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Dusts and Residues from Machining and Incinerating Graphite/Epoxy Composites A Preliminary Study

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A Preliminary Study

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by

Jack Wagman, Henry R. Berger, John L. Miller, and William D. Conner

Emissions Measurement and Characterization Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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PREFACE

Environmental protection depends on efforts to detect, identify and quantify specific pollutants and to assess their effects. As part of this Laboratory's research to determine the relationships between emissions of pollutants from all types of sources and air quality, the Emissions Measurement and Characterization Division conducts studies to identify and elucidate the chemical and physical nature of pollutants emitted to the atmosphere and develops methods and instrumentation for their measurement.

Projections of greatly increased use of carbon fiber composites in aerospace, automotive and industrial applications and in a variety of consumer products give rise to concern about future environmental problems that may be posed. Releases of carbon fibers that may occur in large scale manufacturing and in the ultimate disposal of carbon composite materials could constitute significant hazards because of the susceptibility of electronic and electrical power equipment to damage from exposure to these highly conducting fibers. The potential health hazard of these fibers is of less concern at this time. This preliminary study of dusts and debris from the machining and incineration of graphite/epoxy composites is intended as a prelude to the research program being conducted by the U. S. Environmental Protection Agency to characterize carbon fibers released during manufacturing, handling and disposal of carbon fiber products, develop measurement technology needed for source and ambient air monitoring of released carbon fibers, and develop safe methods for disposal of discarded consumer goods and industrial scrap.

ABSTRACT

Preliminary laboratory experiments were carried out to obtain some information on the nature of potential carbon fiber emissions resulting from the machining and incineration of graphite/epoxy composites. Examination of residues by scanning electron microscopy following exposure of graphite fiber products in a laboratory furnace showed the high resistance of graphite fibers to combustion at temperatures up to 1000°C. Resins and binders in the composites are destroyed rapidly at elevated temperatures, but one can predict that the disposal of composite waste materials by conventional refuse incineration would result in the release of large amounts of both intact and partly degraded and thinned graphite fibers. In other experiments, dusts generated by sawing and drilling of graphite/epoxy composites contained large numbers of fibers free of the resin matrix and generally about 50 to 100 μm in length. There was also evidence of longitudinal cleavage of some fibers by sawing; the potential thus exists for the formation of more respirable fiber fragments with diameters smaller than those (about 6 to 8 μm) established in the fiber manufacturing process.

INTRODUCTION

The development of high strength carbon and graphite fibers in the 1950's followed by their embedment in resin matrices resulted in the production of materials called composites with highly desirable properties. Attracted by their light weight and high strength, the aircraft industry has found steadily increasing applications for these composites in various structural components of military and commercial aircraft. The necessity for achieving improved fuel economy in passenger cars is expected to induce the automotive industry to become by far the largest user of graphite composites, and projected decreases in graphite fiber production costs are expected to lead to increased use of fiber composites in industrial applications, sporting goods and other consumer products.

Evidence has been obtained that carbon fibers such as those used in advanced composites can cause failures in exposed electrical, electronic, and power equipment. For example, the burning of carbon composites can release carbon fibers to the environment and may result in damage to electronic or electrical equipment. While current usage of carbon composites poses only a very limited hazard, projected increases in usage could result in significant hazard. A NASA Technical Memorandum (1) outlines the Federal Government's plan involving many agencies to study all aspects of this and other potential problems associated with carbon fibers. As its part of this plan, the U. S. Environmental Protection Agency has initiated a program with the following objectives: (a) to determine the concentration and size distribution of carbon fibers released during manufacturing, handling, and disposal of carbon fiber products; (b) to develop measurement technology for monitoring carbon fiber emissions; (c) to assess the transport and deposition of carbon fibers in the atmosphere and relate ambient concentrations to source emission rates; (d) to assess the likelihood of damaging releases of carbon fibers from conventional solid waste processing, resource recovery, and disposal technologies; and (e) to modify these technologies or develop new technology to safely dispose of carbon fiber containing materials.

The program outlined above will be carried out primarily through contracts, grants and/or interagency agreements. Since extramural research programs require significant lead times before they can be implemented, some preliminary experiments were carried out in this Laboratory, using available facilities and instrumentation, with the objective of obtaining a rough characterization of dusts and other debris resulting from the machining and incineration of graphite/epoxy composites. While these experiments involved only labortory simulations of actual or projected operations, it was felt that they could yield some useful information on the nature of potential carbon fiber emissions.

SUMMARY AND CONCLUSIONS

Examination of residues after exposure of graphite fibers and fiber/epoxy composites to elevated temperatures in a laboratory furnace demonstrate the high resistance of graphite fibers to combustion at temperatures up to 1000°C. Resins and binders in composites are destroyed rapidly but the fibers remain intact for significant periods even at 1000°C. Resistance of fibers to damage varies from product to product and probably depends on degree of graphitization. Damage is first observed in the form of dimpling and thinning of the fibers after exposure for some minutes at 1000°C. One can predict from these results that the disposal of graphite/epoxy composite waste materials by conventional refuse incineration would result in the release of large amounts of both intact and partly degraded graphite fibers.

Dusts generated by sawing or drilling of graphite/epoxy composites contain significant numbers of fibers free of the resin matrix. These fibers generally have lengths of about 50-100 μm. There is also evidence that sawing can cause longitudinal cleavage of the fibers, thereby making possible the generation of more respirable fiber fragments with diameters less than that (about 6-8 μm) determined in the fiber manufacturing process.

MATERIALS AND METHODS

Assorted samples of carbon fiber and carbon fiber composite materials were kindly provided by several manufacturers. The types of samples obtained are listed in Table I including the trade designations and some specifications given by the manufacturers. It can be seen that these samples included fibers with a broad range of physical properties in terms of tensile strength and elasticity, thus reflecting varying degrees of graphitization. Properties of composites are dependent not only on fiber characteristics but also on fiber surface treatment, type of resin matrix, proportions and geometry of the fiber-matrix combination, and resin curing procedure.

Scanning electron micrographs of typical carbon fiber production samples are shown in Figure 1. The fibers appear to be smooth circular cylinders with diameters varying from about 5 to 8 μm, though the actual cross-sectional morphology of different samples vary and include circular, elliptical and dogbone shapes. Some manufacturers expose fiber surfaces to a roughing etch to improve interlaminar sheer strength in the composite. Also, a sizing or coating of resin is often added to enhance the bonding capability of the fibers in the composite medium.

Our laboratory-simulated incineration process consisted of the use of a single-zone tube furnace, shown in Figure 2, to heat carbon fiber and fiber composite samples to temperatures up to 1000°C. Samples were placed in ceramic combustion boats which were inserted and heated within a quartz combustion tube. Temperature was monitored with a thermocouple. Following various combustion intervals, fibers were collected on glass fiber filters for microscopic analysis after becoming airborne by purge air circulated through the quartz tube. In some instances residues remaining in the combustion boats were also analyzed.

In other tests, samples of composite were subjected to cutting with a hacksaw blade and drilling with carbide-tipped drills in a press. Settled dust samples thus generated were collected for microscopic analysis.

Fiber residues and dusts were examined with a Bausch and Lomb light microscope and with an AMR-900 scanning electron microscope (SEM).

TABLE 1. TENSILE STRENGTH AND MODULUS OF CARBON FIBER SAMPLES[a]

Product Designation	Manufacturer	Tensile Strength (10^3 psi)	Tensile Modulus (10^6 psi)	Remarks
GY-705E	Celanese	270	75	surface treated, sized
Celion 6000	Celanese	400	34	surface treated, sized
Panex 1/4 CF	Stackpole	325	30	chopped form, sized for nylon resins
Panex 30	Stackpole	225[b]	18[b]	epoxy composite
Panex PWB-6	Stackpole			cloth, for high heat resistance
Magnamite AS3	Hercules	360	30	sized with epoxy resin
Magnamite A370-8H/3501-6	Hercules	90[b]	10.5[b]	8-harness satin-weave composite
Thornel 300 WYP 30 1/0	Union Carbide	360	34	surface treated, sized
Fortafil 3U (fiber)	Great Lakes Carbon	360	27	no surface treatment
Fortafil 3U (composite)	Great Lakes Carbon	190[b]	16[b]	60% fiber volume in epoxy
Fortafil 5 (fiber)	Great Lakes Carbon	400	48	no surface treatment
Fortafil 5 (composite)	Great Lakes Carbon	160[b]	23.5[b]	60% fiber in epoxy

[a] Manufacturer's data

[b] Composite properties

RESULTS

INCINERATION EFFECTS

Exposure of raw carbon fiber samples to temperatures of 200° to 220° C for 30 to 60 minutes caused little or no damage. As shown in Figure 3, there were no discernible changes in the appearance of the fibers when observed in the SEM. At a temperature of 1000° C, however, the fibers showed definite signs of degradation after a short period. Dimples or pits in the fibers appeared after 1 minute (Figure 4) and were deep and numerous after 3 1/2 minutes (Figure 5). A general thinning of the fibers even in undimpled portions was also noted.

When samples of carbon fiber composite in epoxy resin matrices were subjected to elevated temperatures, the epoxy matrix material was incinerated first, leaving the fibers virtually intact at temperatures of 300 - 600° C and delaying the degradation of fibers at 1000° C. Examination of composite samples after 5 minutes at 1000° C showed some charred remains of the epoxy matrix adhering to apparently unaffected fibers (Figure 6), as well as some fiber clusters completely free of epoxy residue with little, if any, significant damage to the fibers (Figure 7).

Another type of carbon fiber product subjected to incineration was a woven cloth (Panex PWB-6 manufactured by Stackpole) designed for high heat resistance. After exposure for 23 minutes at 1000° C, the cloth fibers were still in remarkably good condition (Figure 8) though showing very definite signs of damage including thinning and pitting.

MACHINING EFFECTS

Microscopic examination of dust generated by drilling a sample of composite (Fortafil 3U manufactured by Great Lakes Carbon) showed (Figure 9) the presence of free fibers in lengths mainly from about 50 to 100 μm in addition to particles of epoxy debris.

Dust from sawing another sample of composite (Magnamite A 370-84/3501-6 manufactured by Hercules) also contained free fiber fragments (Figure 10). These were generally shorter than those seen in drill dusts, and the micrographs also show evidence that some were cleaved longitudinally, probably along the graphitic planes.

DISCUSSION

This preliminary laboratory study has demonstrated the high resistance of graphite fiber products to combustion at temperatures up to 1000° C. There is no doubt that the disposal of graphite fiber composite waste materials by conventional refuse incineration would result in the release of airborne graphite fiber residues. Released fibers will be intact in some instances and partly degraded and thinned in others. The resistance of carbon fibers to incineration is dependent on their degree of graphitization. It is clear that the control of carbon fiber emissions from the incineration of waste composite materials will require either high efficiency fiber trapping or incinerator designs that permit more complete combustion of fibers.

Although free graphite fibers may be released by the sawing or drilling of composite materials, these generally have lengths less than 100 μm and are therefore likely to have a very low potential for causing electrical equipment failure. On the other hand, fibers released by these and other types of machining operations (cutting, grinding, etc.) are in a size range that requires an assessment of potential health hazards. Since most of the fibers generated have diameters (about 6-8 μm) that are predetermined in the fiber manufacturing process, their health effects are likely to be limited to skin, eye, and upper respiratory tract irritation. However, the evidence that longitudinal cleavage of fibers can occur requires that due consideration be given to the possible generation, during manufacturing operations, of significant numbers of smaller diameter fibers which can penetrate more deeply into the lungs and therefore constitute a greater respiratory hazard.

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1 Carbon Fiber Study. Technical Memorandum 78718, National Aeronautics and Space Administration, Washington, D. C. 20546, May 1978.

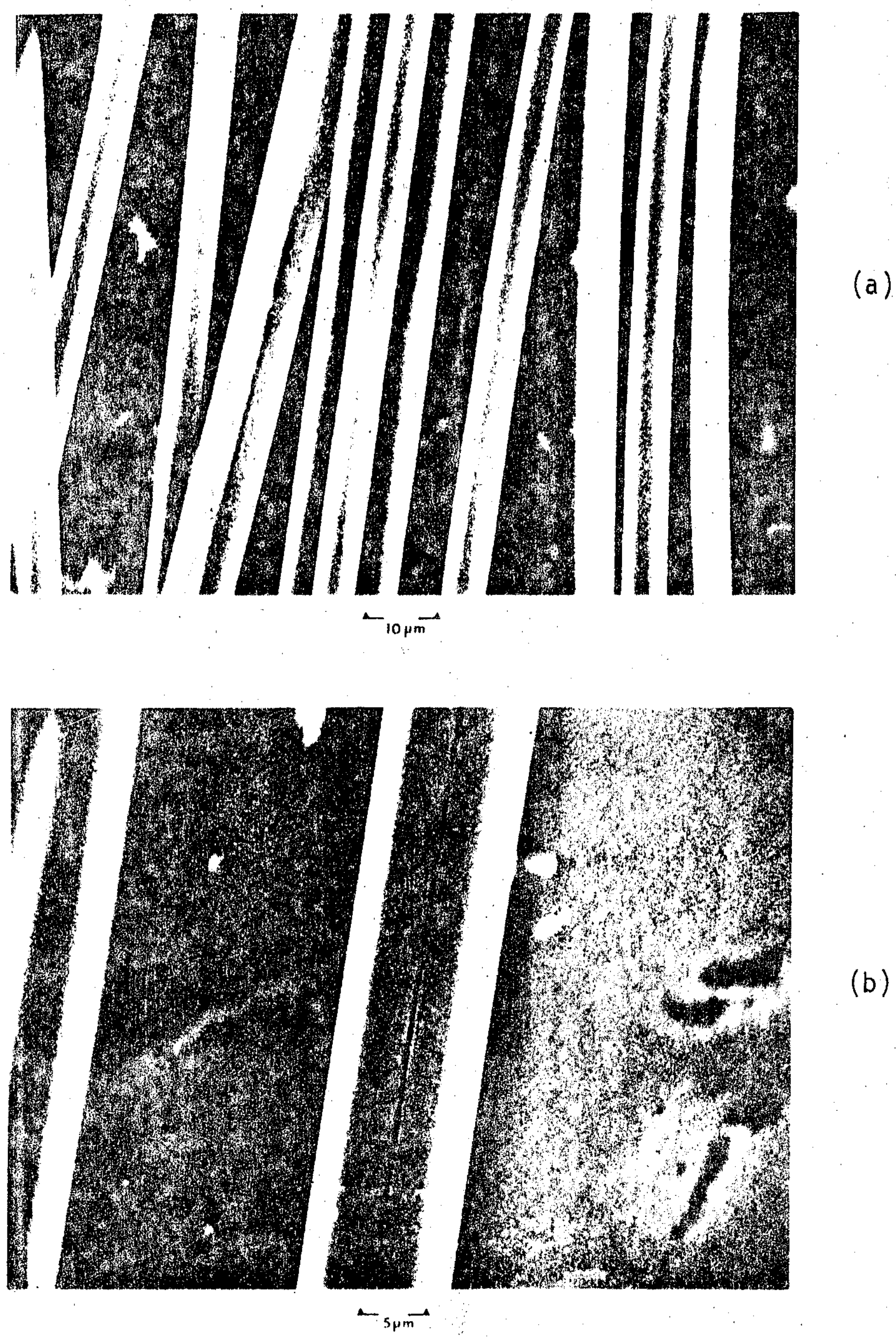


Fig. 1 SEM micrographs of carbon fiber samples: (a) Panex 1/4 CF (Stackpole); (b) Magnamite AS3 (Hercules).

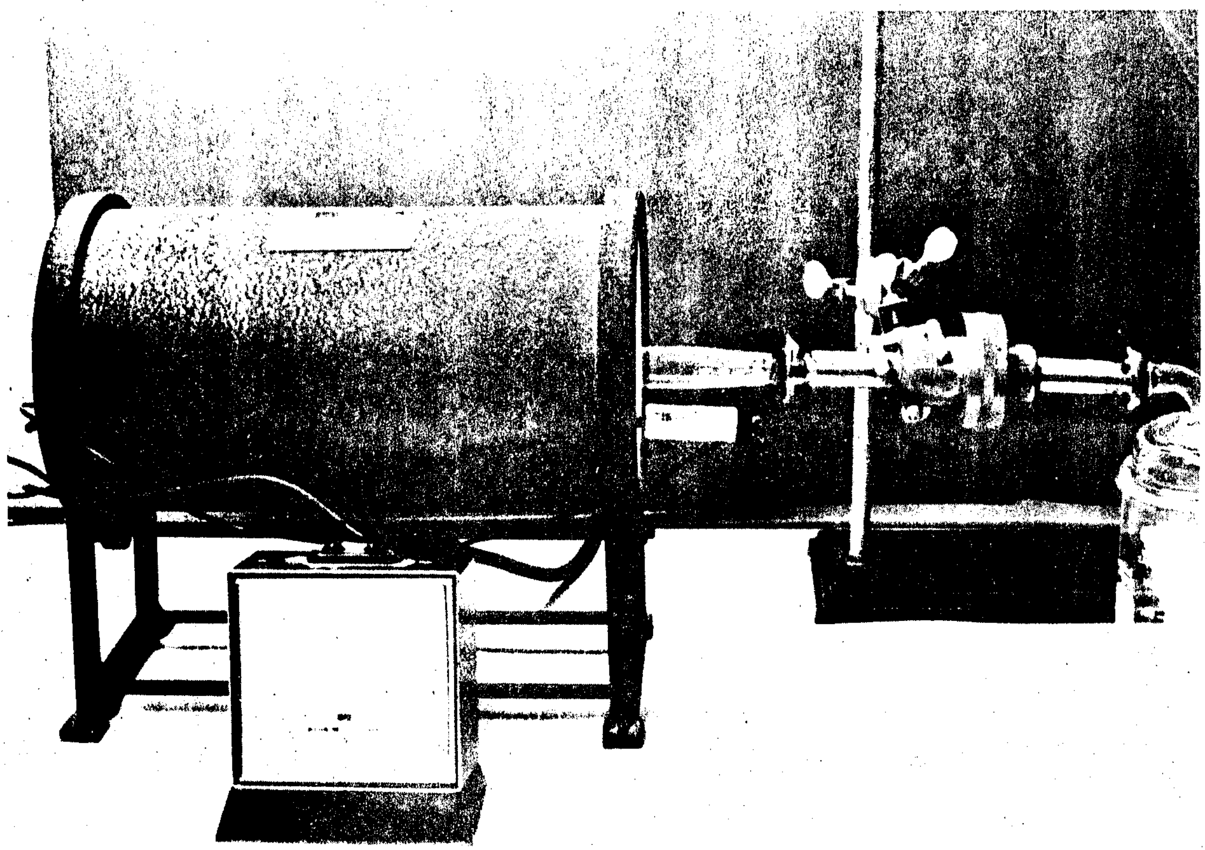


Fig. 2 Laboratory quartz tube combustion furnace.

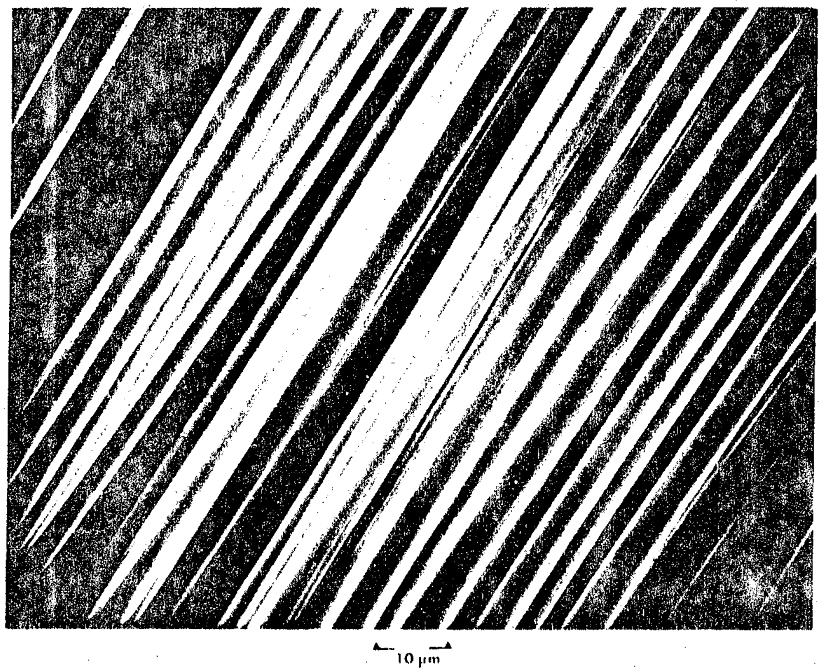


Fig. 3 SEM micrograph of carbon fiber [Thornel 300 (Union Carbide)] sample after exposure for 30 minutes at 200-220°C.

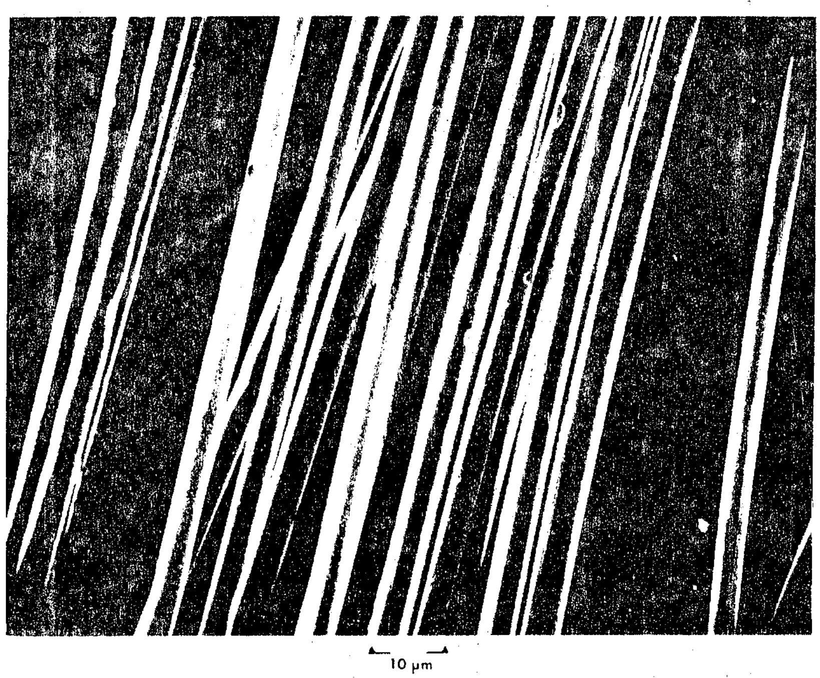
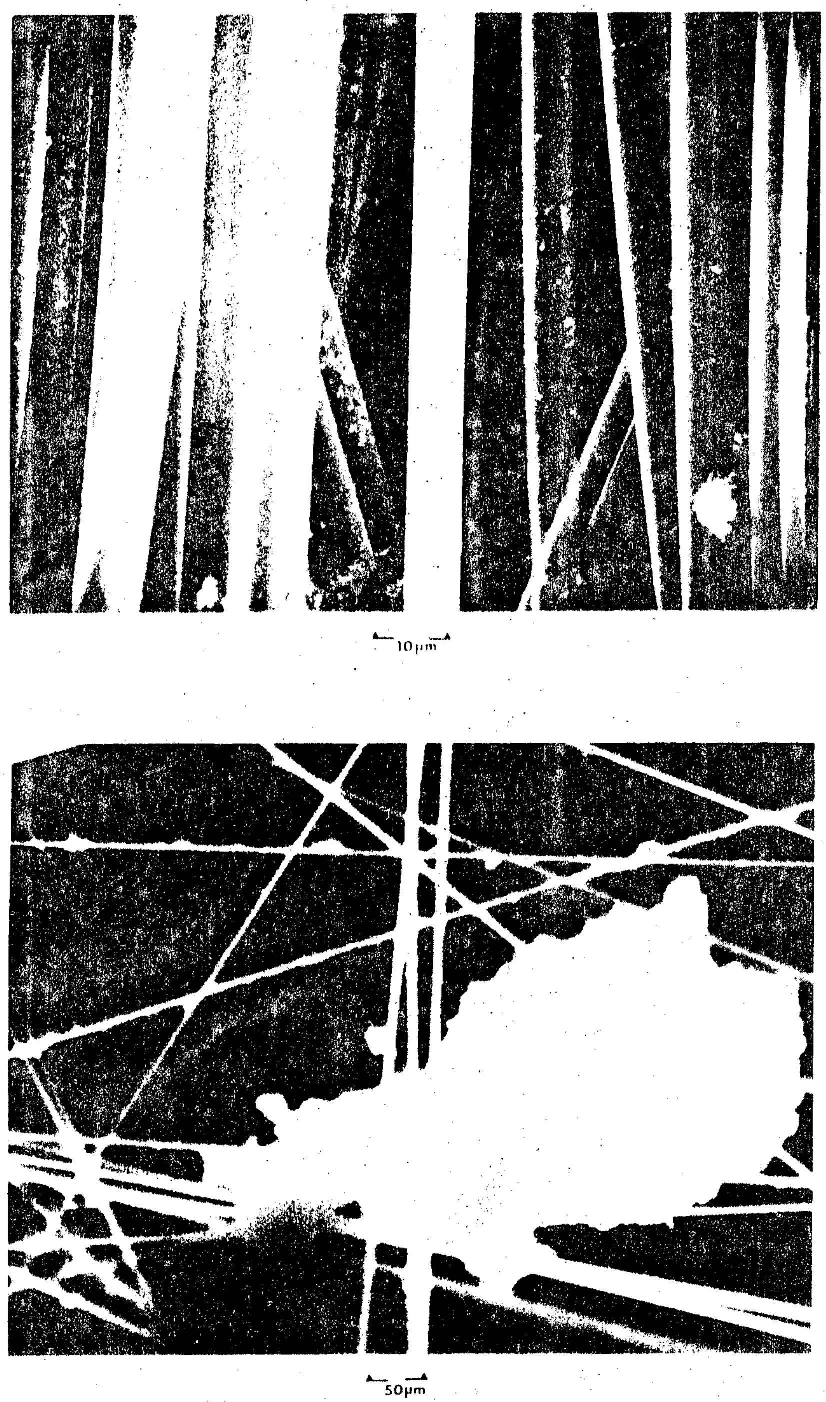


Fig. 4 SEM micrograph of carbon fiber [Thornel 300 (Union Carbide)] sample after exposure to a temperature of 1000°C for 1 minute.

Fig. 5 SEM micrograph of carbon fibers [Thornel 300 (Union Carbide)] after exposure for 3.5 minutes at 1000°C.



(a)

(b)

Fig. 6 Micrographs of residues after exposure of graphite/epoxy composite sample [Fortafil 5 (Great Lakes Carbon)] for 5 minutes at 1000°C: (a) SEM micrograph; (b) optical micrograph.

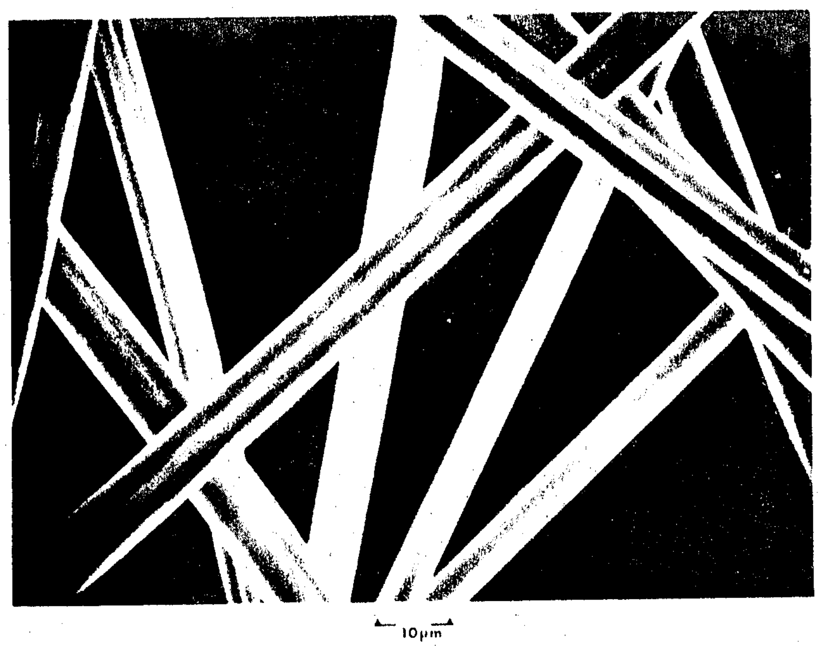


Fig. 7 SEM micrograph of fiber residue following exposure of graphite/epoxy sample [Fortafil 5 (Great Lakes Carbon)] for 5 minutes at 1000°C.

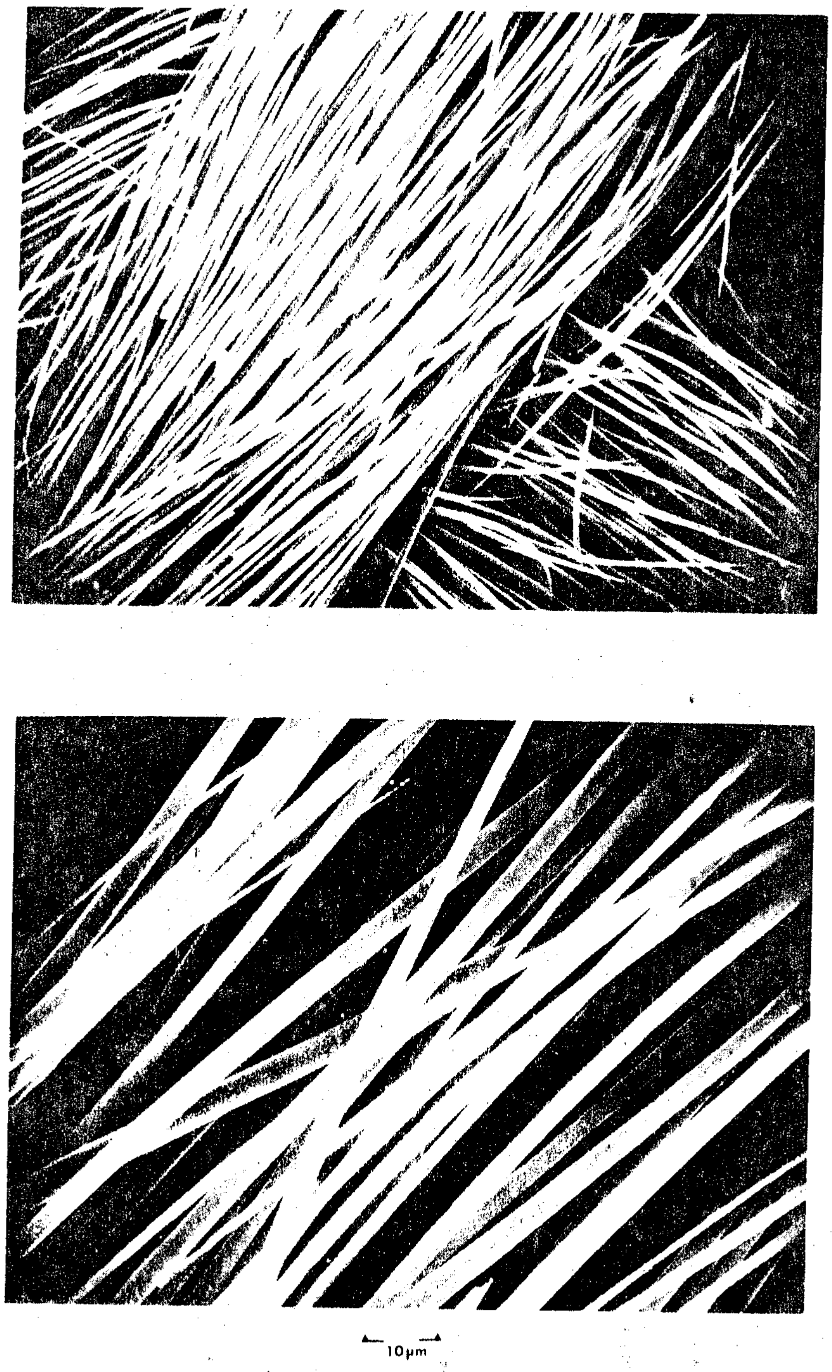
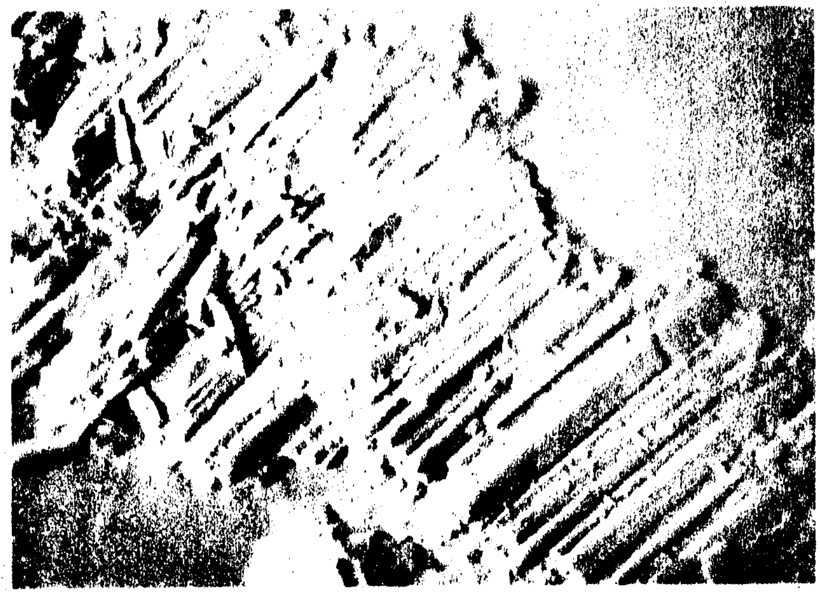
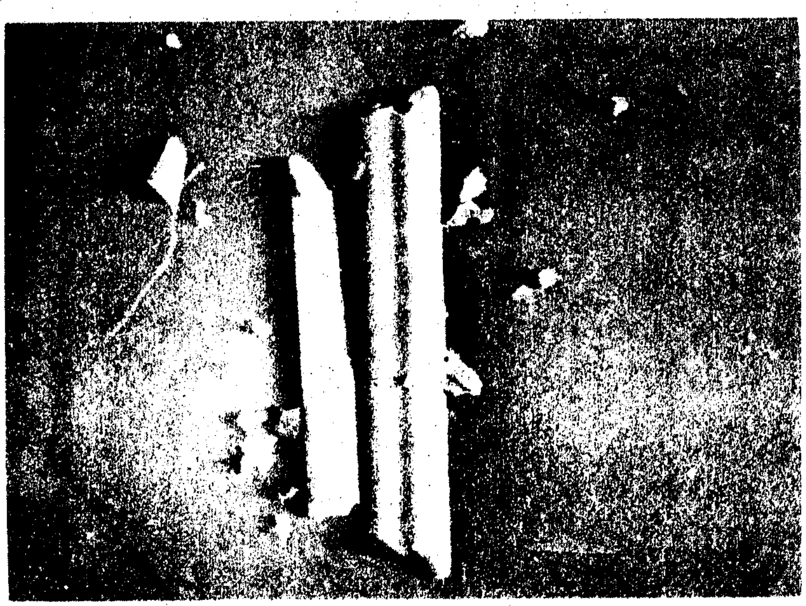


Fig. 8 Woven cloth sample [Panex PWB-6 (Stackpole)] after exposure for 23 minutes at 1000°C: SEM micrographs at two different magnifications.

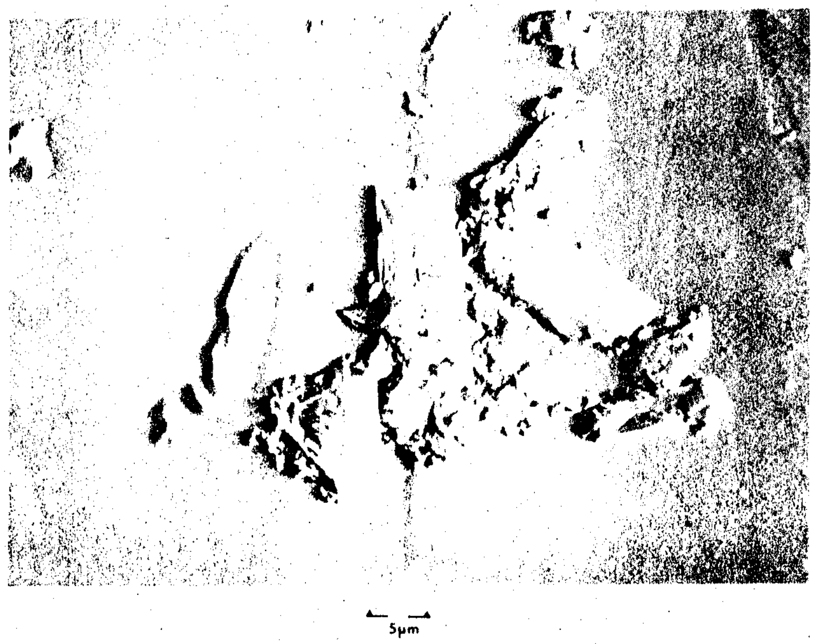


(a)



(b)

Fig. 9 SEM micrographs of dust particles from drilling a sample of graphite/epoxy composite: (a) large particle containing fibers still bound in resin; (b) free fibers.



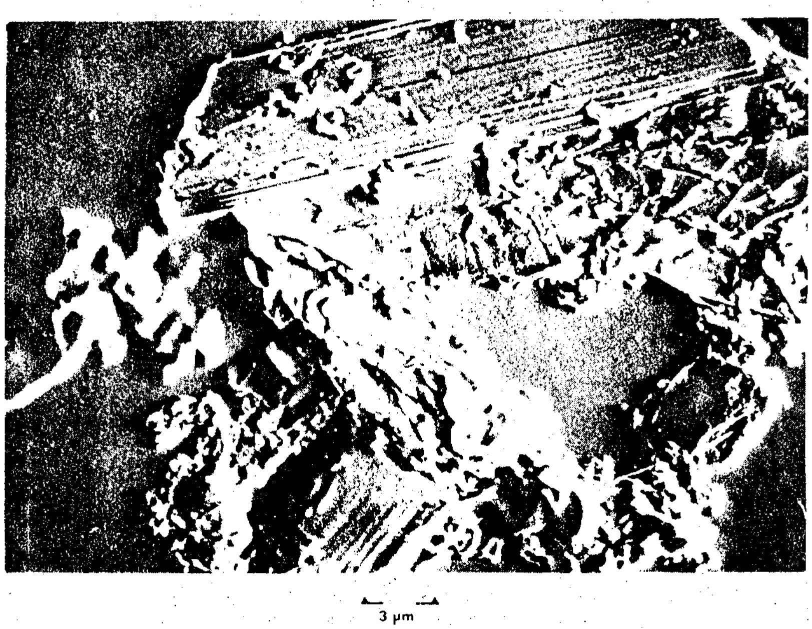


Fig. 10 SEM micrographs of dust particles from sawing a graphite/epoxy composite sample.