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MAY-JUNE, 1969

NO. 16

CURRENT AWARENESS BULLETIN

- NEW R & D
- SELECTED ACCESSIONS
- TECHNICAL MEETINGS CALENDAR

SPECIAL REPORT: CARBON/GRAPHITE FIBER

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NEW R and D

APPLICATIONS

Flightworthy Graphite Reinforced Aircraft Primary Structural Assembly
Northrop Corporation, Norair Division
Hawthorne, California 90250
Contract No. F33615-69-C-1490
Air Force Materials Laboratory

Advanced Composite Engine Components
United Aircraft Corporation, Pratt & Whitney Division
East Hartford, Connecticut 06108
Contract No. F33615-69-C-1651
Air Force Materials Laboratory

Develop the Analysis, Materials, Design, Fabrication, and Test Technology of Advanced Composites Related to Gas Turbine Engine Components
General Motors Corporation, Allison Division
Indianapolis, Indiana 46206
Contract No. F33615-69-C-1652
Air Force Materials Laboratory

Frangible Canopy Program and Data
Corning Glass Works
Corning, New York 14830
Contract No. F33657-69-C-1000
Aeronautical Systems Division

R&D on Efficient Infrared Laser Material and Devices in Two Task Areas Defined by Two Separate Wavelength Regions
Hughes Aircraft Company, Hughes Research Laboratories
Malibu, California 90265
Contract No. F33615-69-C-1500
Air Force Avionics Laboratory

Study of Armor Penetration and Shielding for Projectiles
Systems, Science and Software
San Diego, California 92121
Contract No. DA-OAG07-68-C-0931(R)
U. S. Army, Los Angeles Procurement Agency

Anode Electrolyte Composites for Test and Evaluation
Clevite Corporation, Aerospace Division
Cleveland, Ohio
Contract No. DAAB07-69-C-0035(E)
U. S. Army Electronics Command

R&D Work on High-Quality NAG:VAG Laser Material
Raytheon Company, Microwave and Power Tube Division
Waltham, Massachusetts
Contract No. DAAB07-69-C-0258(E)
U. S. Army Electronics Command

Development of Aircrew and Aircraft Armor Protection
AVCO Corporation
Lowell, Massachusetts
Contract DAAG17-69-C-0121
U. S. Army Natick Laboratories

Integral Dual Armor for Critical Aircraft Components
Whittaker Corporation
West Concord, Massachusetts 01781
Contract No. DAAJ02-69-C-0058
U. S. Army Aviation Materiel Laboratories

Development of 400°-2200°F Fibrous-Type Insulations for Radioisotope Power Systems
Johns-Manville Research and Engineering Center
Manville, New Jersey
Contract No. AT(30-1)-3633
Albuquerque Operations Office, U. S. AEC

PROCESSING

Development of Manufacturing Processes for the Application of Rain-Erosion-Resistant Coating
Goodyear Aerospace Corporation, Arizona Division
Litchfield Park, Arizona 85340
Contract No. F33615-67-C-1349, Continuation
Air Force Materials Laboratory

Exploratory Development on the Formation of High-Strength, High Modulus-to-Density Substrateless Filament Reinforcements for Use in Structural Composites
Tyco Laboratories, Inc.
Waltham, Massachusetts 02154
Contract No. F33615-69-C-1369
Air Force Materials Laboratory

Exploratory Development of New and Improved Elastomers, Plastics, and Special Composite Systems of Materials in the Areas of Fluid or Chemical Resistance, Retention of Physical and Mechanical Properties Under Extremes of Temperature and Pressure
University of Dayton
Dayton, Ohio 45400
Contract No. F33615-69-C-1465
Air Force Materials Laboratory

Research on Development of High-Resistance Films
Arthur D. Little, Inc.
Cambridge, Massachusetts 02140
Contract No. F33615-69-C-1567
Air Force Materials Laboratory

Research to Develop New and Improved Surface Treatments for Graphite Fiber Reinforcements
Monsanto Research Corporation
Dayton, Ohio 54507
Contract No. F33615-67-C-1728
Air Force Materials Laboratory

Epitaxial Growth of Ferrimagnetic Garnets
North American Rockwell Corporation
Anaheim, California 92803
Contract No. F33615-69-C-1520
Air Force Avionics Laboratory

Exploratory Development Effort to Achieve the Capability for Designing and Fabricating High-Frequency Gallium Arsenide Junction Field Effect Transistors
McDonnell-Douglas Astronautics Company, Western Division
Huntington Beach, California 92647
Contract No. F33615-69-C-1589
Air Force Avionics Laboratory

Investigation of Voids in Carbon-Fiber Epoxy Composites
AVCO Corporation, Space Systems Division
Lowell, Massachusetts
Contract No. N00019-69-C-0208
Naval Air Systems Command

Investigate the Effects of Surface Finishing Treatments on the Properties of Structural Ceramics
Stanford Research Institute
Menlo Park, California
Contract No. N00019-69-C-0229
Naval Air Systems Command

Graphite-Metal Carbide Composites
IIT Research Institute
Chicago, Illinois 60616
Contract No. NASR-65(09), Continuation
NASA Headquarters

Low-Linear Thermal Expansion Carbide-Graphite Composites Studies
McDonnell-Douglas Corporation
Huntington Beach, California
Contract No. SNPC-67
NASA, Lewis Research Center

Developing Methods of Fabricating Spheres and Composite Materials in Zero-Gravity Environment
Arthur D. Little, Inc.
Cambridge, Massachusetts 02140
Contract No. NAS 8-21402
Marshall Space Flight Center

PROPERTIES

Defects and Their Role in Determining Bulk Properties of Crystals
Texas Instruments, Inc.
Dallas, Texas 75222
Contract No. F44620-67-C-0073, Continuation
Air Force Office of Scientific Research

Research on Assessment of Slurry Silicide Coatings for Refractory Metal Alloys
McDonnell-Douglas Corporation
St. Louis, Missouri 63166
Contract No. F33615-67-C-1574, Continuation
Air Force Materials Laboratory

Analytical and Experimental Investigation to Assess the Role and Importance of Emittance in Determining the Overall Suitability of Oxidation-Resistant Coatings for Protection of Refractory Metal Alloys From Degradation in High-Temperature Environments Associated With Prospective Service Application
North American Rockwell Corporation, Los Angeles Division
Los Angeles, California 90009
Contract No. F33615-69-C-1618
Air Force Materials Laboratory

Research on the Stability of Oxides as Filamentary Reinforcements in a Metal or Metal Alloy Matrix
General Electric Company, Missile & Space Division
Philadelphia, Pennsylvania 19101
Contract No. F33615-69-C-1635
Air Force Materials Laboratory

Studies and Investigations on Single Crystal SnTe/PbSe
General Electric Company, Imaging Devices Department
Syracuse, New York 13201
Contract No. DAAG-69-C-0525
U. S. Army Engineers Research and Development Command

Determination of Physical and Structural Properties of Mixed Modulus Composite Materials
The Boeing Company, Vertol Division
Philadelphia, Pennsylvania 19142
Contract No. DAAJ02-69-C-0059
U. S. Army Aviation Materiel Laboratories

Investigation and Testing Program on Factors Controlling Strength of Composite Structures
The Board of Trustees of The University of Illinois
Urbana, Illinois
Contract No. N00019-69-C-0289
Naval Air Systems Command

Study to Determine the Effect of Adhesives on Strength of Sandwich Structures
Whittaker Corporation, Research & Development
San Diego, California 92123
Contract No. NOO156-69-C-1735
Naval Air Engineering Center

Investigation of the Ignition and Burning of Materials in Space Atmospheres
General Electric Company
Philadelphia, Pennsylvania 19101
Contract No. NAS W-1725
NASA Headquarters

Measurement of Vacuum Ultraviolet Radiation of Ionized Carbon
Cornell Aeronautical Laboratory, Inc.
Buffalo, New York 14221
NAS2-5330
NASA, Ames Research Center

TEST METHODS

Investigate and Determine Nondestructive Methods for the Evaluation of Graphitic and Ceramic Materials
AVCO Corporation, Space Systems Division
Lowell, Massachusetts 01851
Contract No. F33615-68-C-1185, Continuation
Air Force Materials Laboratory

Development of an Analytic Technique for Predicting Graphite Recession in a Solid Propellant Rocket Motor
Aerotherm Corporation
Mountain View, California 94040
Contract No. F04611-69-C-0081
Air Force Flight Test Center

Research on Holographic Characterization of Ceramics
TRW Systems Group
Redondo Beach, California
Contract No. N00019-69-C-0228
Naval Air Systems Command

FUNDAMENTAL BEHAVIOR

Study Diffusion in Ternary Multiphase Systems Using Polyphase Diffusion Couples
The Ohio State University Research Foundation
Columbus, Ohio 43212
Contract No. F33615-68-C-3948, Continuation
Air Force Materials Laboratory

Research in the Area of Ferroelectric Phenomena in Crystals
The Pennsylvania State University
University Park, Pennsylvania 16802
Contract No. F33615-69-C-1446
Air Force Avionics Laboratory

Continuation of Research Entitled Material Properties in High-Velocity Impact
Washington State University
Pullman, Washington 99163
Contract No. 44620-67-C-0087
Air Force Office of Scientific Research

Research in Defects and Mass Transport in Oxide Crystals
Columbia University
New York, New York 10029
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SELECTED ACCESSIONS

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ABSTRACTS

3926-5 Graphite-Fiber Composite Development

This third annual report of integrated research by Union Carbide Corporation, Case Western Reserve University, and Bell Aerosystems Company on advanced graphite-fiber-reinforced metal-matrix and resin-matrix composites, their properties and applications, presents detailed studies of fabrication variables (pressure, temperature, and time).

Physical properties of nickel-graphite fiber (Thornel) composites were studied as a function of hot-pressing conditions (1500 to 5000 psi, 750 to 1125 C, 5 min to 2 hr). Density, Young's modulus, and shear modulus approached their highest values at the upper range of these conditions, but tensile strengths were best at low forming pressures (~2000 psi). For composites containing 50 vol % Thornel 50, the combined effect of low pressure and well-collimated fibers resulted in minimum fiber breakage and tensile strengths up to 115,000 psi and Young's modulus of 35×10^6 psi. Other composites fabricated with 80×10^6 psi modulus graphite yarn reached tensile strength and modulus values of 120,000 psi and 45×10^6 psi, respectively. Under tension, these composites failed in shear; presumably they can stand even higher stress with proper specimen geometry.

The variation in tensile strength with test angle for uniaxial specimens follows trends established in other composite systems. Values are highest when the tension axis is parallel to the fiber axis. The tensile strength decreases with test angle as the failure mode changes from tensile to shear failure (at the matrix-fiber interface). The average transverse strength is 5000 psi, much less than expected for matrix tensile failure. Young's modulus decreased similarly; for the transverse direction, the modulus was 5.5×10^6 psi. Young's modulus in unidirectional composites was lower than the values predicted by Whitney's micromechanics model for orthotropic filaments. This discrepancy apparently is not related to a decrease in fiber modulus as a result of processing or to errors in the sonic measurements. Various fiber properties were considered in Whitney's model without achieving satisfactory agreement and adequate correlation was established between sonic and preliminary ultrasonic data.

In epoxy-matrix composite studies, surface properties of carbon and low-modulus graphite fibers, as well as those of Thornel 25 and 40 fibers, were studied at Union Carbide. Total pore volume, surface area, pore-size distribution, and density were determined. Oxidative treatment of graphite fibers with either chromic acid or ozone does not increase surface area but changes pore-size distribution by increasing the volume fraction occupied by large pores. This may be important in adhesion since either method increases the shear strength of epoxy composites. Evidence of graphitic pyrolytic deposits on some fibers was noted in the ozone oxidation experiments.

To measure tensile strength and Young's modulus of graphite fibers, a fiber-strand test was preferred to single-filament tests because it can be performed more quickly, the data show less scatter, and the test results correlate better with the properties of uniaxially reinforced composites.

The interlaminar shear strength of the composites was determined by torsion shear tests of uniaxially reinforced composite rods. This test is relatively quick and inexpensive, requires only 70 feet of yarn, and the composite always fails in shear no matter how high the shear strength. The torque-versus-angular displacement curves are quite different for high (~10,000 psi) and low (~4000 psi) shear strength composites. High-shear-strength materials exhibit only moderate nonlinearity, indicating catastrophic failure or severe and erratic specimen degradation. The displacement curves for low-shear-strength composites bend over into a plateau region; thus the ultimate failure condition is rather arbitrary.

Integrated Research on Carbon Composite Materials, Union Carbide Corporation, Carbide Products Division, in association with Case Western Reserve University and Bell Aerosystems Company, a Textron Company, Technical Report AFML-TR-66-310, Part III, Contract No. AF 33(615)-3110 (January 1969).

4037-13 Diboride Improvements by SiC and Carbon Additions

ManLabs presents mechanical, physical, and oxidation and thermal stress resistance properties and hot-pressing characteristics for zirconium and hafnium diborides and for several diboride composites formulated with additives of silicon carbide or carbon, or both. These additives, alone and combined, enhance fabricability and improve overall diboride material properties; silicon carbide improves oxidation resistance and carbon lowers the elastic modulus and effects improved thermal stress resistance. Property data include bend strength to 1800 C, elastic modulus to 1400 C, mechanical deformation above 1800 C, linear expansion to 2000 C, cold gas/hot wall oxidation characteristics to 2200 C, and steady-state thermal stress resistance. The test specimens were 3-in.-diameter by 1-in.-high billets fabricated with selected microstructural and compositional variations. Bend strength data to 1800 C are reported for specimens obtained from 6-in.-square by 1- to 2-in.-high billets.

Research and Development of Refractory Oxidation-Resistant Diborides, E. V. Clougherty and E. V. Peters, ManLabs, Inc., Semiannual Report No. 3, Contract No. AF 33(615)-3671 (December 1968).

4160-8 High-Modulus, Low-Silica Glasses

UARL has developed 11 glass compositions with Young's modulus in excess of 20 x 10^6 psi and another 24 with Young's modulus from 18 to 20 x 10^6 psi. Possibly the most significant of these glasses is UARL 350, which, while not having the highest Young's modulus ($E = 19.8 \times 10^6$ psi), has a specific modulus of 197 x 10^6 in. Experiments on the fiberization of these new glasses are not yet complete. At this reporting time, the best data on the experimental glass compositions in fiber form are for UARL 331, which has a Young's modulus of 19.8 x 10^6 psi and a specific modulus of 150 x 10^6 in.

The batch composition of UARL 350 was SiO_2, 144.7 g; Al_2O_3, 133.1 g; MgO, 52.7 g; $BeCO_3$, 174.5 g; Li_2CO_3, 96.2 g; and $CaCO_3$, 130.8 g. For UARL 331, the batch composition was SiO_2, 148.8 g; Al_2O_3, 77.5 g; $Y_2(C_2O_4)_3$, 460 g; $BeCO_3$, 113 g; and $ZnCO_3$, 95.4 g.

Generally, high-modulus glass fibers are best achieved with SiO_2 content held to a minimum. Thus, as a class the highest moduli are achieved with invert analog glasses, in which the SiO_4^{-4} tetrahedra share fewer than two corners with each other, rather than 3 to 3.5 corners as in most stable glasses.

Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems, J. F. Bacon, United Aircraft Research Laboratories, H901373-14, Contract NASW-1301 (April 1969).

4165-4 Plastic Effects in Alumina Fracture

This investigation at the University of Newcastle upon Tyne, United Kingdom, was guided by the concept that the development of stronger alumina requires an understanding of the details of its fracture. In particular, the investigators were interested in the possibility that alumina is not perfectly brittle, that is, that some plastic deformation might be associated with its fracture. If, for example, fracture is initiated by microscopic plastic flow, then it should be possible to raise the fracture strength by inhibiting plastic deformation.

The authors measured the fracture stress of thin drill-cracked plates of polycrystalline alumina (Lucalox) between -196 C and 500 C. To eliminate the influence of small differences in crack size, the fracture stress (σ_f) was expressed in terms of γ', the apparent surface energy for fracture initiation, obtained from the Griffith equation, $\sigma_f = (2E\gamma'/\pi c)^{1/2}$, where E is Young's modulus and 2c is crack length.

Two important features of the graph of γ' versus temperature were:

(1) The magnitude of γ' is from 5 to 15 times the intrinsic surface energy

(2) γ' shows a minimum at 250 C.

The first observation suggests an association of plastic work with the fracture crack. The second suggests an association between temperature-dependent plastic deformation and fracture.

From these observations, the authors conclude that alumina fracture is not perfectly brittle, and that the initiation, and possibly the propagation, of fracture in alumina requires dislocation movement at the crack tip, either by slip or twinning.

The authors explain the observed temperature dependence of fracture stress on the basis of the ease of dislocation motion at the crack tip. Below 250 C the fracture stress decreases with increasing temperature because dislocation motion becomes easier (the flow stress decreases). At higher temperatures, additional dislocation motion associated with crack extension becomes a progressively important impediment to crack growth, and causes the fracture stress to rise with increasing temperature. Other details of the fracture of alumina can be explained on this basis as well, including the temperature of minimum strength and dependence of strength on orientation for single crystals, and the propagation of intergranular fracture in polycrystalline alumina.

Detailed fractography by both scanning and transmission electron microscopy confirmed that plastic deformation is associated with the fracture surface and that even in single crystals, the fracture follows a devious path and generates numerous flakes. These flakes break free from the surface by plastic tearing when the crack front unites. The dislocation density at the edges of the flakes is often 10^9 to 10^{10} cm^{-2}.

The effect of small alloying additions on the notched bend strength of single crystal alumina was also reported. It was felt that such additions would alter the ease of dislocation motion and thereby influence fracture strength without appreciably altering Young's modulus or the intrinsic surface energy. The alloying additions studied were: 0.05 to 1.0% chromium, 0.05% titanium, or 1.0% vanadium.

Chromium altered the strength of alumina, the effect depending on temperature and the amount of alloying element. Small additions (up to 0.5% Cr) produced strengthening (up to 70% increase at -196 C) but a 1.0% Cr addition produced weakening. The vanadium-doped alumina (0.1% V) was consistently stronger than the pure aluminum, while the 0.05% Ti-doped alumina was generally weaker than the pure material. The authors hesitated to discuss the possible reasons for the strength changes until the alloyed rods could be more fully characterized with respect to microporosity, homogeneity of additive distribution, etc.

The notched bend testing of doped alumina also showed that annealing at 1250 C after notching reduces the weakening effect of the notch, that is, the specimen is almost as likely to fail under the loading point as at the ground-in notch. Accompanying this was an increase in bend strength of two to three times. The authors suggest that on the basis of this evidence, accidental surface damage introduced during the manufacture of an alumina part might be remedied by annealing.

The Brittle Fracture of Alumina, J. Congleton, M. R. Holdsworth, and N. J. Petch, University of Newcastle upon Tyne, United Kingdom, AD843775, Contract No. DAJA37-67-C-0522 (April 1968).

4454-5 NbC-Graphite Composite Properties

A factorially designed experimental scheme was used to investigate the niobium carbide-graphite composite system at the Carborundum Company. Density, thermal expansion, modulus of rupture, elastic modulus and oxidation recession were characterized to temperatures as high as 2500 C and related to experimental variables of fabrication, NbC:C ratios, and graphite type.

High fabrication temperatures of >3000 C and hold times of 45 min produced 95 to 97 percent dense composites with high modulus and high strength. Anisotropy was developed by varying the shape of the graphite phase, which enabled properties to be tailored for specific applications.

Graphite was introduced in flake (needle coke), fiber, and spherical (powdered nuclear grade) form in concentrations of 20 or 50 vol %. Generally the most desirable properties were found with the flakes of needle coke. Strength, stiffness, thermal expansivity, density, and oxidation resistance were all relatively low composites reinforced with fiber. Strength and stiffness tended to increase with decreased graphite content, being highest for the pure NbC, but graphite addition tended to reduce the temperature dependence of these properties, thereby increasing thermal shock resistance.

Advanced Ceramic Systems for Rocket Nozzle Applications, D. A. Speck and B. R. Miccioli, The Carborundum Company, Summary Report on Contract No. N00017-67-C-2406 (October 1968).

4764-9 CVD Boron Nitride for Microwave Applications

For the Army Electronics Command, workers at Raytheon have established process parameters for depositing BN by CVD with a density greater than 1.6 g/cm^3. The mechanical, chemical, and electrical properties are superior to standard isotropic CVD BN (density, 1.25 g/cm^3) for many applications, particularly as microwave windows, grid spacers, and substrates for slow-wave structures.

The key to high-density deposition lies in preventing nucleation in the vapor phase, which is accomplished with high temperature (above 1900 C versus 1750 to 1800 C for the standard 1.25 g/cm^3), and reduced boron or ammonia vapor pressure. With the lower reactant concentration, however, deposition rates were only 2 mils/hr for consistent deposition of 1.6 g/cm^3 material. There is some indication that more useful rates are possible.

The higher density increases thermal expansivity (to about 6 x 10^{-6} at 1.6 g/cm^3), flex strength (to roughly 20 to 22 x 10^3 psi at 1.6 g/cm^3), and dielectric constant to about 3.3 at 1.4 g/cm). The high density isotropic CVD BN also showed negligible corrosion in boiling water and SF_6 up to 450 C.

BN windows were brazed to Cu-glass pump-out tubes using Ag-Cu eutectic braze and a molybdenum cylinder to grade the thermal expansion, and retained a vacuum of 5 x 10^{-8} torr at room temp. For metallizing the coating before brazing, several Si-Zr and Si-Ti compositions, with or without molybdenum, were found suitable, 88% Ti-12% Si, for example. Contaminated BN windows can be cleaned by vacuum firing to 1300 to 1800 C and admitting a few bursts of air followed by several bursts of NH_3 and then re-evacuating before cooling. BN parts should be stored in dry argon.

To form slow-wave patterns ZrB_2 or Ti was sputtered onto the BN substrate. For greater uniformity of coating, CVD was tried for ZrB_2, although promising, early attempts were unsuccessful.

Chemical Vapor Deposition Materials for Electron Tubes, S. R. Steele, J. Pappis, H. Schilling, and J. Simpson, Raytheon Company, Research Division, Technical Report ECOM-0156-F, Contract No. DAAB07-68-C-0156 (April 1969).

5375-2 Improved $BaTiO_3$ Dielectrics

The New Jersey Ceramic Research Station of Rutgers investigated the controlling factors in the development of ceramic dielectrics with dielectric constants >200 ± 10 ppm/°C and loss tangents <0.0005 at microwave frequencies over the temperature range -40 to +85 C. $BaTiO_3$ containing various additions of $SrSnO_3$ was studied to determine the shape of the dielectric constant versus temperature curves and location of the Curie points. Theoretical curves were calculated for combinations of two or more of these compositions. Specimens were made from various combinations using both a layered type configuration and a superficial mixing of the end members. The layered type specimens closely approximated the theoretical curves, indicating little interaction between the layers. The superficially mixed materials interacted much more. Quite flat dielectric constant versus temperature curves were obtained between 25 and 900 C using equal weight layers of end members containing 3 and 9 mole percent $SrSnO_3$.

To reduce grain size and increase bulk density of specimens of ultrapure $BaTiO_3$, Ta_2O_5 was added at 0.1, 0.5, 1.0, and 1.5 mole percent levels. Batches were prepared by passing wet-milled and dried compositions through a jet mill to thoroughly incorporate the additives. Specimens were fired to 1275, 1310, and 1345 C in air and in various vacuum atmospheres. The air firings resulted in room-temperature dielectric constants as high as 3780 with dissipation factors of 1%. The vacuum firings yielded room-temperature dielectric constants as high as 62,500 with approximately 3% dissipation.

The effect of varying the time and temperature of the initiation soak on the bulk density and electrical properties of ultrapure $BaTiO_3$ was studied. Higher fired bulk densities and higher dielectric constants were obtained using certain initiation soak temperatures and times, particularly with soaking at 1175 C for 3 or 5 hr, or at 1200 C for 1 hr, where bulk density >5.60 g/cm^3 and dielectric constants >4100 were regularly achieved.

Experiments with devitrified specimens of the BaO-TiO_2-B_2O_3 system showed that for any given B_2O_3 content the highest dielectric constants were obtained when moles BaO = moles TiO_2 + moles B_2O_3.

Inorganic Dielectrics Research, E. J. Smoke, E. L. Kastenbein, et al., New Jersey Ceramic Research Station, Rutgers, Technical Report ECOM-0232-2, Contract DAAB07-67-C-0232 (October 1968).

5751-3 p/n Silicon Carbide Diodes

Using $AlCl_3$ or B_2H_6 as dopants, Stanford Research Institute has succeeded in preparing p/n SiC by CVD depositing doped SiC epitaxially from CH_3SiCl_3-H_2 vapors on solution-grown single-crystal SiC.

The minimum $AlCl_3$ vapor pressure to obtain p-type deposits was 0.005%, or about 10% of the CH_3SiCl_3 vapor concentration. The minimum diborane gas doping level is about 3% of the CH_3SiCl_3 level. Without such doping CVD with CH_3SiCl_3 produces n-type epitaxial layers. In the n-type layers the electron carrier concentration can be increased by doping with nitrogen, introduced in the vapor as a 99.5% H_2-0.5% N_2 mixture.

It has been difficult to prepare diodes from these materials. Surface preparation by lapping or edge grinding apparently damaged the surface at the junction, and neither evaporated or sputtered contacts adhered very well, although sputtered gold or platinum contacts could be used experimentally.

Comparison of photoluminescence and electroluminescence in several diodes showed no correlation between the properties.

Growth, Processing and Characterization of -Silicon Carbide Single Crystals, R. W. Bartlett and R. A. Mueller, Stanford Research Institute, AFCRL-69-0114, Contract F19628-67-C-0243 (February 1969).

5769-5 Depositing SiC Using IR Radiant Energy

A unique method for the chemical vapor deposition of 3 to 5-mil SiC filaments onto an electrically nonconductive substrate, fused silica, has been developed by Tyco Laboratories using infrared radiant energy. Carbon-opacified SiO_2 substrates, 0.4 and 0.7 mil in diameter, are radiantly heated by a quadelliptical mirror wall furnace with four line-source tungsten lamps. SiC deposits, produced by the pyrolysis of CH_3SiCl_3, are attained at a furnace power input of ≈4 kw. Other deposition parameters for the system are 470 ± 5 cm^3/min total gas flow rate, coolant air pressure of 1.5 psi, and gas composition of 292 cm^3/min argon, 96 cm^3/min H_2, and 78 cm^3/min CH_3SiCl_3.

Optimal SiC on SiO_2 filaments have smooth, glass-like surfaces with fine-grained surface. The deposits are highly oriented, with the (111) crystallographic planes normal to the radial direction of the substrate. The filament cross sections showed both radial columnar and circumferential lamellar grains existing singly and in combination. The modulus of elasticity for SiC on SiO_2 filaments ranged between 56 and 70 x 10^6 psi. The maximum room-temperature fracture strength was ≈300,000 psi. Limited elevated-temperature tensile testing indicated fracture strengths above 116,500 psi at 1200 C in air.

While SiC on SiO_2 filaments lost some hardness after 300-hr heat treatments at 1100 and 1200 C in air, no change in hardness was observed from that of the as-deposited structure after a 600-hr heat treatment in argon at 1200 C. The "softening" in air has been related to an oxidation effect. Neither treatment produced substrate-deposit interaction.

Infrared radiant heating was also used to vapor deposit SiC on Thornel graphite yarns at power inputs from 2.4 to 2.8 kw.

TiC, a potential reaction barrier for SiC filament in Ni-base matrices, was vapor deposited on silica substrates by the infrared radiant energy technique. The optimum parameters for its deposition in the present experimental system are a total gas flow rate of 738 to 752 cm^3/min and a gas composition of 420 cm^3/min H_2, 278 to 292 cm^3/min argon, 12 cm^3/min CH_4, and 8 cm^3/min $TiCl_4$. The furnace input was 2.8 kw and the coolant air pressure was 6 psi. Single-phase, randomly oriented polycrystalline deposits of TiC were obtained. The formation of a TiC-coated SiC on SiO_2 filament by sequential vapor depositions is feasible in the infrared radiant furnace. Based upon known phase equilibrium data for stoichiometric TiC and Nickel, a duplex filament of this type should be stable in a Ni-base matrix up to 1200 C.

Silicon Carbide Filaments, S. J. Michalik and M. Weinstein, Tyco Laboratories, Final Technical Report, Contract No. N00019-68-C-0177 (February 1969).

6078 Forging Oriented Ferrites

Studies at Avco proved that press forging or single-step hot press forging can be used to prepare highly dense $Ba_3Co_2Fe_{24}O_{41}$ and $BaFe_{12}O_{19}$ with significant crystallite orientation.

$Ba_3Co_2Fe_{24}O_{41}$ was hot pressed at 1100 C and 15,000 psi for 50 min, press forged at 1150 to 1200 C and 30,000 psi for 4 to 30 min, and single-step hot-press-forged at 1150 C and 30,000 psi for 30 min. $Ni_{0.64}Zn_{0.36}Fe_2O_4$ was hot pressed at 1100 to 1150 C and 15,000 to 20,000 for 52 min, and $BaFe_{12}O_{19}$ was single-step hot press forged at 1150 C and 30,000 psi for 30 min, not including 3 min for gradual application of pressure. For all three materials these processes yielded highly dense bodies; press-forging and single-step hot-press-forging efforts failed for the NiZn ferrite. The NiZn ferrite crystallites were not successfully oriented and hot pressing did not succeed in orienting the BaCo ferrite.

In the press-forged and hot-press-forged $Ba_3Co_2Fe_{24}O_{41}$ and the $BaFe_{12}O_{19}$, crystallites were obtained with the basal planes of the hexagonal unit cells aligned perpendicular to the forging direction. The microstructure of the forgings consists of platelets with the small dimension parallel to both the forging direction and the c-axis of the crystallographic unit cell. The magnetic permeability of the oriented $Ba_3Co_2Fe_{24}O_{41}$ (7 at 2000 MHZ) is two and a half to three times greater than it is with the randomly oriented body prepared by hot pressing.

Magneto-Crystallographic Orientation Produced in Ferrites by Hot Working, R. M. Haag, Avco Corporation, Space Systems Division, Annual Report AVSSD-0047-69-CR, Contract N0014-68-C-0364 (March 14, 1969).

6079 Aspect Ratio for BN Fiber Reinforcement

In Monsanto/Washington University studies, the flexural fatigue characteristics of boron-fiber-reinforced epoxy were found to depend strongly on the aspect ratios of the reinforcing fibers.

Composites with a fiber-to-matrix modular ratio of 120 and 50 to 55 v/o of 4.5-mil-diameter fiber were cycled to failure at various stresses and the fatigue life at 60, 70, 80, and 90% of the single-cycle strength determined. The fiber lengths used were 1/4, 1/2, 1, and 4 in. At each stress level the fatigue life rapidly increased with increasing aspect ratio up to a ratio of about 200 (the ratio for the 1-in. fiber). Only moderate increases in the fatigue life were found at the higher aspect ratio tested (about 900). Static strengths show similar relationships. The investigators conclude that an aspect ratio of 200 is sufficient for outstanding static and dynamic mechanical properties; the difficulties of fabricating higher aspect fibers can be avoided. The fatigue failure was a combination of interfacial failure and brittle rupture of the matrix at 45 deg to the fiber axis. The fatigue cracks resulted in debonding of the outer fibers, which reduced the effective moment of inertia of the specimen.

The Effect of Aspect Ratio on the Fatigue Life of Short Boron Fiber Composites, R. E. Lavengood and L. B. Gulbransen, Monsanto/Washington University Association, HPC 68-66, Contract No. N00014-67-C-0218 (February 1969).

6083 Joining Dissimilar Materials

For the NASA Office of Technology Utilization, Battelle has prepared a comprehensive state-of-the-art review with 161 references plus a supplemental bibliography with 32 entries. Ceramic-to-metal joining in the electronic industry and graphite joining in the nuclear and aerospace industries are emphasized, since these have been the principal sources of development. Among the topics included are materials selection, joint configuration, surface preparation, bonding theory and method, and methods of evaluating joints.

Joining Ceramics and Graphite to Other Materials, H. E. Pattee, R. M. Evans, and R. E. Monroe, Battelle Memorial Institute, NASA SP-5052 (1968).

6084 Resistance Switching in Vanadium Oxide Films

Electrical characteristics of thin-film resistive elements of VO_2 were investigated at RPI. Interest in this material is due to a known pronounced drop in electrical resistance at about 68 C apparently associated with a transition from a monoclinic to a tetragonal structure.

Films 5000 A thick with a density of 4.25 g/cm were prepared by RF sputtering from a vanadium oxide cathode onto an as-fired 96 percent alumina substrate. Electrodes 10 mils apart were provided on 100- by 50-mil diced specimens by evaporating gold pads.

For a typical sample, resistivity decreased from about 20 ohm-cm to 0.1 ohm-cm in only a few degrees around 68 C. Static current-voltage curves obtained by varying the applied dc voltage showed the initial resistance to be somewhat ohmic, with a value of about 500 Kohms. However, at a certain critical threshold voltage the unit rapidly switched to a resistance averaging about 20 Kohms. Decreasing the voltage sufficiently reversed the switching. It was said that the devices could be cycled "repeatedly" very consistently. Dynamic tests using 60 Hz voltage showed similar switching. Extrapolation of threshold voltage as a function of ambient temperature showed, as expected, a zero threshold voltage at about 68 C. With a relaxation circuit using a dc voltage source, relaxation oscillations were generated at a frequency and amplitude dependent on the circuit parameters selected. All devices tested could be made to oscillate at 100 KHz, some at up to 500 KHz.

The switching proceeds by supplying the heat for crystal transformation. Although basically a current-controlled, thermal process, the switching of the vanadium oxide films was said to take place in the order of a microsecond. Although tests were not extensive the experience with several dozen models was said to be satisfactory in dependability, reliability, and stability. The temperature dependence is a dominant factor for potential applications. Applications suggested include sensitive infrared detection, temperature sensing, and nonlinear circuit modulation.

A Vanadium Oxide Film Switching Element, T. N. Kennedy and F. M. Collins, Rensselaer Polytechnic Institute, Technical Report No. 2, Contract N00014-67-A-0117-0005 (February 1969).

6086 Weathering of Quartz Crystal Units

The Army Electronics Command has investigated the durability of military quartz crystal units in the frequency range of 4.3 to 100.0 MHz. These units were stored for 4-1/4 yr under climatic conditions representative of field conditions in most of the United States. An overall failure rate of .2%/1000 hr (60% confidence level) was derived. It can be expected in such a group of military crystal units that 2.5% will be catastrophic failures and 3.3% will be degradational failures over a 4-yr period. This is considered high for present-day reliability requirements. However, the current Military Specification MIL-C-3098 requires internal inspection of the crystal unit, leak testing of the enclosure, and a 30-day aging requirement, which should eliminate many of the defects found in this investigation. With this increased quality control more reliable crystal units should become available. PEM programs now being conducted on high-reliability general-purpose military crystal units require a reliability of .1%/1000 hr with a 60% confidence level.

Reliability of Military Crystal Units Under Climatic Environmental Conditions, L. Nelson, U. S. Army Electronics Command, Technical Report ECOM-3066, DA Task No. 1H6-62705-A-058-01-15 (November 1968).

6114 Better Bipolar Transistors

By improvements in the quality of thin-film silicon, coupled with gettering techniques and a new bipolar transistor structure, RCA Laboratories have developed greatly improved devices. In the new structure, the emitter is deposited through a hole in the oxide covering the base, which greatly simplifies fabrication and eliminates the emitter-to-collector spikes in the earlier structure. Gettering increases minority-carrier lifetime by a factor of 3 to 10, yielding values in the range 10 to 40 nsec. Preliminary measurements made on transistors fabricated with the improved technology show a current gain of 25 at $I_C = 5$ mA and a cut-off current less than 1 nA at $V_{CB} = 10$ V. High-frequency and field-effect measurements are reasonably consistent with a base width of about 0.5 μm. Fall-off of h_{FE} with frequency is less than 6 dB/octave. f_T is 580 MHz at $I_C = 10$ mA.

Silicon on Sapphire Bipolar Study, F. P. Heiman, P. H. Robinson, and P. S. Rosenblum, RCA Laboratories, Technical Report AFAL-TR-69-58, Contract F33615-68-C-1368 (February 1969).

6116 Carbothermic Reduction of Silica

Bureau of Mines investigators found that graphite did not reduce silica in vacuum appreciably below 1,300 C, but above 1,445 C carbon monoxide formed so rapidly that it was difficult to retain unreacted sample in the crucible. Maximum interaction was obtained at a silica-to-graphite molar ratio of about 1.5, and with reactant particle diameters of 0.06 to 0.13 mm. With finer reactants, the gas permeability of the charge was too low to liberate the gaseous products freely. For particle sizes larger than 0.13 mm, the amount of reaction correlated better with the number of particles than with the surface area of the reactants.

At 1400 C for 5 hr, over 80% of the total oxygen was extracted from an equimolar powdered mixture containing Wausau silica and graphite particles of approximately 0.15 mm diameter. Carbonized dextrose provided a better reductant than graphite.

Effect of Physical Parameters on the Reaction of Graphite With Silica in Vacuum, L. A. Haas and S. E. Khalafalla, Bureau of Mines, RI 7207 (December 1968).

6118 In-Depth Heating of Ablators

The primary concern in this GMC study to develop techniques for coupling high strain-rate testing with the high reentry temperatures was to eliminate, or at least minimize, all effects on the strain-rate behavior other than high temperature. Carbon-, quartz- and silica-reinforced phenolic resin were used as test materials as well as graphite. Existing techniques for heating ablator materials to very high temperatures, such as plasma jet, arc-image, and radiant infrared heating, can heat materials to 5000 F and higher, but these techniques deposit the energy on the surface of the material. Since there is no direct in-depth penetration, large thermal gradients arise producing stresses that superimpose on the mechanical stresses during high strain-rate testing. Smaller samples or slower heating are unacceptable solutions, since the ablator materials possess definite size-effect limitations and time-at-temperature effects.

In-depth heating, that is, heating within the material volume, reduces thermal gradients to acceptable limits, although small thermal gradients are always present in the ablator materials because of the electrical differences between the fiber and matrix constituents.

Primary effort in this study was placed on developing in-depth heating. Resistive and inductive techniques were investigated because the ablators to be tested include graphite and carbon phenolic, which are electrically conductive. In addition, the carbonaceous char from the decomposition of the phenolic matrix is conductive. Both techniques worked very well. Potential heating rates as high as 10^4F/sec were realized up to the graphite sublimation temperature (~6500 F).

Dielectric (microwave) heating proved satisfactory for non-conductive silica and quartz phenolic. Heating in-depth stops as charring begins and surface heating takes place in the form of a plasma on the surface. Potential solutions to this problem appear to be in combining microwave heating with resistive or inductive heating. Rapid heating (~10^3F/sec) is possible with higher power generators.

High-energy (2 Mev) electron-beam heating proved to be potentially useful especially for very rapid heating (~10^4 - 10^5F/sec) of dielectric materials.

Dynamic Mechanical Properties at Ablative Temperatures-Techniques, S. G. Babcock, P. A. Hochstein, and W. F. Dais, Materials and Structures Laboratory, General Motors Corporation, SAMSO TR-68-71-Vol. IV, Contract No. F04694-67-C-0033, AD 842 605 (January 1968).

6119 Ceramic Filament Production

Babcock and Wilcox has defined an overall process for routinely producing a ceramic oxide continuous filament of approximately 75% Al_2O_3 20% SiO_2, and 5% B_2O_3 from a fiberizable salt solution.

The initial salt solution is prepared by dissolving aluminum metal in concentrated inorganic acids or an inorganic acid salt solution or both until the dissolution rate becomes very slow. Colloidal SiO_2 boric acid or phosphoric acid are added, depending on the desired finished-fiber properties.

By extruding 200 to 800-poise solutions through 3-mil orifices, 8- to 20-μ diameter unfired fibers of uniform diameter can routinely be produced for collection at a rate of 600 to 1000 ft/min. The extrusion pressure and temperature for this processing are 250 psig and 80 to 105 F, respectively. Close control of the extrusion temperature to insure optimum solution viscosity (~300 poise) should allow routine production of uniform fibers 8 μ or less in diameter. No effort has been directed toward collection of continuous lengths of fiber. A maximum of 4-ft-long fiber swatches are currently produced.

After extrusion, the fiber is only dried enough to allow convenient collection. Fiberizable solutions are about 35% oxide solids and must be dried to at least 45% solids content for the fiber to maintain integrity after initial fiber formation.

The final step, calcination, determines the chemical and physical structure of the ultimate fiber and thus has a large effect on the tensile strength and modulus of elasticity of the fiber. Different calcination procedures are required for different diameter fibers. By firing slowly (25 to 50 F/hr) to 1850 or 1950 F, fiber strengths greater than 100,000 psi tensile strength were achieved for fibers 12 to 40 μ in diameter.

With an improved fiber extrusion-attenuation system and 0.002- to 0.004-in.-diameter spinnerettes, green fibers from 6 to 15 μ in diameter could be produced. These green fibers could be fast-fired in a tunnel kiln at 1850 or 1950 F to 5 to 10 μ in diameter and resulted in fibers with 175,000 to 230,000 psi average tensile strength and 22 to 30 x 10^6 psi average modulus of elasticity.

The tensile strength of the fibers increases with a decrease in fiber diameter. The modulus of elasticity is independent of fiber diameter. The fibers lose strength during storage and handling but appear to be unaffected by atmospheric humidity.

Development of a High-Strength, High-Modulus Ceramic Fiber, R. N. Fitterwolf, Babcock and Wilcox Company, B&W Report No. 5114, Contract No. NAS8-21186 N69-13872 (September 1968).

TECHNICAL MEETINGS CALENDAR

July 7-11; Paris, France. *INTERNATIONAL COLLOQUIUM ON STRUCTURE AND PROPERTIES OF SOLID SURFACES* [sponsored by Centre National de la Recherche Scientifique] (Information: Prof. J. Benard, Ecole Nationale Superieure de Chimie 11, rue Pierre-Curie, Paris 5, France)

July 14-18; Andover, New Hampshire. *GORDON RESEARCH CONFERENCE, CHEMISTRY AND METALLURGY OF SEMICONDUCTORS* [Topics: Epitaxial growth-kinetic studies, Compositional control of compound crystals, Doping distributions, Amorphous switching devices, Electronic conduction in noncrystalline solids, and General discussions] (Information: A. M. Cruickshank, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island 02881)

July 16-18; Pasadena, California. *4TH NATIONAL CONFERENCE ON ELECTRON MICROPROBE ANALYSIS*

July 21-25; Meriden, New Hampshire. *GORDON RESEARCH CONFERENCE, CHEMISTRY AT INTERFACES* [Topics: Molecular beams, Interfacial dynamics, and Short topics and discussions] (Information: A. M. Cruickshank, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island 02881)

July 27-August 1; Haifa, Israel, *QUANTITATIVE RELATION BETWEEN PROPERTIES AND MICROSTRUCTURE* [sponsored by International Metallographic Society and other organizations] (Information: Dr. A. Rosen, Department of Materials Engineering, Technicon City, Haifa, Israel)

August 4-8; Meriden, New Hampshire. *GORDON RESEARCH CONFERENCE, SOLID STATE STUDIES IN CERMICS* [Topics: Bonding models, Interatomic forces in oxides, Mossbauer studies, Paramagnetic states, Neutron diffraction, Optical properties, Ramau studies, and Band structure and physical properties] (Information: A. M. Cruickshank, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island 02881)

August 6-8; Denver, Colorado. *18TH ANNUAL DENVER CONFERENCE ON APPLICATIONS OF X-RAY ANALYSIS* [papers invited on any aspect of x-ray analysis] (Information: Dr. J. B. Newkirk, Metallurgy Division, Denver Research Institute, University of Denver, Denver, Colorado 80210)

August 11-13; Gaithesburg, Maryland. *ACCG CONFERENCE ON CRYSTAL GROWTH,* sponsored by American Committee for Crystal Growth and National Bureau of Standards [Topics: Impurity distribution in crystal growth, New results in vapor phase growth, New results in melt and solution growth, Polymer and molecular crystals, and Dendrites, Eutectics, and Morphological stability] (Information: C. S. Sahagian, Air Force Cambridge Research Laboratories, L. G. Hanscom Field, Bedford, Massachusetts 01730)

August 13-21; Buffalo, New York. *INTERNATIONAL UNION OF CRYSTALLOGRAPHY 8TH GENERAL ASSEMBLY AND CONGRESS* (see also August 23-27 meeting at Buffalo, below)

August 18-22; Tilton, New Hampshire. *GORDON RESEARCH CONFERENCE, THIN FILMS* [Topics: Formation and Diffusion induced changes] (Information: A. M. Cruickshank, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island 02881)

August 23-27; Buffalo, New York. *SYMPOSIA AT STONY BROOK AND UPTON* (Information: Mrs. U. Fiess, Congress Headquarters, c/o State University of New York at Stony Brook, Stony Brook, New York 11790)

August 23-27; Lehigh University. *THE NATIONAL SYMPOSIUM ON FRACTURE MECHANICS* [Includes half-day lectures by an authority in the field and papers on research and advanced applications] (Information: Mrs. Barbara DeLazaro, Del Research Corporation, 427 Main Street, Hellertown, Pennsylvania 18055)

TECHNICAL MEETINGS CALENDAR

August 25-28; Stanford, California. *SCIENCE OF SUPERCONDUCTIVITY, INTERNATIONAL CONFERENCE* [sponsored by Air Force Office of Scientific Research] (Information: Lt. Col. R. A. Houidobre, Air Force Office of Scientific Research (SRPS), 1400 Wilson Boulevard, Arlington, Virginia 22209 or Prof. W. M. Fairbank, Stanford University, W. W. Hansen Laboratory of Physics, Stanford, California)

August 25-29; New Hampton, New Hampshire. *GORDON RESEARCH CONFERENCE, SCIENCE OF ADHESION* [Topics: Adhesion systems and their mechanisms, Fracture mechanics, Surface chemistry, Composites, and Specific systems] (Information: A. M. Cruickshank, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island 02881)

August 25-29; Newark, Delaware. *INTERNATIONAL CONFERENCE ON LUMINESCENCE* [cosponsored by International Union of Pure and Applied Physics and American Physical Society] (Information: Program chairman, R. B. Murray; conference chairman, Fred Williams, both of department of physics, University of Delaware)

August 26-29; St. Paul, Minnesota. *ELECTRON MICROSCOPY SOCIETY OF AMERICA 27TH ANNUAL MEETING* (Information: E. C. Shaffer, Central Research 3M Company, 2301 Hudson Road, St. Paul, Minnesota 55119)

September 2-6; Columbus, Ohio. *24TH ANNUAL SYMPOSIUM ON MOLECULAR STRUCTURE AND SPECTROSCOPY* (Information: K. Narahari Rao, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210)

September 3-6; Toronto, Canada. *INTERNATIONAL COMMISSION ON GLASS ANNUAL MEETING* (Information: Mr. T. A. Tinmuth, c/o Consumers Glass Company Ltd., 249 Kipling Avenue South, Toronto 18, Ontario, Canada)

September 8-10; Warwick, New England. *MEETING ON ELECTRICAL AND MAGNETIC CERAMICS* (Information: British Ceramic Society, Basic Science Section, University of Warwick)

September 9-10; Rochester, New York. *3RD SYMPOSIUM ON THE DEPOSITION OF THIN FILMS BY SPUTTERING* [sponsored by University of Rochester and Bendix Corp.'s scientific instrument and equipment division, University of Rochester] (Information: Robert K. Lohwater, Bendix Corporation, 1775 Mt. Read Boulevard, Rochester, New York 14603)

September 9-11; Seattle, Washington. *1969 NATIONAL SAMPE TECHNICAL CONFERENCE* (Information: Program chairman M. A. Disotell, Boeing Aircraft Company, P. O. Box 707, Renton, Washington 98055)

September 9-13; Rolla, Missouri. *SMALL ANGLE X-RAY SCATTERING CONFERENCE*, University of Missouri (Information: Norbert J. Kreidl, Ceramic Engineering Department, University of Missouri-Rolla, Rolla, Missouri 65401)

September 16-19; Rolla, Missouri. *CONFERENCE ON SMALL-ANGLE X-RAY SCATTERING IN GLASSES AND HIGH-TEMPERATURE MATERIALS*, University of Missouri

September 24; Montreal, Quebec, Canada. *JOINT AIChE-CSChE-IChE MEETING ON STRUCTURAL COMPOSITES FROM WHISKERS, FILAMENTS, FLAKES AND FILMS*

October 6-10; Anaheim, California. *SOCIETY FOR APPLIED SPECTROSCOPY, 8TH NATIONAL MEETING* (Information: W. T. Barnes, General Dynamics, Pomona Division, P. O. Box 2507, Plant Mail Zone 6-56, Pomona, California 91766)

October 13-16; Philadelphia, Pennsylvania. *AMERICAN SOCIETY FOR NONDESTRUCTIVE TESTING, ANNUAL NATIONAL CONFERENCE* (Information: ASNT, 914 Chicago Avenue, Evanston, Illinois)

October 19-23; San Francisco, California. *AMERICAN SOCIETY FOR INFORMATION SCIENCE 32ND ANNUAL MEETING* (Information: Dr. C. Bourne, Programming Services, Inc., 493 Middlefield Road, Palo Alto, California 94301)

October 20-24; Anaheim, California. *AMERICAN INSTITUTE OF AERONAUTICS AND ASTRONAUTICS SIXTH ANNUAL MEETING AND TECHNICAL DISPLAY* (Information: 1290 Sixth Avenue, New York, New York 10019)

October 21-24; Columbus, Ohio. *FIRST INTERNATIONAL CONFERENCE ON QUALITY CONTROL* (Information: American Ceramic Society, 4055 N. High Street, Columbus, Ohio 43214)

NEW COMPILATIONS BY DCIC

Ceramic-Armor Technology, DCIC Report 69-1, Part I, Proceedings of Symposium, 21 articles, 124 pages, Edited by V. G. Dunleavy and W. H. Duckworth, and Part III, Bibliography, 270 references, compiled by E. R. Smith (May, 1969).

The field of ceramic-armor technology is one of the most rapidly growing areas of ceramics, spurred by the Department of Defense need for tough, lightweight armor, either opaque or transparent, for many applications. To help organize efforts in this field and to provide a unified view of the technology involved, a symposium was held in January of 1969 at the Columbus Laboratories of Battelle Memorial Institute under the joint sponsorship of the Air Force Materials Laboratory and the Defense Ceramic Information Center. These DCIC reports contain the unclassified papers presented at this symposium and a bibliography of recent reports and papers published in this area.

The proceedings of this symposium provide the only available coherent, up-to-date review of the theoretical and engineering basis of ceramic armor technology and its present state of development. Likewise, the bibliography is the only available compilation of recent references. Together they are indispensable as introductions or source works for anyone who wants to participate in the growth of this important and interesting field of ceramic application.

Parts I and III are unclassified and can be obtained only from DCIC. Part II, the classified proceedings, will soon be available from the Defense Documentation Center.

The price for Parts I and III together is $15.00. These parts cannot be ordered separately. Make out check to Battelle Memorial Institute and send request with remittance to:

Defense Ceramic Information Center
Battelle Memorial Institute
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201.

Summary of Papers—Ninth Biennial Conference on Carbon, June 16-20, 1969, cosponsored by The American Carbon Committee, 218 pages.

DCIC has compiled extended abstracts of the technical papers presented at the 9th Carbon Conference that provide significant results and conclusions or precisely delineate the content of the papers. This compilation reflects current advances in carbon/graphite science and technology.

The abstracts (159 papers) are arranged alphanumerically according to conference session subjects. Author and corporate author indexes also are provided.

This document is available at a nominal cost from

The American Carbon Committee
102 Mineral Industries Building
The Pennsylvania State University
University Park, Pennsylvania 16302
Attn: Dr. P. L. Walker, Jr.

CARBON/GRAPHITE FIBER

INTRODUCTION

Although glass fiber-reinforced resins have been used widely for several decades, the relatively low stiffness of these materials has prevented their application to many aerospace structural elements. Advances in fiber technology during the last five years, however, have produced filaments that are five to seven times stiffer than glass fibers. These new filaments have been used to develop fiber-reinforced composites which are not only stiffer than fiber glass-reinforced resins, but also offer weight reductions of 25 - 50% compared to conventional materials. For example, boron, the first of the high-performance filaments, has an elastic modulus of 60 million psi. A unidirectionally boron fiber-reinforced resin-matrix composite can have an elastic modulus two to three times greater than that of aluminum, yet be about 25% lighter. Compared to titanium, a boron fiber-reinforced resin could be equally strong and stiff but would weigh only half as much.

Of the many filamentary materials other than boron which have been investigated as reinforcements, carbon/graphite* fibers are rapidly emerging as the leading high-performance filaments. However, many composite fabricators believe that no single filament will satisfy all design requirements and that boron, graphite, and some of the other advanced filaments will always be used because of the different and unique properties that each fiber may impart to a composite. It seems likely, however, that economics will always be a limiting factor in fiber selection and current technology suggests that graphite fibers have greater potential for more economic production than does boron.

Recent developments in Great Britain, Japan, and the United States are demonstrating the properties and the performance potential offered by graphite fiber-reinforced resins. The purpose of this paper is to review briefly the status of graphite fibers including current applications for graphite fiber-reinforced composites.

BACKGROUND

Graphite fiber is not a recent development. Edison and Maxim (U.S. Patents 223, 898, and 230,309) produced it in small quantities late in the 19th century for use as incandescent lamp filaments. However, the first concentrated efforts to produce continuous graphite fibers were probably made by a research group at Wright-Patterson Air Force Base in the late 1950's. During the same period, graphite whiskers, produced in a d.c. arc (U.S. Patent 2,957,756), clearly demonstrated the strength potential that existed in fibrous graphite. Tensile strengths of three million psi reported from this work undoubtedly stimulated other groups active in graphite filament research. Late in 1961, Shindo [1] and co-workers described the preparation of continuous graphite fibers from polyacrylonitrile (PAN) precursor, but Watt et. al. [2] in 1963 were the first group to make high-strength, high-modulus graphite fibers. Developments since than have been extremely rapid and recent announcements of graphite fibers having tensile strengths of 400,000 psi and elastic modulus of 80 million psi [3] are approaching the goal of one million psi tensile strengths and 100 million psi elastic modulus set by British scientists [4]. In fact, laboratory material meeting the 100 million psi modulus goal has already been reported in this country and abroad [5], but commercially available fibers have properties considerably below this figure.

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*Although carbon/graphite is more descriptive, the term "graphite" will be used in reference to these fibers throughout this paper. Definitions for both carbon and graphite can be found in Reference 13.

AVAILABILITY

High-strength, high-modulus graphite fibers are now produced commercially by Courtaulds, Ltd., HITCO, Morganite Research and Development, Ltd., and Union Carbide Corporation. Celanese Corporation and other domestic and foreign organizations are also active in this technology but have not announced commercial quantities. Rolls-Royce, Ltd. also manufactures graphite fibers but uses the entire production in-house.

The three British firms were licensed by the National Research Development Corporation to produce fibers according to the process developed by Watt et al. of the Royal Aircraft Establishment who pioneered graphite fiber work in England. In a move to exploit the American market, NRDC arranged licensing agreements between the three British firms and three firms in the United States [6]. Although direct licensing through NRDC would have been more profitable, this arrangement was made on the basis that a full flow-back of American experience would return to England. Courtaulds, Ltd. and Hercules, Inc. reportedly have an agreement whereby the latter has an exclusive license to sell Courtaulds, Ltd. fiber in the United States with an option to manufacture it later. MRD, Ltd. and Whittaker Corp. have announced the formation of a joint company in Los Angeles which will manufacture graphite fibers by the British process. Rolls Royce, Ltd. and Lockheed Aircraft Company have also reportedly just signed a technical collaboration agreement which gives Lockheed the British fiber technology for which in return, Lockheed will provide composite impregnation feedback and certain manufacturing techniques relevant to gas turbine applications [7].

Recent news releases indicate that these licensing agreements have caused quite a furor in England. The concern of many persons is that the current British leadership in graphite fiber technology could be lost. So great is the concern that the Select Committee of the House of Commons on Science and Technology is investigating the licensing agreements [6, 8, 9].

All of the graphite fiber suppliers, domestic and foreign, offer various grades covering a wide range of properties. This information, together with current prices, is shown in Table I. Recent predictions [10, 11] estimate price reductions based on the economics of large scale production to as low as $12 a pound by the early to mid 1970's.

FIBER STRUCTURE AND PROPERTIES

Although graphite fibers are polycrystalline, they exhibit a high degree of preferred orientation which polycrystalline materials do not generally possess. The preferential arrangement of the hexagonal graphite crystallites parallel to the fiber axis is responsible for the high strength exhibited by some of the currently available fibers [12-15]. Preferred orientation is achieved by applying stress to the precursor at some stage in its thermal decomposition. However, various precursors require different treatment as Bacon [16] points out: acrylic precursors or other polymers possessing a continuuous "backbone" of carbon atoms may be stretched in the early stages of heating because the strength of such fibers is not seriously degraded by pyrolysis. With rayon or other cellulosic fibers, the necessity for removal of oxygen linkages in the chain precludes the application of significant tension to the filament early in pyrolysis because fiber strength is initially lowered. Rayon precursors may, however, be stretched during the later stages of heating. The effect of stress graphitization on the tensile strength and elastic modulus of British-made (Pan precursor)

TABLE I: COMMERCIALLY AVAILABLE GRAPHITE FIBER

SUPPLIER	Diameter (Microns)	Density (D) (lbs/in^3)	Strength (S) (10^3 psi)	Modulus (E) (10^6 psi)	S/D (10^6 in)	E/D (10^6 in)	Cost ($/lb)
Courtaulds, Ltd*.							
Type HM	7.5	0.070	250-350	50-60	3.6-5.0	715-850	260-450**
Type HT	7.5	0.068	300-400	32-40	4.4-5.9	470-590	260-450**
Type A	7.5	0.067	250-300	25-32	3.7-4.5	370-480	260-450**
Morganite R&D, Ltd.*							
Type I	7.5	0.072	200-300	55-65	2.8-4.1	760-900	425-595**
Type II	7.5	0.063	350-450	35-45	5.6-7.1	560-710	425-595**
HITCO							
HMG 25	7.4	0.054	150	25	2.8	460	250***
HMG 40	7.4	0.061	250	40	4.1	650	325
HMG 50	6.9	0.065	300	50	4.6	770	350
Union Carbide Corp.							
Thornel 25	7.4	0.051	180	25	3.5	490	325
Thornel 40	6.9	0.056	250	40	4.5	710	325
Thornel 50	6.6	0.059	285	50	4.8	845	350
Thornel 50-S	6.6	0.060	220	50	3.8	834	400
Thornel 75	6.4	0.068	375	75	5.5	1100	****

* Courtaulds, Ltd. Markets in USA through Hercules, Inc.

* Morganite R&D, Ltd. markets in USA through Whittaker Corp.

** Lower price for long staple; higher price for continuous fiber. Both prices include surface treatment.

*** Add $194 to each price for surface-treated fiber.

**** Laboratory quantities, prices on request.

fiber is shown in Figures 1, 2, and 3 [17]. The dependence of tensile strength on the elastic modulus of American-made graphite fiber also prepared by a precursor stretching method is shown in Figure 1 [18].

The exact procedure for converting an organic precursor fiber into a high-strength, high-modulus graphite fiber is, of course, proprietary and rather complex. However, a simplified schematic arrangement of a basic process is shown in Figure 5 [19].

The relationship between the structure and properties of graphite fibers has been the subject of much study. Brydges et al. [12] suggest that the elastic behavior which these fibers exhibit up to fracture results from the restriction of dislocation motion imposed by the small crystallite size. These workers further suggest that a graphite fiber with perfect orientation of its crystallites would possess an elastic modulus approaching 160 x 10^6 psi, compared to an elastic modulus of 130 x 10^6 psi exhibited by an a-axis graphite single crystal. The large difference can be attributed, they say, to the constraints which exist between the crystallites. Ruland [15] studied three models in an attempt to determine the type of cross linking which holds the graphite crystallites together as a possible explanation for the high modulus. He reports, however, that further work is necessary before a final conclusion can be made. Ezekiel [13] did not observe any correlation between interlayer spacing and tensile strength or modulus of elasticity in graphite fibers produced from rayon-derived yarn. Gibson and Langlois [20] found that graphite crystallites appear to be more densely packed in the structure of fibers having an elastic modulus of 50 x 10^6 psi than in fibers having a modulus of 25 x 10^6 psi.

Surface and internal flaws have been observed in graphite fibers made from PAN precursor and have a pronounced effect on fiber tensile strength [14]. Apparently the surface defects can be removed readily but the internal flaws appear to be intimately related to the presence of flawed structures in the precursor.

In summary, it appears that while much progress has been made in determining structure-property relationships in graphite fibers much remains to be done in order to understand fully the phenomena that control fiber structure and consequently the fiber properties. It is reasonable to assume that a better understanding of precursors and additional refinements of the carbonization-graphitization stages of production will result in improved fibers, or perhaps completely different precursors may be found.

RESIN-MATRIX COMPOSITES

Early efforts to reinforce resins with graphite fibers were disappointing because of the low interlaminar shear strengths obtained. This is undesirable because low shear strength allows fiber microbuckling and results in compressive failure at low stresses. Shear strengths as low as 2300 psi were reported for early graphite fiber-reinforced epoxy composites [21]. Poor fiber-matrix bonding was identified as the cause for this behavior and fiber surface treatments were investigated as a means for overcoming this deficiency. Herrick [22, 23] used an acid etch followed by a polymeric coating on the fiber and obtained shear strengths as high as 7500 psi. Composite shear strengths can also be improved by subjecting the fibers to an air oxidation treatment [24]. As a result of these and other studies, shear strengths ranging from 8000 to 10,000 psi are now being obtained [25] and are considered adequate for many applications, although higher values can be obtained in other composite systems (e.g. boron-epoxy).

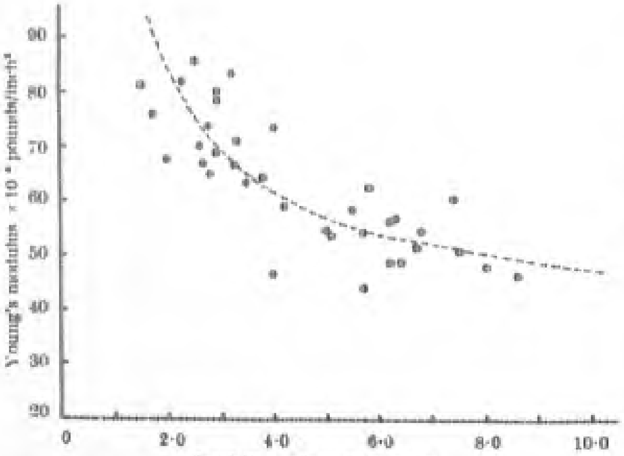

Fig. 1. Possible relationship of Young's modulus to c-axis orientation is shown for the unstretched controls (○) and the stress graphitized samples (●).

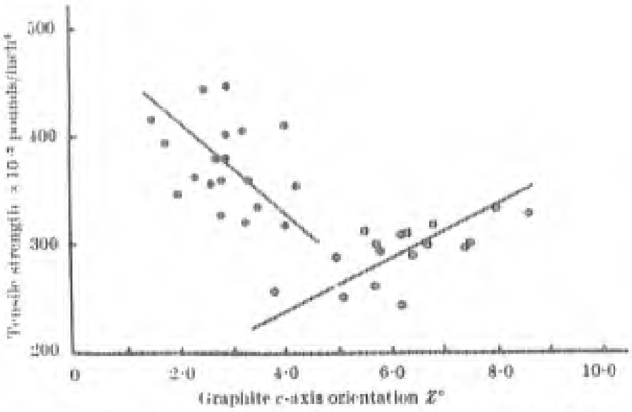

Fig. 2. The relationship between carbon fibre strengths and preferred orientation is transformed by stress graphitization; the inverse relationship for the unstretched fibre (○) is converted to one of direct proportionality for the stretched fibre (●).

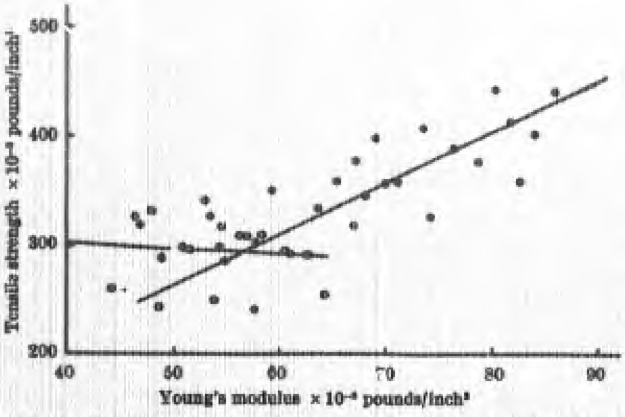

Fig. 3. Tensile strength is almost independent of Young's modulus for unstretched fibre (○) at these heat treatments. The stretched fibre (●) shows a linear dependence.

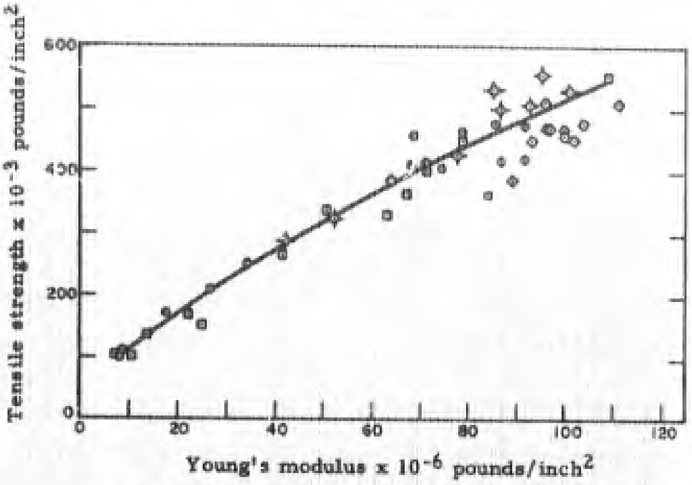

Fig. 4. Dependence of tensile strength on Young's modulus for an American-made fibre.

Figures 1, 2, and 3 used with permission of publisher [17]

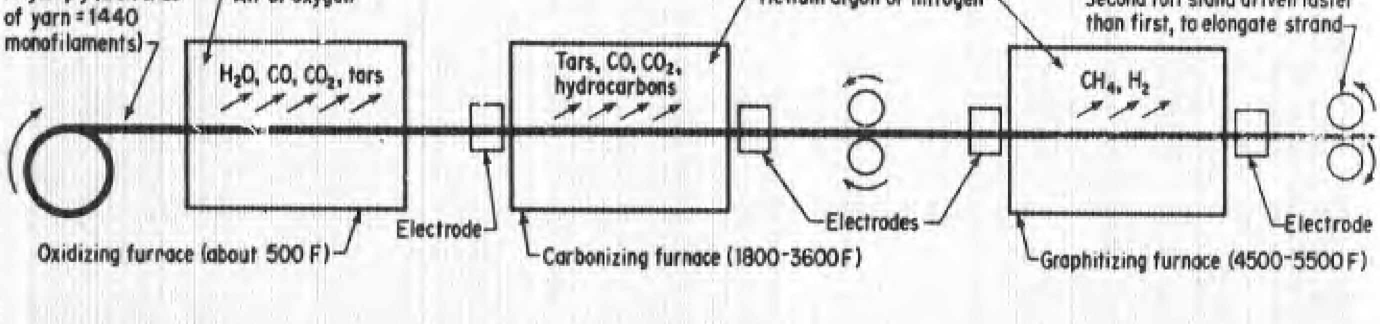

Fig. 5. Schematic diagram of carbon fiber production [19] (Used with permission of publisher)

A rather unusual technique for improving composite shear strength has been achieved by growing silicon carbide whiskers on graphite fiber surfaces perpendicular to the axis of the fiber. Composites of epoxy resin containing "whiskerized" fibers had shear strengths ranging from 6000 - 18,000 psi. When tested, the composites exhibited failure ressembling that of brittle isotropic materials, instead of breaking in the usual shear mode [26].

It appears that, by various surface treatments to the graphite fiber, the shear strength of resin-matrix composites can be improved considerably over that reported several years ago. Unfortunately, these treatments usually impair the fiber tensile strength and consequently have a detrimental effect on other properties of the composite.

The very small (7-10 micron) diameter of currently available graphite fibers makes them amenable to fabricating methods developed for glass fiber-reinforced resins. Like glass (and all small diameter fibers), graphite fibers must be kept under some tension during fabrication to obtain uniform alignment, maximum volume fraction, and consequently maximum properties in the composite. Fabricating conditions can, of course, affect the kinds of applications for which a material is best suited. Thus, composites reinforced with small-diameter fibers (glass, graphite, etc.) perform better in applications where loads are predominately tensile, than under compressive loads. Composites reinforced with large-diameter fibers perform better under the latter conditions.

METAL -MATRIX COMPOSITES

The ability of graphite to withstand extremely high temperatures without loss of strength or stiffness would seem to qualify this material as an ideal reinforcement for metals. However, the highly reactive nature of graphite in contact with many metals and the very small diameter of graphite fibers combine to pose serious problems to fabricators of graphite fiber-reinforced metals. Limited reaction between the fibers and the matrix could be beneficial in that it might improve the fiber-matrix bond and provide a barrier against further interaction [27]; however, the state-of-the-art for graphite-metal systems has not advanced to the point where limited fiber-matrix interaction can be assured.

Composites of graphite fiber in cobalt and in nickel have been made by swaging and hot isostatically pressing aligned bundles of yarn which had been plated with these metals [28]. Exposure of the graphite fiber-nickel composites to 1000°C for 100 hours in a nitrogen atmosphere had no deleterious effect on the composite microstructure. However, nickel-coated graphite fibers heated in vacuum for 24 hours at 1100°C were found to recrystallize [29]. More recent compatibility studies between graphite fibers and Al, Ni, Co, Cu, Pt, and Ni-Cr confirmed the recrystallization tendency of the fibers [27]. All of these studies strongly indicate the need for applying protective coatings to graphite fibers when they are to be used in metal matrices. One source [6] reports that alumina and certain other oxides are promising candidates for this purpose.

There is no doubt that the potential payoff of graphite fiber-reinforced high temperature metals is outstanding. Calculations based on a 60 v/o graphite fiber-reinforced cobalt composite show that on a strength-to-weight basis such a material would be four times stronger than Inconel at 1800°F [30]. Realistically though, considerably more development and evaluation studies must be conducted to determine the degree to which the theoretical potential can be matched experimentally.

CERAMIC–MATRIX COMPOSITES

Graphite fiber-reinforced ceramics seem attractive for several specialized applications. For example, where a ceramic material is desirable but where fracture toughness and thermal shock resistance are important, fiber reinforcement can improve these properties. In general, though, fiber reinforced ceramics are not suggested as widespread substitutions for present metallic parts nor as alternates for advanced filament-reinforced resins or metals. However, fiber reinforced glass composites have been considered as the high temperature analog of, and perhaps the answer to present studies on fiber-reinforced high-temperature resin-matrix composites.

Graphite fiber-reinforced graphite is available commercially and holds great promise for certain high-temperature applications. Unfortunately, these composites exhibit shear failure at the fiber-matrix interface which limits their utilization in many application [31]. Recent studies indicate that improvement of the fiber-matrix bond is possible and should eliminate this undesirable behavior.

Three-dimensional composites consisting of graphite fibers in a graphite matrix have been prepared. Preliminary data indicate that this material possesses excellent mechanical strength and is both impact and thermal shock resistant [32].

Bowen [33] reports that the incorporation of continuous high-strength, high-modulus graphite fibers in hot-pressed magnesia appreciably increases the work of fracture of the composite compared to the unreinforced magnesia. Amorphous silica reinforced with 50 v/o aligned graphite fibers exhibited elastic modulus values ranging from 22 - 35 x 10^6 psi. The composites were thermally shocked by being heated to 1200°C, then quenched in water. None of the samples cracked and when they were subsequently tested at room temperature in three-point bending, their mechanical properties were found to be the same as those samples which had not been thermally shocked [34].

APPLICATIONS

Rapid progress in the development and design of graphite fiber-reinforced resin composites has resulted in the application of these materials to prototype hardware for aircraft and several other uses. The development of metal-matrix and ceramic-matrix graphite fiber composites is considerably less advanced.

Northrop Aviation Company has been conducting in-flight tests on an 8 in. x 5 in. graphite fiber-epoxy composite section of the leading edge of an F-5 fighter aircraft. Based on these and other data, Northrop plans to proceed with experimental wing flaps nine feet long [4].

Rolls-Royce, Ltd. has been producing a graphite fiber reinforced epoxy known as Hyfil for almost two years. In collaboration with BOAC, twenty Conway engines are being progressively fitted with blades of this material throughout the first stage of the low pressure compressor rotor [11]. In May 1968, VC 10 aircraft on African routes began using the material in one of their four engines. By 1971, when the Lockheed 1011 enter service, Rolls-Royce, Ltd. should have about 140,000 hours of data on the in-flight performance of the Hyfil blades. Limited experience indicates that erosion might be a problem, but the British firm feels it has solved this situation by plating the blade leading edge with nickel [35].

Glass Fiber Engineering, Ltd. replaced part of the glass fiber with graphite fiber in a racing car body and found that the weight was reduced from 140 pounds to about 80 pounds. The extra stiffness of the graphite fiber reinforced polyester body also resulted in improved performance at high speed [36].

The foregoing examples are only a few of the applications in which graphite fiber-reinforced resins appear to be showing great potential. Numerous other uses have been predicted. Phillips [37] believes that graphite fiber-reinforced resins will become the preferred materials of construction where strength/weight is important and that they will find wide application in jet engines, industrial fans and compressors, hovercraft propellers and ducting, and helicopter rotor blades. Hom and Couch [38] suggest that high-modulus fibers such as graphite are attractive reinforcements for pressure vessel hulls in future hydrospace applications.

Graphite fiber-reinforced resins may play an important role in bearing technology. A variety of thermosetting and thermoplastic resins has been reinforced with randomly oriented, chopped graphite fibers and their friction and wear properties examined. Results show that both the coefficient of friction and the wear rate, during continuous sliding against steel, are reduced to levels which are almost independent of the matrix material [39]. Another study of graphite fiber-reinforced polyester resin revelaed that both coefficient of friction and wear rate reductions were maximum when the fiber axes were oriented normal to the sliding surface [40]. A similar study of metal-matrix composites found no change in the coefficient of friction but observed reduced wear rates at low temperatures. At temperatures near 500°C, the wear rates no longer showed reductions [41].

Gunston [11] list the following as some of the potential applications for graphite fiber-reinforced materials; a cable for electric grid transmission lines consisting of graphite fibers (50-50) in an oxide-free aluminum, prosthetic devices, electronic aerials, hydrofoil foils, skis, fishing rods, golf clubs, yacht masts, and nuclear construction.

Although it is still too early to establish the full potential of graphite fiber-reinforced materials, the performance of these first generation composites is very encouraging. When this new technology advances to the degree of refinement that exists in glass fiber-reinforced resins, present limitations in the materials horizon should be extended considerably.

SUMMARY

High-strength, high-modulus graphite fibers are available commercially from several suppliers at prices which are rapidly approaching a level competitive with boron. The lower density and higher modulus of graphite fibers presents a definite improvement in specific properties over boron, filaments, and considerably over glass.

Additional study of the precursors as well as the carbonization-graphitization stages of manufacturing could result in commercially available graphite fibers with tensile strength approaching one million psi and elastic modulus over one hundred million psi.

Some of the pros and cons of graphite fiber-reinforced resins are beginning to emerge as more experience with hardware accumulates. Overall, this new information supports the view that graphite fibers will probably assume the leadership among the new high-performance reinforcements. Some of the principle reasons for this view are:

1. Potential for low-cost fibers when the production level increases to several hundreds of thousands of pounds or more per year.
2. The small diameter of graphite fibers lends itself to composite fabrication methods developed by the glass fiber-reinforced resin industry.
3. Compared to boron or glass fibers, graphite is less hard, therefore, composites containing graphite fibers should be easier to machine or trim.

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INFORMATION
on
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The overall response was about 60%. This figure seems small; nonresponse presumably means that the recipient is no longer interested in receiving the CAB, but the responses received tend to express a favorable opinion of the Bulletin. The contrast is probably due to a poorly developed distribution list, rather than a poorly received Bulletin.

Even though most readers are willing to pay for the CAB, it seems unwise to market it in the very near future. The potential return, less than $2000, seems far too small to justify the narrowing of information dissemination that would result.

DCIC thanks all who responded to the questionnaire. All suggestions for improvement will be considered carefully.