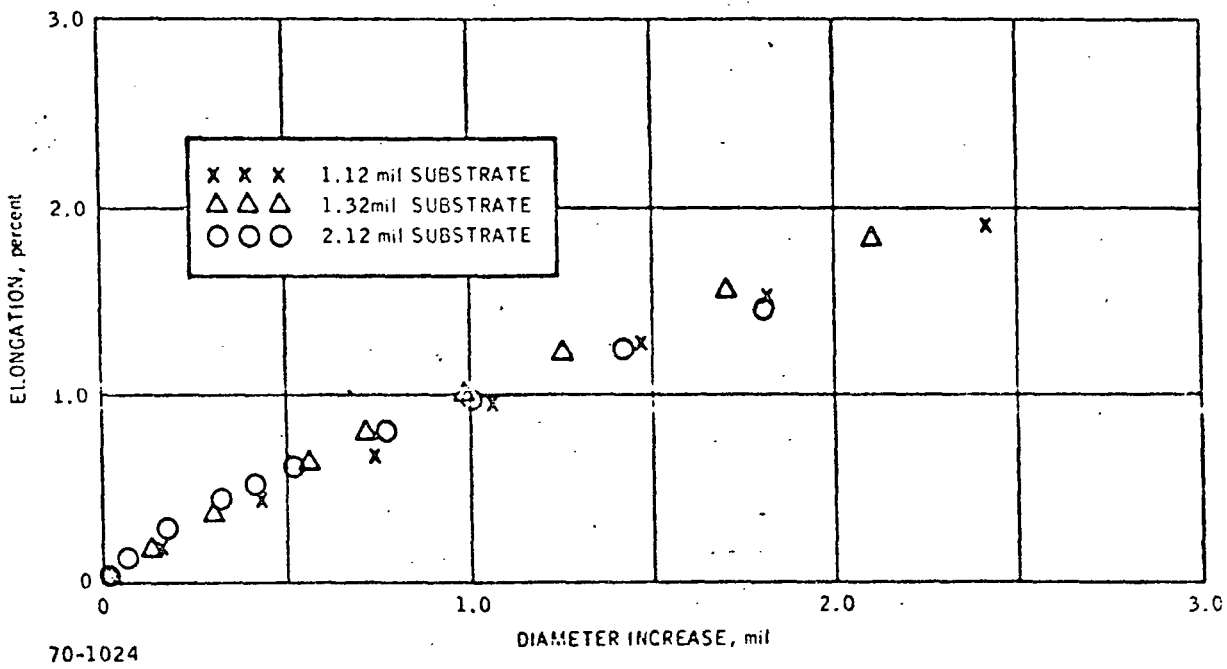

Figure 2. Boron Elongation Versus Thickness of Boron Added (Round Substrate)

strain capabilities were exceeded. This fracture phenomenon was named the "light-bulb" flaw because of the appearance of numerous closely-spaced hot spots along the filament at points whereat the current path shifted to the boron sheath.

When boron is deposited in ribbon form, boron expansion phenomena also result in similar deposition problems; for example, typical distortion anticipated is shown in Figure 3, resulting in high local stresses, with attendant low filament strength. After many boron deposition tests were carried out such distortion was found. At temperatures of about 1350°C, i.e., normal deposition conditions for boron filament, several (but not all) cross-sections of ribbon boron evidenced this stress-separation. Figure 4 is a photomicrograph of a polished cross-section of ribbon boron showing the separation that boron deposition is seen to be fairly uniform, even at the edges of the ribbon. This uniformity results when the ribbon is first coated with PG at 2500°C and is probably due to heat transfer considerations.

On the previous AFML boron-on-carbon program, reported in AFML-TR-72-271 it was found that boron deposited at temperatures higher than 1350°C did not undergo as much expansion as that deposited at 1350°, and it was felt that one way to circumvent some of the boron expansion difficulties in ribbon boron was to deposit at very high temperature say 1400-1500°C. The boron deposit at this temperature is crystalline rather than amorphous as stated above, and it was found that virtually no expansion occurs during deposition at these conditions. When (round) boron-on-carbon filament is produced under these conditions, it is relatively weak, 100-140 KN/cm^2 (150-200 Ksi) compared to about 340 KN/cm^2 (500 Ksi) for normal 100 micron (4 mil) boron-on-carbon. However, 100-140 KN/cm^2 level is very near the target goal for this current ribbon program, and therefore, deposition of crystalline boron was given further consideration.

Another option that was considered during the early phases of the program was the deposition of silicon carbide in ribbon form. On the parallel AFML funded program[2] directed to establishing an improved economic process for producing SiC filament, it was found that no expansion occurs at normal deposition temperatures, and typical strength levels of 350 KN/cm^2 (500 Ksi) on both

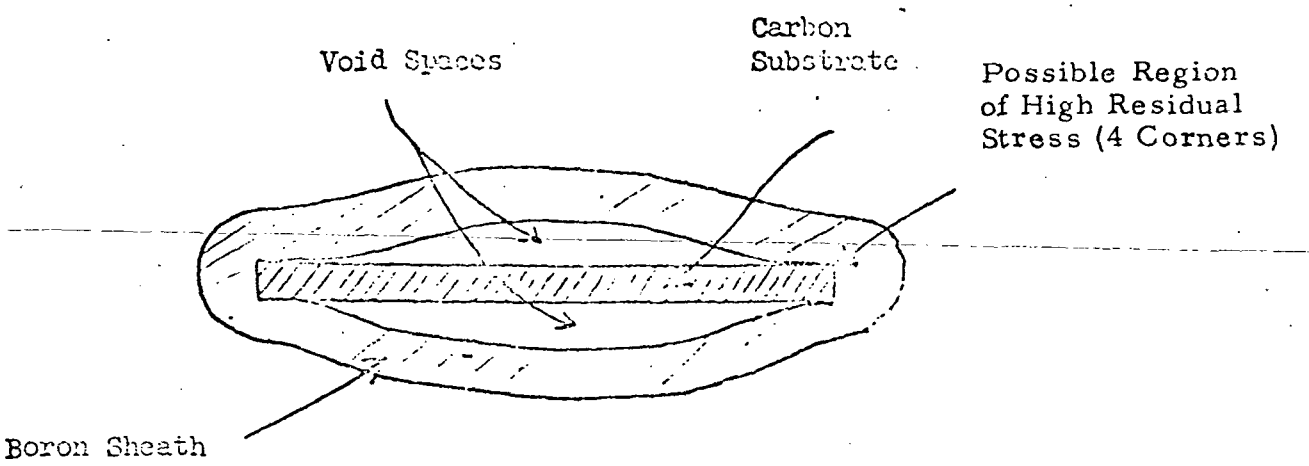

Figure 3. Distortion of Ribbon-shaped Boron as a Result of Boron Expansion during Deposition.

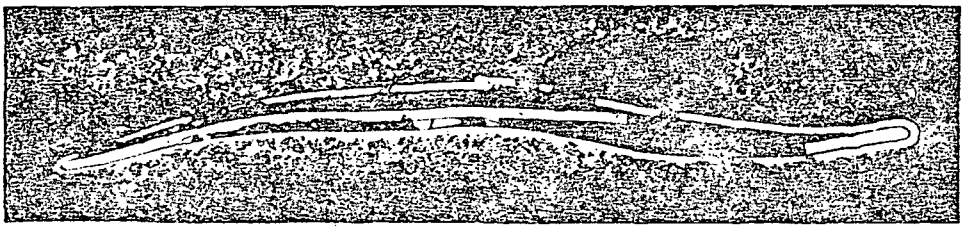

Figure 4. Cross-Section Photograph of Boron/Carbon Ribbon Showing Separation.

tungsten substrate and round carbon monofilament substrate have already been achieved. After approval of the Army program monitor, the program scope was broadened to include ribbon of SiC on carbon as one of the reinforcement materials to be considered.

Table 1 shows the results of some early attempts at boron and SiC deposition. Most of the tests involved the deposition of boron over PG-coated carbon ribbon. For all the runs PG was deposited at about 2500°C, and temperatures of 1300°C, 1350°C and 1400°C were used for boron deposition. Boron which was deposited at 1300°C was amorphous and a surface photograph is shown in Figure 5. Amorphous boron, however, underwent the severe growth strains as explained above. Curved surfaces resulted with light bulb flaws seen during the deposition sequence, and the ribbon was usually so fragile that even delicate handling resulted in breakage before tensile tests could be made. At 1350°C the surface was partially amorphous with frequent crystalline spots, and Figure 6 shows the surface texture of β-rhombohedral boron in the amorphous boron matrix. This ribbon was also very fragile. At 1400°C, the surface was more fully polycrystalline but the boron ribbon produced was still weak and friable. The test pieces broke as the tensile test jaws were closed and no strength determinations could be made. A photomicrograph of the typical fully polycrystalline ribbon produced at 1400°C is shown in Figure 7.

The first silicon carbide ribbons showed a surface which was very rough as seen in a typical photomicrograph, Figure 8, and was marked with closely spaced bumps. As will be brought out, optical microscopy tools were used in analyzing low strength fractures and were also used in determining the morphology of the ribbon. These bumps when present on round silicon carbide filament have always resulted in low strength fractures; there was, however no evidence of anything on the carbon ribbon which should form these bumps. The same bumpy surface was observed on SiC ribbons made without PG coating and these bumps were also present on a ribbon made with only PG coating. One suspected cause for these bumps was the growth of whiskers at sites where residual copper catalyst was present at the surface. A copper compound catalyst is present during the production of carbon ribbon which aids the carbonization and graphitization steps. It has been found on the previous boron-on-carbon filament program that a metal

TABLE 1

RIBBON FILAMENTS MADE DURING APRIL, 1973

Run No.	Coating	Temp. °C	Tensile Strength KN/cm^2	(Ksi)	Comments and Observations
R 1, 2, 3, 4, 5	PG, boron	1300	0	(0)	Amorphous boron coating, fragile
R 6, 7, 8	PG, boron	1350	0	(0)	Partially crystalline boron, more fragile
R 9, 10, 11	PG, boron	1400	0	(0)	Fully crystalline boron, also fragile
RS 1	PG, silicon carbide	1350	12	(18)	Surface showed frequent bumps
RS 2	PG, silicon carbide	1350	12	(18)	Surface showed frequent bumps (repeat test)
RS 3	Silicon carbide only	1350	10	(15)	Same surface
RS 4	PG only	2500	No test was made.		Also bumpy surface
RS 5	Clean, PG, silicon carbide	1350	16	(23)	Much less bumpy

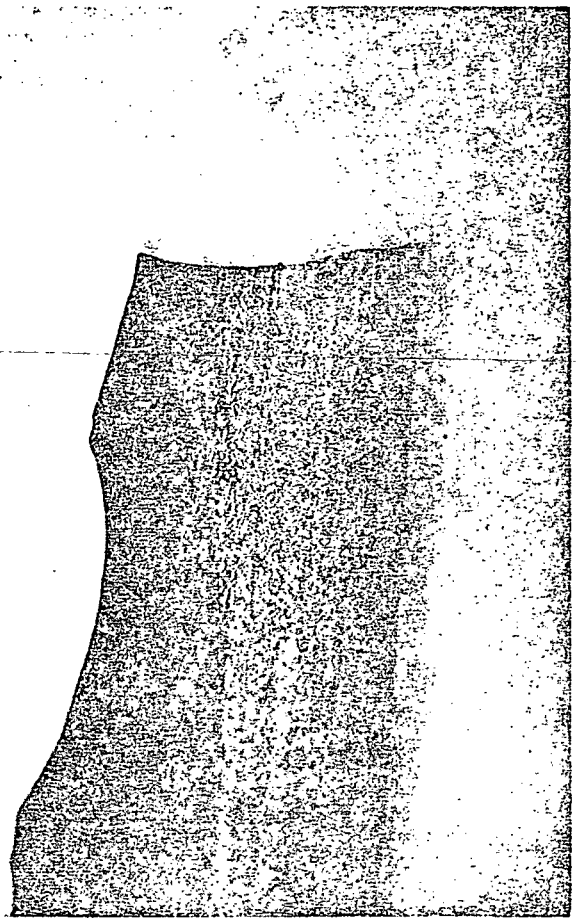

Figure 5. Amorphous Boron Ribbon
Temperature = 1300°C 50X

Figure 6. Partially Crystalline Boron Ribbon
Temperature = 1350°C 50X

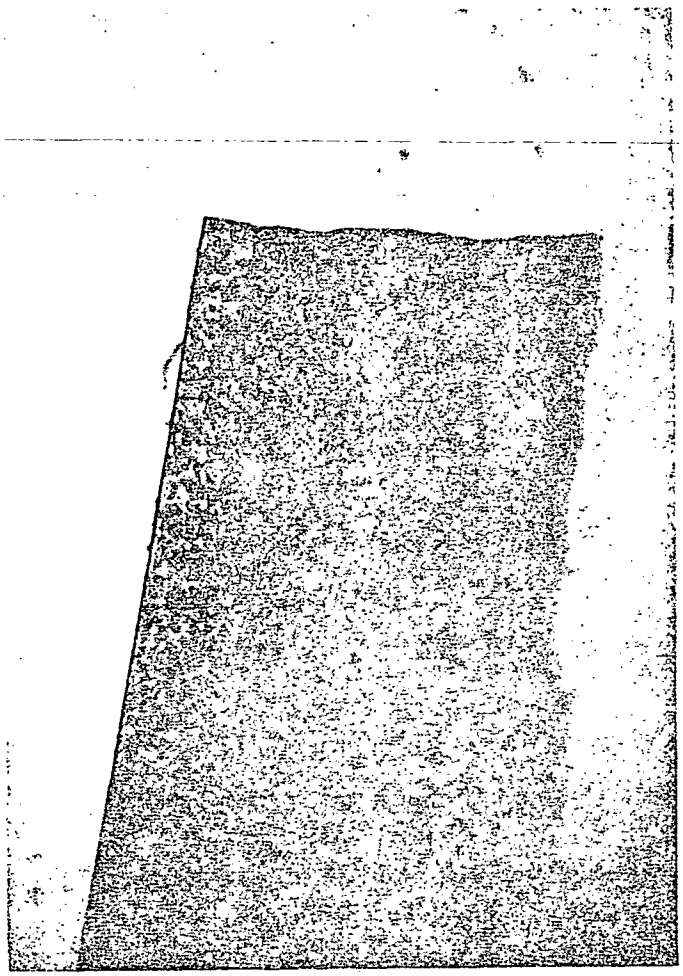

Figure 7. Polycrystalline Boron Ribbon
Temperature = 1400°C 50X

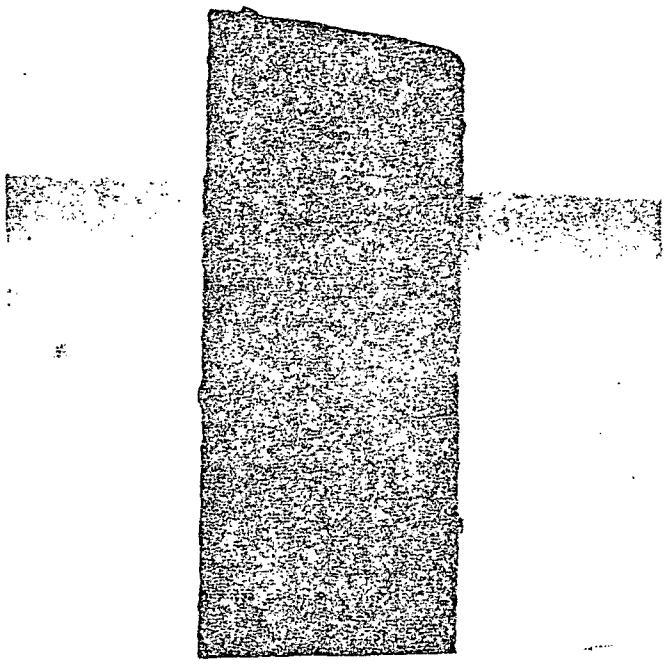

Figure 8. Silicon Carbide Ribbon
Temperature = 1300°C 50X

impurity site can lead to VLS (vapor-liquid-solid) whisker growth mechanisms during vapor deposition processes. Therefore, the final deposition tests in this series included a cleaning step consisting of first heating the carbon ribbon to about 2000°C in N_2 for about 3 minutes to "clean" the substrate, followed by the PG and the silicon carbide deposition steps. This ribbon showed no bumps over much of its area, and also produced a somewhat higher tensile strength, 16 KN/cm^2 (23 Ksi), instead of 12 KN/cm^2 (18 Ksi). A cross-section photomicrograph of SiC/C ribbon is shown in Figure 9. The substrate for this deposition was about 2 mils thick. It can be seen from the photomicrograph that about 2-3 mils of SiC have been deposited.

In addition to the major bumps observed on the surface of the early tests, there were also present smaller bumps and signs of surface irregularities, especially lines running parallel with the axial long dimension of the ribbon. End views of broken pieces of these filaments showed an irregular cross-section which followed the contour of the substrate.

Later, GE Research Labs produced carbon ribbon substrate made with a continuous rather than the static process, and this material was used for static deposition studies; the results of the deposition tests are shown in Table 2. The substrate designation GE-2 refers to the first shipment of substrate carbonized with the continuous process. This lot of carbon substrate was about 900 by 38 microns (35 x 1.5 mils), and optical microscopy showed that it was smoother and more uniform in cross-section than the material carbonized statically. Tensile tests on each piece of SiC ribbon were made on 10 inch gage lengths, and when available, on the residual pieces of shorter length.

The tensile tests of the SiC ribbon made with this lot of carbon ribbon substrate showed a substantial improvement over the earlier ribbon. The tensile stresses in the SiC sheath at fracture measured as high as 35 KN/cm^2 (50 Ksi) on several tests. Optical microscopy studies of the surface of these ribbons, however, showed a rough texture on a scale of about 2 to 10 microns, with the roughness aligned parallel with the longest dimension of the ribbon. The substrate showed this lineal surface texture, which was clearly visible on broken cross-sections; the external surface of the SiC was a magnified replica of the substrate. In spite of this surface roughness very encouraging results were obtained (see Table 2). Although the strengths were far short of the target goal of 140 KN/cm^2 (200 Ksi), they were moderately strong compared with the boron ribbon.

Figure 9. End View of Silicon Carbide Ribbon
100X

TABLE 2

RIBBON FILAMENTS MADE DURING MAY, 1973

Run No.	Substrate	Cleaning Gas	PG Coating	°C Deposition Temperature	Deposition Time Sec	Propane Treatment Start Sec	Propane Treatment End Sec	Tensile Strength KN/cm^2	Tensile Strength (Ksi)
RS 6	GE-2 900 x 38 microns (35 x 1.5 mils)	N_2	Yes	1350	20	0	0	11	(16)
RS 7	GE-2	N_2	Yes	1350	20	0	0		Low
RS 8	GE-2	N_2	Yes	1350	30	0	3	18	(26)
RS 9	GE-2	N_2	Yes	1400	30	3	3	34	(49)
RS 10	GE-2	N_2	Yes	1425	22	2	2	21	(30)
RS 11	GE-2	N_2	No	1225	30	2	2		Low
RS 12	GE-2	N_2	No	1450	20	10	10		Low
RS 13	GE-2	N_2	Yes	1300	21	1	4	14	(20)
RS 14	GE-2	$H_2 + N_2$	Yes	1300	20	2	2	26	(37)
RS 15	GE-2	N_2	Yes	1300	20	2	2	23	(33)
RS 16	GE-2 with a layer of SC 1008 phenolic resin added	N_2	Yes	1300	20	0	0		Low

TABLE 2 (Concluded)

Run No.	Substrate	Cleaning Gas	PG Coating	°C Deposition Temperature	Deposition Time Sec	Propane Treatment Start Sec	Propane Treatment End Sec	Tensile Strength KN/cm^2 (Ksi)
RS 17	Same as RS 16	N_2	Yes	1300	20	0	0	Low
RS 18	Same as RS 16	N_2	Yes	1300	20	0	0	Low
RS 19	Same as RS 16	N_2	Yes	1300	20	0	0	Low
RS 20	Kapton	N_2	Yes	1300	20	0	0	Low
RS 21	VYB Yarn	N_2	Yes	1300	20	0	0	Low
RS 22	VYB Yarn	N_2	Yes	1300	20	0	0	Low
RS 23	VYB Yarn	N_2	Yes	1300	20	0	0	Low
RS 24	Graphoil	N_2	Yes	1300	20	0	0	Low
R 12	35 x 1.5	N_2	Yes	1300	30 (Boron)	0	0	Could not handle

Only one test was made with boron deposition using the new continuous substrate. The deposition of amorphous boron at 1300°C was attempted. However, severe growth strains were again experienced and the boron ribbon was too fragile to test.

In the following month a new shipment of carbon ribbon substrate 1470 by 17 microns cross-section (58 by 0.66 mils) was received from GE. This material was made with still further improved processing which resulted in substantially smoother carbon ribbon substrate. The new ribbon also had a wider, thinner, and more uniform cross-section. The first few static reactor runs exhibited problems of curling, twisting, and wrinkling because of the thinner substrate; these problems were corrected by cleaning in hydrogen instead of nitrogen and by increasing the tension on the ribbon during both cleaning and SiC deposition. The results of these tests are shown in Table 3. Note that several tests showed tensile stresses up to about 35 KN/cm^3 (50 Ksi), but none exceeded the 35 KN/cm^2 level. The broken ends of these tests were studied carefully by optical microscopy to determine the causes of the low strength failures. Generally, at the broken ends there were observed localized enlarged growths giving rise to large stress concentrations. Figure 10 shows a side view and Figure 11 an end view of a typical fracture surface which show the irregular bead growth responsible for the reduced strength. Also in the figure the improved cross-sectional shape of the new substrate compared with the earlier ribbon shown in Figure 9 is evident.

The lack of improvement in tensile strength in spite of a substantial improvement in quality of the substrate led to the postulate that the enlarged growths responsible for the low strength failure may be caused by external dirt contamination. It was therefore decided to discontinue the static deposition method of making ribbon specimens in favor of a continuous or moving substrate reactor similar to that used to deposit SiC on round carbon or tungsten substrates.

Continuous Reactor Deposition Studies

A continuous deposition reactor shown schematically in Figure 12 was put into operation (see Figure 13). It included the following features:

1. The reactor was designed to operate continuously, similar to full-scale round filament reactors. It has been found during the last six years of research and development at Avco that continuous operation has always

TABLE 3

RIBBON FILAMENTS MADE DURING JUNE, 1973

Run No.	Substrate	Cleaning Gas	PG Stage H_2	PG Stage N_2	Deposition Temp. (°C)	Deposition Time (Sec)	Propane Treatment Start Sec	Propane Treatment End Sec	Tensile Strength KN/cm²	Tensile Strength (Ksi)	Comments
RS 25	KAPTON Carbonization Exp.									Low	
RS 26	Steel									Low	
RS 27	GE-3 1470 x 17 microns (58 x 0.66 mils)	N_2	No	Yes	1300	20	0	2		Low	Twisty
RS 28	GE-3	N_2	No	Yes	1325	20	0	2		Low	
RS 29	GE-3	N_2	No	Yes	1350	20	1	2	5	(8)	
RS 30	GE-3	N_2	No	Yes	1350	20	1	2	14	(20)	
RS 31	GE-3	N_2	No	Yes	1300	40	0	2	14	(20)	
RS 32	GE-3	N_2	No	Yes	1300	37	0	0		Low	Twisty
RS 33	GE-3	N_2	No	Yes	1300	35	2	0		Low	
RS 34	GE-3	N_2	No	Yes	1300	30	2	2	6	(9)	
RS 35	GE-3	N_2	No	Yes	1375	20	0	2	7	(10)	
RS 36	GE-3	H_2	Yes	No	1300	40	5	2	35	(50)	Straight
RS 37	GE-3	H_2	Yes	Yes	1300	30	2	2	31	(45)	

TABLE 3 (Concluded)

Run No.	Substrate	Cleaning Gas	PG Stage H_2	PG Stage N_2	Deposition Temp. (°C)	Deposition Time (Sec)	Propane Treatment Start Sec	Propane Treatment End Sec	Tensile Strength KN/cm^2	Tensile Strength (Ksi)	Comments
RS 38	GE-3	H_2	Yes	Yes	1300	40	0	2	14	(20)	
RS 39	GE-3	H_2	No	No	1300	40	0	2	2	(3)	
RS 40	GE-3	H_2	Yes	Yes	1300	30	0	2	10	(15)	
RS 41	KAPTON Exp.									No Test	
RS 42	KAPTON Exp.									Low	
RS 43	KAPTON Exp.									No Test	
RS 44	GE-4 1450 x 15 microns (57 x 0.6 mils)	H_2	Yes	Yes	1325	40	0	2	8	(12)	
RS 45	KAPTON 970 x 20 microns (38 x 0.8 mils)	H_2	Yes	Yes	1325	40	0	2		Low	
RS 46	KAPTON									No Test	
RS 47	GE-4	H_2	Yes	No	1350	33	3	3	38	(40)	
RS 48	GE-4	H_2	Yes	No	1325	40	3	2	10	(15)	

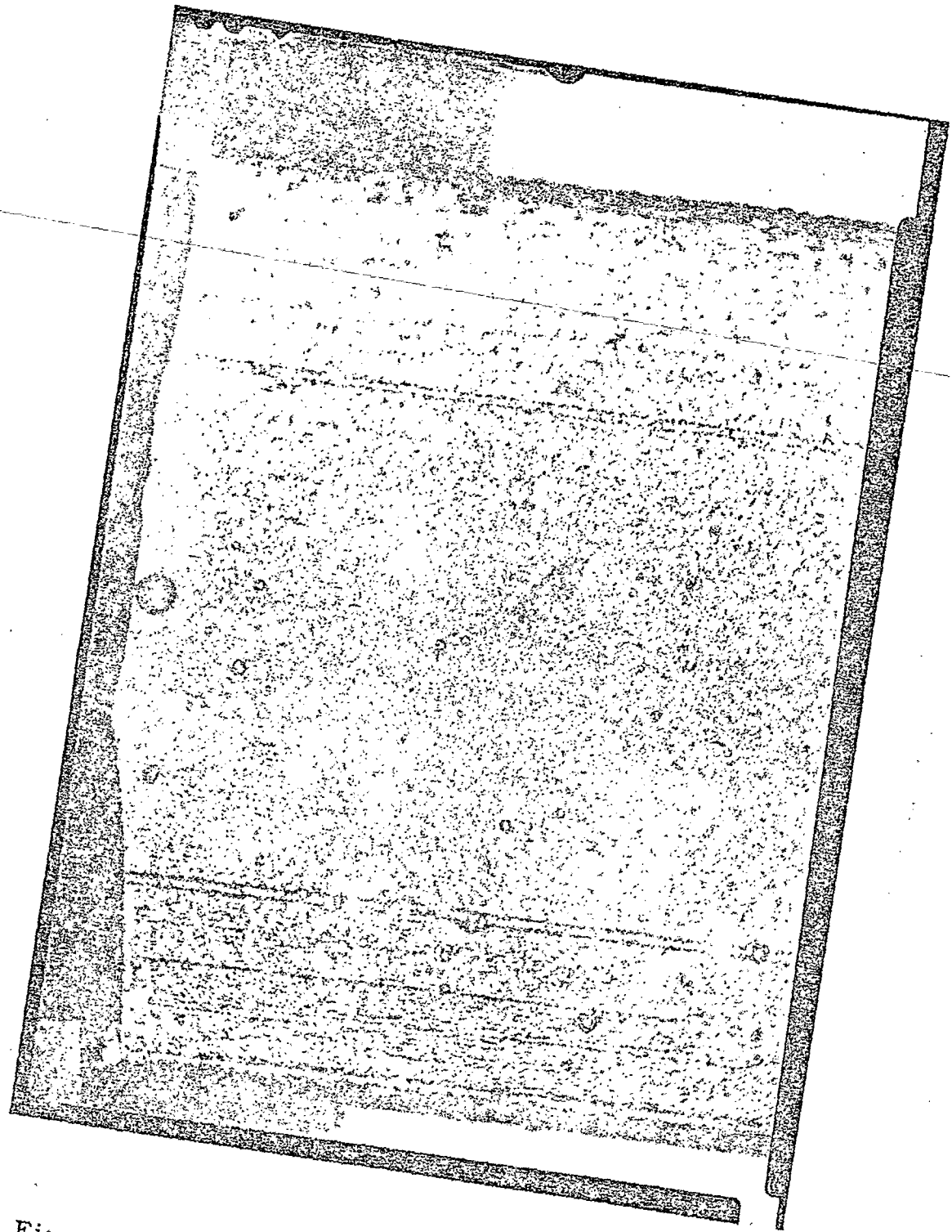

Figure 10. Side View of a Typical Fracture Surface of SiC Ribbon Showing the Large Growth Flaw which caused the Break.

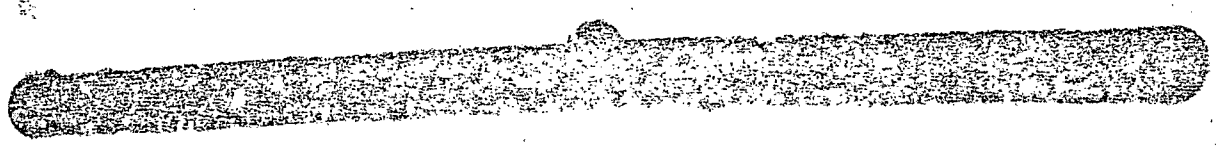

Figure 11. End View of a Typical Fracture Surface of SiC Ribbon Showing the Large Growth Flaw which caused the Break

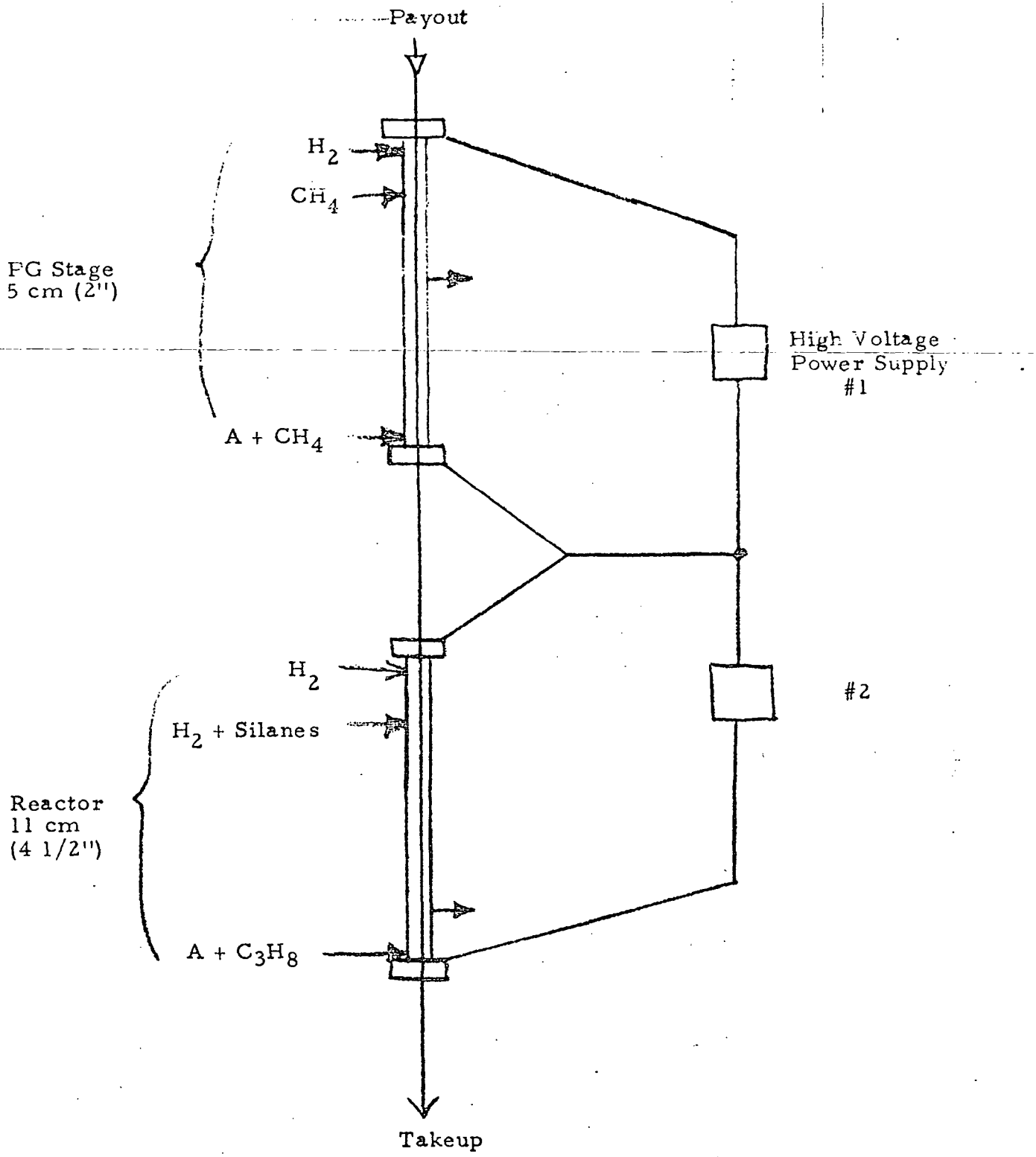

Figure 12. Schematic of Continuous Reactor for SiC Deposition on Ribbon Substrate.

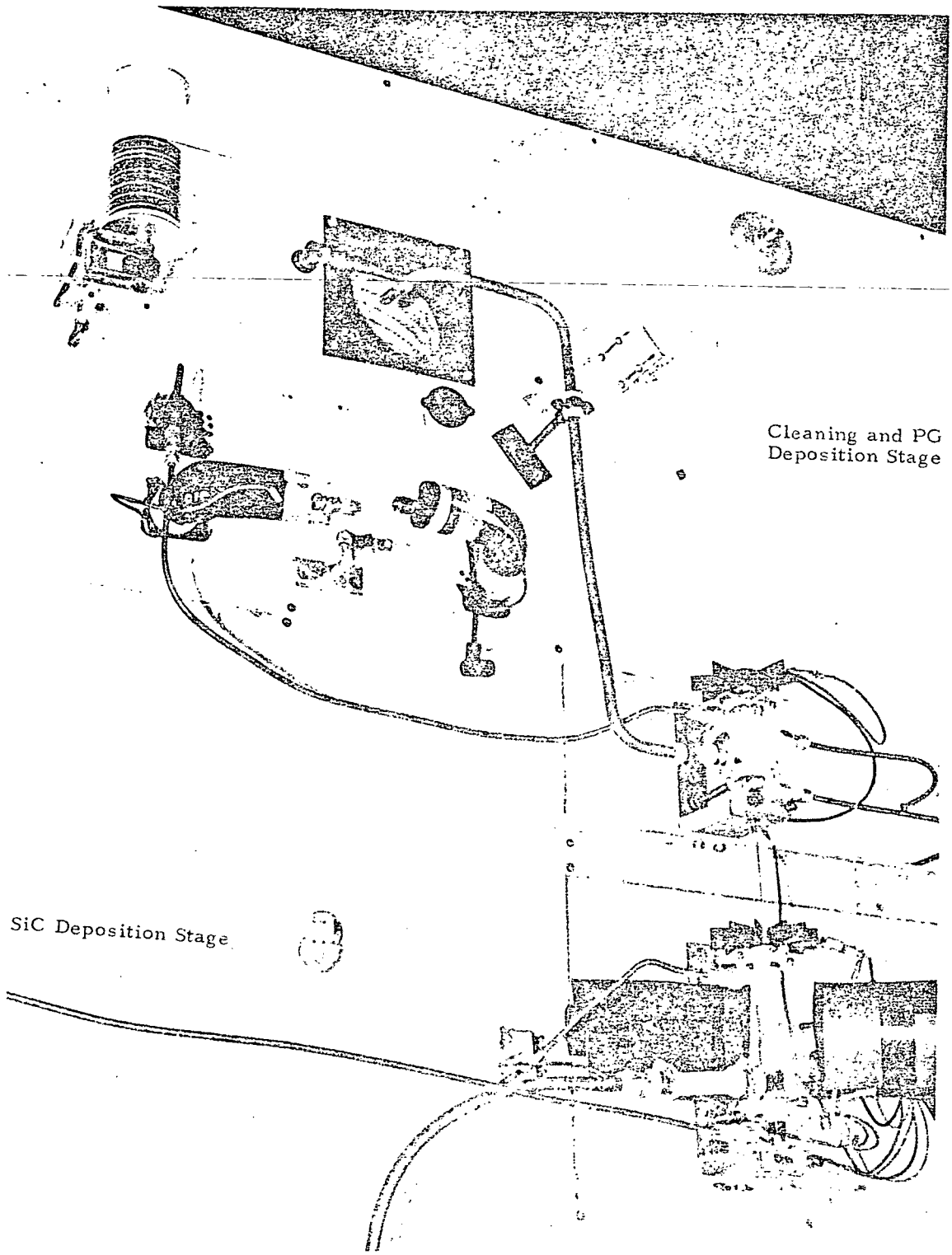

Figure 13. Continuous Ribbon Reactor in Operation.

yielded better quality material than static reactors in boron-on-tungsten, boron-on-carbon and silicon carbide reactors using round substrates, with rapid quality improvement being observed with time after start-up of the continuous reactor over the first 5-10 minutes. This quality variation has always been attributed to foreign material pickup in the reactor from the gas lines and the mercury electrodes during the first few minutes.

2. The incoming silane-hydrogen mixture was preheated, and the flowing gas stream in the reactor cooled to obtain a more nearly flat temperature profile. The static reactor, without these features, showed a substantial temperature gradient, viz., cooler at the incoming gas end and hotter at the exhaust end.

3. The reactor was shorter than the static reactor, 4 1/2 inches long compared with 15 inches, so as to provide a ratio of SiC deposition rate to gas flow rate the same as has been used in round SiC deposition reactors. It is not yet known how important this factor was in filament quality, but it was considered conservative practice to limit this ratio, at least for the first tests.

4. A surface treatment procedure as nearly identical to that used on round SiC filament manufacture as possible, considering the scale of the system, was used to enhance the surface strength of the ribbon. Previously this procedure had been simulated in the static reactor by introducing propane in the reactive mixture at the beginning or end of the experiment, or both, as shown in Table 2.

The results of the tests with this reactor were highly encouraging as shown in Tables 4 and 5. Note in these tables that ultimate tensile stresses in the SiC sheath as high as 105 KN/cm^2 (150 Ksi) were obtained in the first few tests as shown in Table 4, with average strengths near 70 KN/cm^2 (100 Ksi) for a group of about 10-15 tests on a given run. For these measurements, a gage length of 2.5 cm (1 inch) was used. Another feature of the tests beginning with Run RS 56 was that rubber cushions were used between the ribbon and the jaws of the tensile test machine to prevent crushing of the slightly bowed ribbon when the jaws closed.

TABLE 4

RIBBON FILAMENTS MADE DURING JULY, 1973

(Continuous Reactor)

Run No.	Substrate	Temp.	Tensile Strength High KN/cm^2	(Ksi)	Tensile Strength Average KN/cm^2	(Ksi)	No. Tests	Comments
RS 49		1375	100	(150)			6	
RS 50	Round CMF	1350	40	(60)			3	
RS 51		1350	110	(160)			8	
RS 52		1350	140	(210)			11	
RS 53		1350	120	(170)			12	
RS 54	GE-5 1450 x 15 microns (57 x 0.6 mils)	1350	55	(80)			6	
RS 55	GE-5	1350		(0)			8	Crushed in Jaws
RS 56	GE-5	1375	80	(120)			13	
RS 57	GE-5	1375	100	(150)	65	(95)	15	
RS 58	GE-5	1425	70	(100)	55	(80)	8	

TABLE 5

RIBBON FILAMENTS MADE DURING AUGUST, 1973

Run No.	Substrate	Temp.	Tensile Strength KN/cm^2 (Ksi) High		KN/cm^2 (Ksi) Average		No. of Tests	Comments
RS 59	GE-6 1457 x 17 microns (58 x .66 mils)	1450	75	(110)	60	(86)		Smooth & Straight
RS 60	GE-6	1450	60	(84)	40	(60)		Twisty
RS 61	GE-6	1450	100	(150)	65	(95)		Smooth & Straight
RS 62	GE-6	1450	90	(135)	65	(95)		
RS 63	GE-6	1450	85	(122)	60	(90)		
RS 64	GE-6	1450	61	(89)				
RS 65	GE-6	1450	63	(91)				
RS 66	GE-6	1450						
RS 67	GE-6	1450	75	(110)	59	(85)		
RS 68	GE-6	1450						
RS 69	GE-8 1457 x 17 microns (58 x .66 mils)	1450	50	(72)				
RS 70	GE-8	1450	140	(200)				
RS 71	GE-8	1450	100	(145)				

Crushing had been observed when strips of aluminum had been used as cushions. The carbon substrate was fed to the upper cleaning and PG deposition stage and then to the SiC deposition unit at a rate of about 18 cm (7 inches) per minute. It is interesting (and potentially very important) to point out that the one 10 cm (4 inch) long reactor produces as much silicon carbide product as one normal 180 cm (6 ft) long production reactor which currently produces 100 micron (4 mil) SiC/W substrate. Stated differently one ribbon reactor of production scale could produce the same throughput as 30 SiC/W reactors!

The ends of all tensile breaks were studied under the optical microscope to determine the causes of the breaks so that action could be taken to avoid the causes of the low strength flaws. The flaw type of Figures 10 and 11 was nearly always observed at the ends of the ribbon where the break occurred. These large growths were generally spaced at much shorter intervals than the 2.5 cm (1 inch) gage length, hence their probability of occurence in any test section was high. Furthermore, the flaw severity of the ribbon as observed under the optical microscope was similar to that of the ribbon made on the static reactor. This suggested that the continuous reactor made higher strength ribbon because of its ability to deposit stronger SiC rather than to make ribbon with less severe flaws. As mentioned previously, similar results have been found in early studies with boron deposition where continuous reactors always produced filament with tensile strength greater than filament made in static units.

Another substrate cleaning scheme was attempted in which the cleaning was done at high temperature in argon saturated with water vapor. The water vapor etched about 25% of the ribbon away, and it was the intent of the etching reaction to remove any thin carbon whiskers. However, the SiC ribbon tensile strengths obtained under these etching conditions were less than with no etching of the substrate.

The highest strength value obtained (as shown in Table 5) was 142 KN/cm^2 (206 Ksi). For this test, the gage length was 2.5 cm (1 inch) and the strength value shown was the ultimate stresses in the silicon carbide layer. It was noted that on that run, there was a region several inches long on which the frequency of the large growth flaws was very low, and within this region the highest ultimate tensile stress was obtained.

These results, together with the exceptional strength values up to 550 KN/cm^2 (800 Ksi) recently obtained with SiC deposited on round, very smooth carbon monofilament substrate which are discussed subsequently are promising. Another promising aspect of SiC ribbon is its potentially very low cost. Table 6 shows a projected cost breakdown for SiC ribbon, indicating that when production levels reach those now experienced for boron, the cost of SiC ribbon can be in the range of a few tens of dollars per pound.

TABLE 6

PROJECTED COST ANALYSIS, SiC RIBBON, 10,000 LB/YEAR

(Costs/lb of SiC Ribbon)

Raw Materials	
Substrate	$ 5.00
Silane (with recycling)	5.50
H_2	4.00
Miscellaneous (Caustics, etc.)	2.00
	$16.50
Labor	
Production	$ 7.00
Testing	2.00
	$ 9.00
Other	
G&A (at 20%)	$ 5.00
Depreciation	12.00
Profit (15%)	6.50
TOTAL	$49.00

CONCLUSIONS AND RECOMMENDATIONS

SiC on a carbon ribbon substrate has demonstrated strength levels as high as 140 KN/cm^2 (200 Ksi), the program target. Results from other work on SiC on round carbon monofilament show that the strength potential of SiC on carbon ribbon is at least 400-550 KN/cm^2 (600-800 Ksi).

The above results were achieved using carbon ribbon substrate provided by GE Research Center, a material which is still in the very early stages of development. It is considered that improvements in the carbon ribbon surface smoothness will translate into stronger SiC ribbon.

Further work is considered justified on the SiC on carbon ribbon concept, and it should be promulgated vigorously. The next step is to improve the strength further, with 275 KN/cm^2 (400 Ksi) as the next target strength level. It appears that the most fruitful approach to increasing the tensile strength is to investigate the causes and the means of prevention of the large irregular growths that occur on the ribbon fiber surfaces. Then a sufficient quantity of material should be produced to make several composite samples, both in epoxy and in aluminum. These composites should be tested in both longitudinal and transverse directions to demonstrate the strength and moduli levels achievable with the ribbon concept.

APPENDIX

Other studies were conducted on this and a related program at Avco which was worthy of note in this report. First are some highly promising results obtained on Avco-sponsored work with SiC on round carbon monofilament. Another concept that appears promising is the carbonization of polyimide ribbon, Du Pont's Kapton film. The other studies reviewed below proved negative, but are included here for completeness -- the use of resin coating of the ribbon as a means of improving surface finish, the use of Union Carbide's Graphoil as a substrate, and the use of nickel and nichrome ribbon as a substrate.

SiC on Round Carbon Monofilament Substrate

Avco has had underway for over a year, a program to develop a process for depositing SiC on a round carbon monofilament substrate. Some work was done on this during the AFML-sponsored program[2] to improve the process for the manufacture of SiC filament. Strength levels obtained through January, 1973 were in the 170 KN/cm^2 (250 Ksi) range, at which time the silanes combination was a mixture of $MeSiCl_3$ and $MeHSiCl_2$. Later in the first quarter of 1973, strength levels of 250 KN/cm^2 (350 Ksi) were achieved, when the silanes comprised Me_2SiCl_2 and $MeHSiCl_2$. Then process improvements in July, 1973 suddenly achieved a significant breakthrough, when strength levels up to 550 KN/cm^2 (800 Ksi) were measured with average strength levels as high as 480 KN/cm^2 (700 Ksi). Much additional work is needed to optimize the process for depositing SiC on carbon monofilament and when optimization is complete these high strength levels are expected to be routine. It is acknowledged that much work is needed to demonstrate that these same strengths can be achieved with SiC on carbon ribbon substrate because within a given gage length, such as one inch, there is 10-30 times as much filament area on which a low strength flaw might be located, making the task proportionately more difficult to achieve the same strength. It does, however, follow from the SiC on carbon monofilament results, that very high strength levels are attainable with SiC on carbon ribbon substrate.

Carbonization of Polyimide Film

The carbonization and graphitization of polyimide film, sold by Du Pont as Kapton ribbon, has been reported[3] and it was felt that polyimide film may be suitable as a precursor to make substrate for boron or SiC ribbon deposition. A few preliminary tests were conducted at Avco to investigate this possibility. Some as received film was inspected under the optical microscope which showed that it is smooth; one side is very highly glossy and the other side is pocked with only very small and shallow blemishes. The side with these blemishes was less glossy than the other, although the difference for the time being appears unimportant in this application. This film was carbonized by wrapping it on a graphite cylinder about 3 1/2 inches in diameter and heating to about 1000°C (1800°F). This material in the initial carbonization broke because of shrinkage during carbonization, but microscopic inspection revealed that the surfaces were still highly glossy after carbonization. The shrinkage phenomenon was also reported in Reference 3. Another carbonization was done by hanging a Kapton ribbon vertically in the muffle furnace in nitrogen and heating to 1000°C (1800°F); this carbonized Kapton also exhibited a smooth surface; however, the ribbon wrinkled badly during carbonization and emerged in a very brittle state. Some deposition tests with the wrinkled ribbon were not successful.

Several experiments were conducted in June to determine the conditions required to carbonize polyimide film. The last and most nearly successful experiment consisted of raising the filament temperature to 1050°C (1900°F) in a hydrogen atmosphere in about 1 hour. The filament ends were free until the temperature exceeded 650°C (1200°F). This permitted about 15% shrinkage before affixing the ends and putting the filament in tension. The filament was enclosed in a quartz tube with flowing hydrogen during the heating of the center 100 cm (40 inches) of a 180 cm (75 inch) long ribbon.

The ribbon made during this experiment was coated with SiC, but it was weak (see Run RS 45 of Table 3). The surface of the SiC ribbon was marked with large growths, similar to those observed on filaments made with GE carbon ribbon, even though the carbonized ribbon surface was very smooth and free of blemishes. Another problem observed was non-uniform ribbon resistance leading to cold zones.

in the ribbon in localized regions when it was heated electrically. Third, the ribbon was curved considerably; i.e., it was shaped like a 970 micron (38 mil) wide by 20 micron (0.8 mil) thick strip cut from a cylindrical surface, with a radius of curvature of about 1500 microns (60 mils). This curved shape resulted in high stresses when the tensile test machine jaws were closed on the SiC-coated ribbon. More work is needed to determine theproper carbonization procedure for the polyimide film for use as a substrate for SiC ribbon.

Resin Coating of Carbon Ribbon

Studies were undertaken during May to determine if a viscous liquid resin coating could produce a smoother surface on the carbon ribbon substrate. The coating method used was to lower a 0.6 meter (2 foot) section of the 970 by 38 micron (38 by 1 1/2 mil) GE carbon ribbon into a resin bath by weighting the bottom end and then lifting it out slowly. The resin film was subsequently cured in air to about 200°C using a muffle furnace oriented vertically. The average heating rate used was about 3-5°C/min. The resin mixture which was first investigated was a 50-50 mixture of phenolic resin, Monsanto SC 1008, and ethyl alcohol but it did not coat the ribbon uniformly. Pure SC 1008 resin was tried next and coated quite well yielding a smooth very glossy surface after curing. The resin layer was thicker in the middle of the ribbon, however, resulting in a ribbon cross-section that was elliptical. When this coated ribbon was raised to SiC deposition temperature quickly it did not retain its integrity and led to a crazed surface which produced a very fragile SiC ribbon. It will be necessary to carbonize the phenolic under other conditions in order to determine if a suitable substrate can be achieved in this manner. This particular coating study was undertaken because SC 1008 resin had been successfully carbonized on splice joints of carbon monofilament substrate. These SC 1008 coated splices were cured at about 200°C and subsequently heated quickly during the very short contact time in the reactor before boron deposition. They had a very smooth surface free of cracks and physical degradation. More work along this line is considered justified because of the previous splice results.

Other Ribbon Substrate Tests

Some graphoil from Union Carbide was used as a substrate for one test, RS 24 of Table 2. This material was about 125 microns thick, and was sliced with a razor blade into a ribbon about 3200 microns wide (1/8 inch). A heating current of about 10 amperes was required to reach deposition temperature, and 60 Hz AC power was used. The surface of the graphoil is very rough as was the finished SiC ribbon and the strength was very low. This approach was not considered promising.

A few brief runs were conducted using a carbon yarn as a substrate, the yarn containing either 720 or 1440 individual filaments each about 8 microns in diameter as shown in Table 2, runs RS 21-23. These were coated with SiC, but the end product did not look particularly promising as a first step toward a ribbon cross-section. In round form the SiC penetration was not complete, the inner fibers being only partially coated before the outer SiC layer closed. Even if the filaments could be arranged in a flat configuration the surface might suffer from the periodic change of curvature, which would probably result in low transverse strength. The potential low cost of this approach is attractive, of course, and means to avoid the disadvantages should be considered in later work.

A few brief tests, (Run RS 26 of Table 3), were conducted using nickel and nichrome ribbons as substrates. These were unsuccessful. If the temperature was held below the ribbon burnout point, the coating was non-adherent. The nickel reacted with the SiC deposit and burned out at a temperature above about 1200°C, lower than the normal deposition temperature of SiC on carbon or tungsten.

References

1. C.N. Krutchen, D.G. Flom, B. Gorowitz, and B.W. Roberts,"Large Diameter High Strength, High Modulus Carbon Fibers from Polyacetylenes", 11th Biennial Conference on Carbon, June 1973, pp. 263-264.

2. H. DeBolt and V. Krukonis, "Improvement of Manufacturing Methods for the Production of Low Cost Silicon Carbide Filament", AFML-TR-73-140.

3. R.G. Bordeau, "High Modulus Carbon Ribbon", 11th Biennial Conference on Carbon, June 1973, pp. 265-266.