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A STUDY TO IMPROVE THE MECHANICAL PROPERTIES
OF SILICON CARBIDE RIBBON FIBERS

By

Harold E. DeBolt
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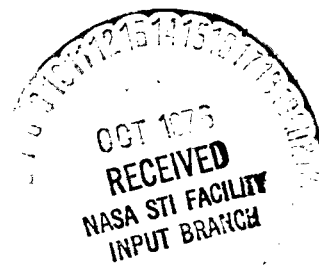Prepared under Contract NAS 1-13018

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Prepared for
National Aeronautics & Space Administration
Langley Research Center
Langley Station
Hampton, Virginia 23365

Submitted by

Avco Systems Division
Lowell Industrial Park
Lowell, Massachusetts 01851

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FOREWORD

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

Preliminary deposition studies of SiC ribbon on a carbon ribbon substrate showed that the dominant strength limiting flaws were at the substrate surface. Procedures for making the carbon ribbon substrate from polyimide film (DuPont Kapton) were improved, providing lengths up to 450 meters (1500 ft.) of flat carbon ribbon substrate 1900 microns (75 mils) wide by 25 microns (1 mil) thick. The flaws on the carbon ribbon were smaller and less frequent than on carbon ribbon used earlier. SiC ribbon made using the improved substrate, including a layer of pyrolytic graphite to reduce further the severity of substrate surface flaws, showed strength levels up to the 2068 MPa (300 Ksi) target of the program, with average strength levels over 1700 MPa (250 Ksi) with coefficient of variation as low as 10% for some runs.

INTRODUCTION

To date most of the high strength, high modulus reinforcements such as boron or silicone carbide (SiC) have consisted primarily of round filaments each 100, 140, or 200 microns (4, 5.6 or 8 mils) in diameter. Besides the inorganic fibers, graphite yarns, consisting of a large number of individual round filaments each about 8 micron (0.3mils) diameter, have also found wide utilization in advanced composite applications. These round filaments provide high composite strengths in a direction parallel to 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 technical advantage of increased transverse strength, ribbon shaped filaments offer a substantial cost reduction potential 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.

An earlier program[1] demonstrated that the SiC ribbon on a carbon ribbon substrate was a viable reinforcement material, although its tensile strength was low and variable. Another related program[2] added support to the concept. Still another program[3] studied an alternative concept for ribbon reinforcement manufacturing methods.

The objective of the program reported herein was to improve the carbon ribbon substrate and the SiC deposition procedures using it, to achieve a SiC ribbon with a 2070 MPa (300 Ksi) tensile strength. Also, composites were to be fabricated to demonstrate the potential of the ribbon concept. The planned approach was to construct a longer reactor than the one used on the earlier program (30-60 cm length rather than 10 cm), with a plastic ribbon to captivate the SiC ribbon as it was produced, and with pinch rollers preceding the take-up spool to avoid run stops in the event the SiC ribbon should break. It was originally planned to obtain the carbon ribbon substrate from the G. E. Research Laboratory, but this source of carbon ribbon was no longer available at the time of program initiation. Production procedures using polyimide film precursor (DuPont Kapton)[4] were then planned. The results of the program are discussed in the results section below. Recommendations to carry the program further are presented following the discussion of results.

RESULTS

The research and development program consisted of two major
subdivisions. During the first part the deposition of SiC on a substrate
made from 0.3 cm (1/8 inch) wide by 12 micron (1/2 mil) thick Kapton
film was studied, first with the 10 cm (4 inch) long deposition reactor
and soon thereafter with the 35 cm (14 inch) long version. Several methods
of cleaning the substrate were tested in an effort to avoid the large flaws at
the substrate surface. Despite these efforts the target strength was not
reached. Some composites were made and tested during the first part of
the program. During the second part of the program studies were carried
out to improve the methods of carbonizing the Kapton film to make a carbon
ribbon substrate with less severe surface flaws. SiC deposition studies on
this improved substrate were then carried out, including the deposition of
a layer of pyrolytic graphite on the substrate before SiC deposition. The
target tensile strength of 2068 M Pa (300 Ksi) was achieved and average
strength levels in the range over 1700 M Pa (250 Ksi) were obtained on
some runs.

The discussion below is subdivided into four sections. The first section
describes the early SiC deposition studies; the second covers the composite
fabrication and testing using the SiC ribbon made during the earlier part of
the program. In the third section the studies to improve the carbon ribbon
substrate are reported, and finally, the fourth section describes the results
of the later SiC deposition studies using the ribbon made by the improved
methods.

Series A Production Studies

The first series of SiC ribbon production runs were conducted on a system shown schematically in Figure 1. The carbon ribbon substrate was payed out from the 7.6 cm (3 inch) OD by 17.8 cm (7 inch) long cardboard substrate holding spool, using a simple friction brake to control tension. Initially the carbon ribbon substrate was wound directly on the spool. Without protection, the substrate often was scratched or twisted and broken. It was later found that if a 1-1/4 cm (1/2 inch) mylar ribbon was wrapped on the spool with the carbon ribbon, these breakage problems were eliminated. The carbon ribbon was passed over pulleys to guide it to the reactor stages, one pulley driving a tachometer which provided a power shutoff interlock when the ribbon stopped for any reason. The first stage served as a ribbon finishing reactor in which the ribbon was heated to a temperature well above SiC deposition temperature, without which the carbon ribbon was unstable during SiC deposition (i.e., small circular spots of SiC would break out and separate after part of the deposition was completed). The next step in the sequence was substrate cleaning, when used. The first cleaning procedure consisted of passing the ribbon through rubber slits through which a high air flow was passed. Later, another step was added consisting of polishing both sides by rubbing with rubber wheels as shown schematically in Figure 2. The reactor is shown in operation in Figure 3 where the key parts are shown.

The silane supply and recovery system used for the SiC deposition studies is shown schematically in Figure 4, developed during an earlier program[5]. The silanes mixture, consisting of a blend of dimethyldichlorosilane (Me_2SiCl_2) and methyldichlorosilane ($MeHSiCl_2$), together with the volatile

PAYOUT

TACHOMETER

Hg ELECTRODE (4)

VARIABLE
dc POWER
SUPPLY (2)

H$_2$

PG STAGE

EXHAUST

Ar, CH$_4$

EXHAUST
THROUGH SLITS

SLIT

GAS BLOWING STAGE

AIR

SLIT

H$_2$, SILANE, Ar, C$_3$H$_8$

H$_2$, SILANE

DEPOSITION STAGE

EXHAUST

Ar, C$_3$H$_8$

PINCH ROLLS

MYLAR TAPE

8" DIA. TAKEUP SPOOL
(TRAVERSING)
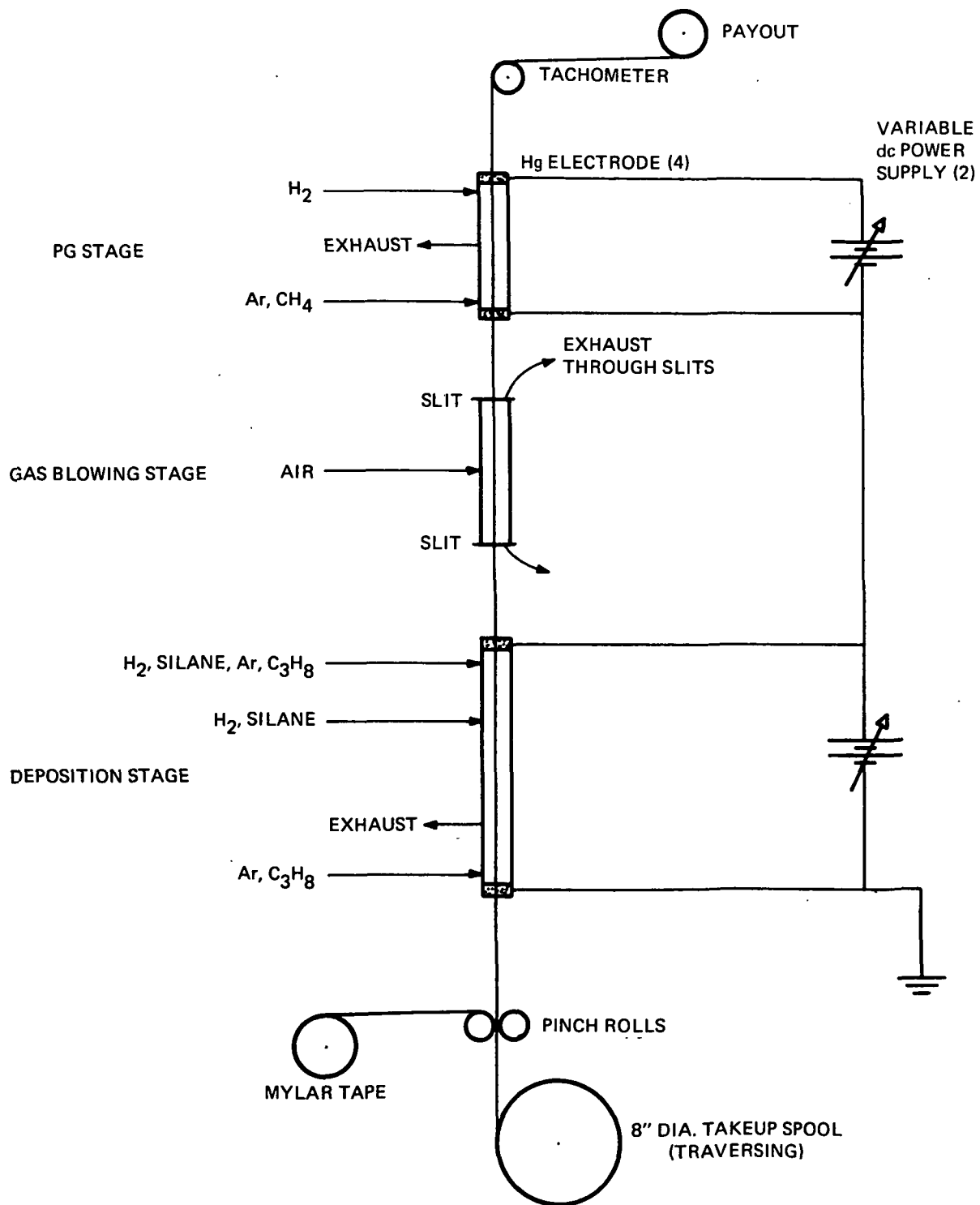
86-1524

Figure 1 SCHEMATIC DIAGRAM OF SiC RIBBON DEPOSITION REACTOR

PAYOUT   IDLER AND TACHOMETER DRIVE

IDLER

ARGON →

12" HEAT TREATMENT STAGE

IDLER

RUBBER-COATED
POLISHING WHEELS

IDLER

SLITS   AIR

H_2 + Si + A + C_3H_8 →   ← H_2 + Si

14" REACTOR

← A + C_3H_8

PINCH ROLLS AND GUIDE

MYLAR TAPE

8" DIA. TAKEUP SPOOL
0.5 – 3.5 f/m
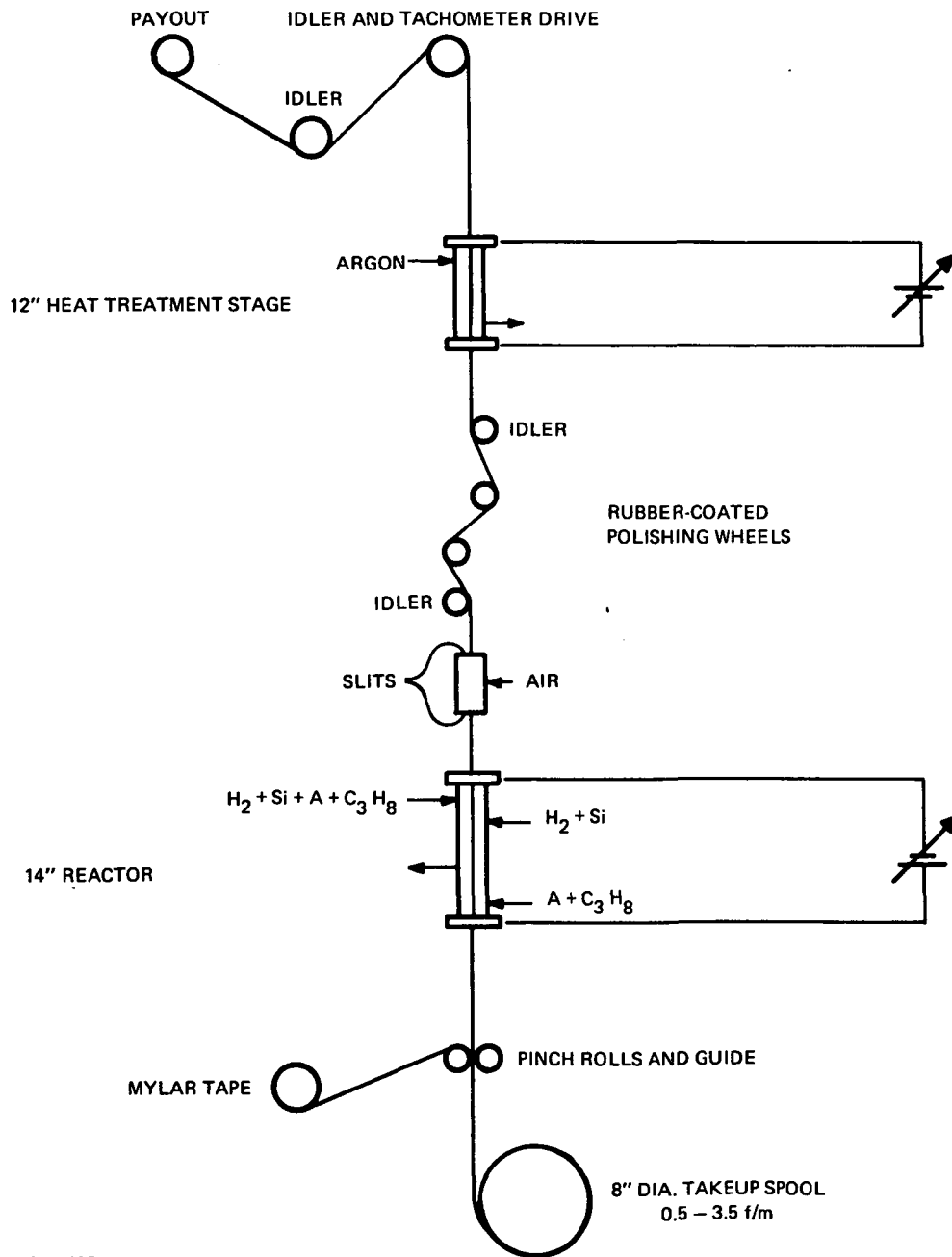
86-1525

Figure 2 SCHEMATIC DIAGRAM OF THE SiC RIBBON DEPOSITION REACTOR
AS OF AUGUST 31, 1974

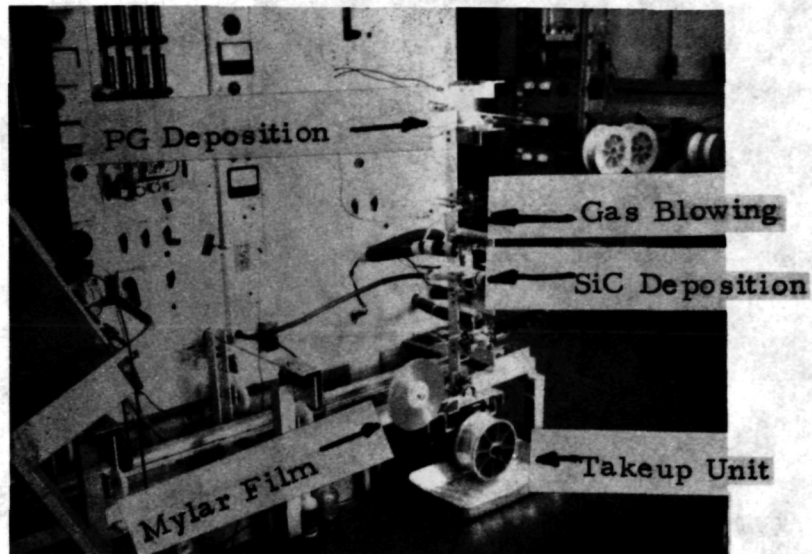Figure 3 SiC RIBBON DEPOSITION REACTOR IN OPERATION

SiC FILAMENT PRODUCTION PROCESS SCHEMATIC
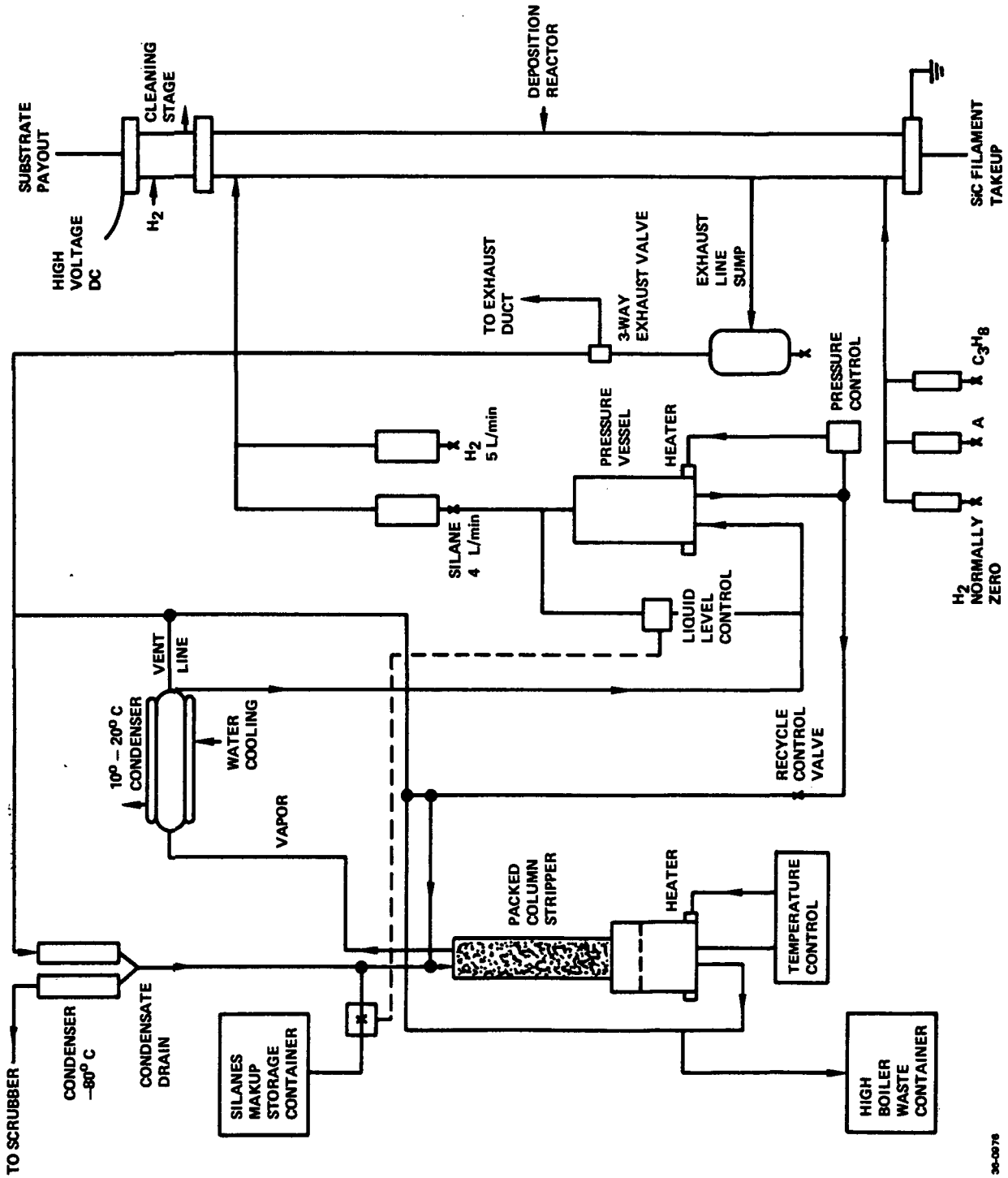
Figure 4 SiC FILAMENT PRODUCTION PROCESS SCHEMATIC

-9-

decomposition products of the reaction (primarily trichlorosilane, $HSiCl_3$, and silicon tetrachloride, $SiCl_4$) are supplied as vapor from the reboiler vessel. This vapor, with a dew point of about 65°C (150°F), was metered through heated flowmeters, mixed with hydrogen and other gases when used, and sent to the reactor. The unused silanes and reaction products were condensed in condensers cooled with dry ice and freon and packed with Raschig rings or small glass beads. The hydrogen and HCl by-product were exhausted to atmosphere. The condensate was distilled in a packed distillation column to reject the high boiling products synthesized in the reactor (primarily disilanes -Si-Si- and disilmethylenes -Si-CH_2-Si-). The volatile components, with boiling points below about 100°C (212°F), were returned to the reboiler vessel.

The two power suppliers shown in the schematic of Figure 2 were both three phase full wave rectified 60 cycle power supplies rated at 3 amperes, and controlled with 3 phase ganged autotransformers. The supply for the cleaning stage was rated for 750 volts and the supply for the SiC deposition reactor for 4000 volts. These provide adequate voltage and current for this program.

The SiC deposition reactor included three zones, each supplied with a different mixture. The top zone, about 2.5 cm (1 inch) long, was supplied with a mixture of hydrogen, silane, argon, and propane. An additional mixture of hydrogen and silane, each of much higher flow rate than those in the first section, was added at the beginning of the second section. The second section

was about 10 cm (4 inch) long in the initial work, and about 30 cm (1 ft) long for the rest of the program. The third section, about 3-3/4 cm (1-1/2 inch) long was supplied with a mixture of argon and propane to apply an external surface treatment. This surface treatment has been found to reduce the sensitivity of the ribbon to surface abrasion, and to increase the surface strength by about a factor of two (in round SiC filament, from about 4800 M Pa or 700 Ksi to about 11,000 M Pa or 1600 Msi).

After SiC deposition, the ribbon filament was passed through a guide, then through rubber coated pinch rollers where a 1-1/4 cm (1/2 inch) mylar ribbon was also added. This mylar ribbon served the dual purpose of separating adjacent layers of SiC ribbon on the takeup spool, and preventing run stops in case of SiC ribbon breakage on the takeup spool.

The takeup spool can be operated over the takeup speed range of 15 to 105 cm/min (0.5 to 3.5 f/min) which was sufficient for the current program. The takeup spools used were about 20 cm (8 inch) in diameter.

Table 1 presents the results of the first series of runs. For the first four runs the cleaning stages were not present, and the SiC ribbon produced was of low strength. The initial runs served to demonstrate the operability of the pinch roll and windup apparatus and the low strength which was measured and which was caused by large anomalous growths, justified the need for the cleaning steps. Runs 5 through 13 included the heat treatment and pyrolytic graphite stage, but not the physical cleaning (gas blowing) stage, and again low strengths were observed. Runs 14 and beyond used both cleaning steps, and

TABLE I

RESULTS FROM SiC RIBBON PRODUCTION THROUGH JUNE 1974

Run, 9S No.	Cleaning Gas	Air Cleaning	PG Coating	Speed M/min (f/min)	Tensile Strength, M Pa (Ksi)		Coefficient of Variation σ/Average, %
					High	Average	
1	None	None	None	0.335 (1.1)			
2	None	None	None	0.335 (1.1)			
3	None	None	None	0.335 (1.1)			
4	None	None	None	0.335 (1.1)			
5	H_2 + Ar	None	Yes	0.335 (1.1)			
6	H_2 + Ar	None	Yes	0.335 (1.1)			
6A	H_2 + Ar	None	Yes	0.335 (1.1)			
7	H_2 + Ar	None	None	0.168 (0.55)	606 (88)	404 (58.7)	35
8	H_2 + Ar	None	None	0.335 (1.1)			
9	H_2 + Ar	None	None	0.335 (1.1)	620 (90)	427 (62)	27
10	H_2 + Ar	None	None	0.335 (1.1)	848 (123)		
11	H_2 + Ar	None	None	0.335 (1.1)			
12a	H_2 + Ar	None	None	0.335 (1.1)	1048 (152)	876 (127)	15
12b	H_2 + Ar	None	None	0.335 (1.1)	689 (100)	455 (66)	32
12c	H_2 + Ar	None	None	0.335 (1.1)	793 (115)	593 (86)	23
12d	H_2 + Ar	None	None	0.335 (1.1)	1034 (150)	758 (110)	26

TABLE I (continued)

RESULTS FROM SiC RIBBON PRODUCTION THROUGH JUNE 1974

Run, 9S No.	Cleaning Gas	Air Cleaning	PG Coating	Speed M/min (f/min)	Tensile Strength, M Pa (Ksi)		Coefficient of Variation σ/Average , %
					High	Average	
13a	H_2 + Ar	None	None	0.335 (1.1)	1330 (193)	876 (127)	23
13b	H_2 + Ar	None	None	0.274 (1.1)	1350 (196)	958 (139)	22
13c	H_2 + Ar	None	None	0.390 (1.28)	938 (136)	641 (93)	29
13d	H_2 + Ar	None	Yes		Poor	—	
14a	H_2 + Ar	Yes	None	0.335 (1.1)	814 (118)	593 (86)	19
14B	H_2 + Ar	Yes	Yes	0.335 (1.1)	820 (119)	648 (94)	24
15a	H_2 + Ar	Yes	Yes	0.335 (1.1)	717 (104)	572 (83)	22
15b	H_2 + Ar	Yes	Yes	0.335 (1.1)	827 (120)	689 (100)	14
15c	H_2 + Ar	Yes	Yes	0.335 (1.1)	876 (127)	627 (91)	22
16	H_2 + Ar	Yes	None	0.335 (1.1)	1027 (149)	765 (111)	22
17	H_2 + Ar	Yes	None	0.335 (1.1)	1096 (159)	841 (122)	16
18	H_2 + Ar	Yes	None	0.274 (0.9)	972 (141)	814 (118)	14
19	H_2 + Ar	Yes	None	0.274 (0.9)	1047 (152)	841 (122)	13
20a	H_2 + Ar	Yes	None	0.274 (0.9)	1206 (175	910 (132)	18
20b	H_2 + Ar	Yes	None	0.274 (0.9)	1413 (205)	1020 (148)	18

TABLE I (concluded)

RESULTS FROM SiC RIBBON PRODUCTION THROUGH JUNE 1974

Run, 9S No.	Cleaning Gas	Air Cleaning	PG Coating	Speed M/min (f/min)	Tensile Strength, M Pa (Ksi)		Coefficient of Variation σ/Average, %
					High	Average	
21	H_2 + Ar	Yes	None	0.335 (1.1)	1448 (210)	1213 (176)	10
22a	H_2 + Ar	Yes	None	0.335 (1.1)	1089 (158)	958 (139)	12
22b	H_2 + Ar	Yes	None	0.335 (1.1)	1082 (157)	979 (142)	12

better strengths were then obtained. The gas mixtures, particularly in the first 2.5 cm (1 inch) of the SiC deposition stage, were varied, as well as the filament speed and the input power. Runs 20b and 21 showed the best results up to that time with a high value of 1447 M Pa (210 Ksi) an average of 1213 M Pa (176 Ksi), and a coefficient of variation of 10%.

The substrate used for all of the tests of Table I was 12 micron (0.5 mil) thick by 0.18 cm (70 mils) wide made by carbonizing Kapton polyimide film 12 micron (1/2 mil) thick by 0.3 cm (1/8 inch) wide. Sufficient material was carbonized successfully to provide substrate for these preliminary check out runs. A photograph of carbonized Kapton film is shown in Figure 5. These early results showed that the carbonized Kapton film was capable of higher quality than the substrate used on the earlier program, but still showed evidence of flaws and difficulties such as holes, protrusions, and residual curvature or lack of flatness. The 12 micron (1/2 mil) thick by 0.3 cm (1/8 inch) wide Kapton film carbonized into a ribbon of about 12 micron x 0.18 cm (1/2 x 70 mils), an aspect ratio which met the specification target of this program; with these starting substrate dimensions, one can deposit a 150 micron by 0.19 cm (6 mil by 75 mil) SiC ribbon which is greater than the 10:1 aspect ratio target. Also, the volume fraction of the substrate would be below the prescribed upper limit of 10% of the total filament volume.

Examination of the ends of the tensile breaks by optical microscopy proved to be the most effective process analysis tool and indicated that the tensile strength was limited by enlarged growths caused by external debris or irregularities in the carbon ribbon substrate; the growths observed on SiC ribbon

Figure 5 CARBONIZED KAPTON FILM (100x)

during these early results were substantially smaller in size than those observed on the SiC ribbon made on the previous program. The substantial improvement in the reduced frequency of large growths after inclusion of the physical rubbing and gas blowing cleaning step (included before Run 14) suggested that external debris was responsible for many of these asperities, and the strength improvement showed that at least some of this foreign material can be removed. However, the frequency of these still observed on tensile ends showed that removal was not yet complete.

The results of Run 21, i.e., the highest average tensile results, and the observed smooth SiC surface showed that the physical removal of debris should be done before pyrolytic graphite (PG) deposition. When the PG stage was used only for heat treatment, the material was much more nearly free of large growths, suggesting that deposition of pyrolytic graphite on the debris made it impossible to remove these asperities. Figure 6 is a photograph of the smooth surface of SiC ribbon produced under the best conditions through June 1974. Note that the lines visible on the Kapton film seen in Figure 5 are replicated on the vapor deposited SiC ribbon. Figure 7 is a photomicrograph of a SiC ribbon facture end; in the figure the top surface is SiC, the next layer (a small chip visible) is the carbonized Kapton, and the last layer is the "other" side of the SiC ribbon. Note that the surface morphology of the Kapton was replicated on both the outside and inside surfaces of the SiC layers.

During July 1974, several changes were made in the cleaning and deposi-tions, giving the results of Table II. The highest tensile data obtained in this series were from Runs 28 and 29, with a high individual tensile value of
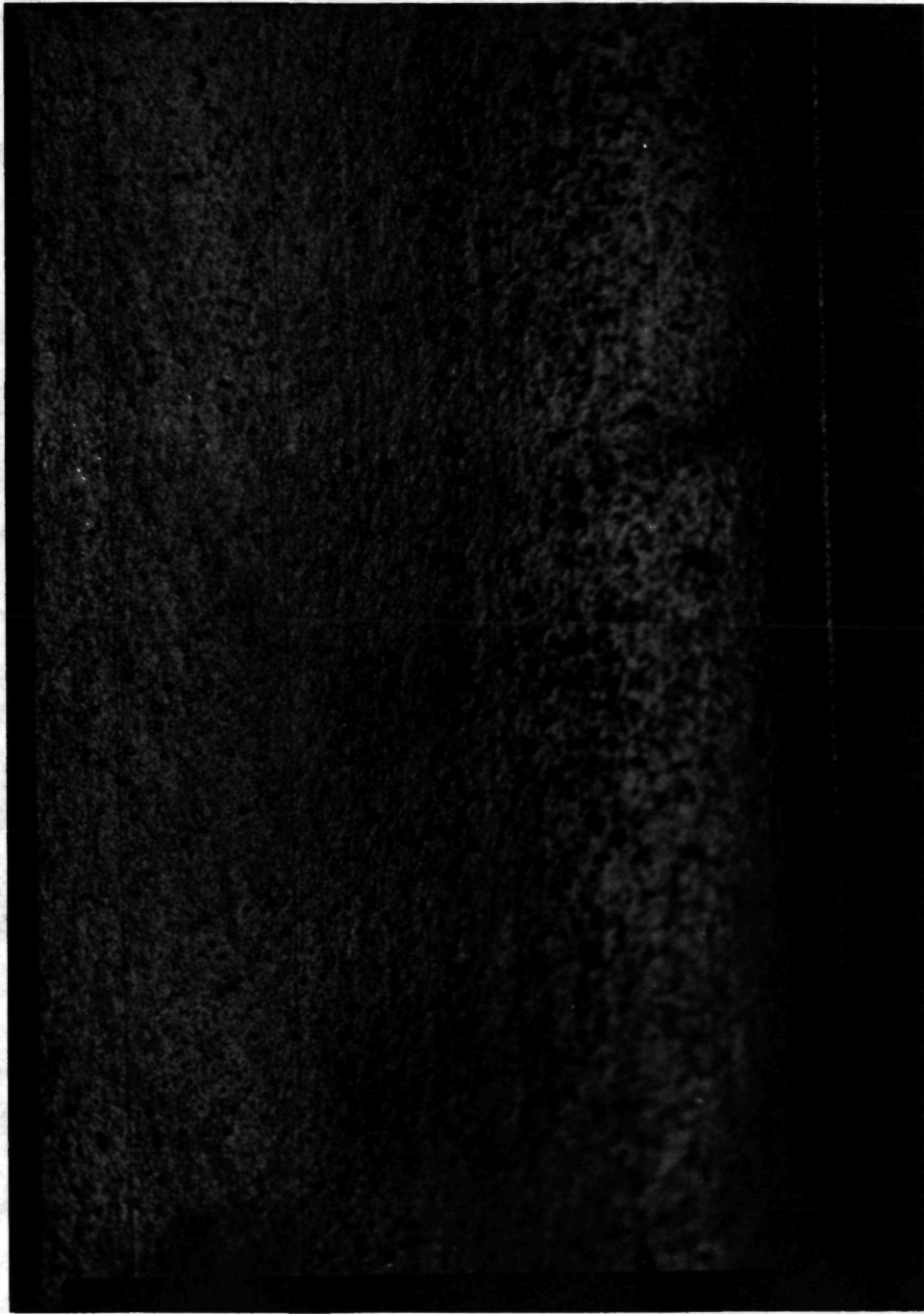
Figure 6 SURFACE STRUCTURE OF SiC RIBBON (100x)

Figure 7 SIDE VIEW OF THE BROKEN END OF A SiC RIBBON

TABLE II

RESULTS OF SiC RIBBON PRODUCTION IN JULY 1974

Run No. Start	Speed f/min.	Tensile Strength, M Pa (Ksi)			Notes See Note 1
		High	Average	Std. Dev. %	
23	1.1	1322 (192)	1193 (173)	9	Material used for Composite Making
24	1.1	No Test			
25	1.1	1241 (180)	1076 (156)	9	
26	1.1	1241 (180)	1041 (151)	13	
27	1.1	No Test			
28	1.1	1537 (223)	1144 (166)	16	
29	1.1	1489 (216)	1241 (180)	15	See Note 2
30	1.1	1027 (149)	841 (122)	12	See Note 3
31	1.1	1068 (155)	931 (135)	10	
32	2.6	1323 (192)	1089 (158)	24	See Note 4
33	2.6	1385 (201)	1192 (173)	9	
34	2.6	No Test			
35	2.6	476 (69)	372 (54)	24	
36	2.6	731 (106)	579 (84)	18	
37	2.6	1027 (149)	751 (109)	20	
38	2.6				Material used for Composites. These runs were done consecutively without stopping the reactor.
39	2.6				
40	3.0				
41	3.7				

NOTES TO TABLE II

Note 1: At the start of the runs of Table II, the reactor included a 10 cm (4 inch) heat treating stage, the first half in H_2, the second half in argon; an air cleaning stage through two rubber slits; and a 11.4 cm (4-1/2 inch) long SiC deposition reactor, including a surface treatment step using an argon-propane mixture.

Note 2: For Run 29 and thereafter, a substrate polishing step using driven rubber rollers against each side was used.

Note 3: From Run 30 on, the heat treatment stage was lengthened from 10 cm (4 inch) to 30 cm (12 inch).

Note 4: From Run 32 on, the SiC deposition reactor was lengthened from 11.4 cm (4-1/2 inch) to 35.5 cm to (14 inch) with no change in the gas flows.

1551 M Pa (223 Ksi), and the highest average of 10 tests of 1240 M Pa (180 Ksi). In the table it is to be noted also that the variability was relatively low with the standard deviation being as low as 10% on some runs. The tensile values still fell short of the 2068 M Pa (300 Ksi) target value, indicating that more needed to be done to optimize the operating conditions to achieve better tensile strength.

Note the encouraging operability of runs 38 through 41 shown in Table II. These runs were conducted consecutively without shutdown while cutting specimens off the takeup reel for examination during operation for a total duration of over 45 minutes. Examination of the ribbon during the latter stages of these runs showed a surface relatively free of the large growths observed earlier at closely spaced intervals on the ribbon. The flexural strength of the surface of this ribbon as measured by a bending test was well over 2068 M Pa (300 Ksi). For example, the ribbon could be bent to a diameter of 2.5 cm (1 inch) or less, and the surface stress calculates to be 2688 M Pa (390 Ksi) from the formula,

$$\sigma = \frac{dE}{D}$$

where

σ is the surface stress

d   is the filament diameter or ribbon thickness

D   is the filament loop diameter

E   is the modulus of SiC

The tensile strength as measured by straight axial stress, however, was about 1378 M Pa (200 Ksi), but the end view showed non-uniform interior texture.

The above results concluded the runs of Series A of the program. Several runs noted in Table II were used to make composite specimens discussed in the next section below. The conclusion from the results shown in Tables I and II was that improvements were needed in the process of making the carbon substrate before the target strength of 2068 M Pa (300 Ksi) could be obtained from the SiC ribbon. The studies on improvement of the carbon ribbon are described following the composite studies, and the results from SiC deposition on the improved ribbon are discussed after that.

Fabrication and Testing of Composites

During July 1974, as shown above in Table II, sufficient SiC ribbon material was made to fabricate several composite specimens for both longitudinal and transverse composite measurements. The SiC ribbon material laid up in the composites measured about 0.18 cm (70 mils) wide by about 0.009 cm (3.5 mils) thick. The matrix material was 5505 epoxy, used routinely in boron composites fabrication. The first set were transverse specimens. The SiC ribbon was cut into 2.5 cm (1 inch) long pieces and laid up by hand into 2.5 cm (1 inch) wide by 15 cm (6 inch) long specimens. The specimens were 6-ply, with $\pm$ 15° skew on alternate layers, i.e., the first layer was laid up with a 15° skew lower left to upper right, the next with a 15° skew lower right to upper left, etc. The skew was introduced to ensure good overlap between layers, or, stated another way, the skew avoids the possibility of no overlap at all at some point on all six layers of the specimen.

The above 6-ply specimens were tensile tested to measure the transverse strength and Table III presents the results of these tests.

TABLE III

PROPERTIES OF TRANSVERSE SiC RIBBON COMPOSITES - FIRST SET

Specimen	Load (lbs)	Tensile Strength, MPa (Ksi)		Modulus, MPa (Msi)	
86-1	380	59.5	(8.640)	51,000	(7.4)
86-2	385	57.7	(8.370)	50,300	(7.3)
86-3	350	51.3	(7.450)	55,150	(8.0)
86-4	420	56.8	(8.240)	68,253	(9.9)

The results of Table III indicated a transverse strength below that which was expected based upon the axial tensile strength of the SiC ribbon. The ribbon which was produced had an average tensile strength over 1034 MPa (150 Ksi), with a number of individual pulls over 1378 MPa (200 Ksi) range. However, the modulus values indicated the improvement in transverse modulus to be expected by using ribbon reinforcement.

One reasonable explanation for the low transverse strength of the composite was that the strength of each ribbon piece was degraded at the ends where it was broken to make 2.5 cm (1 inch) pieces, and these breaks, which were ragged, served as stress raisers. To test whether this or some other effect resulted in the relatively low transverse strength, specimens of a different arrangement were tested. First, some specimens were made using nickel ribbons 0.16 cm (1/16 inch) wide by 78 microns (3.1 mils) thick, which was very close to the same dimensions as the SiC ribbons. These specimens were not sensitive to degradation due to the end cut, and were intended to demonstrate the upper limit strength of a ribbon-reinforced epoxy matrix. Second, a transverse specimen was made using 7.6 cm (3 inch) long pieces of SiC ribbon, but the specimen was laid up with epoxy matrix only in the center 2.5 cm (1 inch) portion of the ribbon. The outer portions added little or no strength or stiffness to the composite, but provided a means to measure the failure strength of a SiC composite free of the stress-raising end effects of 2.5 cm (1 inch) pieces. This technique is similar to that developed by Kreider, Sardi, and Prewo, of United Aircraft Research Labs, Metal Matrix Composite Technology, AFML-TR-71-204, in their study of

premature B/Al fracture in transverse specimens, fracture which was initiated by filament splitting. In addition to the additional transverse specimens discussed above, two longitudinal (or nearly longitudinal) specimens were fabricated. One had a ± 15° skew, the other no skew.

The composite specimens discussed above were constructed during December 1974, two of which were tested in December and three during January 1975. The results of these composite tests are shown in Table IV.

TABLE IV

RESULTS FROM COMPOSITE SPECIMENS - SECOND SET

Specimen	Reinforcement Material	Orientation	Tensile Strength MPa (Ksi)	Comments
N1	75 micron x 0.16 cm (3 mil x 1/16") Ni	Transverse ± 15° Skew	45.3 (6.580)	Failed in grip
N2	75 micron x 0.16 cm (3 mil x 1/16") Ni	Transverse ± 15° Skew	76.5 (11.100)	Failed in grip
0-1	89 micron x 0.19 cm (3.5 mil x 75 mil) SiC Ribbon	Longitudinal ± 15° Skew	147.5 (21.400)	Failed in grip
0-2	89 micron x 0.19 cm (3.5 mil x 75 mil) SiC Ribbon	Longitudinal	355 (51.500)	Failed in guage length
D	89 micron x 0.19 cm (3.5 mil x 75 mil) SiC Ribbon	Transverse ± 15° Skew	64.3 (9.330)	2.54 cm (1") Specimen with 2.54 cm (1") extended ends on reinforcement ribbon

Longitudinal Specimen 0-2 failed at a total load of 2370 lbs, which is an average stress of 862 MPa (125 Ksi) on each ribbon at failure. This agrees quite well with the average tensile strength of 1034 MPa (150 Ksi) for the ribbon. Specimens N1, N2, D, and 86-1 through -4 (Table III) showed a transverse modulus in the range 48,000-69,000 MPa (7-10 Msi) which is substantially higher than the transverse modulus for round reinforcement of 20,000 MPa (3 Msi). The transverse failure stress of 68,900 (10 Ksi) is lower than expected for ribbon reinforcement, and the reasons for this are not yet known.

In conclusion, the longitudinal composite specimen without skew (0-2) showed a breaking strength consistent with the value expected for the ribbons used in the composite. The transverse modulus was also as expected. More work needs to be done on transverse specimens to demonstrate what can be achieved for transverse strength of composites made with SiC ribbon reinforcement.

Carbon Ribbon Substrate Improvement Studies

In December 1974, the emphasis was shifted from SiC deposition studies to studies of methods to improve the carbon ribbon substrate. The need for this shift in emphasis was pointed up by the results of the Series A SiC deposition studies which showed that strength was limited by flaws at the carbon substrate surface, and that improvement of the carbon ribbon was needed to provide stronger SiC ribbon. The precursor for the carbon substrate was still Kapton[R] polyimide film, as before, but 12 micron x 0.3 cm (1/2 mil x 1/8 inch) dimensions. The carbonization method used during the

Series A studies was to carbonize the ribbon in two sequential muffle furnaces, the first held at 750°C (1380°F), and the second at about 1050°C (1920°F). The ribbon was held flat in both of these furnaces by winding it over and under the rungs of a quartz "ladder", i.e., a device with rungs over and under which the Kapton film traveled during its residence in the furnace. The ladder device was designed to decrease curling of the ribbon. The N_2 gas in the furnace tube was admitted in counter-flow, i.e., it flowed in a direction opposite to the direction of travel of the ribbon being carbonized.

The improvement studies undertaken next were aimed at avoiding some of the difficulties encountered in the previous carbonization procedure. The friction between the carbonizing ribbon and the rungs of the ladder proved excessive, causing frequent breaks. To reduce this problem, a quartz ladder was designed with roller wheels which rotated on their axles, thus providing a mechanical advantage to overcome the friction as the ribbon traveled over them. Additionally, it was felt that the wheels would provide more contact with the ribbon to hold it flat during carbonization. A second feature incorporated into the furnace was co-flow of the gas, i.e., the N_2 (or air) was introduced to flow in the same direction as ribbon motion. It was considered that co-flow would reduce the contamination of the ribbon with carbonized tar condensate transferred to the ribbon from the ladder; for example, it was felt that the previously observed (but intermittent) surface irregularities on the carbonized ribbon could have been caused by condensation of high molecular weight imide material on the cold Kapton ribbon surface entering the tube furnace.

Carbonization of Kapton was conducted using a four oven arrangement, as shown schematically in Figure 8 below. Partial carbonization of polyimide ribbon was achieved at rates of 0.15 to 0.45 meters/min (1/2 to 1-1/2 ft/min). Both air and nitrogen gases were used in co-flow. No excessive tar build-up occurred which could drop off onto the ribbon. Transverse curling was reduced by using the quartz wheel and roller assembly, shown in Figure 9, instead of the ladder arrangement. There were some ribbon tension problems in the system from the rollers; however, the overall tension was lower as compared with the previous quartz ladder arrangement.

During January 1975, several stages of improvements were evolved on the roller-wheel guide concept, and the wheel guide system as developed then is shown in Figure 10. The roller guides, as stated above, were installed to maintain flatness in the ribbon by preventing curling of the polyimide film during the dimensional change which occurs at the 500-1100°C (930-2010°F) treatment temperature and were changed to graphite to prevent sticking. The first successful configuration used was a furnace with two heating zones, using a 3-wheel guide in the second zone. The first zone was operated at 500°C (930°F) and the second at 1100°C (2010°F) and the N_2 flow was in the same direction as (concurrent with) the ribbon motion. The first run was about 45 meters (150 ft.) long and was limited only by the initial length of polyimide film on the test roll. One very interesting observation about this configuration was the absence of exhaust smoke as was observed from the first half of the two-stage furnace which was used previously.
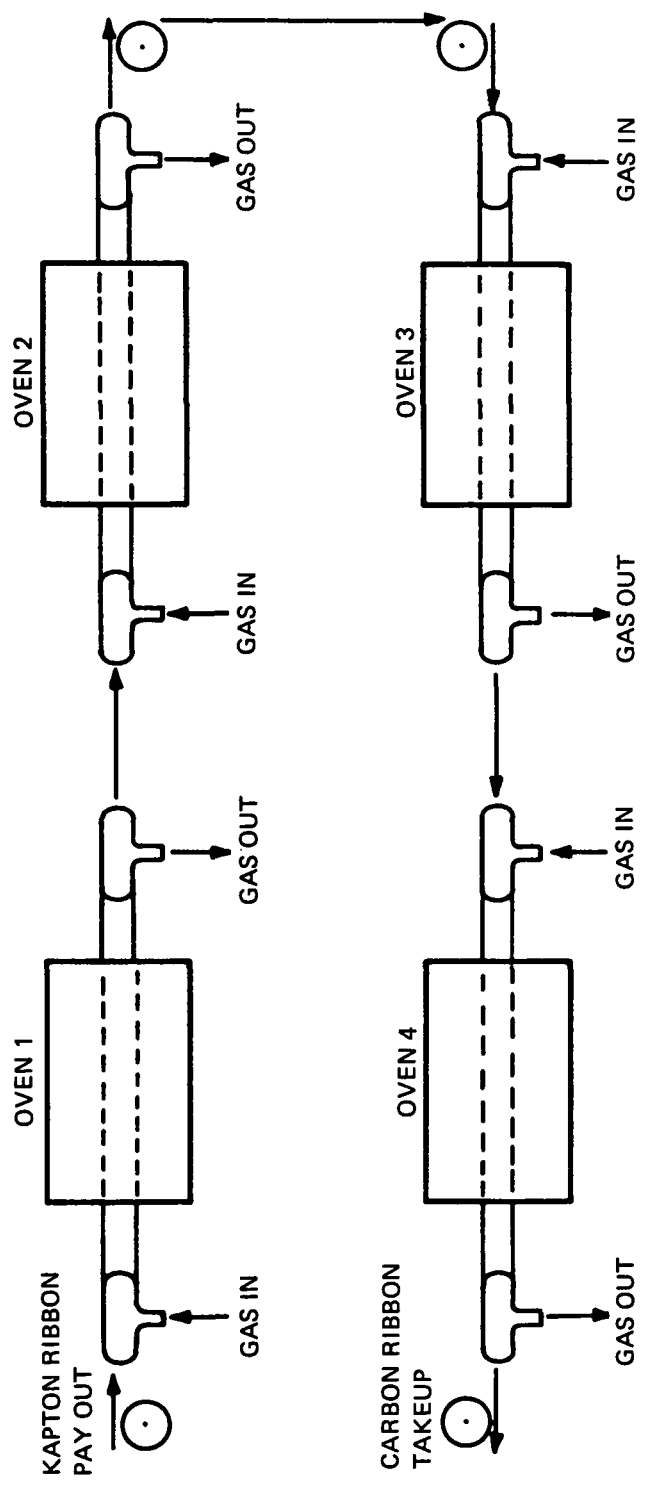
Figure 8 TUBE FURNACE ASSEMBLY

86-1526

-30-

TOP VIEW

QUARTZ WHEELS

SIDE VIEW
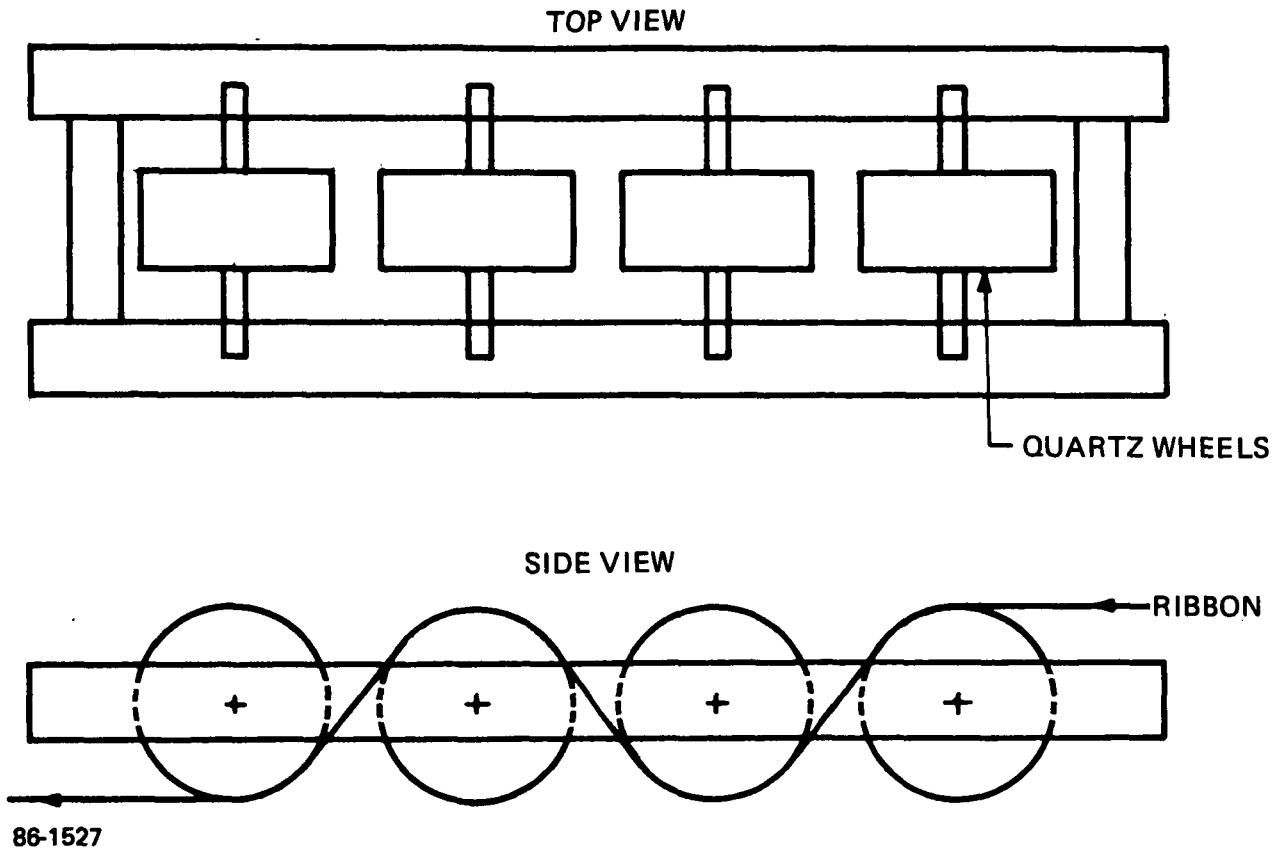
RIBBON

86-1527

Figure 9 TOP VIEW AND SIDE VIEW OF THE CARBON RIBBON ROLLER ASSEMBLY

TOP VIEW

GRAPHITE WHEELS
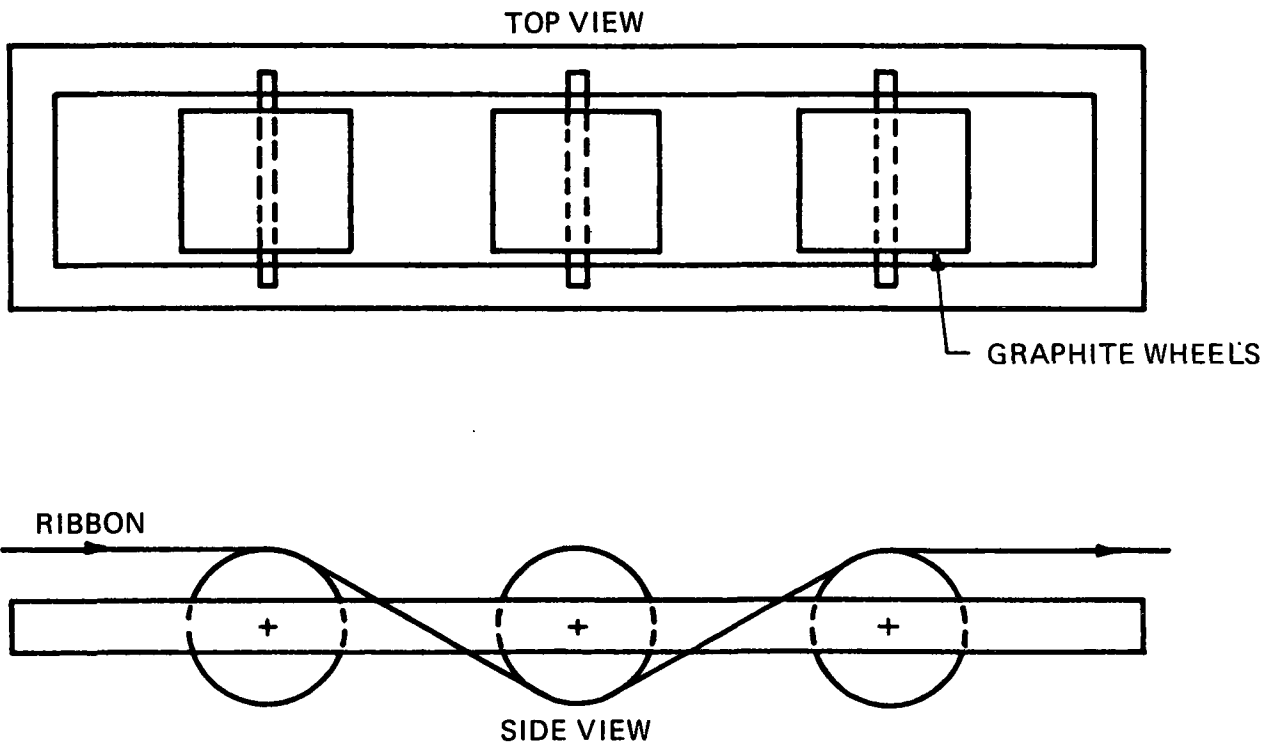
RIBBON

SIDE VIEW

86-1528

Figure 10 TOP VIEW AND SIDE VIEW OF CARBON RIBBON ROLLER ASSEMBLY

-32-

The gases which evolved from the ribbon did deposit a carbonaceous layer on the furnace walls, however, indicating that the ribbon effluent was completely decomposed into carbon and gases before it left the furnace. A second observation was that the carbon ribbon that was made appeared to be free of sooty material picked up in the furnace. (These sooty deposits which previously were found on the ribbon were the motivation for changing the gas flow configuration as described above.)

The first configuration tested used quartz wheels about 0.6 cm (1/4 inch) wide. However, the ribbon slipped off the side of the wheels in spite of the presence of guides near the wheels. A second version tested used wheels about 2.5 cm (1 inch) wide, which guided the ribbon successfully if the wheels were properly aligned (although "proper" alignment is somewhat difficult to achieve.) In addition, if there were a break during carbonization, it was noted that the ribbon stuck to the quartz liner surface. Successful pulleys were made of graphite supported on graphite axles, which result in low turning friction and furthermore, resulted in no tendency to cling to the ribbon. These pulleys, in addition, provided a high surface area contact with the ribbon in order to hold it flat during carbonization. The carbonization of Kapton polyimide film reported previously[4] showed that the carbonization per se presented no operational problems, but the requirement for a flat and smooth SiC substrate presented some special problems.

Several variables had to be optimized during the ribbon carbonization process. Tension throughout the furnace assembly had to be optimized to improve the flatness of the finished ribbon, even with the use of the graphite wheels. The number of pulleys was increased to further improve the contact

with the ribbon. The operating speed was varied to determine the optimum residence time. Argon, N_2, and H_2 gases were studied, but no difference was noted. The total gas flow rate was varied also with no variation in quality. The finished filament resistance, its flatness and its surface texture was observed as a diagnostic indication of optimum conditions.

It was not practicable with the furnaces available to finish the carbon ribbon to a high enough temperature to stabilize it adequately. The final finishing step had to raise the ribbon temperature well above the SiC deposition temperature (about 1350°C or 2470°F) to avoid catastrophic damage in the form of circular areas of SiC breakage. This final finishing was carried out by resistively heating the ribbon in hydrogen first to about 1200°C (2200°F), then in argon to about 2000°C (3650°F). This final finishing stopped the damaging SiC deposition tendencies, but resulted in a tendency to make a ribbon with a preset twist characteristic. Unsuccessful attempts were made to heat the ribbon electrically in the final section of the carbonization oven, by insulating the graphite rollers on boron nitride supports. The final solution to prevent the twist characteristic was to keep the ribbon under a tension of about 50 grams (0.11 lbs) during the final 2000°C (3650°F) finishing and SiC deposition.

During July 1975, the oven system was used to produce flat, twist-free carbon substrate with an average run length of about 100 m (328 ft) and a high of about 370 m (1214 ft). It was found that a pulley assembly was not necessary in the second or higher temperature oven to produce a flat substrate (it was needed only in the first oven), but that residence time in the oven could affect the flatness of the substrate. The oven was used successfully with modifications as discussed below throughout the rest of the program.

Series B SiC Ribbon Production Runs

The SiC deposition reactor system was put into operation in July 1975, using the improved carbon substrate. Twenty-three samples were made at various operating conditions as shown in Table V. An ultimate tensile strength of 1606 MPa (233 Ksi) was achieved. Various methods of preparing samples for tensile tests were tried due to the fact that the smooth ribbon would slip when conventional methods were used.

During August 1975 several long runs of carbon ribbon substrate were produced in the two-stage carbonization oven system described above. The material produced was flat and curl-free, suitable for SiC deposition studies.

Twenty-six SiC deposition runs were made in August 1975, and the results are tabulated in Table VI. The primary objective of these runs was to optimize the reactor operating conditions, with the aim of improving the tensile strength. The highest strength obtained was on run 9S85, where a tensile strength of 1480 MPa (215 Ksi) was obtained. This is comparable with, but not better than the maximum obtained in July of 1610 MPa (233 Ksi).

During January 1976, several long runs of carbon ribbon substrate were produced in the two-stage carbonization oven system described above. Two modifications were made to the system. First, a new set of entrance and exit seals was made, which allowed ribbon with widths up to 4.76×10^{-3} m (3/16 inch) and thicknesses up to 2.54×10^{-5} m (1 mil) to be carbonized. Second, a new low-friction payout was added which allowed the material to be pulled through the furnaces with less tension than previously possible.

TABLE V
RIBBON FILAMENTS MADE DURING JULY 1975

Run No.	PG Stage Current (A)	SiC Stage Current (A)	Tensile Strength MPa	(Ksi) High	Deposition Time (sec)	SiC Thickness micron	(mil)
9S-47	1.20	1.20		-	13.5		-
9S-48	0.85	1.20		-	31.3		-
9S-49	1.00	1.20	740	(108)	13.5	50.8	2.0
9S-50	1.00	1.20	1430	(208)	13.5	43.2	1.7
9S-51	1.20		-	-	13.5		-
9S-52	1.00	1.50	-	-	13.5		
9S-53	1.00	1.00	690	(100)	13.5	27.9	1.1
9S-54	1.00	1.25	-	-	13.5		-
9S-55	1.00	1.30	-	-	13.5		-
9S-56	1.25	1.35	800	(116)	13.5	43.2	1.7
9S-57	1.25	1.35	610	(88)	13.5	66.0	2.6
9S-58	1.50	1.50	670	(97)	13.5	94.0	3.7
9S-59	1.60	1.50	1160	(168)	19.2	71.1	2.8
9S-60	1.50	1.50	1040	(151)	21.7	68.6	2.7
9S-61	1.50	1.50	1380	(200)	21.7	68.6	2.7
9S-62	1.50	1.70	660	(96)	21.7	68.6	2.7
9S-63	1.50	1.50	1530	(222)	17.2	50.8	2.0
9S-64	1.50	1.60	1380	(200)	17.2	58.4	2.3
9S-65	1.50	1.60	1080	(156)	21.7	58.4	2.3
9S-66	1.50	1.60	1240	(180)	21.7	71.1	2.8
9S-67	1.75	1.75	880	(127)	21.7	76.2	3.0
9S-68	1.50	1.75	1610	(233)	13.5	35.6	1.4
9S-69	1.75	2.00	1400	(203)	13.5	43.2	1.7

TABLE VI

SiC RIBBON FILAMENTS MADE DURING AUGUST 1975

Run II	PG Stage Current (A)	SiC Stage Current (A)	Tensile Strength		Deposition Time (sec)	SiC Thickness	
			MPa	Ksi		micron	mils
9S70A	1.5	1.75	1206	175	17.2	71	2.8
9S70B	1.5	1.5	1393	202	17.2	69	2.7
9S71	1.5	1.5	1427	207	13.5	48	1.9
9S72	1.25	1.25	1124	163	17.2	51	2.0
9S73	1.25	1.5	1427	207	21.7	84	3.3
9S74	1.75	1.5	717	104	33.3	86	3.4
9S75	1.75	1.75	552	80	33.3	130	5.1
9S76	1.75	1.5	1048	152	13.5	46	1.8
9S77	1.75	1.25	655	95	45.4	84	3.3
9S78	1.75	1.5	1227	178	45.4	91	3.6
9S79	1.75	1.5	827	120	31.2	91	3.6
9S80	1.75	1.5	765	111	31.2	91	3.6
9S81	1.5	1.5	448	65	45.4	109	4.3
9S82	1.5	1.5	993	144	21.7	99	3.9
9S83	1.5	1.5	1413	205	20.8	64	2.5
9S84	1.5	1.3	1420	206	19.2	46	1.8
9S85	1.5	1.4	1482	215	19.2	56	2.2
9S86	1.5	1.25	1117	162	31.2	61	2.4
9S87	1.5	1.15	751	109	31.2	41	1.6
9S88	1.5	1.20	917	133	31.2	64	2.5
9S89	1.5	1.25	965	140	31.2	66	2.6
9S90	1.5	1.3	1227	178	17.2	38	1.5
9S91	1.25	1.25	1427	207	17.2	41	1.6
9S92	1.25	1.25	1448	210	17.2	38	1.5
9S93	1.25	1.25	1434	208	15.1	46	1.8
9S94	1.25	1.25	1268	184	13.5	41	1.6

With this new apparatus, three packages of carbon ribbon substrate were produced, with an average length of 1.60×10^{2} m (525 ft). Because this precursor was thicker than any previously used (25 micron or one mil) the drawing rate of the ribbon was reduced from 0.9 meters (3.5 inch) per minute to 0.16 meters (6.2 inch) per minute. This rate produced an excellent substrate.

One of the packages of substrate was used to study the performance of a new vertical heat treatment and pyrolytic graphite (PG) coating reactor. In this reactor, the substrate was heated in an atmosphere of argon and hydrogen, where it approached temperatures used to deposit PG. This heat treatment evolved volatiles before any attempt was made to deposit pyrolytic graphite (PG). Only after the substrate was exposed to this high temperature did it enter the PG stage where a mixture of methane and argon was used to deposit the PG.

Ten runs were made to find suitable conditions to deposit PG and are shown in Table VII. The final run produced a substrate free of any curl, twist, or bumps, which had a 2.54×10^{-6} m (0.1 mil) layer of pyrolytic graphite deposited on it.

During February and March 1976, a series of runs were carried out to optimize the PG and SiC deposition parameters. Table VIII shows the results of runs during February. The first series of runs, 11 through 21, studied the effect on tensile strength of varying the PG current. The conclusion from this series was that the strength was not particularly

TABLE VII

PG RUNS MADE DURING JANUARY 1976

Run No.	Speed Meter/Minute	H_2 L/min.	Ar Top L/min.	Ar Bottom L/min.	CH_4 L/min.	Current (Amps)
1	5.49×10^{-1}	0.1		1.7	0.16	2.25
2	5.49×10^{-1}	0.1		1.2	0.11	2.50
3	5.49×10^{-1}	0.1		1.2	0.11	2.80
4	5.49×10^{-1}	0.1		1.2	0.16	2.80
5	5.49×10^{-1}	0.1		1.2	0.16	2.80
6	5.49×10^{-1}	0.1		1.2	0	2.80
7	5.49×10^{-1}	0.1		1.7	0.11	2.80
8	5.49×10^{-1}	0.1	0.7	1.0	0.08	2.40
9	5.49×10^{-1}	0.1	0.7	1.0	0.08	2.40
10	5.49×10^{-1}	0.1	0.7	1.0	0.13	2.40

TABLE VIII

SiC RIBBON FILAMENT MADE DURING FEBRUARY 1976

Run No.	PG Current (A)	SiC Current (A)	PG Gas Flow (L/min)	Avg. Tensile Strength MPa	(Ksi)
11	1.80	1.80	1.20	896	(130)
12	2.10	1.80	1.20	703	(102)
13	2.40	1.80	1.20	627	(91)
14	1.75	1.80	1.20	841	(122)
15	2.00	1.80	1.20	614	(89)
16	2.35	1.80	1.20	641	(93)
17	2.00	1.80	1.20	614	(89)
18	1.50	1.80	1.20	820	(119)
19	2.25	2.25	1.20	586	(85)
20	2.00	2.25	1.20	800	(116)
21	1.75	2.25	1.20	882	(128)
22	1.75	2.25	1.20	607	(88)
23	1.75	2.25	2.40	641	(93)
24	1.75	2.25	0.60	745	(108)
25	1.75	2.25	0.60	882	(128)
26	1.75	2.25	1.20	772	(112)
27	1.75	1.75	1.20	510	(74)
28	1.80	1.80	1.20	724	(105)
29	1.80	1.80	1.20	490	(71)
30	2.10	1.80	1.20	936	(136)
31	2.00	2.00	1.20	816	(118)
32	1.75	2.00	1.20	786	(114)
33	1.75	2.00	1.20	607	(88)
34	1.75	1.75	1.20	670	(97)
35	1.75	2.00	1.20	710	(103)
36	1.75	2.25	1.20	765	(111)
37	2.40	2.00	1.20	1110	(161)
38	2.40	2.30	1.20	1151	(167)

sensitive to the thickness of PG deposited, but it was sensitive to the temperature at which the SiC was deposited. The second series, 22 through 26, studied the effect of varying the gas flow rate in the PG stage, but no significant effect was observed. The third series (27 through 38) studied the effect of varying both the PG current and the SiC deposition reactor current, with the conclusion that the higher current ranges for both PG and SiC deposition were preferable.

The optimization studies of SiC ribbon deposition were continued during March 1976, with the results shown in Table IX. The first part of this series (through Run 68) showed a tensile strength pattern much like that of earlier studies. The flaws observed at the tensile breaks appeared sometimes to be external to the PG layer. A possible source of debris that could cause this flaw was the top slit electrode of the SiC deposition reactor. To suppress the collection of debris at this point, the reactor configuration of Figure 11 was constructed and used, which prevents the formation of soot and silane from the mixture of silane and propane originally used there. In addition, a routine cleaning procedure was instituted before each run in which the reactor tube and top electrode slit were cleaned thoroughly. Another change was to reduce the silane concentration in the second zone (the first zone being pure H_2) where the mixture is rich in propane. These changes resulted in a substantial improvement in the tensile strengths obtained. Note in Run 79 that the target tensile strength of 2068 MPa (300 Ksi) was achieved, and many runs showed strength levels above 1723 (250 Ksi).
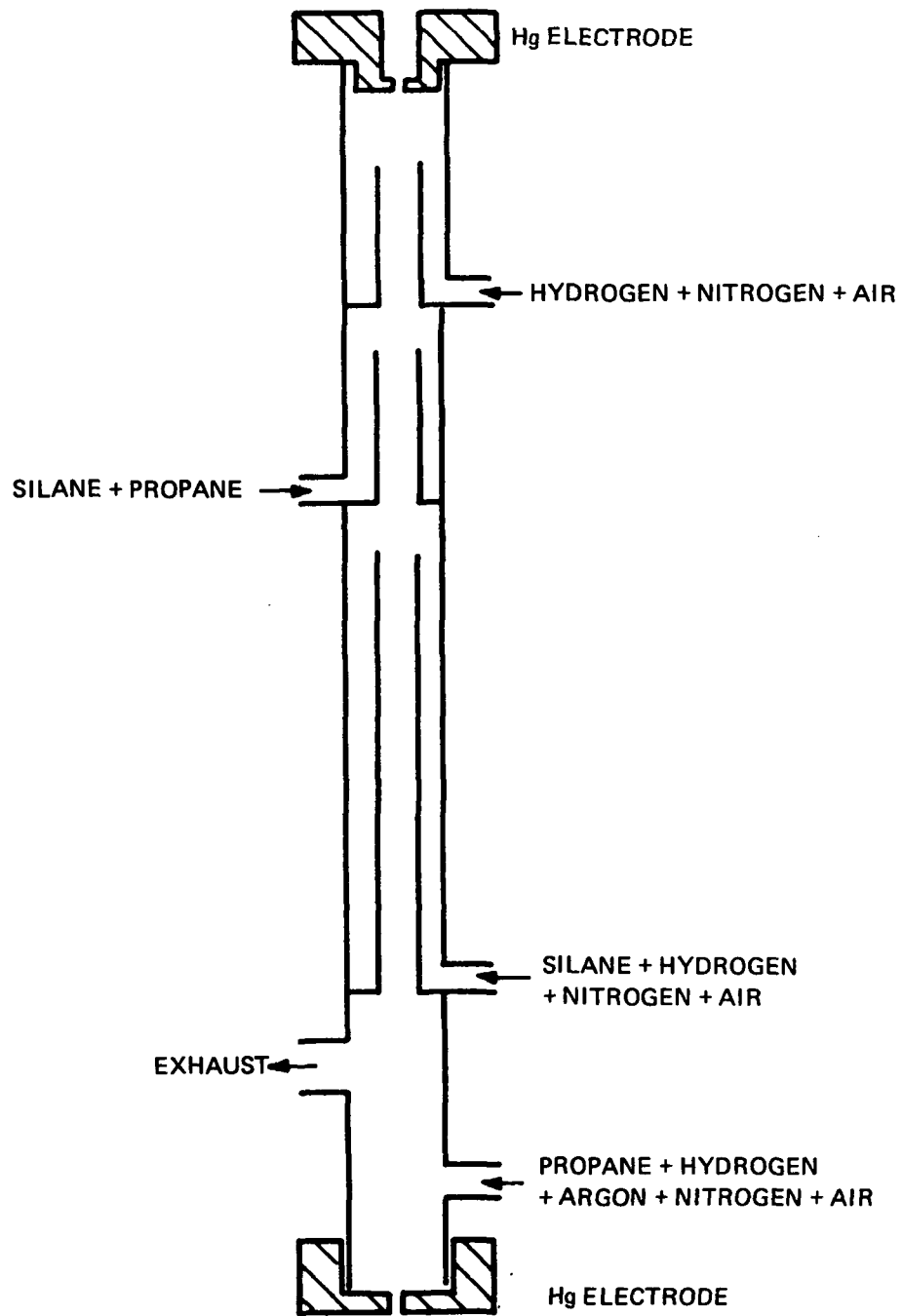
TABLE IX

SiC RIBBON FILAMENTS MADE DURING MARCH, 1976

Run No.	PG Current (A)	SiC Current (A)	Tensile Strength (High)		Speed (M/min.)	SiC Thickness	
			MPa	Ksi		Micron	Mil
39	2.4	2.4	545	79	0.07	102	4.0
40	2.4	2.4	889	129	0.07	102	4.0
41	2.4	2.4	689	100	0.09	76	3.0
42	2.4	2.4	841	122	0.06	119	4.7
43	2.4	2.4	882	128		89	3.5
44	2.5	2.0	1172	170	0.06	79	3.1
45	2.5	2.0	1034	150	0.07	69	2.7
46	2.5	1.8					
47	2.5	2.0	772	112	0.06	97	3.8
48	2.5	2.0	620	90	0.06	97	3.8
49	2.5	2.0	1144	166	0.07		
50	2.5	2.0	1117	162	0.07		
51	2.5	2.0	1103	160	0.06		
52	2.0	2.0	1089	158	0.06	84	3.3
53	2.0	2.5	855	124	0.12	66	2.6
54	2.0	2.5	855	124	0.13	64	2.5
55	2.0	2.2	1234	179	0.13	38	1.5
56	2.0	2.5					
57	2.2	2.0	1296	188	0.07	51	2.0
58	2.2	2.0	1427	207	0.07	46	1.8
59	2.2	2.5	1517	220	0.07	64	2.5
60	2.2	2.5	676	98	0.07	58	2.3
61	2.2	2.5	855	124	0.07	84	3.3
62	2.2	2.5	869	126	0.07	84	3.3
63	2.2	2.5	814	118	0.07		
64	2.2	2.5	827	120	0.09	84	3.3
65	2.3	2.5	1034	150	0.09	76	3.0
66	2.3	2.5	1317	191	0.09	71	2.8
67	2.3	2.5	1517	220	0.06		
68	2.3	2.5	1730	251	0.09	64	2.5

TABLE IX (CONCLUDED)

SiC RIBBON FILAMENTS MADE DURING MARCH 1976

Run No.	PG Current (A)	SiC Current (A)	Tensile Strength (High)		Speed (M/min.)	SiC Thickness	
			MPa	Ksi		Micron	Mil
69	2.3	2.8	1462	212	0.09		
70	2.2	2.5	1613	234			
71	2.2	2.5	1551	225	0.09	53	2.1
72	2.3	2.5	1868	271	0.09	64	2.5
73	2.3	2.5			0.09		
74	2.3	2.5	1138	165	0.09		
75	2.3	2.5	1310	190	0.09	69	2.7
76	2.3	2.5	1813	263	0.09	51	2.0
77	2.3	2.5	1510	219	0.09	61	2.4
78	2.3	2.2	1462	212	0.09	51	2.0
79	2.25	2.5	2075	301	0.09	53	2.1
80	2.25	2.7	1724	250	0.09		
81	2.25	2.7	1468	213	0.09	58	2.3
82	2.25	2.5	1586	230	0.09		
83	2.25	2.5	1192	173	0.09		
84	2.25	2.5	1503	218	0.09		
85	2.25	2.5	1813	263	0.09		
86	2.25	2.5	510	74	0.09	71	2.8
87	2.25	2.5	1186	172	0.09		
88	2.25	2.5	1544	224	0.09		
89	2.5	2.4	662	96	0.09		
90	2.25	2.5	1351	196	0.09		
91	2.25	2.5	1034	150	0.09		

Hg ELECTRODE

HYDROGEN + NITROGEN + AIR

SILANE + PROPANE

SILANE + HYDROGEN
+ NITROGEN + AIR

EXHAUST

PROPANE + HYDROGEN
+ ARGON + NITROGEN + AIR

Hg ELECTRODE

86-1529

Figure 11 MODIFIED SILICON CARBIDE REACTOR

CONCLUSIONS AND RECOMMENDATIONS

SiC on carbon ribbon substrate has shown strength levels as high as 2068 MPa (300 Ksi), the program target. SiC on round carbon monofilament substrate has shown a strength level over 5500 MPa (800 Ksi), indicating that SiC ribbon has a potential well above the values obtained to date.

Strength levels do not yet appear to be limited by flaws on the substrate itself, but rather by external debris on the outside surface. Therefore, improvements are still obtainable using the carbonized Kapton ribbon. It will eventually be necessary to improve the substrate itself, but not immediately. Improvements should be sought first by continuing the optimization studies using the carbonized 25 micron (1 mil) thick Kapton in widths in the range 0.3 to 0.9 cm (1/8 inch to 3/8 inch).

Additional work on the SiC ribbon concept is considered justified and should be promulgated vigorously. The next tensile strength target recommended is 2750 MPa (400 Ksi), with average strengths above 2068 MPa (300 Ksi), and the program should include the production of sufficient quantities of material to evaluate it in both epoxy and aluminum composites.

Additional studies are needed in the area of determining the transverse strength levels obtainable with SiC ribbon reinforcement. Reinforcements with ribbons of other materials such as steel should be included as reference standards.

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