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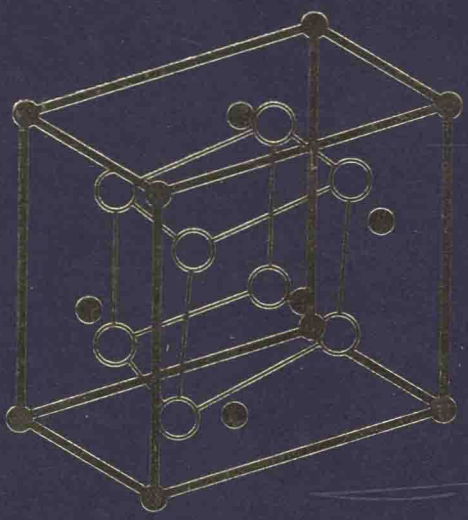

Science and Technology I

Edited by

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sponsored by the Surface Modification and
Coatings Technology Committee,
held at the Fall Meeting of
the Mineral, Metals & Materials Society
in Rosemont, Illinois, October 3-6, 1994

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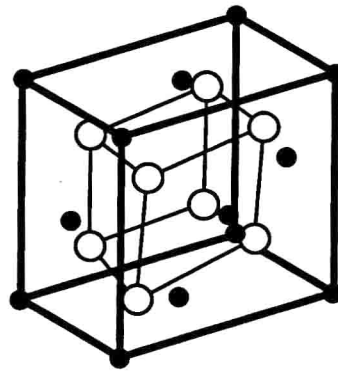

Science and Technology I

PREFACE

In the applications of advanced materials such as composites, intermetallics and ceramics, operating conditions are far extended beyond their traditional limits. Materials development has provided a wide range of cost effective and efficient applications for these materials. However, in order to make existing applications even more cost effective and efficient, various approaches to physically and chemically modifying the advanced materials have been adopted. One such approach is the placement of coatings on the materials which provide physical and chemical barrier without altering bulk materials properties. The usefulness of coatings to tailor advanced materials for required purposes has propelled an outburst of research activities in the last decade which continues to grow. In light of this, the present symposium on High Temperature Coatings-I was organized, in order to provide a forum for the exchange of information on high temperature coatings.

This volume consists of invited and contributed papers presented in the first symposium in the series, "High Temperature Coatings-I," held in Rosemont, Illinois on October 3-6, 1994. The symposium was sponsored by the newly formed Surface Modification and Coatings Technology Committee under the Materials Design and Manufacturing Division of TMS. The principal objective of this symposium was to provide a platform for state-of-the art aspects of high temperature coatings. A better understanding of the performance of high temperature coatings was promoted through the presentations on processing and characterization with regard to physical, chemical and engineering properties. The importance of high temperature coatings was emphasized from the perspective of materials rather than the processes used to synthesize them. Accordingly, specific materials topics covered were: ceramic, intermetallic, metallic and composite coatings. Papers on novel and innovative techniques of producing coatings were also included. In order to explore environmental issues, a full session was dedicated to "Removal of Coatings" in compliance with environmental requirements. The papers were presented by a broad group of researchers and scientists representing universities, federal laboratories and industries in USA and countries such as Canada, France, and Poland. All manuscripts were critiqued by one or more technical reviewers and an editor. We thank the reviewers for their time, diligence and promptness.

We wish to gratefully acknowledge all authors, presenters and participants. We also thank the session leaders for their assistance in coordinating and conducting the symposium. Our special thanks go to Dr. T.S. Sudarshan for his support, encouragement and willingness to share his experience. One of the organizers (NBD) would like to extend his gratitude to several people at the University of Tennessee Space Institute

including, Dean K.C. Reddy, for institutional support, Ms. Melissa Weatherford for secretarial support and colleagues, Vice President and Professor T. Dwayne McCay, and Professor Mary Helen McCay for their support during the organization of this symposium. We are grateful for the continuing assistance from TMS on the High Temperature Coatings symposia.

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ADVANCED SiC FIBER TOW VIA CVD

W. Jack Lackey

Georgia Institute of Technology, Atlanta, Georgia 30332

Abstract

Economical, high strength, thermally stable fiber tow is needed for reinforcement of ceramic and metal matrix composites. As an introduction, this paper reviews commercially available and developmental fibers. The feasibility of preparing a superior SiC fiber by the continuous chemical vapor deposition of SiC onto carbon fiber tows was experimentally evaluated.

Statistically designed and analyzed processing studies quantitatively showed the influence of key CVD process variables (temperature, pressure, and flow rates of CH_3SiCl_3 and H_2) on fiber attributes such as coating thickness and uniformity, surface roughness, percent agglomeration, and strength. Emphasis was given to conceiving and evaluating various fiber spreading devices in order to enhance coating uniformity and to minimize filament agglomeration within a tow. Uniform coatings and fiber tensile strengths in excess of 4 GPa were achieved. A cost analysis indicates that the process is very economical.

Introduction

Ceramic fiber-ceramic matrix composites offer potential for use as structural materials in high temperature oxidizing environments. However, three factors currently limit their application. First, an inexpensive, thermally stable fiber is not available. This point is made in Table 1; the fibers are either very expensive or are limited to processing and use temperatures of 1200°C, or lower if long exposure times are considered. Second, fiber coatings such as carbon and boron nitride which are used to tailor the fiber-matrix interfacial mechanical and chemical properties are not oxidation resistant. Finally, many processes for fabricating ceramic matrix composites tend to mechanically, thermally, or chemically degrade the fiber, and they are often time consuming and expensive. This paper addresses the first of these problems, the need for an inexpensive, high performance fiber.

Small diameter ceramic fibers are needed for use in ceramic and metal matrix composites in defense and industrial applications. Stoichiometric SiC is a useful candidate material because of its low density, high temperature strength, and resistance to oxidation and creep. By depositing a 5 μm layer of SiC onto a 5 μm diameter carbon fiber by chemical vapor deposition (CVD), the fiber properties become dominated by SiC since the composite

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fiber is 89% SiC. A stoichiometric CVD coating possesses high strength and low porosity along with chemical purity which is lacking in available fibers which are made by sol gel[1] or melt spinning[2] processes. By studying the coating of multifilament tows, small diameter fibers can be developed for potential use in ceramic and metal matrix composites. The small diameter fibers are favored over large diameter fibers; the size of large diameter filaments such as monofilament SiC fiber (150 μm diameter) renders them undesirable for reinforcement of ceramics.

Table I Cost and Strength of Available Ceramic Fibers

FIBER TYPE	PROCESS	CHEMISTRY	DIA. (μm)	PRICE ($/lb)	TENSILE STRENGTH (GPa)	APPROX MAX. USE TEMP(°C)
Nicalon	Polymer	SiC+C+O	12-15	300	2.0	1200
Dow Corning HPZ	Polymer	Si-N-C-O	10-12	5,000	2.6	--
3M Nextel 610	Sol-gel	Al_2O_3	10-12	1,500	1.9	1200
Textron	CVD	~Stoich. SiC	50-142	5,000	3.9	1400
Saphikon	Melt	Single Crystal Al_2O_3	125	24,000	2.0	1500

A large body of work has been completed for use in depositing coatings on both monofilament and fiber tows. Several fibers, including large diameter SiC[3,4] and B[5] monofilaments are fabricated using CVD techniques. Most of the fiber development work, however, has emphasized depositing thin layers (<0.1 μm) in order to modify the surface of the fiber. The prior work includes efforts to enhance fiber pull-out in a matrix structure[6,7] and to chemically tailor the interface of reinforcing fibers to enhance the bonding of the fiber/matrix.[8,9] This current work extends the deposition in order to nearly triple the fiber diameter, thereby essentially developing a new fiber. Current small diameter fibers, including Nicalon SiC fibers (12-15 μm diameter), have been shown to degrade at ~1200°C due to nonstoichiometry.[10] In addition, they are expensive, i.e., $300/lb.

The CVD of SiC has been extensively studied for both thin planer films as well as fiber coatings and matrix applications.[11-20] Prior experimental work determining the effects of different reagent gases, and deposition temperature and pressure has been completed for both hot and cold walled deposition systems.[11,12,14,16,18] Work by Brennefleck et al.[11] for coating of carbon fiber tows with SiC at atmospheric pressure using methyltrichlorosilane was completed in order to provide a protective layer for subsequent processing with the coated fibers. The room temperature filament tensile strengths were reported to decrease as the coating thickness was increased; the thicker coatings were about 1 μm thick. For coatings deposited with H_2 as a diluent, the tensile strength also decreased with increasing temperature up to the maximum value, 1100°C, investigated. It was hypothesized that hydrogen attack of the carbon substrate fiber contributed to the latter effect.

Experimental Procedure

The calculation of thermal and bending stresses which would be present in the coated fibers was completed by analyzing the differences in the coefficients of thermal expansion of CVD SiC versus that of several types of commercial carbon fiber tows considered for use as substrates. The calculation procedure has been described elsewhere[21,22] and generally involves considering the thermal stresses (ΔT = 1200 K) for the fiber/coating system as a function of the radial positions in the coating. Table 2 contains the material properties required for the stress calculations. Effects caused by some fibers having cross-sections that are not circular were not considered. A comparison of the two Amoco[a] carbon fibers, T-50 and T-300, was completed in order to analyze radial, tangential, and axial stresses which would develop upon cooling due to thermal expansion mismatch between SiC coatings and the fiber substrate.

Table II Physical and Mechanical Properties of Fibers and Coatings

	Thermal Expansion		Young's Modulus	Poisson Ratio	Fiber Radius
	Radial	Axial			
	(10^{-6} K^{-1})		(GPa)		(μm)
Fibers					
Carbon					
T-50	6.70	0.352	391	0.2	3.5
T-300	8.85	0.932	232	0.2	3.5
Coating					
SiC	5.5	5.5	428	0.2	

In order to determine the optimal conditions for depositing a thick (5 μm) SiC coating uniformly on individual filaments of a carbon fiber tow by CVD, temperature, reagent concentration, and H_2 flow rate were varied using a statistically designed and analyzed experiment involving 17 coating runs (Table 3). Processing-property relationships were determined using the STATGRAPHICS[b] statistical analysis program. The analyses consisted of linear and multiple regression using the least squares technique. The STATGRAPHICS program was also used to analyze coating results for ~ 100 additional deposition experiments where different types of fiber spreaders were evaluated.

Deposition experiments were performed on Amoco T-300 unsized carbon fibers (3000 filaments/tow) using a hot wall continuous fiber coating furnace previously described.[23] For all the experiments, methyltrichlorosilane (MTS = CH_3SiCl_3) was decomposed to SiC in an excess of H_2. Hydrogen was used to carry the MTS vapor into the furnace; H_2 was also added as a diluent to the reagent gas stream. Exhaust gases, including mainly HCl and H_2, were passed through a soda lime scrubber and then vented to the atmosphere.

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[a] Amoco Performance Products, Inc.
P.O. Box 849
Greenville, SC 29602

[b] Manugistics, Inc.
211 East Jefferson St.
Rockville, MD 20852-9950

Table III Operating Conditions and Fiber Attributes for the Statistical Processing Study for SiC Deposition

Run #	Temperature (°C)	H_2 Flow (sccm)	MTS Flow (sccm)	Pressure (kPa)	Tensile Strength average range (GPa)	Weight for 15.2cm fiber (g)	Coating Thickness (μm)	Fiber Agglomeration %
Uncoated fiber	-	-	-	-	3.6	0.0290	-	-
Handling Test*	roomT	0	0	101	$\overset{2.68}{1.91 \rightarrow 3.1}$	-	-	-
SC-18	1050	2000	281	20.0	$\overset{1.67}{0.82 \rightarrow 2.35}$	0.0336	<1	0
SC-19	1150	~2800	479	23.3	$\overset{1.33}{0.77 \rightarrow 2.35}$	0.0356	<1	0
SC-20	1250	1500	0	16.7	$\overset{1.95}{1.35 \rightarrow 2.36}$	-	-	-
SC-22	1250	2500	875	20.2	$\overset{1.04}{0.63 \rightarrow 2.02}$	0.062	4	30
SC-23	1400	2000	297	13.3	$\overset{1.35}{1.08 \rightarrow 2.07}$	0.073	5	90
SC-24	1150	2000	264	12.0	$\overset{1.62}{0.75 \rightarrow 2.51}$	0.033	<1	0
SC-26	1350	3000	1321	16.7	$\overset{5.68^{**}}{3.11 \rightarrow 8.52}$	0.093	2	90
SC-27	1350	900	1305	14.7	$\overset{3.62^{**}}{2.26 \rightarrow 3.82}$	0.132	7	90
SC-28	1350	2000	330	16.0	$\overset{2.22}{1.82 \rightarrow 2.61}$	0.047	2	50
SC-29	1250	2500	1206	18.7	$\overset{0.98}{0.52 \rightarrow 1.62}$	0.099	3	50
SC-30	1350	2800	297	21.3	$\overset{1.74}{1.35 \rightarrow 2.16}$	0.034	<1	0
SC-31	1150	2800	1190	23.3	$\overset{1.09}{0.44 \rightarrow 1.38}$	0.058	1.5	80
SC-32	1150	2000	1222	26.7	$\overset{1.59}{0.91 \rightarrow 2.67}$	0.040	<1	60
SC-33	1150	3500	574	26.7	$\overset{1.19}{0.41 \rightarrow 1.86}$	0.0337	<1	0
SC-34	1150	2000	145	10.0	$\overset{0.85}{0.62 \rightarrow 1.42}$	0.0354	<1	0
SC-35	1150	2000	1042	13.3	$\overset{0.58}{0.46 \rightarrow 0.73}$	0.0506	4	90
SC-36	1150	1500	236	13.3	$\overset{1.55}{1.04 \rightarrow 2.20}$	0.0320	<1	0

*Fiber pulled through room temperature coating furnace to evaluate potential strength degradation.

**Tensile samples had 2 cm gauge lengths.

The box statistical study was designed and completed to find the optimal conditions for SiC deposition. The temperature was varied from 1050 to 1400°C, H_2 flow rate was varied from 1.5 to 3.5 ℓ/min, and MTS flow rate was varied from 0.15 to 1.35 ℓ/min. The pressure inside the furnace and the fiber speed were kept constant at 13.3 kPa and 10 cm/min, respectively. During each experiment, a fiber vibration device was used which cyclically applied and released tension, at one second intervals, along the axis of the fiber tow in an attempt to spread the tow and to minimize agglomeration of the individual filaments within the tow.

Several other fiber spreading techniques were also experimentally evaluated. Gas jets and both stationary and moving rollers were used in conjunction with cyclic tension to spread the fiber tow to over twice the initial diameter. In addition, several spreaders that used "knife-edges" to split the tow into two or four segments were tested. Other novel nonmechanical spreading techniques were also evaluated. A pneumatic technique, which was designed by modifying the spreader presented by Kim and Gray,[24] utilized a "Venturi-like" reduction in pressure within a cylinder that surrounded the fiber tow. This apparatus was placed in the lower spool enclosure of the continuous fiber coater as were the previously described mechanical spreaders. A high flow rate of gas was used to force the filaments apart inside the cylinder as schematically shown in Figure 1. The operation principle involved using a vacuum pump to provide a high throughput of gas down restricted inlets (points A and B in the figure) and utilized the flow to force the filaments apart. For the study of fiber spreader types, the deposition temperature and fiber speed were held constant at 1250°C and 19 cm/min, respectively. The H_2 and MTS flow rates were typically about 2 and 0.9 ℓ/min but were deliberately varied over the ranges 0.2 to 8 ℓ/min and 0.15 to 1.8 ℓ/min, respectively. The total reactor pressure was typically about 24 kPa but was varied to a low of 4 and a high of 30 kPa.

Another spreading technique utilized electromagnetic forces to spread and vibrate the fiber.[25] This work was completed in a smaller cold walled CVD system for a fixed length (15 to 30 cm) of fiber tow. The technique (Figure 2) involved passing an alternating electrical current of about 3 amperes through the fiber tow using either a 100 Watt frequency generator or a variac connected to a 110 volt, 60 Hz power outlet. Four 500 Gauss permanent horseshoe magnets were positioned along the outside of a fused silica reactor tube.

Hitachi S4100 and Cambridge 150 scanning electron microscopes were used to characterize the coated fibers at magnifications of 200 to 7000 X. Micrographs taken at 200 X were used to study the infiltration, uniformity, and agglomeration of filaments; the higher magnification was used to estimate the coating thickness, diameter, surface roughness, and to compare outer to inner fiber coating thickness for the tow. Fiber agglomeration refers to the percent of the filaments that were stuck to one or more adjacent filaments in the coated tow as determined by counting the number of stuck filaments and dividing by the total number of filaments viewed. The phase identification of the deposited material was determined using a Rigaku "Geiger flex" D/Max-B x-ray diffractometer, scanning from 5 to 75 degrees 2θ. Tensile specimens were made by extracting at least ten 6 cm length filaments from each coated tow. These single filaments were glued with M-bond 200 onto aluminum tabs. An Instron model 1331 tensile testing machine was used in conjunction with pneumatic grips to pull the samples to fracture at a rate of 0.038 cm/s.

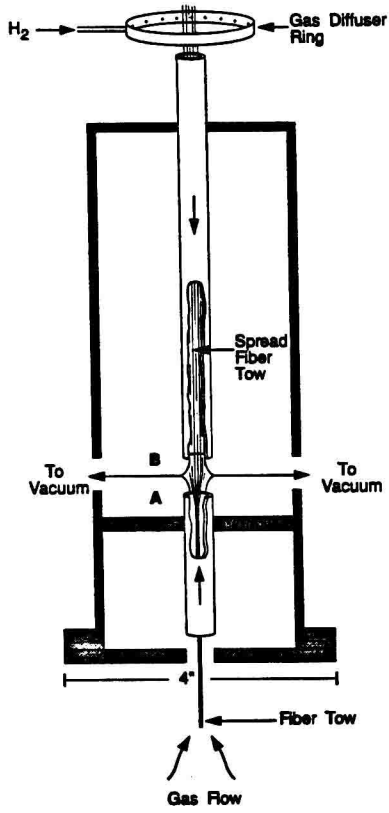

Figure 1. Schematic of the pneumatic device used to spread the fiber tow.

Results and Discussion

Stress Analysis

Calculations were performed to analyze the stresses which develop due to thermal expansion mismatch between SiC coatings and the T-50 and T-300 carbon fiber substrate.[22] Figure 3 compares the maximum stresses versus coating thickness for each fiber. It can be seen from Figure 3 that the axial stresses in the T-50 coating are greater than the corresponding stresses in coatings applied to the T-300 fiber for a range of coating thicknesses from 0 to 5 μm. The high axial stress for T-50 at the fiber/coating interface (2.5 GPa) was the highest tensile stress until the coating thickness exceeded 3.9 μm. As the coating thickness increased, the axial stresses decreased. For the target coating thickness of 5 μm, the stresses are appreciably smaller than the fracture strength (~2-4 GPa) of CVD SiC. It should be noted that cracked coatings were never observed experimentally, even when the coating thickness was 1 μm or less.