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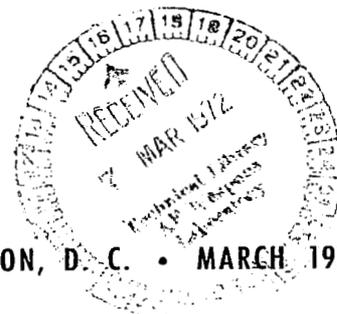
**IMPROVED OXIDATION-RESISTANT
CARBON AND GRAPHITE MATERIALS**

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for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1972





0061304

1. Report No. NASA CR-1970		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle IMPROVED OXIDATION-RESISTANT CARBON AND GRAPHITE MATERIALS				5. Report Date March 1972	
				6. Performing Organization Code	
7. Author(s) Hugh M. Muir				8. Performing Organization Report No. ARC-R-411	
9. Performing Organization Name and Address Astro Research Corporation Santa Barbara, California 93103				10. Work Unit No.	
				11. Contract or Grant No. NAS7-728	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered Contractor Final Report	
				14. Sponsoring Agency Code RWS	
15. Supplementary Notes					
16. Abstract Studies and experiments on silicon-carbide treated carbon and graphite fibers, tapes, felts, forms, and bulk materials for improved oxidation resistance and increased mechanical properties when used in composites. <i>1. Oxidation Resistance</i> <i>2. Carbon</i> <i>3. Graphite</i>					
17. Key Words (Suggested by Author(s)) Composite materials, carbon, graphite, oxidation resistant materials			18. Distribution Statement Unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 19	22. Price* \$3.00



SUMMARY

A variety of silicon-carbide treated carbon and graphite products have been prepared, and oxidation and strength properties determined. Carbon and graphite materials used in this preliminary study include fiber, tape, felt, foam, bulk, and laminar configurations. The silicon-carbide treatment used in preparing the oxidation resistant specimens employs either vacuum or ultrasonic impregnation of various silicone-silicon mixtures into the matrix material. The impregnation phase is followed by controlled thermal reaction at which time the silicon carbide is synthesized and takes the form of an integral protective boundary layer. Thickness of the layer ranges from a fraction of a mil to 10 mils, depending on the matrix material and processing parameters.

Oxidation resistance of all the silicon-carbide-treated specimens investigated to date has been found to be significantly improved. Mechanical strengths of the laminar composites were also found to be somewhat improved. At room temperature the specific strength of the silicon-carbide treated fibers and tapes was degraded to some extent; however, their relative strengths were significantly increased at elevated temperatures in oxidizing atmosphere.



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INTRODUCTION

For some time, silicon carbide has been utilized quite successfully to improve the oxidation resistance properties of various carbon and graphite products. Two types of oxidation-resistant carbon and graphite products are commercially available, namely, the inhibited and the chemical vapor-deposited (C.V.D.) grades. A wide range of oxidation resistance and mechanical properties exists in products prepared by the use of these two types of processing.

The inhibited grades are generally produced by the incorporation of elemental zirconium and boron, as well as silicon, into the carbon base during the premix stage. In the subsequent graphitization stage of the process, these elements are converted to the respective carbides. The end product is a molded, or extruded, dispersed carbide bulk form of graphite having significantly improved oxidation resistance over that of pure bulk graphite, especially at temperatures over 1500°C (Refs. 1 and 2). Union Carbide's JTA grade is representative of this type of process.

The C.V.D. silicon-carbide grade is produced by the thermal decomposition of a gaseous molecule containing carbon and silicon onto a heated graphite substrate. The end product is in the form of a graphite matrix having a very pure, dense coating of SiC. These bodies possess much better oxidation resistance than the inhibited form, especially at the lower temperature regions from 800°C to 1300°C. Excellent oxidation resistance is retained with the C.V.D. product (Ref. 3) up to the 1800°C range. A critical restriction exists, however, in the C.V.D. type process. A very close thermal expansion matching of the matrix material with that of the deposited SiC must be maintained; otherwise, excessive thermal cycling stresses can develop. Inherent in this type of process is a very discrete interface between the matrix and the SiC coating. Any fracture in this impervious coating due to expansion stresses during thermal cycling leads to catastrophic oxidation at the unprotected carbon-SiC interface and integrity of the entire coating layer is rapidly lost.

Severe processing limitations are evident in applying either the inhibiting or the C.V.D. process to improve carbon or graphite products such as foam, felts, tapes, cloths, or laminated

composites. It was felt that a need existed for additional process development to extend the oxidation resistance of various forms of graphite to a level as close as possible to that of the C.V.D. SiC, without the process or material restrictions inherent in both the inhibiting and the C.V.D. techniques.

Two silicon-carbide processes being investigated in this preliminary study have produced significant oxidation improvements in a wide variety of carbon and graphite configurations in the 1200°C range. The first process (Astro I) is characterized by the formation of a SiC boundary layer as an integral part of the matrix material. No addition to the original dimension of the component results in this processing phase. The second process (Astro II) is a combination of the integral SiC boundary layer developed in Astro I plus an overlay coating of SiC, utilizing silicone-silicon-carbon mixtures.

MATERIALS

The following carbon-graphite materials were investigated in this study.

Fibers

Carborundum Corporation	CY-5 carbon yarn
Carborundum Corporation	CY-2 20% SiC yarn
Hitco Co.	CY-2-1 carbon yarn
Union Carbide	VYB-70-1/2 carbon yarn

Tape

Union Carbide	WCB graphite tape
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Laminar Composites

Carborundum Corporation	Carbitex-700 graphite-graphite
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Foam

Union Carbide	Pyrofoam FPA-20 graphite
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Felt

Union Carbide	UCAR VDG carbon
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Bulk

Union Carbide	ATJ graphite
Poco Company	AXM graphite
Poco Company	AXZ graphite

SILICON-CARBIDE TREATMENT

Silicone-Silicon Impregnation Materials

A 99.9 percent, 325 mesh elemental silicon powder is reclassified using a liquid separation method to reduce the average particle size to a low micron range. This product is then mixed with a silicone fluid. A typical impregnating mixture employed for a tape or cloth configuration would be 10 percent silicon solids dispersed in a silicone fluid having 5 to 10 centistokes viscosity. The silicon solids content and silicone viscosity can be balanced to establish optimum impregnation parameters for the specific matrix materials or applications of interest.

Silicone-silicon-carbon mixtures employed in conjunction with Astro I treatment are also being investigated. These are being utilized in producing overlay silicon carbide coatings when greater thicknesses are desired.

Impregnation Phase

Two types of silicone-silicon impregnation processing are currently being used. For products such as yarn, cloth, felt, and foam (open, low-density configurations) an ultrasonic impregnation technique has been found to be quite effective. A typical yarn impregnation process consists of passing the yarn through an ultrasonically agitated bath consisting of a silicone-silicon mixture which has a 1-10 percent content of silicon solids. Through-put rates are adjusted to established the desired reactant pick-up levels on the specific yarn of interest. No further treatment of the yarn is required prior to the SiC thermal reaction cycle.

For materials of higher density, a vacuum impregnation process has been determined to be effective. A typical process for a laminar composite type material consists of preheating the material to about 500°C and impregnation at a partial pressure of 30 in. Hg. The silicone-silicon mixture is adjusted to a specific viscosity-solids content dependent, again, on the degree and characteristic of SiC protective treatment desired. The parts are drip drained after the vacuum impregnation phase and are then ready for the thermal reaction procedure.

Thermal Reaction Cycles

The silicone-silicon thermal reaction can be looked upon as a combination of a pseudomorphic chemical vapor deposition, followed by a liquid silicon diffusion, and finally, a thermal-chemical reaction to form a fairly dense silicon-carbide protective boundary layer as an integral part of the original matrix configuration. The carbon-graphite bodies are reacted in a resistance-heated graphite pressure furnace. The furnace is loaded, purged with an inert gas, and back filled to a slight positive pressure. The actual thermal reaction is completed in three phases.

Phase one consists of a rapid heat-up, under pressure, to about 1000°C; a soak period of from 1 - 5 minutes is made at this temperature. The silicone is vaporized in this phase and chemically reacts with the matrix to form the initial SiC dispersion in the body. A pressure of approximately 10 psi is employed in this phase of the process.

The second reaction phase, the liquid diffusion, is also carried out at a pressure of 10 psi but at a temperature of 1420°C, the melting point of silicon. A soak at this temperature is maintained to allow liquid silicon to flow and impregnate the matrix. The pressure is released at this point and a 1 ft³/hr flow of inert gas is initiated and maintained during the remainder of the process.

In the third phase of the process, the temperature is raised to 1600° - 1800°C to complete the final silicon carbide reaction. Soak time at this point is in the order of 1 - 10 minutes, depending on the materials being processed.

TEST PROCEDURES

Compressive and Flexure Strength

Bar specimens 0.400 x 0.400 x 2.0 inches long were employed in both the compressive and flexure strength determinations. Specimens whose long axis is parallel to the laminar orientation are labeled W.G. (with grain) and those with their long axis perpendicular to the laminar orientation are labeled A.G. (against grain).

Compressive strengths were determined at room temperature. Loading was applied across the 0.400 x 0.400 inch faces. Three specimens for each test were evaluated and the average value used for calculating variations due to processing. Variations were less than 3 percent in all cases.

Flexure strength was determined at room temperature, by means of the three-point method. An inner span of 1.75 inches was used in all tests. Averages of three specimens from each test were utilized for the calculations. Variations of less than 6 percent were obtained in all cases.

Breaking Strength

The breaking strength of yarns and tapes was determined by using dead-weight loading to failure. All breaking strength tests were made at room temperature.

The relative strengths of yarns and tapes at elevated temperatures were determined in the following manner. The specimens were preloaded to 200 grams and suspended in a vertically mounted, open ended, tubular, resistance furnace. The furnace was maintained at 700°C, within $\pm 5^\circ\text{C}$. The time required for the treated specimen to fail, in air at this temperature and loading, was directly compared with that of an untreated control specimen.

Oxidation Resistance

Oxidation resistances of the untreated controls and SiC treated specimens were determined in air, in an open ended 1.5 in. o.d. x 14 in. long tubular, resistance-heated furnace.

Temperatures in this study ranged from 1100°C to 1230°C. The test specimens were dried at 200°C for 30 minutes to establish reference weights upon which the oxidation resistance calculations were based.

RESULTS

Yarns and Tapes

Union Carbide's VBY-70-1/2, Carborundum's CY-5, Hitco's CY-2-1 yarns, and Union Carbide's WCB tape were all silicon-carbide treated utilizing the Astro I ultrasonic impregnation technique for applying silicone-silicon mixtures to the fibers. A summary of the data resulting from this treatment is given in Table I.

A rather dramatic increase in the oxidation resistance of Astro I SiC-treated Carborundum CY-5 yarn was obtained as evidenced by its lifetime of 82 minutes at 700°C. This represents an improvement factor some 23 times that of the CY-5 control and better than 5 times that measured for the Carborundum CY-2 20-percent SiC C.V.D. treated product. This oxidation improvement was accomplished, however, at the expense of a 40-percent decrease in room-temperature breaking strength. Ultimate processing variables have not been investigated to determine what portion of the original strength of the base yarn can be maintained.

The lifetime of 31 minutes determined for Hitco-CY-2-1 Astro I SiC-treated yarn becomes even more impressive when one considers the control yarn had a 0.2-minute lifetime at 600°C with only 100 grams loading. The 31 minutes represents an improvement factor >150 times that of the control. A loss of approximately 35 percent of the original breaking strength was observed with this particular SiC treatment.

The Union Carbide VBY-70-1/2 yarn did not respond to the Astro I SiC process as well as the Carborundum and Hitco products. An improvement factor of about three times the control was measured. The Union Carbide WCB tape also showed a more modest improvement factor (approximately four times that of the control); however, its breaking strength was reduced by only 15 percent at this level.

When an equal percentage of silicone-silicon solids was used for treating Carborundum and Hitco yarns, a much greater brittleness was developed in the Union Carbide VBY-70-1/2 yarn. This effect necessitated a reduction in silicon percentages when SiC treating WCB tape. Each manufacturer may use a slightly different process to produce the carbon and graphite materials used as samples. The resulting variation in surface characteristics may

significantly affect the specific Astro SiC treatment. Further evaluation of this point is required.

Laminar Composites

The Carborundum Carbitex-700 laminar composite was prepared using the Astro I SiC vacuum impregnation process. Table II presents the summary of the oxidation resistance and mechanical properties determined for both the control and SiC-treated material.

An improvement factor of about 3.3:1 was obtained in the oxidation resistance of the SiC treated resistance control material exposed at 1230°C. The recession rate was decreased by a 4.3:1 ratio, indicating that some internal oxidation of the SiC treated body was occurring. This suggests a degree of porosity in the boundary layers.

Compressive strengths of the SiC-treated A.G. specimens showed an increase of about 10 percent over the control specimens. Compressive strengths of the SiC-treated W.G. materials showed an 8 percent decrease. The flexure strength in the A.G. orientation was essentially unchanged, while that in the W.G. orientation increased more than 20 percent.

The physical property data might well be improved with the utilization of the Astro II process, where the additional SiC overlay thicknesses would be expected to contribute some significant strength increase to the body. This possibility will be explored.

Felt, Foam, and Bulk Materials

Table III presents a summation of the oxidation resistance data determined for various SiC treated felt, foam, and bulk materials.

At 1000°C exposure, the SiC-treated Pyrofoam FPA-20 and the UCAR VDG carbon felt have oxidation improvement factors of 17:1 and 12:1, respectively, over the control. These values would seem to indicate that significant extension in the usefulness of these products for various higher temperature insulating applications is attainable.

The bulk graphite materials, Union Carbide's ATJ and Poco's AXZ and AXM, show improvement factors of 4:1 for ATJ at 1000°C, and about 3:1 for AXZ and AXM at 1050°C. These materials are all fairly high-density products. Greater oxidation resistance might be possible with the SiC treatment, starting with special lower density products specifically designed for this treatment.

CONCLUSIONS

This preliminary study has indicated that significant improvement in both the oxidation resistance and physical properties of a variety of carbon-graphite configurations, at temperatures in the order of 1200°C, can be realized with the silicone-silicon processes described. The following areas are felt to merit further study:

- 1) Investigation of the relative merits of the processes with carbon versus graphite material configurations. The carbon systems, because of their higher chemical activity, might be more responsive to the silicone-silicon process than the graphite materials.
- 2) The use of lower density bulk and composite materials, to allow increased reactant pick-up and diffusion penetration.
- 3) Evaluation of the effectiveness of an Astro II type SiC overlay coating utilized in conjunction with the integral SiC boundary layer formed in the Astro I process.
- 4) The development of a C.V.D. silicon-carbide coating on materials previously treated with silicone-silicon (Astro I process).

The provision of a strong diffusion-bonded SiC surface on a carbon/graphite substrate could reduce the critical nature of the coefficient of thermal expansion which is now so evident in all C.V.D. SiC processing. Catastrophic failure of the C.V.D. coating, which normally occurs at the interface of the SiC and the substrate if a crack or pinhole develops, could be greatly retarded with the silicone-silicon pretreatment. Such an improvement could be of great importance, especially in applications which involve large-order thermal cycles in reactive environments.

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2. Graphite J.T.A. Graphite Composite, Union Carbide Corporation Bulletin No. 509-BD.
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TABLE I. SUMMARY OF RESULTS - YARN AND TAPE PRODUCTS

Material	Product Weight (grams/in.)	Breaking Strength @ 20°C (grams)	Specific Strength (10 ⁶ in.)	Relative High Temp. Endurance (1) (minutes)
Carborundum CY-5 Control Yarn	0.00491	2426	0.505	3.5
Carborundum CY-2 20% SiC Yarn	0.00383	1400	0.373	15.1
Astro I SiC Treated CY-5	0.00480	1267	0.258	81.6
Hitco CY-2-1 Control	0.00292	1925	0.663	0.22 ⁽²⁾
Astro I SiC Treated CY-2-1 Yarn	0.00291	1239	0.427	31.2
Union Carbide VBY-70-1/2 Yarn	0.00423	2774	0.660	2.37
Astro I SiC Treated VBY-70-1/2 Yarn	0.00328	1804	0.563	6.00
Union Carbide WCB Tape	0.11191	7701	0.068	4.0
Astro I SiC Treated WCB Tape	0.12996	6444	0.048	13.1

(1) Test Parameters 700°C with 200 gram loading

(2) Special Test Case 600°C with 100 gram loading

TABLE II. SUMMARY OF OXIDATION RESISTANCE AND MECHANICAL PROPERTIES OF SiC TREATED LAMINAR COMPOSITE

Carbitex - 700

Mechanical Properties		
Compressive Strength (psi)		% Change in Strength
Control, A.G. (1)	8,650	
Astro SiC, A.G.	9,500	+10
Control, W.G.	11,750	
Astro SiC, W.G.	10,812	- 8
Flexure Strength (psi)		
Control, A.G.	10,000	
Astro SiC, A.G.	9,800	--
Control, W.G.	632	
Astro SiC, W.G.	836	+20
Oxidation Resistance		
Weight Loss (%)		
Control	63	
Astro SiC	19	
Recession Rate (mils/min)		
Control	4.3	
Astro SiC	1.0	
Oxidation parameters: 60 minutes at 1230°C in air		

(1) A.G.: Across grain; W.G.: Parallel to grain

TABLE III. SUMMARY OF OXIDATION RESISTANCE DATA
FELT, FOAM, AND BULK MATERIALS

Materials	Oxidation Temp (°C)	Weight Loss (gm/min)	Improvement Factor
Pyrofoam Graphite FPA-20 Control	1000	0.069	
Astro SiC - Pyrofoam FPA-20	1000	0.004	17:1
UCAR VDG Carbon Felt Control	1000	0.080	
Astro SiC - UCAR VDG Carbon Felt	1000	0.007	12:1
ATJ Graphite Control	1000	0.013	
Astro SiC - ATJ Graphite	1000	0.003	4:1
AXZ Graphite Control	1050	0.042	
Astro SiC - AXZ Graphite	1050	0.017	2.5:1
AXM Graphite Control	1050	0.045	
Astro SiC - AXM Graphite	1050	0.015	3:1