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Fiber Coatings for the Fabrication
of Graphite-Reinforced Magnesium Composites

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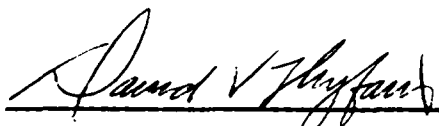
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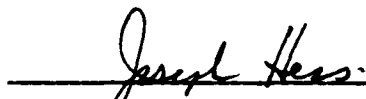This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-85-C-0086 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by R. W. Fillers, Director, Materials Sciences Laboratory. Captain David Thyfault, Space Division/YNSA, was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) Program.

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A new fabrication technique for graphite-fiber-reinforced magnesium is presented. An air-stable silicon-dioxide coating is deposited on the fiber surfaces from an organometallic precursor solution. The fibers are passed through this solution followed by hydrolysis or pyrolysis of the organometallic compound to form silicon dioxide on the fiber surfaces. The silicon-dioxide coating facilitates wetting and bonding when the fibers are immersed in molten magnesium. A modification of this coating technique was developed for coating fibers with amorphous carbon, which was found to

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20. ABSTRACT (Continued)

improve the adhesion between the graphite fibers and the silicon-dioxide coating. Composites containing either T300, P55, or P100 graphite fibers in pure magnesium, magnesium - 1% silicon, and magnesium alloy AZ91 have been fabricated. Preliminary mechanical property data are presented.

PREFACE

The author would like to thank The Aerospace Corporation, Aerospace Sponsored Research, for financial support; C. S. Hoover, Jr., R. A. Brose, and J. C. Uht for technical support; and G. L. Steckel, H. L. Marcus, J. S. Evangelides, A. B. Chase, M. F. Amateau, and D. M. Goddard for many helpful suggestions. The XPS analysis was performed by H. Hensen at Oak Ridge National Laboratory, and the TEM of the amorphous carbon coating was performed by L. T. Drzal, currently at Michigan State University.

CONTENTS

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FIGURES

I. INTRODUCTION

Graphite-fiber-reinforced magnesium is emerging as a valuable new struc-
tural material. It combines high specific strength and stiffness with a near-
zero coefficient of thermal expansion, has high electrical and thermal
conductivity, and is nonoutgassing. The primary difficulty with fabricating
this material is that molten magnesium does not wet or bond to graphite
fibers. Because molten magnesium does not wet or bond to graphite fibers, it
is impossible to achieve load transfer from the matrix to the fibers. To
overcome this problem the fibers must be coated with a material that is wet by
molten magnesium, and which also protects the fibers against chemical
degradation during processing and use.

The currently used process relies on the chemical vapor deposition (CVD)
of a thin layer of titanium and boron onto the fibers to achieve wetting.[1]
However, there is an inherent problem associated with this process. The
titanium-boron coating is rapidly oxidized when exposed to air, and molten
magnesium does not wet the oxidized coating. Consequently, the coated fibers
cannot be exposed to air before immersion in molten magnesium. This severely
limits the material shapes that can be fabricated by using this process. To
date, only fiber-reinforced magnesium wire has successfully been made. This
wire must then undergo costly secondary fabrication to produce useful struc-
tural shapes such as plates or tubes. In fact, the final shapes have been
limited to plates and tubes due to the rigidity of the wires.

We have solved this fabrication problem for graphite-fiber-reinforced
magnesium with the development of an air-stable coating of silicon dioxide,
which is easily wet by magnesium. The coatings are deposited on the fiber
surfaces using silicon-based organometallic compounds. Fibers are simply
passed through a solution of the organometallic, which is then chemically
converted by either hydrolysis or pyrolysis to form the silicon-dioxide
coating. The flexible, coated fibers may then be wound or layed up and held
in place with a removable binder for selective reinforcement. They are then
incorporated into the magnesium by casting near-net-shape structures.[2] Not

only can complex structural shapes be made by this method, but the fiber
volume fraction can be controlled to a much greater degree than possible using
the earlier CVD technique. Fiber volume fraction is critical in determining
the thermal expansion, strength, and stiffness of the composite.

II. FIBER COATINGS

A. TECHNIQUE

We have deposited thin, uniform oxide coatings on graphite fibers by using alkoxides, a class of organometallic compounds in which metal atoms are bonded to hydrocarbon groups by bridging oxygen atoms.[3] These compounds are currently being widely investigated as precursors for ceramics and glasses.[4,5] They hydrolyze when exposed to water or water vapor to form hydroxides or hydrated oxides, which can then be converted to oxides by heating to relatively low temperatures. Alternatively, alkoxides can be pyrolyzed at similarly low temperatures to yield oxides directly. Elements for which alkoxides are commercially available include aluminum, boron, lithium, magnesium, niobium, potassium, silicon, sodium, tantalum, titanium, vanadium, and zirconium. These compounds can be dissolved in various organic solvents (toluene, for example), and solutions which hydrolyze to produce various mixed oxides can easily be made.

The chlorides of boron, silicon, and titanium are also easily hydrolyzed by water or water vapor. These compounds are generally more reactive than alkoxides and are also soluble in toluene. Therefore, a mixture of chlorides and alkoxides can be used to control the reactivity of the toluene solution.

A continuous process that takes advantage of this chemical behavior was developed for coating fibers with various oxides (Fig. 1). It is a solution coating process in which the fibers are passed through a furnace in which the sizing on the fibers, applied by the manufacturer to aid in handling, is vaporized and removed. This is followed by immersion in an ultrasonic bath containing the organometallic solution. Ultrasonic vibration insures that the solution penetrates into the fiber bundle and that each of the many thousand filaments is equally coated. The uniformity and thickness of the resultant coating is controlled by the concentration and reactivity of the solution as well as the time and temperature of immersion. The alkoxide-coated fibers are then passed through a chamber containing flowing steam in which the alkoxides are hydrolyzed, followed by an argon-atmosphere drying furnace in which the
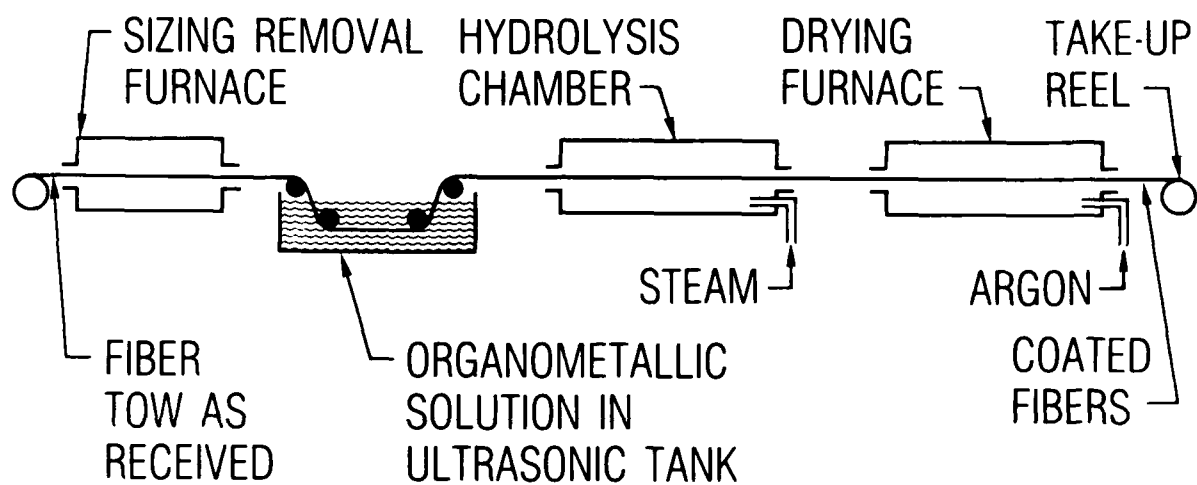
Fig. 1.   Schematic of the Solution Coating Process Used to Coat
          Fibers with Various Oxides.

10

hydrated oxide is converted to an oxide. Any residual solvent or water is vaporized, and any unhydrolyzed alkoxide is pyrolyzed in this last step.

B. EXPERIMENTAL

We have found that a silicon-dioxide coating on carbon fibers facilitates wetting by molten magnesium.[6] Three carbon fibers were investigated: T300,[*] P55,[*] and P100.[*] The SiO_2 coatings were applied using the solution coating process previously described. The fibers were passed through a furnace containing argon at 475°C to remove their sizing, followed by immersion in an ultrasonically vibrated toluene solution containing 5 vol % tetraethyoxy silane[**] [$Si(OC_2H_5)_4$, also called tetraethyl orthosilicate] and 5 vol % silicon tetrachloride[**] ($SiCl_4$). The $SiCl_4$ increases the reactivity of the solution which is kept at 25 to 30°C. The silicon compounds are hydrolyzed by passing the coated fibers through a chamber containing flowing steam. They then travel through a furnace at 550°C containing flowing argon, which serves to transform the hydrated oxide to a SiO_2 coating on each fiber surface. The fibers move at a rate of 2 to 10 ft/min, which results in a residence time of 5 to 30 sec for each step. The most efficacious coatings were obtained by repeating the process and applying the coating twice.

C. CHARACTERIZATION OF COATED FIBERS

Coated fibers were examined with scanning electron microscopy (SEM) equipped with energy dispersive x-ray analysis (EDX), transmission electron microscopy (TEM), scanning Auger microscopy (SAM), x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and x-ray diffraction (XRD). Scanning electron microscopy (Fig. 2a) shows that each fiber is uniformly and continuously coated and that there is no bridging or joining of the fibers due to the coatings. The coated fibers remain pliable, and the coatings adhere to the fibers even after flexing. No differences in tensile strengths were found between coated fibers and as-received fibers indicating that the coating process does not degrade the strength of the fibers.

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[*] Union Carbide Corporation.
[**] Alfa Products, Danvers, Mass.

(a)   (b)
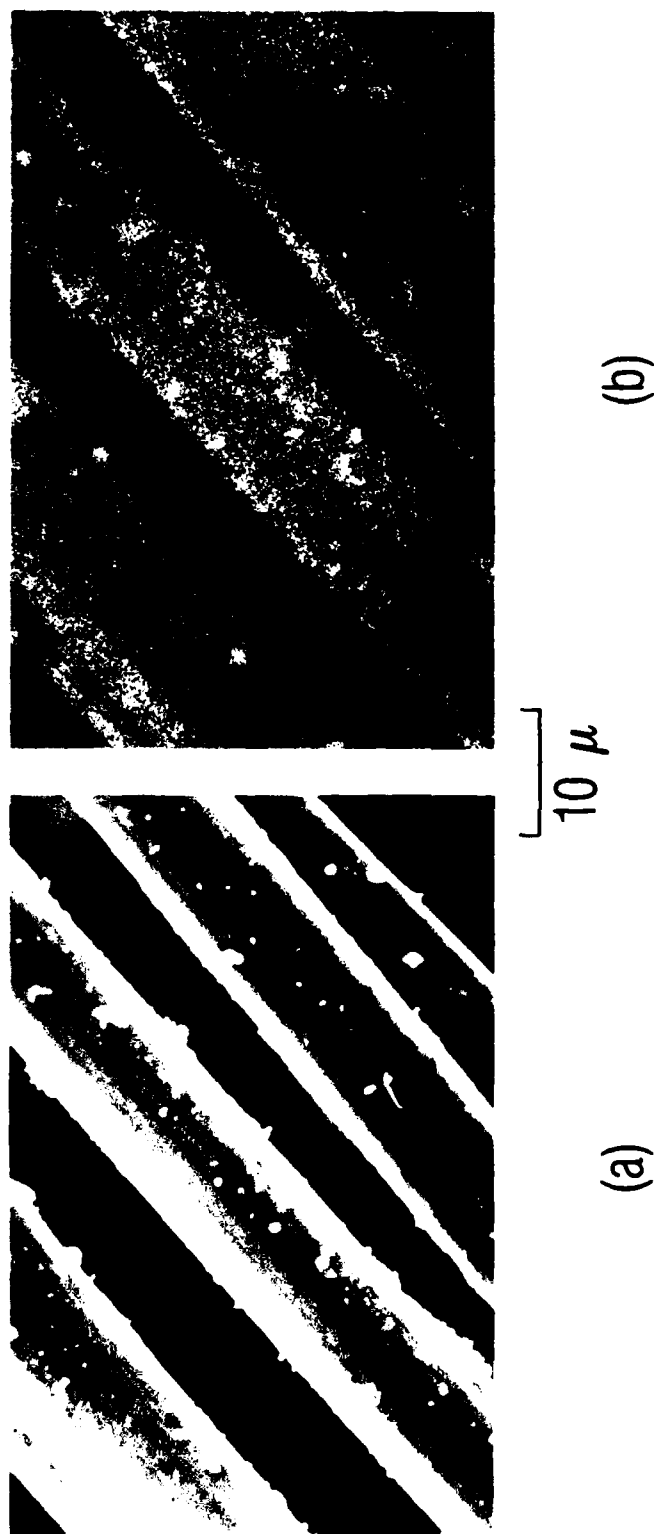
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Fig. 2. (a) Scanning Electron Photomicrograph of Silicon-Dioxide-
Coated P55 Fibers and (b) An Energy Dispersive X-ray
Silicon Map of the Same Area. The light areas correspond
to x-rays emitted by silicon.

12

Energy dispersive x-ray analysis (Fig. 2b) shows that every fiber in the bundle is coated and that even the bare-looking areas are coated. No residual chlorine is found in the SiO_2 coatings by EDX, SAM, or XPS. Scanning Auger microscopy depth profiles (Fig. 3) indicate that the thickness of the coatings varies from 700 to 1500 Å with an average value of approximately 1000 Å. The argon-ion sputter rate for the depth profiling was calibrated with tantalum oxide standards. The thickness values are verified by TEM (Fig. 4). In Fig. 4 the edge of the as-coated fiber is illuminated with electrons from behind. The grey area adjacent to the black fiber is the coating. Both electron and x-ray diffraction indicate that the coatings are amorphous.

The SAM elemental depth profiles (Fig. 3) show that the oxide coatings contain some carbon. Elemental concentrations were estimated using handbook sensitivities.[7] The carbon originates in the carbon fiber, not the organometallic compound or solvent since similarly applied coatings on FP alumina fibers* contain no carbon. X-ray photoelectron spectroscopy was employed to determine the chemical nature of this carbon as well as to determine the nature of the bonding between the coating and the fiber. The XPS spectra (Fig. 5) show that the silicon in the coating is present only as SiO_2, not SiC.[8] The carbon spectrum (Fig. 5b) shows a main peak corresponding to graphitic carbon with a shoulder indicating some carbon-oxygen bonding. However, after argon-ion sputtering for 15 min (Fig. 5d), only the graphitic carbon peak remains. The binding energy of the silicon 2p peak is unchanged after sputtering (Fig. 5c). This indicates that the coating is SiO_2 with some graphitic carbon from the fiber dispersed in it.

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*DuPont Corporation.

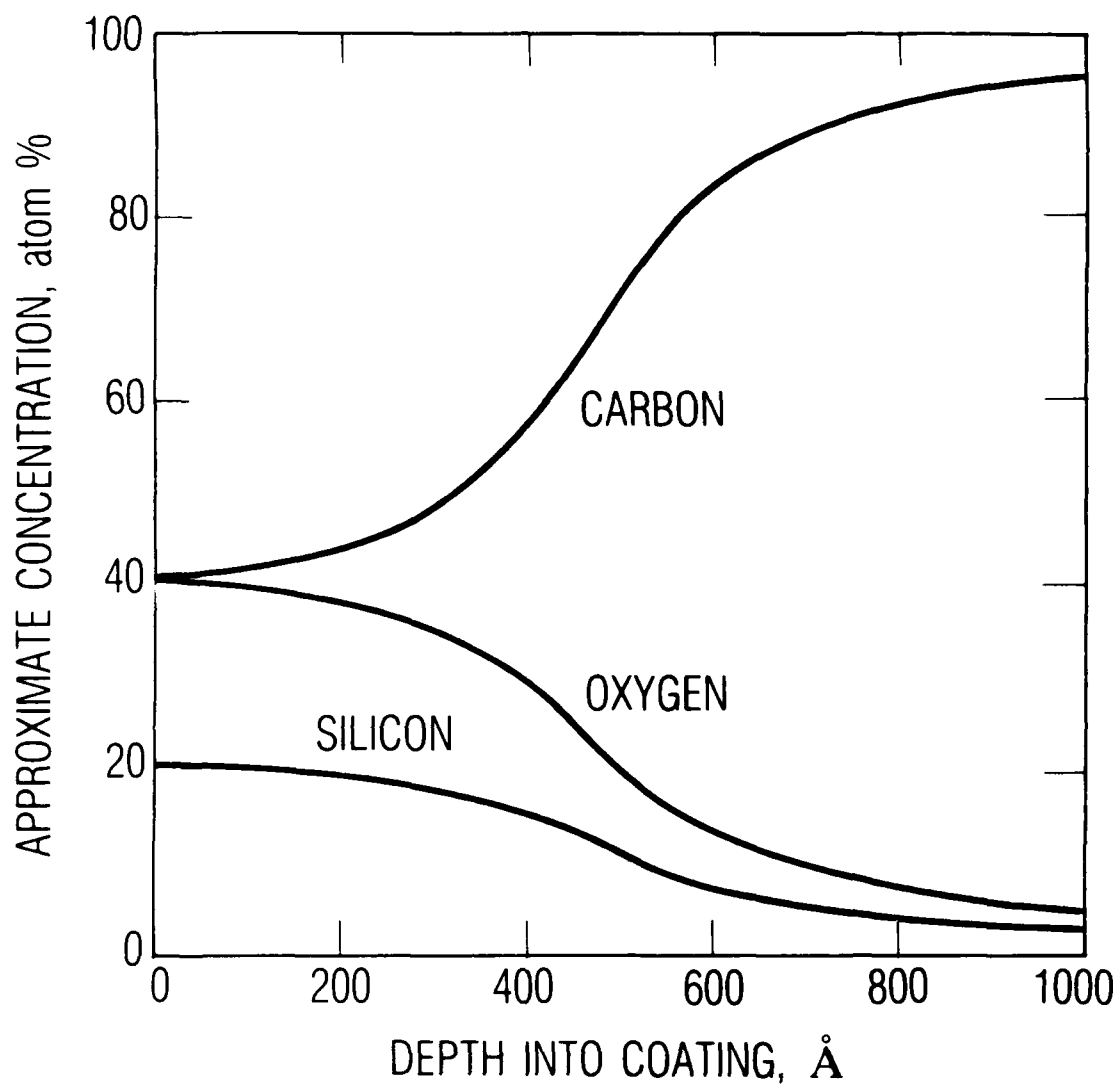Fig. 3.   Scanning Auger Microprobe Elemental Depth Profiles of a
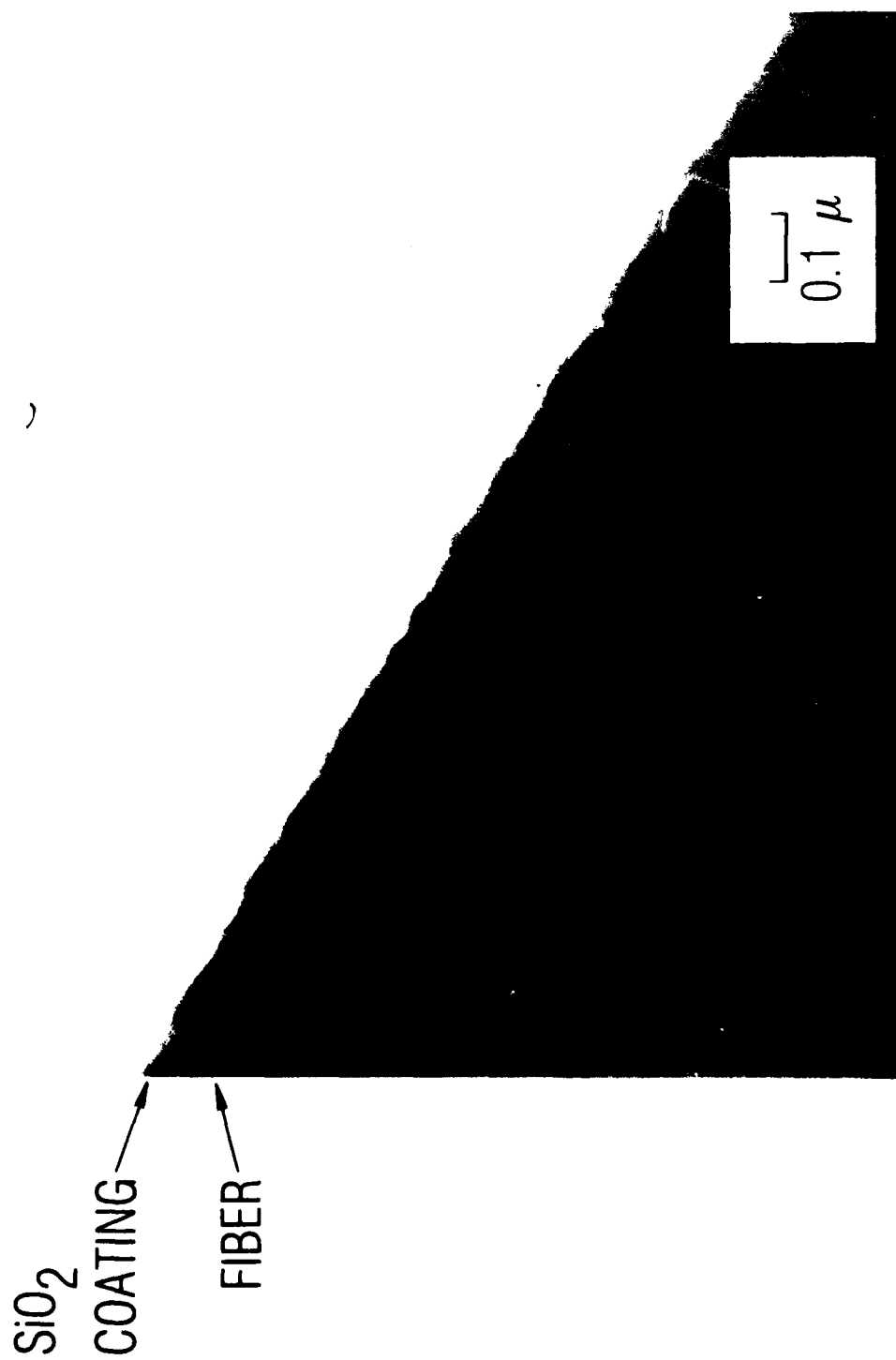Carbon Fiber Coated with Silicon Dioxide.

14

SiO$_2$
COATING

FIBER

$\overline{}$
0.1 μ

Fig. 4. Transmission Electron Photomicrograph of a T300 Fiber
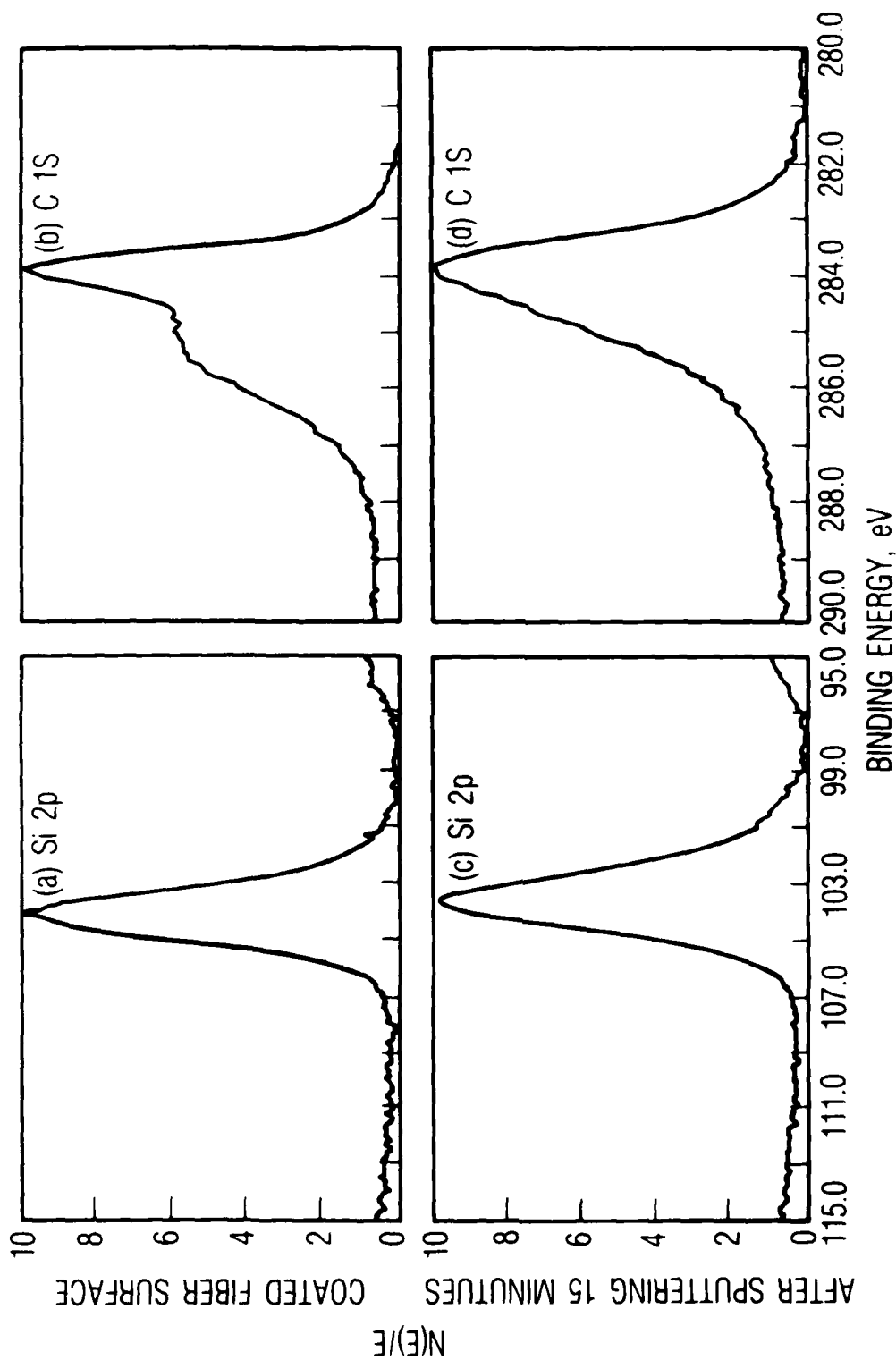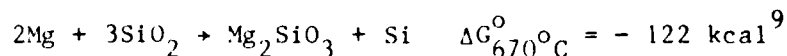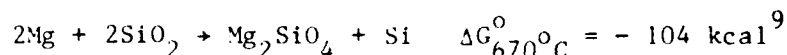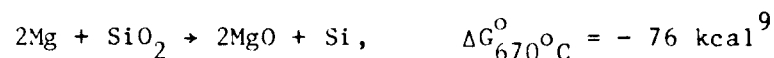Coated with Silicon Dioxide.

Fig. 5. X-ray Photoelectron Spectra of a Carbon Fiber Coated with Silicon Dioxide. (a) Si 2p Peak from the Coated Fiber Surface, (b) C 1s Peak from the Coated Fiber Surface, (c) Si 2p Peak After Argon-Ion Sputtering for 15 min, and (d) C 1s Peak After Argon-Ion Sputtering for 15 min.

16

A. T300 AND P55 FIBERS IN MAGNESIUM

Silicon-dioxide-coated T300 or P55 graphite fibers are wet, and the fiber bundles are uniformly infiltrated when immersed in molten magnesium at 670 to 700°C for 10 to 30 sec. Figure 6 shows an optical photomicrograph of a polished cross-section of P55 fibers in a pure magnesium matrix. Wetting is achieved by a reaction between the molten magnesium and the silicon-dioxide coating to form magnesium oxide and magnesium silicate:

$$2Mg + SiO_2 \rightarrow 2MgO + Si, \qquad \Delta G^O_{670°C} = -76 \text{ kcal}^9$$

$$2Mg + 2SiO_2 \rightarrow Mg_2SiO_4 + Si \qquad \Delta G^O_{670°C} = -104 \text{ kcal}^9$$

$$2Mg + 3SiO_2 \rightarrow Mg_2SiO_3 + Si \qquad \Delta G^O_{670°C} = -122 \text{ kcal}^9$$

Both SAM and SIMS confirm the presence of magnesium, silicon, and oxygen at the interface between the fiber and matrix (Fig. 7). This mixed oxide phase forms a graded junction and assures good bonding between the magnesium and the fibers.

B. P100 FIBERS IN MAGNESIUM

Higher modulus fibers such as P100 can also be coated with oxides using the solution coating process previously described. Scanning Auger microscopy indicates similar coating thickness and uniformity as for T300 or P55 fibers. However, when silicon-dioxide-coated P100 fibers are immersed in molten magnesium, very little magnesium adheres to the fibers. Scanning Auger microscopy reveals that immersion in liquid magnesium causes the SiO_2 coating to separate from the fibers, indicating that the oxide coating does not adhere to P100 fibers as well as to T300 or P55 fibers.

The difference in adhesion is due to differences in both the surface morphology and chemical reactivity of the fibers. Figure 8 shows SEMs of the
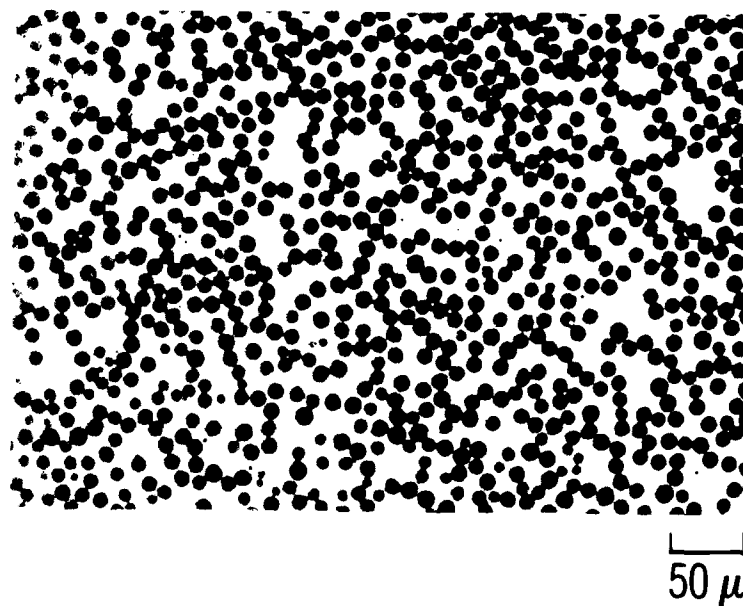
Fig. 6. Optical Photomicrograph of a Polished
Cross-Section of P55 Fibers in a Pure
Magnesium Matrix.

18

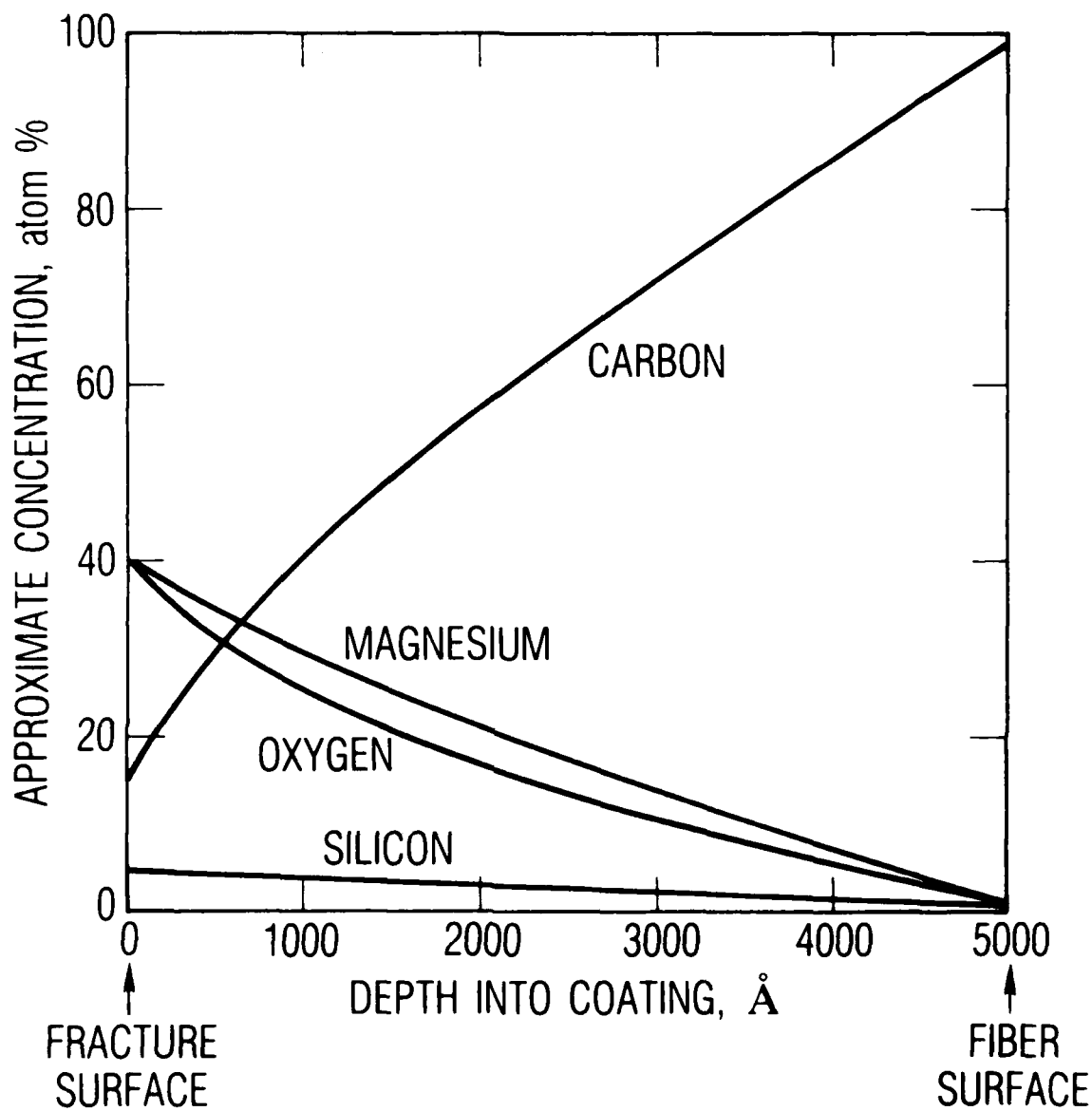Fig. 7. Scanning Auger Microprobe Elemental Depth Profiles
of the Coating Adhering to a Fiber After Fracture.

19

Fig. 8. (a) Scanning Electron Photomicrograph of T300 Fibers and (b) Scanning Electron Photomicrograph of P100 Fibers.

(a)

(b)

10 μ

surfaces of T300 and P100 fibers. The surfaces of higher modulus fibers such as P100 are smooth. Most of the graphite crystallites in the fiber have their basal planes aligned parallel to the fiber direction. Few plane edges are exposed. Lower modulus fibers such as T300 have rougher and more porous fiber surfaces. Also, more plane edges are exposed. Since the edges of the graphite plane are chemically much more reactive than the plane faces, lower modulus fibers are more reactive than higher modulus ones. These differences lead to the difference in adhesion between the silicon-dioxide coating and fibers of various moduli.

We succeeded in improving the adhesion between higher modulus fibers and the silicon-dioxide coatings by precoating the fibers with amorphous carbon. This allowed the production of magnesium reinforced with P100 fibers.[10] The amorphous carbon coating causes the higher modulus fiber surfaces to resemble those of lower modulus fibers, to which the oxide coating adheres very well. A schematic of the coating process is shown in Fig. 9. The carbon coating is applied to the P100 fibers by passing them through a toluene solution of petroleum pitch* (10 to 40 g/l, at 30 to 50°C). The solvent is vaporized, and the pitch is pyrolyzed to carbon in a series of increasing temperature furnaces containing a counter flow of argon. The optimum maximum temperature is 550°C. The carbon-coated P100 fibers are then coated with silicon dioxide twice using the solution coating process previously described. When they are then immersed in molten magnesium, good wetting and infiltration result.

Transmission electron microscopy of the amorphous carbon coating (Fig. 10) shows that the coating is about 200 Å thick. In Fig. 10 the coated fiber has been mounted in epoxy and thinned before analysis. Unfortunately, elemental surface analytical techniques cannot be used to distinguish between the coating and the fiber because the carbon coating is applied to a graphite substrate.

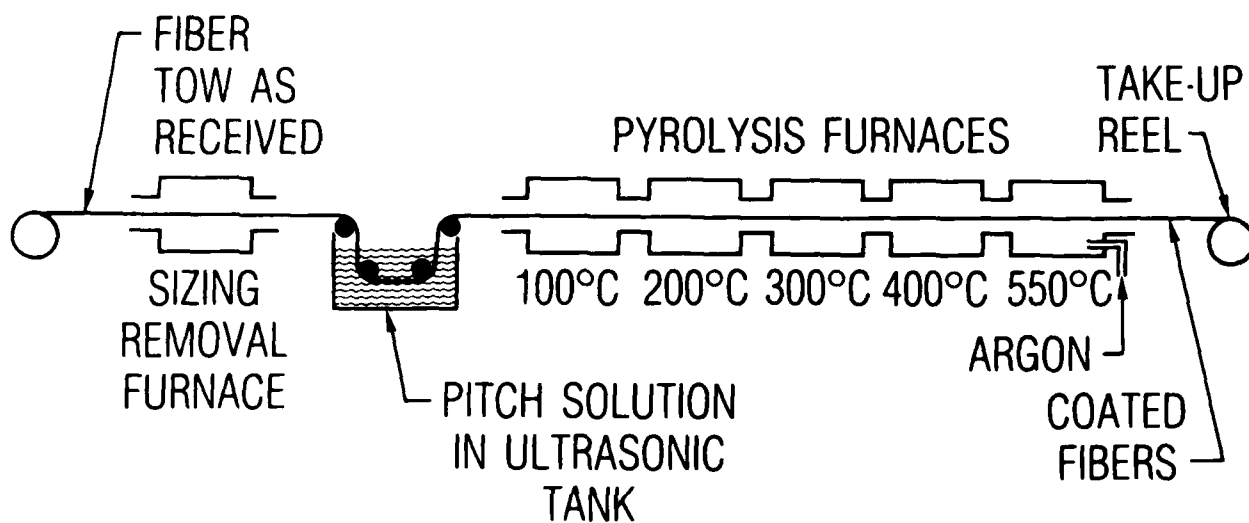---

*Ashland A240.

Fig. 9. Schematic of the Coating Process Used to Coat
Fibers with Amorphous Carbon.
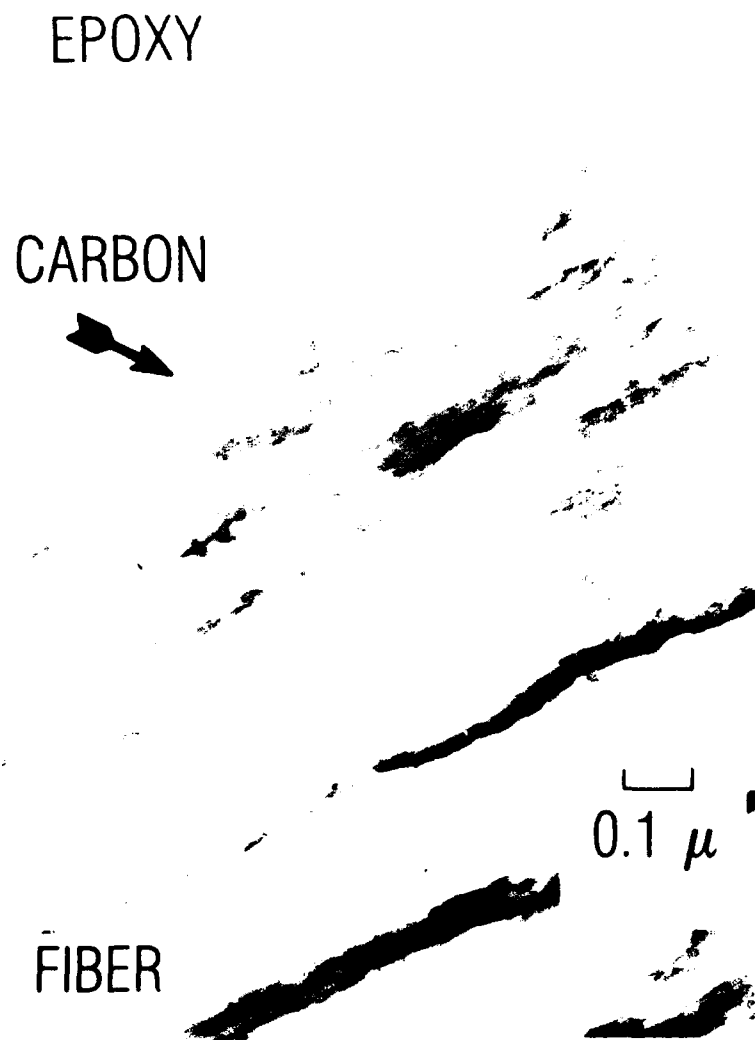
EPOXY

CARBON

FIBER

0.1 μ

Fig. 10. Transmission Electron Photomicrograph
of a Carbon Fiber Coated with Amorphous
Carbon (Mounted in Epoxy).

C. MECHANICAL PROPERTIES

We have successfully fabricated graphite-magnesium composites containing either T300, P55, or P100 fibers in either pure Mg, Mg-1% Si, or Mg alloy AZ91 (Mg-9%Al-1%Zn). Wires of each of these fibers in each of these matrices typically show room-temperature strengths that are 80 to 95% of the rule-of-mixtures values. These are comparable to the strengths measured in our laboratory of material made by the titanium-boron CVD process. A scanning electron micrograph of a tensile fracture surface of a P55/Mg wire is shown in Fig. 11. There is little fiber pullout indicating relatively good bonding between the fibers and matrix. Limited data on plates of P55 in Mg and Mg-1% Si indicate a minimum transverse tensile strength of 2 to 3 ksi (14 to 21 mPa). This contrasts with a maximum of 1 to 2 ksi (7 to 14 mPa) found in material made by the CVD process. Scanning Auger microscopy of samples fractured in situ under high vacuum shows the presence of magnesium, silicon, and oxygen on both the fiber and the matrix side of the fracture. This indicates that the fracture occurs through the interfacial oxide layer.
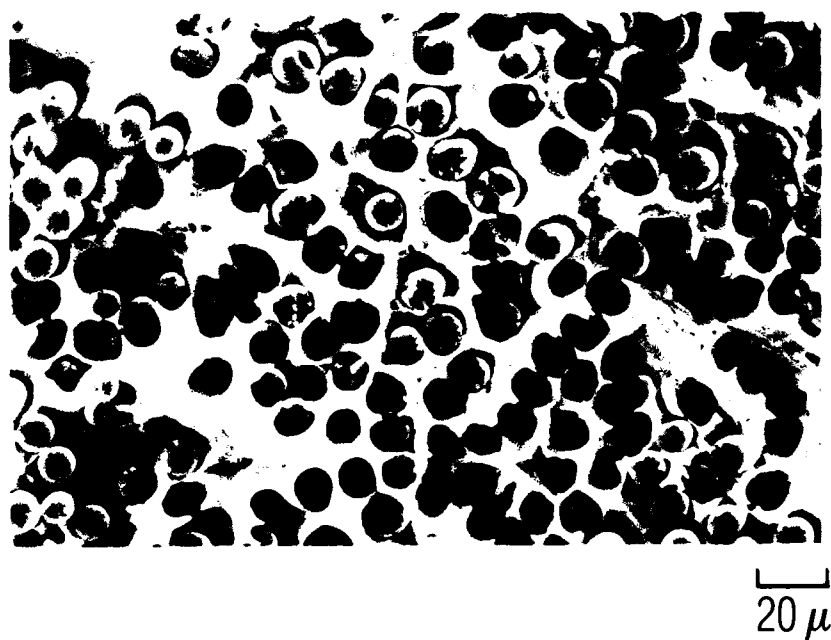
20 μ

Fig. 11. Scanning Electron Photomicrograph of
the Tensile Fracture Surface of a
P55/Pure Mg Composite Plate.

IV. CONCLUSIONS

A technique for the fabrication of graphite-fiber-reinforced magnesium composites has been demonstrated. It relies on the deposition of a thin air-stable coating of silicon dioxide onto the fiber surfaces from an organometallic precursor solution to facilitate wetting when the coated fibers are immersed in molten magnesium. This coating was specifically developed for graphite fibers, but has also been successfully used to fabricate magnesium composites reinforced with FP alumina or Nicalon silicon carbide[*] fibers. A modification of the coating technique can be used to coat fibers with amorphous carbon, which improves the adhesion between higher-modulus fibers and the silicon-dioxide coatings. The amorphous carbon coating is expected to find wider use as fibers with even higher moduli and, therefore, even less reactive surfaces are developed. Finally, we expect that coatings from organometallic precursor solutions will also prove effective in controlling the fiber-matrix bond strength in ceramic matrix composites.

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[*]Nippon Carbon Co.

REFERENCES

1. M. F. Amateau, J. Composite Materials, 10 279 (1976).

2. D. M. Goddard, Metal Progress, 125 49 (1984).

3. D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, "Metal Alkoxides," Academic Press, New York (1978).

4. L. L. Hench and D. R. Ulrich, eds., "Ultrastructure Processing of Ceramics, Glasses and Composites," John Wiley and Sons, New York (1984).

5. C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds., "Better Ceramics Through Chemistry," North-Holland, New York (1984).

6. H. A. Katzman, "Carbon-Reinforced Metal-Matrix Composites," U. S. Patent, No. 4, 376, 803 (15 March 1983).

7. L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, "Handbook of Auger Electron Spectroscopy," Physical Electronics Industries, Eden Prairie, Minnesota, Second Edition, p. 14 (1976).

8. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg (ed.), "Handbook of X-ray Photoelectron Spectroscopy," Perkin Elmer, Eden Prairie, Minnesota (1979).

9. D. R. Stull and H. Prophet, eds., "JANAF Thermochemical Tables," Second Edition, NSRDS-NBS37, U. S. Government Printing Office, Washington, DC (1971).

10. H. A. Katzman, "Pyrolyzed Pitch Coatings for Carbon Fibers," U. S. Patent No. 4,376,804 (15 March 1983).

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