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EFFECT OF CVD TUNGSTEN AND TaC COATINGS ON THE MECHANICAL BEHAVIOR OF SiC(C)

I. Ahmad
N. Hill
W. Heffernan

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BENÉT WEAPONS LABORATORY
WATERVLIET, N. Y. 12189

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Effects of the chemically-vapor-deposited tungsten and TaC coatings on the mechanical properties of silicon carbide (carbon core) filament have been investigated. In the temperature range of interest, because of the possible chemical interaction of tungsten with carbon rich silicon carbide phase on its surface and the columnar grain structure of the coating the filament was found to be embrittled. However, by controlling the initial

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nucleation of tunsten by adjusting the temperature, the direction of flow of reactants and filament speed, the degraduation effect of the coating can be minimized. TaC coating did not decrease the strength of the filament, because it did not react with the filament and had fine grain structure. Coatings of tungsten and TaC decreased the 100 hr 2000°F, rupture strength of the filament from 1.9 GN/M^2 (280 Ksi) to respectively 1.05 GN/M^2 (150 Ksi) and 1.6 GN/M^2 (240 Ksi). The tensile strength of the W coated filament was superior to that coated with TaC in the temperature range 1000 - 1500°C. Thermal cycling (room temperature - 1600°C) induced cracks in the TaC coating while W coating remained unaffected.

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We appreciate very much the contribution of Mr. Richard Warenchak in all aspects of this study, particularly in the measurements of the tensile and stress-rupture properties. The assistance of Mr. Leo McNamara in the examination of fracture surfaces by SEM is also gratefully acknowledged. We also appreciate helpful discussions with Mr. Joseph Cox.

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INTRODUCTION

For the successful fabrication of viable high strength filament reinforced metal matrix composites required for high temperature application, the necessity of overcoming or reducing the filament - matrix interaction during their fabrication and service is now well recognized. Except for the few cases in which this interaction can be minimized by modifying the composition of the matrix (for example, the tungsten filament - tungsten rich nickel[1] and cobalt base alloy[2] composites) the filament has to be protected by means of a thermo-mechanically and chemically compatible coating. During the last fifteen years[3-17*] to develop new high temperature metal matrix composite systems, the compatibility of a number of coating materials for such filaments as tungsten, graphite, boron, silicon carbide, alumina, etc., against a variety of metal matrices has been investigated. For the application of these coatings techniques such as sputtering, chemical vapor deposition, and electroplating have been used. In some cases the effect of these coatings on the room temperature strength of the filament has also been reported. Coatings which interacted with the filament or were thick have been generally found to decrease the mechanical strength, while inert, relatively ductile and thin coatings have been

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[1] Petrasek, D. W. and Signorelli, R. A., "Preliminary Evaluation of W Alloy Fiber - Nickel Base Alloy Composites for Turbojet Engine Application," NASA TN D-5575 1970.

[2] Ahmad, et al, "Metal Matrix Composites for High Temperature Application," Watervliet Arsenal Technical Report 7155, 1971.

[*3-17] See List of References or page

reported to be usually harmless and, in some cases, to have improved[27] the strength of the substrate filament. For example, commercially available "borsic" which is essentially a boron filament with a flash of silicon carbide has about the same strength as the boron filament. Under the conditions reported in reference 3 surface nitriding slightly degraded the boron filament, but it reduced its interaction with nickel. However, according the recent reports[25] the filament strength is not affected by nitriding. Aggour[14] reported no degradation of graphite filament by TiN coatings, although with TiC coating a decrease in strength was noted. More recently Warren and Carlsson[15] found no relationship between the coating thickness or deposition time and the strength of the filament tested after the removal of the TiC coating. The strength of the coated filament, however, fell drastically with an increase in the coating thickness.

Recently AVCO (Mass.) has developed a silicon carbide filament with carbon core which has excellent stress-rupture properties in the

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[3] Sutton, W. H., "Whisker Technology," Editor Albert P. Levitt, Wiley Interscience, NY, 1970, pp. 273-342.

[14] Aggour, et al, Carbon 12, (1974) 358.

[15] Warren, R., and Carlsson, M., "Protective TiC and TiN Coatings on Carbon Fibers in a Nickel Matrix," Proceedings of the Fourth International Conference on CVD, 1973, Electrochemical Soc., Princeton, NJ, p. 611, ibid, "TiC and TiN Coated Carbon Fibers," pp. 623-35.

[25] Debolt, H., AVCO (Private Communication).

[27] F. G. Douglas, E. L. Paradis and R. D. Vellis, "Application of Diffusion Barriers to Refractory Fibers of Tungsten, Columbium, Carbon and Aluminum Oxide," NASA Report CR134466, Sept. 1973.

1000-1200°C temperature range.[20] For example, as shown in Figure 2, at 1093°C (2000°F) its 100 hr 2000°F rupture strength is as high as 1.9 GN/M² (280 Ksi).[19] Its low density (3.7 in/cc) makes it superior to any commercially available high temperature filamentary reinforcement. Consequently, the authors have been involved in exploring the possibility of using this filament as a reinforcement for selected superalloys to develop composite materials for turbine blades for performance at 2000°F or higher. Since investment casting is the conventional process of turbine blade fabrication, it was considered advisable to make the composites by the liquid metal infiltration technique. However, silicon carbide reacts with nearly all metals and alloys at elevated temperatures making it necessary to apply protective coatings on this filament prior to infiltration. Compatibility studies made by the authors[2] showed that tungsten and tantalum carbide could provide protection against cobalt base Mar M322 (20-25%W) and Mar M302 alloys respectively; therefore, techniques to apply coatings of W and TaC on the filament were developed. These techniques involved chemical vapor deposition (CVD) of the respective phases from their halides. In this paper results of a study of the effect of these coatings on

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[2] Ahmad, et al, "Metal Matrix Composites for High Temperature Application," Watervliet Arsenal Technical Report 7155, 1971.

[19] Ahmad, et al, "Silicon Carbide Filaments as Reinforcements for High Temperature Superalloy Matrices," Proceedings of the International Conference on Composites, Geneva, 1975.

[20] Debolt, H. and Krukonis, V., "Improvement of Manufacturing Methods for the Production of Low Cost SiC Filaments," AVCO, AFML-TR-73-140 (1973).

some mechanical properties of the filament will be presented. The process for applying TaC coating has already been reported.[10] Details of the work on the CVD process for applying W coatings on the filament will be reported in a separate publication; in this paper the process will be only briefly described to identify parameters which affect the mechanical properties of the filament.

EXPERIMENTAL PROCEDURES

Filament: SiC(C) filament was supplied by AVCO, Lowell, MA. It has a diameter of 140 microns (5.6 mil), with suppliers' specified room temperature strength in the range 31-49 x 10^8 N/M^2 (450-700 Ksi). This filament is produced on a semi pilot plant scale by a CVD process whereby SiC is deposited on a 25.4 micron (1.0 mil) diameter carbon core which has a prior coat of a thin layer of pyrocarbon. At the exit end of the reactor the filament is given another thin coating of carbon exposing it to a mixture of propane and argon at about 1250°C. This coating apparently helps to protect the filament from surface damage during handling.[20] The exact nature of this coating is not known, though it has been suggested that it is a carbon rich silicon carbide phase, rather than pure carbon. Figure 1 shows a transverse view of a typical filament. The rings represent the thermal and gas composition

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[10] Heffernan, W. J., Ahmad, I., and Haskell, R. W., Proceedings of the Fourth International Conference on Chemical Vapor Deposition, Eds. Wakefield and John M. Blocher, Electro Chem Soc, Princeton, NY, 1973, p. 509.

[20] Debolt, H. and Krukonis, V., "Improvement of Manufacturing Methods for the Production of Low Cost SiC Filaments," AVCO, AFML-TR-73-140 (1973).

Fig. 1 Transverse section of a SiC(C) filament. (X1000)

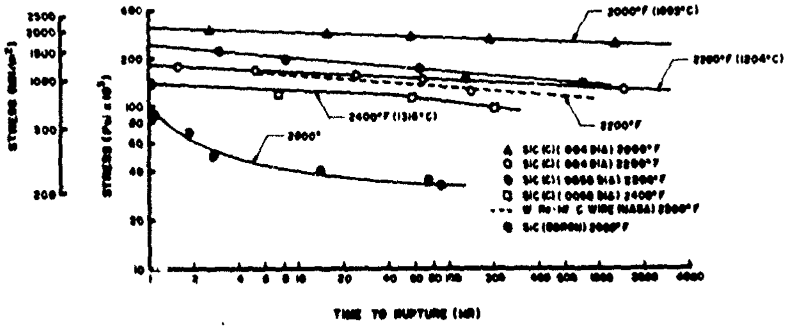

Fig. 2 Stress rupture data for SiC(C) filament in the temperature range 1093-1316 C.

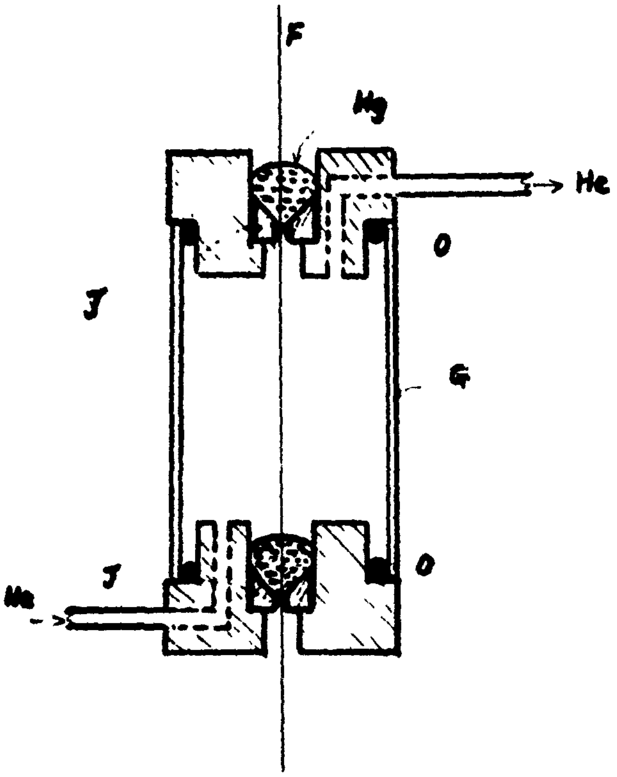

Fig. 3 Schematic of the inert gas envelop used during the measurements of high temperature tensile strength of the filaments: F-Filament, Hg-Mercury Seal, J-Sapphire Orifice, O-Ring, G-Pyrex tube.

fluctuation in the reactor. The process of manufacture of this filament has not as yet been optimized, therefore, the properties along its length could vary.

Because of its ready availability and low price SiC filament with tungsten core SiC(W), also produced by AVCO, was used in the initial studies. This filament has a diameter of 101 microns (4 mil) and an average tensile strength of 2.8 - 3.5 x 10^9 N/M^2 (400-500 Ksi).

Tensile Strength Measurement: The room temperature tensile strength of the filament was measured using a table model Instron Tensile Testing Machine. The diameter of the filament before and after coatings was measured with a microscope equipped with a Vicker's image splitting eyepiece. The specimen with gage length (distance between the grips) of 10 cm was tested at 0.5 cm/min strain rate. The grips were lined with 12.5 micron thick aluminum foil and were air operated. For elevated temperature strength measurements the filament specimen was heated resistively. The heated length was about 5 cm. As shown in Figure 3 inert atmosphere was provided by an arrangement which is a slight modification of the one reported earlier.[19] The electrical contacts to heat the filament resistivity were made through the mercury seals. The filament was aligned by means of a grid positioned accurately at the back side of the glass envelope. Temperature reading was made by a micro-optical pyrometer. Total time of each test after the power to heat the specimen was turned on was approximately two minutes.

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[19] Ahmad, I., et al, "Silicon Carbide Filaments as Reinforcements for High Temperature Superalloy Matrices," Proceedings of the International Conference on Composites, Geneva, 1975.

Elastic Modulus: The elastic modulus of the coated filament was measured by using the vibrating reed technique;[21] the specimen length-to-diameter ratio was found to be in excess of 5000.

Stress Rupture Tests: The apparatus used to measure the rupture life of the filament is described in reference 19.

Thermal Shock Resistance: The apparatus shown in Figure 3 was used to measure thermal shock resistance, however, the filament was not gripped; it was held in place by the surface tension of the mercury in the mercury seals.

Examination of the Coating: Both a high power optical microscope (Leitz) and a scanning electron microscope (Etec) were used to examine the transverse sections of the coatings, interfaces, and the filament and the coated surface after various treatments. The stoichiometry of tantalum carbide was determined from the lattice parameters measured by the standard x-ray diffraction technique using a Debye Sherrer Camera.

CVD Coating Parameters: Tungsten was applied by reacting WF_6 and H_2 on the surface of the filament in a stainless steel tube reactor which was heated externally by means of a continuously moving furnace (Figure 4). The rate at which the furnace was moved was adjusted to eliminate clogging of the reactor during long period runs. The filament

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[19] Ahmad, I., et al, "Silicon Carbide Filaments as Reinforcements for High Temperature Superalloy Matrices," Proceedings of the International Conference on Composites, Geneva, 1975.

[21] Cummarow, R. L., and McDonald, B. P., Journal of Materials JMLSA 7, pp. 286-293 (1972).

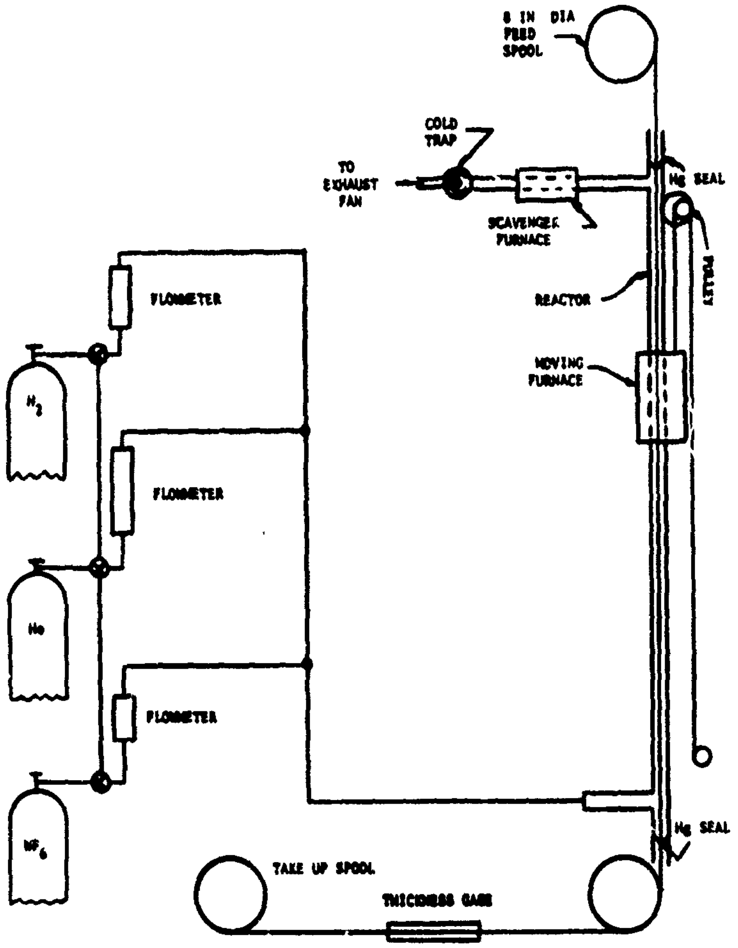

Fig. 4 A sketch showing the CVD set up for coating SiC filaments with tungsten.

passed continuously through the reactor and after receiving the coating was collected on a take up spool. The parameters which were varied included the temperature of the furnace, the filament, and the H_2:WF_6 molar ratio. The flow of He gas was kept constant at 300 cc/min.

The process for the application of TaC has, in principle, already been reported.[10] It essentially consists of reacting $TaCl_{5,(g)}$ H_2, and CH_4 on the resistively heated SiC(C) filament which is continuously passed through a quartz reactor equipped at both ends with water-cooled mercury seals. The quartz reactor is described in reference 10. The stoichiometry of TaC was controlled by the temperature of deposition and molar ratios of the reactants. The thickness of the coating could be varied by adjusting the filament speed.

RESULTS

As previously stated, the process parameters for the manufacture of SiC(C) filament have not yet been optimized by the supplier for uniform quality and the tensile strength of the filament shows some variation along its length. For example, as shown in Figure 6 of reference 19, the scatter of the room temperature tensile strength of this filament is almost 25% (475 ± 105 Ksi). Similar scatter of values was observed in the tensile strength of the coated filament. Hence, the data reported here represent essentially trends and not absolute

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[10] Heffernan, W. J., Ahmad, I., and Haskell, R. W., Proceedings of the Fourth International Conference on Chemical Vapor Deposition, Eds. Wakefield and John M. Blocher, Electro Chem Soc, Princeton, NY, 1973, p. 509.

[19] Ahmad, I., et al, "Silicon Carbide Filaments as Reinforcements for High Temperature Superalloy Matrices," Proceedings of the International Conference on Composites, Geneva, 1975.

property values. No attempt was made to statistically analyze the data. For each data point shown in the graphs, at least five, and usually ten measurements were made with the values reported being the arithmatic mean of each set of data. In general, the standard deviation from the mean fell between 5-25%.

Tungsten Coating:

Effect of the Deposition Parameters: In the initial coating runs a cheaper SiC filament with W core was used. In the process the WF_6 + H_2 + He mexture was introduced counter currently to the filament direction. With a molar ratio of 25:1 (H_2:WF_6) and filament speed of 800 ft/hour, a coating thickness of 5 microns (0.2 mil) was obtained at 850°C. Filament strength calculated on the basis of uncoated filament diameter (i.e., assuming that the coating did not contribute to the strength) was in the range of 350-450 Ksi. In these experiments, however, the filament was flexible and considered acceptable. At the end of the run the reactor tube always contained a dark powdery residue which, on x-ray diffraction analysis, was found to be W_3O, indicating the presence of oxygen in the system. Furthermore, the fracture surface of coated filament showed some porosity in the coating and at the fil-coating interface (Figure 5). Therefore, the system was checked extensively and the leaks were eliminated as far as possible. In subsequent runs ultra pure hydrogen (which gave solid oxide-free coating), was used, however, the coating appeared to be poorly bonded (Figure 6). To improve the adhesion of the coating to the filament, the flow of the reactant gas mixture was reversed and introduced on

Fig 5. A porous tungsten coating on SiC(W) filament applied at 850°C and 800 ft/hr filament speed (X2600). Reactants flow counter current to the filament movement.

Fig. 6 A dense W coating obtained under similar conditions but using ultra pure hydrogen (X4400).

the same side as the filament entrance in the reactor. In addition, SiC(C) filament with better high temperature stability than SiC(W) was used. Under these conditions the coating was solid columnar and was apparently well bonded with the filament (Figure 7). Surprisingly, however, the filament became very brittle. The tensile strength of the filament with a 6 micron (0.24 mil) thick coating dropped from 450 Ksi to 166 Ksi. Even a flash of coating (.005 mil) made the filament brittle.

To determine if the strength deterioration of the filament was due to some interface effect, the coating was dissolved away in Murakamis' reagent (equal parts of aq. 10% NaOH and aq. 30% potassium ferricyanide solutions). The filament completely regained its strength and flexibility thus indicating that the brittleness of the filament was probably the result of stresses at the interface due to the tight columnar growth. For confirmation the direction of the reactant gases was reversed during another run, i.e., they were introduced counter current to the filament. The run conditions and the tensile strength values are summarized in Table I. The filament was, in general, as flexible as the uncoated filament, the strength of the coated filament was also improved. In another series of runs the temperature of deposition and filament speed were optimized to achieve maximum strength in the coated filament. Some of the pertinent data are summarized in Table II and shown in Figure 8. Fracture surfaces of the filaments having high strength, such as those coated at 700-850°C, showed progressively weaker bond. Above 850°C the coating readily debonded

TABLE I: CONDITIONS OF W COATING AND TENSILE STRENGTH OF COATED SiC(C) FILAMENT; SPEED 4550 CM (150 FT) PER HOUR

No.	H_2:WF_6	Temp °C	Gas Flow Direction	Coating Thickness Micron (in)	Mean Tensile Strength $10^9 N/M^2$	Mean Tensile Strength (KSI)	*** SD%
1	10	700	*	6.3 (.00025)	0.779	(113)	27.9
2	25	700	**	10.0 (.00040)	1.883	(273)	19.0
3	25	700	**	10.0 (.00040)	1.662	(241)	14.4
4	35	700	**	12.7 (.00050)	1.517	(220)	16.5
	Uncoated Filament					(537)	20 0

*Same direction as the filament movement.
**Counter to the filament movement.
***Standard deviation from the mean.

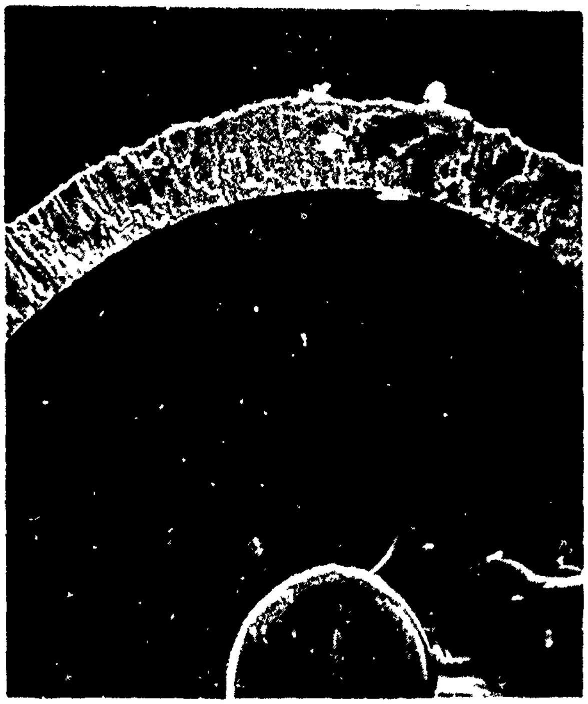

Fig. 7 An adherent coating applied with reactant gas mixture flow in the same direction as the filament (X1000).

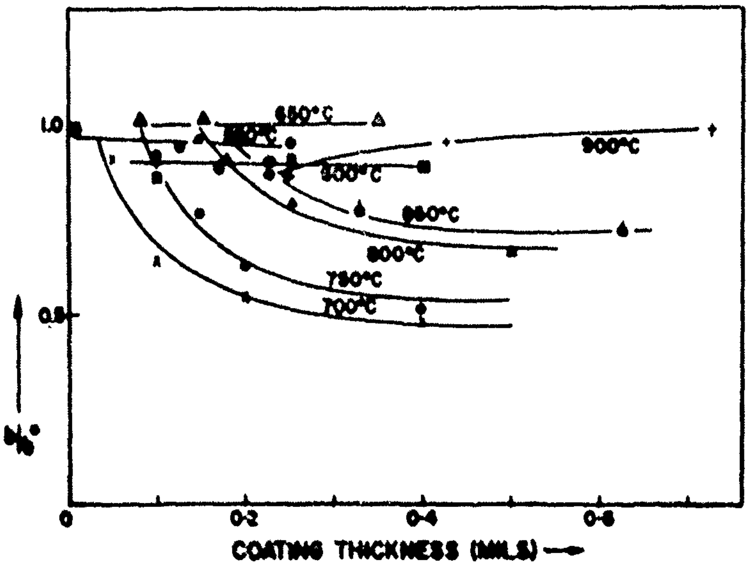

Fig. 8 Normalized tensile strength of SiC(C) filament as a function of W coating thickness showing effect of various temperatures.

when the filament was broken between the fingers (Figure 9a). Figure 9(b) shows the fracture surface of a filament coated at 550°C. Tensile strength measurements made on these filaments after dissolving the coating in the Murakamis Reagent are included in Table II.

Effect of Temperature on the Tensile Properties: The average tensile strength values of tungsten coated silicon carbide filament measured in the temperature range of R.T. - 1600°C are given in Table III. The extent of strength degradation of coated as compared with the uncoated filament is shown in Figure 10 in which the normalized UTS $(\frac{\sigma}{\sigma_0})$ is plotted against temperature. It is apparent that the difference between the average strength of the coated (σ) and uncoated (σ_0) filament decreased with the increase of temperature.

The 1093°C (2000°F) stress rupture values for the filament coated with 12.5 microns (0.5 mil) thick tungsten at 700°C are summarized in Table IV and are shown in Figure 11. Data for the filament to which the coating was applied by passing the reactant gas mixture in the same direction as the filament are also included.

The elastic modulii of the filaments coated at 650°, 700°, and 800°C are summarized in Table V.

Thermal Shock Resistance: As stated earlier, the purpose of applying coatings to the filament was to incorporate it in superalloys by an investment casting process in which the melt temperature could be as high as 1500°C. To ascertain that during this process the coating did not fracture or crack because of thermal shock, the coated filaments were cycled three times from R.T. to 1600°C. After this exposure,

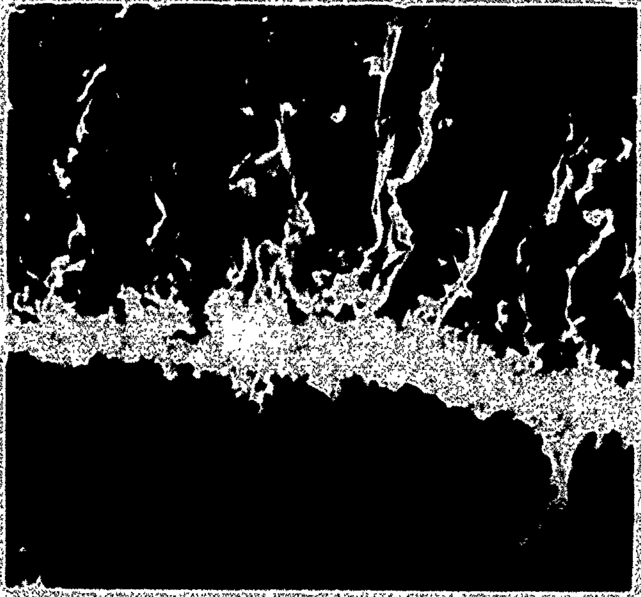

Fig. 9(A) Fracture surface of a filament coated at 800°C, showing interface porosity and poor coating-filament bond (X5600).

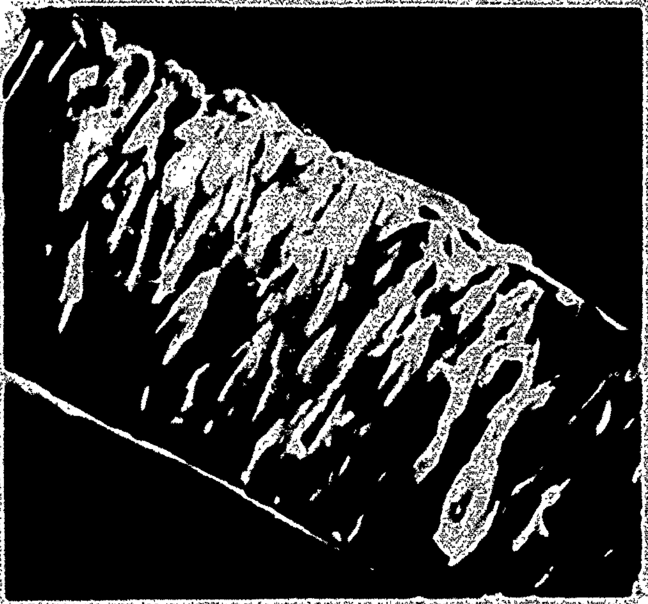

Fig. 9(B) Fracture surface of a filament coated at 550°C showing well adherent coating with dense interface (X5600).

TABLE II: TENSILE STRENGTH (ROOM TEMPERATURE) OF FILAMENT COATED UNDER VARIOUS CONDITIONS OF TEMPERATURE AND FILAMENT SPEED

Run No.	Spool No.	Mean UTS $10^9 N/M^2$ $10^9 lbin^{-2}$	SD%	Deposition Temp °C	Fil Speed Ft/Hr	Coating Thickness x 10^{-3} in	Mean UTS $10^9 N/M^2$ $10^3 lbin^{-2}$	SD%	$\frac{\sigma}{\sigma_o}$
R-16	1S89	3.517 (510)	13.1	550	75	0.25	3.331 (483)	20.6	0.947
					200	0.125	3.311 (480)	23.2	0.941
					400	0.005	3.442 (493)	13.5	0.967
R-17	1S89	3.517 (510)	13.1	600	75	0.4	3.097 (449)	12.2	0.881
					200*	0.25	3.179 (461)	12.0	0.904
					400	0.10	3.000 (435)	21.7	0.853
R-18	1S89	3.517 (510)	13.1	650	200**	0.35	3.621 (525)	15.5	1.03
					400	0.15	3.338 (484)	19.0	0.949
					600	0.08	3.552 (515)	12.2	1.01
R-9	1S85	4.938 (716)	6.9	700	200	0.40	2.345 (340)	4.5	0.475
					400	0.20	2.089 (397)	11.7	0.545
					600	0.10	3.062 (444)	6.7	0.640
					800	.05	4.469 (693)	8.3	.968

TABLE II: TENSILE STRENGTH (ROOM TEMPERATURE) OF FILAMENT COATED UNDER VARIOUS CONDITIONS OF TEMPERATURE AND FILAMENT SPEED (CONT'D)

Run No.	Spool No.	Mean UTS 10^9N/M^2 10^9lbin^{-2}	SD%	Deposition Temp °C	Fil Speed Ft/Hr	Coating Thickness x 10^{-3} in	Mean UTS 10^9N/M^2 10^3lbin^{-2}	SD%	$\frac{\sigma}{\sigma_o}$
R-13	1S75	5.304 (769)	7.0	750	200	0.40	2.704 (392)	9.1	0.509
					400	0.20	3.317 (481)	8.8	0.625
					600	0.15	4.069 (590)	7.9	0.767
					800	0.10	4.062 (705)	8.2	0.917
R-10	1S85	4.938 (716)	6.9	800	200	0.50	3.29 (477)	12.3	0.666
					400	0.25	3.931 (570)	16.8	0.796
					600	0.18	4.456 (646)	15.0	0.902
						0.15	4.98 (722)	3.0	1.009
R-15	1S89	3.517 (510)	13.1	800	200	0.50	3.491 (507)	12.0	0.993
R-14	1S89	3.517 (510)	13.1	850	200	0.62	2.504 (363)	10.7	0.712
					400	0.32	2.69 (390)	9.0	0.765
					600	0.22	3.035 (440)	17.2	0.863
					800	0.17	3.069 (445)	8.6	0.872

TABLE II: TENSILE STRENGTH (ROOM TEMPERATURE) OF FILAMENT COATED UNDER VARIOUS CONDITIONS OF TEMPERATURE AND FILAMENT SPEED (CONT'D)

Run No.	Spool No.	Mean UTS $10^9 N/M^2$ $10^9 lbin^{-2}$	SD%	Deposition Temp °C	Fil Speed Ft/Hr	Coating Thickness $x\ 10^{-3}$ in	Mean UTS $10^9 N/M^2$ $10^3 lbin^{-2}$	SD%	$\frac{\sigma}{\sigma_o}$
R-11***	1S75	5.304 (769)	7.0	900	200	0.72	5.228 (758)	4.7	0.985
					400	0.42	5.014 (727)	9.7	0.945
					600	0.25	4.518 (655)	10.9	0.851
					800	0.22	4.738 (687)	6.9	0.893
					200****	-	4.904 (711)	18.0	0.925

*Average tensile strength of five filaments after dissolving the coating in Murakamis' reagant was 501 KSI.
**Average tensile strength of the filament after dissolving the coating was 539 KSI.
***In general in these runs, the coating bonded very poorly.
****The gas mixture was only H_2 + He without WF_6. Therefore, there was no coating.
SD = Standard deviation from the mean.

TABLE III: HIGH TEMPERATURE TENSILE STRENGTH OF THE TUNGSTEN* COATED AND UNCOATED FILAMENT

	**UTS (Coated)		UTS (Uncoated)		
Temperature °C	$10^9 N/M^2$	(KSI)	$10^9 N/M^2$	(KSI)	$\frac{\sigma}{\sigma_0}$
R.T.	1.835	(266)	2.828	(410)	0.649
800	1.648	(239)	2.359	(342)	0.699
1000	1.531	(222)	2.083	(302)	0.735
1200	1.414	(205)	1.883	(273)	0.751
1400	1.083	(157)	1.359	(197)	0.797
1600	.055	(124)	1.062	(154)	0.805

*Coating thickness 12.7 microns (0.0005 in)
**Mean ultimate tensile strength

TABLE IV: STRESS RUPTURE DATA ON W COATED* SiC FILAMENT AT 1093°C (2000°F)

	Stress		
Gas Flow Direction	$10^9 N/M^2$	KSI	Time (Hrs)
Opposite			
	1.255	182	0.1
	1.117	162	6.1
	0.979	142	693.0
Same			
	0.897	130	0.1
	0.690	100	2.9
	0.552	80	12.9
	0.414	60	105.6

*Coating Thickness 12.7 Micron (0.0005 in)

TABLE V: DYNAMIC MODULUS OF TUNGSTEN COATED SiC(C) FIL

Temp of Deposition °C	Coating Thickness Micron	Young's Modulus $10^{11} N/M^2$ $10^6 lbin^{-2}$
650	5	39.6 (57.5)
700	11.2	41.0 (59.5)
800	9.7	41.3 (59.9)

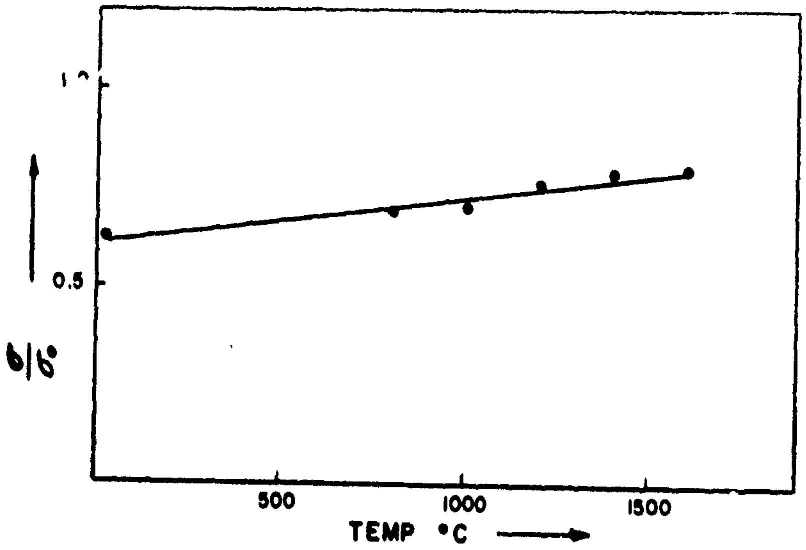

Fig. 10 Normalized tensile strength $\left(\frac{\text{tensile strength of coated filament}}{\text{tensile strength of uncoated filament}}\right)$ of the coated filament as a function of coating thickness.

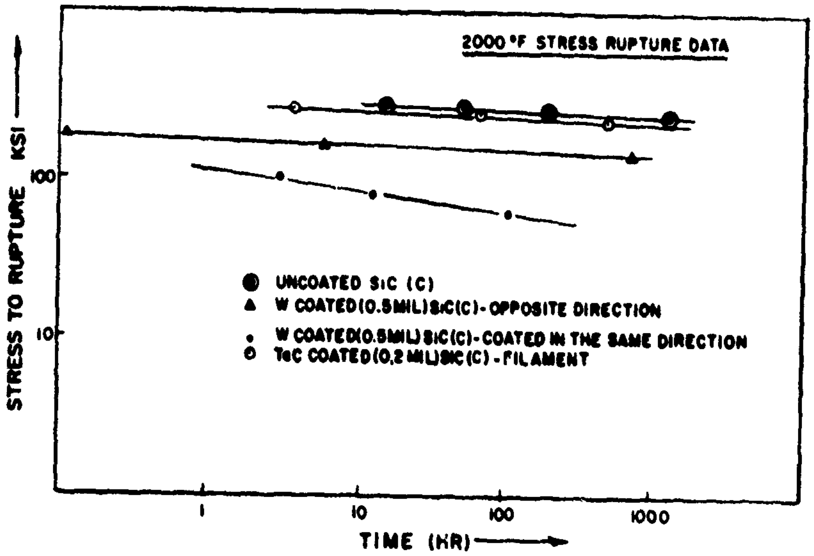

Fig. 11 Stress rupture data of W and TaC coated SiC(C) filament at 1093°C (2000°F).

the coating remained intact and unchanged. The room temperature tensile strength of the coated filament decreased by about 15%, however, cycling at 1500°C did not affect its strength significantly.

TaC Coated SiC(C) Filament:

Tensile Strength: The room temperature tensile strength of tantalum carbide filament with a coating thickness of 5 microns (0.2 mil) did not show any deterioration. In fact, in some cases, the strength of the coated filament (calculated on the assumption that coating did not contribute) was higher than the uncoated filament. The coating was dense and, as shown in Figure 12, its grain size was quite small. The tensile strength values of the coated filament are summarized in Table VI which also includes information on the stoichiometry of TaC, which was calculated from the lattice parameter of the phase, determined by the x-ray diffraction technique. The decrease in strength at elevated temperatures on the coated and uncoated filaments is illustrated in Figure 13.

Stress Rupture Properties: The 1093°C (2000°F) stress rupture data of the TaC coated SiC(C) filament are given in Table VII and compared with the uncoated filament in Figure 11.

Thermal Shock: Tantalum carbide ($TaC_{0.76}$) coated tungsten (Fig. 14 (a), (b)) and SiC(C) filaments (Fig. 15) were thermally shocked at 1600°C. In the former, the coating occasionally developed blisters, folds, and cracks; on the SiC(C) filament the TaC coating showed folding.

A number of coated filaments were annealed at 1000°C for two hours in vacuum to relax stresses. In some of these (about 10%) radial

Fig. 12 Fracture surface of TaC coated SiC(C) filament (X5600).

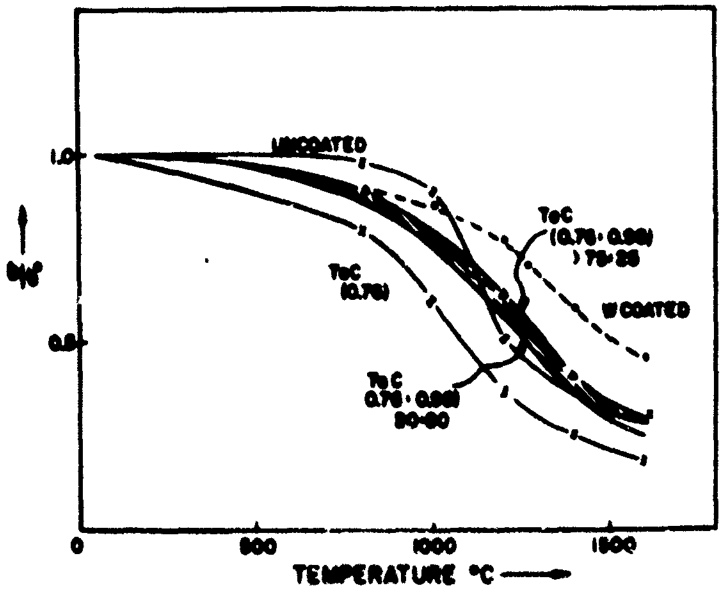

Fig. 13 Normalized tensile strength of TaC coated SiC(C) filament at various temperatures.

TABLE VI: TENSILE STRENGTH* OF TaC COATED SiC(C) FIL AT VARIOUS TEMPERATURES

Run No.	Phase	RT $10^9 N/M^2$ (KSI)	800°C $10^9 N/M^2$ (KSI)	1000°C $10^9 N/M^2$ (KSI)	1100°C $10^9 N/M^2$ (KSI)	1200°C $10^9 N/M^2$ (KSI)	1400°C $10^9 N/M^2$ (KSI)	1600°C $10^9 N/M^2$ (KSI)
Uncoated	SiC(C)	3.662 (531)	3.58 (519)	3.297 (478)	-	2.118 (307)	1.331 (193)	1.110 (161)
116	TaC (0.76)	4.945 (717)	3.959 (574)	3.303 (479)	-	1.814 (263)	1.29 (187)	0.966 (140)
117-4	TaC (0.98)	4.662 (676)	4.662 (676)	-	3.249 (471)	-	1.497 (217)	1.117 (170)
124-1	TaC :TaC (75:25) (0.76) (0.98)	4.330 (628)	3.952 (573)	3.759 (545)	-	2.679 (391)	1.759 (255)	1.317 (191)
124-2	TaC :TaC (60:40) (0.76) (0.98)	4.077 (591)	3.745 (543)	3.524 (511)	-	2.255 (327)	1.49 (216)	1.076 (156)
124-3	TaC :TaC (20:80) (0.76) (0.98)	3.483 (505)	3.18 (461)	2.759 (400)	-	2.021 (293)	1.283 (186)	1.069 (155)

*The standard deviation from the mean values of tensile strength, vary between 5-15%.

TABLE VII: STRESS-TO-RUPTURE OF TaC COATED SiC(C) FILAMENT AT 1093°C (2000°F)

Stress $10^9 N/M^2$	KSI	Time (Hrs)
1.896	275	3.8
1.724	250	67.6
1.586	230	240

Fig. 14 Termally shocked TaC coated tungsten filament showing a blister (a) and crack (b).

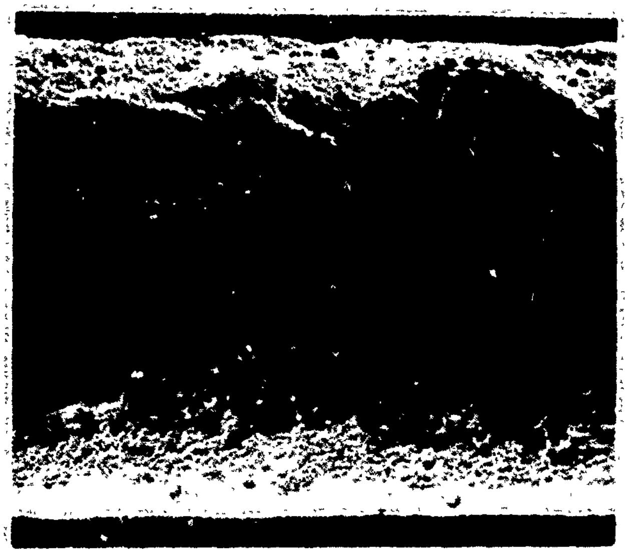

Fig. 15 Termally shocked TaC coated SiC(C) filament showing folding of the coating.

cracks appeared; the rest were unaffected. The crack free filaments when cycled three times between room temperature and 1600°C did not show further cracking or folding.

DISCUSSION

The embrittlement and weakening of the filament in the initial runs of deposition of W appear to be due to two major factors: stress effects due to chemical interactions at W-SiC interface, and the columnar grains of the coating.

As stated earlier, the surface of this filament is carbon rich silicon carbide phase. Very little information is available in the literature on the interaction of WF_6, H_2, C, or carbon rich silicon carbide in the temperature range of interest, i.e., 600-900°C. Burykina[26] identified the formation of WC and W_5Si_3 when SiC powder in contact with W was heated to 1500°C. Randon et al[24] and later Ahmad et al[19] reported formation of an interaction zone at the tungsten core-SiC interface when the silicon carbide filament with tungsten core was exposed to temperatures in the 900-1400°C range. Conceivably, the following reactions can take place at the surface of the filament.

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[19] Ahmad, I., et al, "Silicon Carbide Filaments as Reinforcements for High Temperature Superalloy Matrices," Proceedings of the International Conference on Composites, Geneva, 1975.

[24] Randon, J. L., Salama, G., and Vignes, A., "Silicon Carbide Fibers With Improved Mechanical Properties: Study of Thermal Stability," Proceedings of the Third International Conference on Silicon Carbide, 1973, Ed. Marshall, R. C., et al, University of South Carolina Press, Columbia, South Carolina, p. 386.

[26] Burykina, A. L., Strachinskaia, L. V., and Evtuchok, T. M., Fiziko Chimicheskaia Mechanica Materialov <u>4</u>, 3, 301 (1968).

$$WF_6 + 3H_2 \rightarrow W_{(s)} + 6HF_{(g)} \tag{1}$$

$$WF_6 + 3H_2 + C \rightarrow WC_{(s)} + 6HF_{(g)} \tag{2}$$

$$WF_6 + 3H_2 + 1/2\ C \rightarrow W_2C_{(s)} + 6HF_{(g)} \tag{3}$$

$$11WF_6 + 33H_2 + 3SiC \rightarrow W_5Si_3 + 3W_2C + 66HF_{(g)} \tag{4}$$

$$4HF_{(g)} + SiC \rightarrow SiF_{4(g)} + C + 2H_2 \tag{5}$$

$$3HF_{(g)} + SiC \rightarrow SiHF_{3(g)} + 1\text{-}1/2\ H_2 + C \tag{6}$$

Values of the free energy of formation of all the compounds except W_5Si_3 are available in references 28-30. The heats of formation ($\Delta H°298$) of WSi_2 and W_5Si_3 have been estimated by Brewer and Krikorian[29] to be -26 ± 5 and -63 K cal per mole. Elliott and Gleisen[30] estimate the best values for WSi_2 and W_5Si_3 to be -22.3 ± 4 and -13 to -60 K cal respectively. No data on the entropy are available. The entropy of formation of these compounds because of the large atomic mass of W is expected to be high and to contribute to making free energy of formation of these compounds at high temperatures more negative. Even if this contribution is small, the free energy of the reactions (2) - (4) favor the forward reaction. Figure 16 summarizes the free energy of the reactions (1) to (6) as a function of temperature; it shows that at the temperatures involved in this study, there is a finite possibility of the formation of WC, W_2C and W_5Si_3. This product layer could have microcracks because the presence of growth and thermal stress and could

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[28] Stull, R., et al, JANAF Thermochemical Tables, 1965, PB 168 370, U.S. Dept. of Commerce, Washington, D.C.

[29] Brewer, L., and Kriskorian, O., J. Electrochem Soc., 103 1, 38 (1956).

[30] Elliott, J. F. and Gleisen, Thermochemistry for Steel Making, Vol. 1, p. 233, Addison Wesley Publishing Co., Reading, MA, 1960.

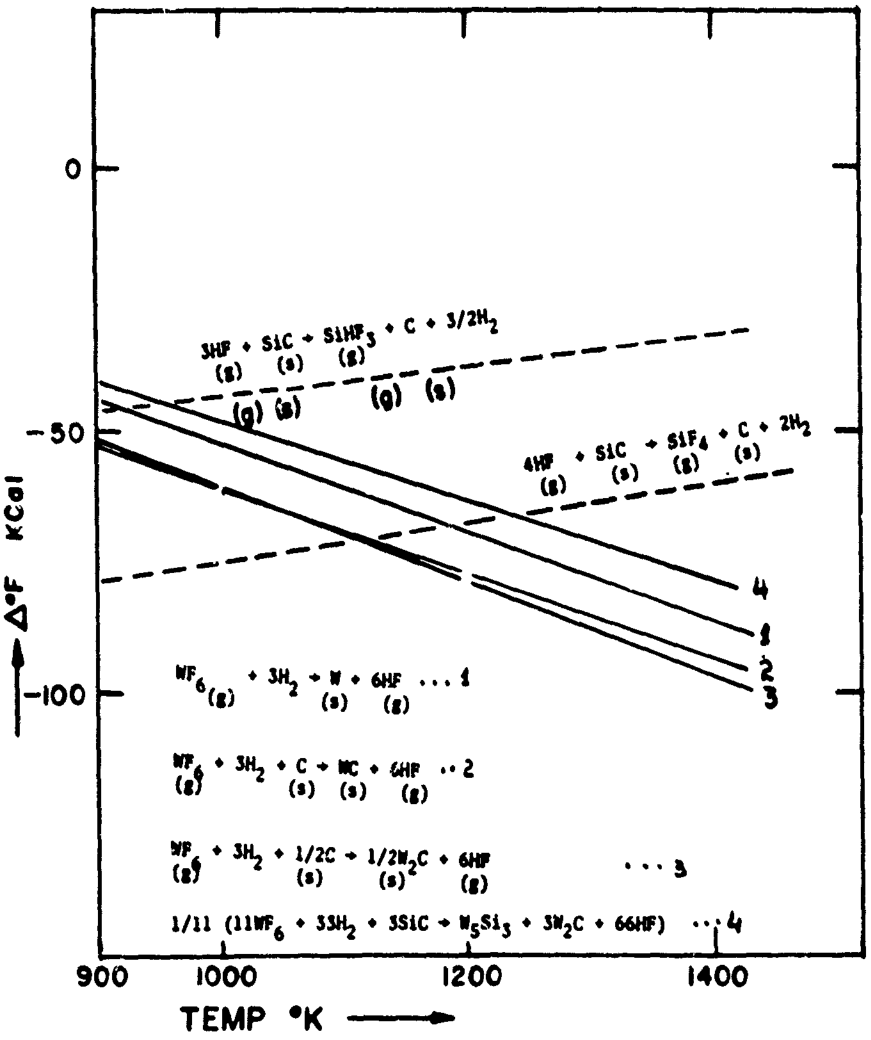

Fig. 16 Free energy of a number of possible reactions of gaseous reaction products with the filament surface as a function of temperature.

embrittle the filament.[24] However, when the gas flow is reversed the filament surface first comes in contact with the products of reaction (1) which contain high concentration of HF, making it possible for both SiF_4 and SiF_3 to form. The surface is thus partially masked with relatively stable flourides of Si reducing the nucleation of tungsten in the WF_6 rich deposition region and, hence, reducing the areas of interaction of tungsten with the substrate surface. The mechanism is schematically illustrated in Figure 17.

The combined effect of these two factors, i.e., chemical interaction and the relative area of coating-filament interface (which is determined by the number of the initial tungsten nuclei on the surface) is schematically illustrated in Figure 18. Values of $\frac{\sigma}{\sigma_0}$ taken from Figure 8 for 10 micron (0.4 mil) thick coating are indicated by small circles. It shows a minimum at 700°C, and then an increase with temperature. However, as has been mentioned earlier, at higher deposition temperatures and filament speed the filament-coating bond becomes weaker, and the coating has a tendency to flake off. In the 550-650°C temperature range the strength of the filament is not effected. After etching off the coating the filament showed original strength. At this temperature apparently there is no chemical interaction, and the bond is purely mechanical. Also, the degradation effective due to

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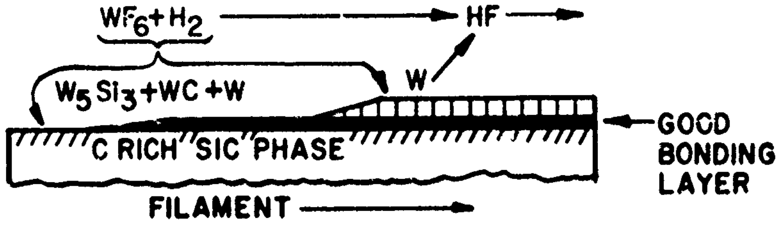
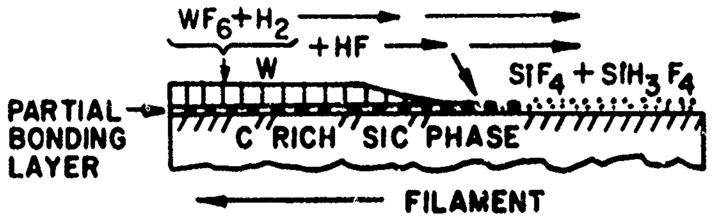
[24] Randon, J. L., Salma, G., and Vignes, A., "Silicon Carbide Fibers With Improved Mechanical Properties: Study of Thermal Stability," Proceedings of the Third International Conference on Silicon Carbide, 1973, Ed. Marshall, R. C., et al, University of South Carolina Press, Columbia, South Carolina, p. 386.



(a) EMBRITTLED PRODUCT



(b) GOOD, FLEXIBLE AND STRONG PRODUCT

Fig. 17 Schematic illustration of suggested mechanism by which the filament is embrittled.

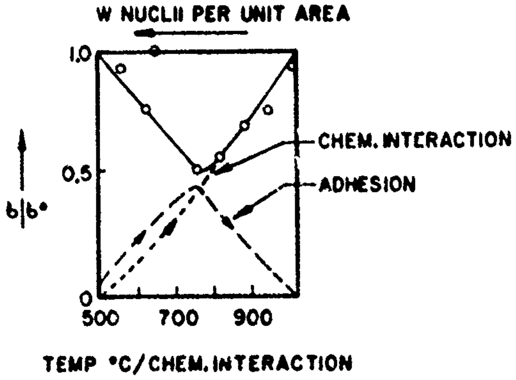


Fig. 18 Schematic illustration of the combined effect of the chemical interaction at the interface and the number of W nuclei per unit area.

the columnar grain structure appears to be small. From these results, 650°C appears to be a good coating temperature. However, the rate of deposition is low. For a more reasonable rate (to obtain large quantity of coated filament) higher coating temperature has to be used, but that will be at the expense of the strength. A careful analysis for the trade offs for maximum payoff is therefore necessary. For example, for our composite fabrication studies, we found 750-800°C at 200 ft/hr to be optimum for obtaining 12 micron thick adherent coating with reasonably good filament strength ($2.8 - 3.5 \times 10^9$ N/M^2).

It must be pointed out here that the data reported in Table II were obtained on more than one batch of the filament. Low temperature data were obtained mostly with IS 89 (UTS 510 Ksi) and IS 75 (UTS about 700 Ksi). It is possible that these filaments could have reacted differently to the coating conditions. Therefore, runs must be made using one single batch of the filament, for all temperatures. However, the data at 200 and 400 ft/hr shows that while IS 89 maintained its strength up to 650°C, it did degrade between 800-850°C. Also, data in Table I were obtained on a batch of filament which was similar to IS 89 (TS of 537) and it showed degradation at 700°C. Nevertheless, more work is necessary to confirm the interpretation given in the foregoing discussion.

Lack of degradation of the toom temperature tensile strength of the filament with TaC coating can also be explained in the light of the above discussion. There was no chemical interaction between TaC and SiC, and the grain size of the TaC coating was very small with no large columnar grains to act as stress risers. Unlike tungsten, the coating of TaC had intrinsic strength because of fine grain structure, and as mentioned in the results, in some runs the strength of the coated filament was higher than that of the uncoated one.

The high temperature strength of the SiC(C) filament was adversely affected by both the coatings, however, the degree of degradation of the W coated filament decreased with increasing temperature (Fig. 11). This decrease may be due to the higher ductility of tungsten coatings at higher temperatures. In the case of TaC coating, the filament retained its original strength up to about 800°C, but then it decreased. The coating with higher carbon content showed higher strength than that with the lower carbon content, perhaps due to the high intrinsic strength of the carbon rich phase. No data on the influence of stoichiometry on the tensile strength of TaC are reported in the literature. Interestingly enough, the tungsten coated filament demonstrated a strength higher than tantalum carbide coated filaments in the temperature range of 1000 - 1600°C. Again, this increased strength may be due to the improved ductility of W.

The stress rupture data illustrated in Figure 11 show the superiority of TaC over W coated filament. Under conditions of extended exposure of the filament to higher temperatures, the tungsten coating probably interacts chemically with SiC. The extent of interaction of W with SiC at 2000°F has been reported by Ahmad et al.[19] The superior

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[19] Ahmad, I., et al, "Silicon Carbide Filaments as Reinforcements for High Temperature Superalloy Matrices," Proceedings of the International Conference on Composites, Geneva, 1975.

stress rupture values of the TaC coated as compared with the W coated filament are due to the lack of chemical interaction of TaC with SiC. In addition, the TaC coating, because of its fine grain size, probably has inherent high temperature strength.

During the thermal cycling of the coated filament, temperature excursion can induce residual stresses both at the interface and in the body of the coating. The stresses at the interface are due to the difference in the thermal expansion coefficient of the coating and the columnar grain orientation in the deposits. The magnitude of these stresses, in general, increases with the increasing thickness of the coating. The tungsten coating was superior to the TaC coating in this respect because its thermal expansion coefficient is closer to that of SiC (SiC 3.9×10^{-6}, W 4.4×10^{-6} cm/cm/°C) and because of its higher ductility at elevated temperatures. The thermal expansion coefficient of TaC is 5.5×10^{-6} cm/cm/°C. The thermal expansion coefficient of $Ta_{0.76}$, which was the coating for the filament cycled here, will probably be higher, thus enhancing the thermal mismatch between the filaments and the coating and, hence, causing the blistering and cracking effects. It is, however, expected that stoichiometric TaC coating will be more compatible. Annealing did help in relieving some of the deposition stresses at the interface and, thus, reduced the propensity of the cracking of the coating. Additional study is necessary to work out parameters to minimize the damaging stresses at the interface.

CONCLUSIONS

This study has shown that in the chemical vapor deposition process of coating tungsten on SiC(C) filament in the temperature range of interest, if the filament movement in the reactor was in the same direction as the reactant gases, the filament became very weak and brittle. To achieve a flexible and high strength product it was necessary to pass the filament counter current to the flow of the reactant gases. It is suggested that the probable chemical interaction of tungsten and its halide with the carbon rich silicon carbide surface combined with the stress risers provided by the columnar nature of the deposit, cause the embrittlement of the filament. In the counter current mode stable gaseous flourides of silicon formed as a result of the interaction of HF with silicon carbide partially mask the surface and reduce the number of tungsten nuclei or, in other words, reduce the surface area affected by the chemical interaction and stress risers. Because of similar effects the 2000°F stress-to-rupture of fine grained chemically inert TaC coated SiC(C) was found to be superior to that for the tungsten coated filament. However, the short period tensile strength of W coated filament, because of the relatively high ductility of W, was higher than that for TaC coated filament in the 1000 - 1600°C range.

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