

# Continuous Pyrolytic Graphite Composite Filaments

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Advances in aeronautics and astronautics have created a need for new and improved structural and thermally protective materials, which are stable or capable of accommodating ultra high temperatures, mechanically erosive forces, and chemically corrosive environments. New physical forms of materials are thus being developed at an urgent pace, and of these, filamentary reinforced composites are among the most promising. For thermally protective use, carbon and graphite fiber reinforced composites have considerable merit, but current forms of the materials have some deficiencies. Through in-house research by the Air Force Materials Laboratory, continuous pyrolytic graphite filaments have now been synthesized in diameters from 25 to 125  $\mu$  and individual lengths up to 2600 ft. They are composed of an inner core of tungsten carbide with an overcoating of a pyrolytic refractory-like highly "turbostatic" carbon. To obtain these filamentous materials, a novel and versatile laboratory apparatus was designed, built, and successfully operated. The newly developed filamentous materials have potential uses in many future Air Force applications, like ablative and reinforced plastic structures, filament-wound composites, thermal insulation inflatable re-entry structures, thermally protective fabrics, and possibly other important uses.

## I. Introduction

ENVIRONMENTS of very high temperature, high shear force and chemical reactivity have been generated by modern rocketry. Ablative and structural composite materials containing fibrous reinforcements have shown great potential for withstanding such environments. However, currently available fibers may not be entirely adequate for future uses because of the ever increasing material property requirements (thermal stability, strength, capability, etc.), and the associated effects of hyperenvironmental constituents on material performance. Highly refractory materials in bulk form have been made available which meet some of the anticipated future needs. Refractory fiber reinforced composites are preferred to bulk materials, however, because of their inherent versatility and the ability to tailor properties to the specific application requirements. Fibrous refractories for these composites are not presently available in proper compositions, physical structure, or amounts, and thus considerable interest exists in preparing such materials.

The objective of this report concerns the preparation of pyrolytic graphite in continuous filament form. The research program designed to fulfill the objective was detailed into the following phases: 1) develop a laboratory apparatus for obtaining continuous pyrolytic graphite filaments; 2) examine the utility of existing chemical vapor-plating processes and improve them in applicable areas; 3) investigate the suitability of various hydrocarbon compounds as the graphite precursor material; and 4) produce continuous lengths of pyrolytic graphite filaments using a tungsten wire substrate.

## II. History of Fibrous Graphite

The preparation of filaments of graphite was first reported in 1890 by Paul and Leon Schestzenberger.<sup>1</sup> These workers passed pure dry cyanogen through a heated porcelain tube. A bulky mass of very slender filaments was formed when nucleated in the hot zone by carbon black and either aluminum metal or cryolite. These workers considered the fibers as a new physical form of carbon, distinct from amorphous

carbon, graphite, and diamond. In 1903 Constant and Pelabon<sup>2</sup> observed the formation of a graphite wool in coke-ovens near the hot gas exits. The wool was noted to consist of bundles of tiny filaments having estimated diameters of 2  $\mu$  and longer filaments with diameters of 30 to 150  $\mu$  and lengths of 2 to 3 in. They concluded that the filaments were derived by pyrolytic deposition from heavy hydrocarbon vapors. Since economic applications for such fibers were not apparent at that time, the filaments were regarded as mere scientific curiosities.

In 1952 Galt and Herring<sup>3</sup> made the now classic discovery that tin whiskers possessed near-theoretical strength. Interest was therefore renewed in all types of whiskers including graphite. The processes employed were many and varied<sup>4</sup> and included thermal decomposition of aluminum carbide whiskers followed by an annealing process<sup>5</sup> and pyrolyzing acetylene on hot carbon filaments at 2000°C and 1.3 mm Hg.<sup>6</sup> Bacon<sup>7</sup> produced graphite whiskers in a d.c. arc at 3650°C under an argon pressure of 92 atm. He reported apparent strengths up to 2.8 million psi and a modulus of 100 million psi.

In 1962 Bourdeau<sup>8</sup> reported the batch preparation of pyrolytic graphite whiskers by the thermal decomposition of methane in the presence of certain catalytic gases. Although such whiskers have not exhibited strengths comparable to those of Bacon, they can be grown in considerably greater quantities. Such whiskers have smooth surfaces and strengths of 0.1 to 0.35 million psi.

In 1959, continuous yarns of pyrolyzed rayon were made commercially available under the generic name of "graphite." These filamentous materials were composed essentially of amorphous carbon<sup>9</sup> and thus are not akin to the highly crystalline graphitic filaments previously discussed. In subsequent research<sup>8</sup> pyrolytic graphite coatings were deposited onto the pyrolyzed rayon filaments to obtain a composite filament with superior properties. Extensive characterization of these coated filamentous materials and preparation of composite specimens are currently underway.

From the preceding history, it may be concluded that filamentous graphite is a unique material with interesting possibilities as a reinforcing agent in composites. Fibers may be obtained by several different processes, and of these, chemical vapor plating may produce a superior material. All of the work has been centered on batch processes in which the fiber yields were relatively small. An obvious need exists for a continuous filament synthesis process to obtain suf-

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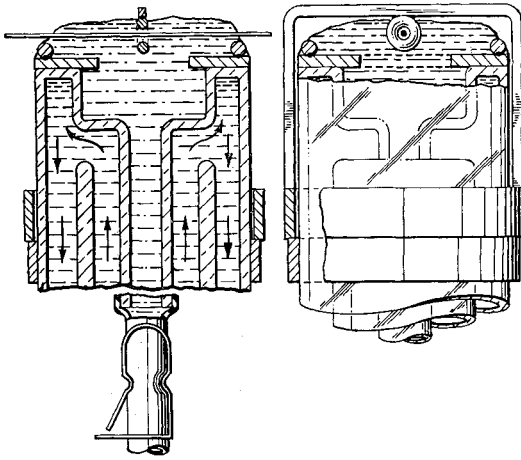


Fig. 1 Diagram of water-cooled electrode.

ficient material for extensive fiber characterization and preparation of composite specimens.

### III. Vapor Plating

This program required an apparatus suitable for continuously vapor plating pyrolytic materials on various filamentous substrates. For maximum utility, the apparatus needed the following design features: 1) suitable for plating temperatures from room temperature to 2500°C. and pressures from high-vacuum through moderate positive pressure; 2) ability to control substrate temperature throughout the plating chamber; 3) ability to control degree of filament vibrations (excessive vibration would increase the cooling rate of the filament with respect to its surroundings as well as generate mechanical stress, for certain operations, for example, when running multiple filaments through the apparatus, slight vibration would be desirable to prevent pyrolytic deposits from bridging adjacent fibers); 4) utilization of ordinary 60-cycle alternating current to resistance heat the substrate; and 5) simplified and trouble-free operation, low maintenance, and ability to handle a wide variety of research requirements. A vapor plating apparatus was successfully developed which met all the foregoing requirements.

The vapor plating apparatus was essentially a long cylinder through which the substrate material could be drawn by means of a powered take-up spool located outside one end of the cylinder. The substrate was fed into the cylinder at the opposite end from a powered spool and tensioning device.

The substrate passed through the cylinder ends via suitable mercury seals. For atmospheric plating chamber pressures, an ordinary Y-type seal was used. The substrate was drawn across a series of electrodes and confined thereon by weighted rider guides (Fig. 1). These guides retained the substrate

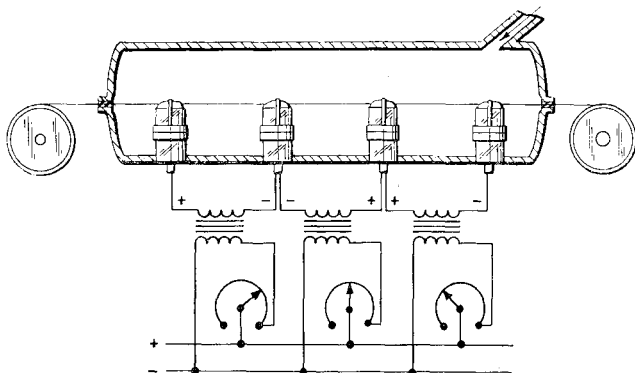


Fig. 2 Partial schematic of electrical system.

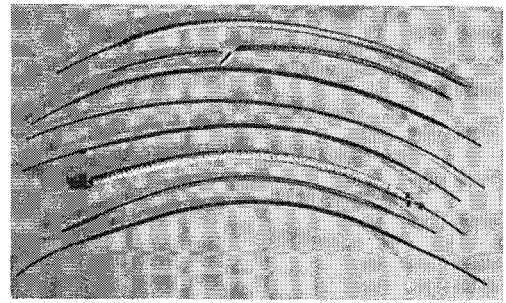


Fig. 3 Pyrolytic graphite deposits.

from vibrating and thus prevent arcing. Such a series arrangement of electrodes prevented vibration, allowed the use of alternating current for resistance heating, and provided temperature control through the entire length of the plating chamber.

The portions or stages of the substrate between successive electrodes could be supplied with independently variable electrode currents (Fig. 2), thus achieving a wide latitude in temperature control. As a result, substrates having widely diversified electrical characteristics could be heated.

### IV. Process

Continuous pyrolytic graphite filaments were formed by deposition of pyrolytic graphite from a hydrocarbon source gas on a resistance-heated tungsten filament as it was drawn through the vapor plating apparatus. Localized pyrolysis of suitable hydrocarbons occurred on the moving filament at temperatures from 1100° to 2000°C. These hydrocarbons were first diluted with argon to mole concentrations of 5 to 30% and then used to sweep the vapor plating zone at atmospheric pressure.

The tungsten filaments, used as substrates, lose considerable strength upon heating to temperatures above 3500°F. In contrast, the pyrolytic graphite coating became strongest with increase in temperature. At 3500°F and above, pyrolytic graphite is much stronger than tungsten. Because of this, it was necessary to heat the filament in every increasing temperature increments. Electrodes were spaced every 100 mm. Several such "staged" heating intervals at a comparatively low temperature were necessary to nucleate and develop an initial pyrolytic graphite coating sufficient to withstand higher temperatures. Subsequent "stages," heated to these higher temperatures, produced the required plating rates.

#### Substrate

Tungsten was chosen over other materials as the substrate upon which pyrolytic graphite was deposited. Factors included in this choice were: 1) strength at the high required pyrolytic graphite deposition temperatures; 2) the availability in very fine diameters to 0.0003 in.; and 3) ability to be

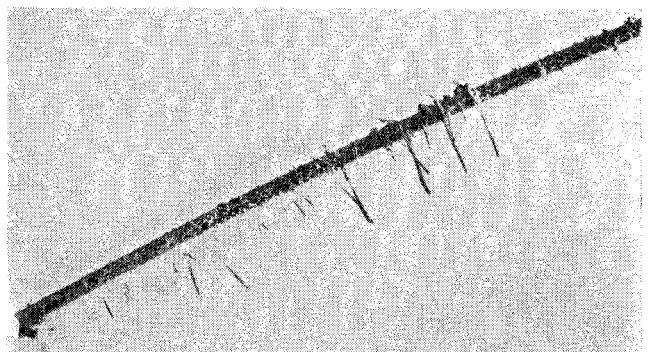


Fig. 4 Pyrolytic graphite deposits.

resistance-heated. Only tungsten fine wires meet all of these factors. Limitations of tungsten fine wires are the moderately high-cost compared with fiber glass and the inherently high-density.

#### Source Gases

Meyer and Gomer<sup>10</sup> observed that a hot, clean, annealed filament covered with graphite of fiber structure is unable to decompose methane, acetylene, or carbon tetrachloride below  $15\mu$  pressure unless the filament surface is first roughened with soot. Above  $15\mu$ , some surface decomposition occurs.

The sensitivity of the pyrolytic deposition upon pressure and surface conditions led to the theorization that the process might be dependent also upon the functional structure of the precursory hydrocarbon molecule. If this were true, such compounds could be directed into the thermal zone that exists around the resistance heated wire substrate. There, pyrolysis would occur with the formation of heavy intermediates to produce concentric gas layers about the hot filament. These layers would function in two ways. First, a protective zone would be formed. This zone would prevent gross pyrolytic soot particles from forming inclusions and resulting defect structures in the pyrolytic graphite. The protective mechanism might be 1) the formation of a soot diffusion barrier, 2) low soot formation by the intermediates themselves, or 3) an erosive chemical action on the soot. Second, the layers of heavy gaseous intermediates may also act as third bodies. The existence of such third bodies near the deposition surface would provide multiple collision sites and guide pyrolytic graphite precursors onto the hot filament surface. Thus, even in the absence of surface roughness and accompanying multiple high energy topographical sites, new layers could be rapidly formed by high angle incident collisions and existing layers completed by low angle incident collisions.

To expedite research and to substantiate the foregoing proposed theory, 27 alkane compounds were investigated by batch processing. The compounds included methane, ethane, and propane, either with or without various functional groups. As anticipated, the resultant pyrolytic

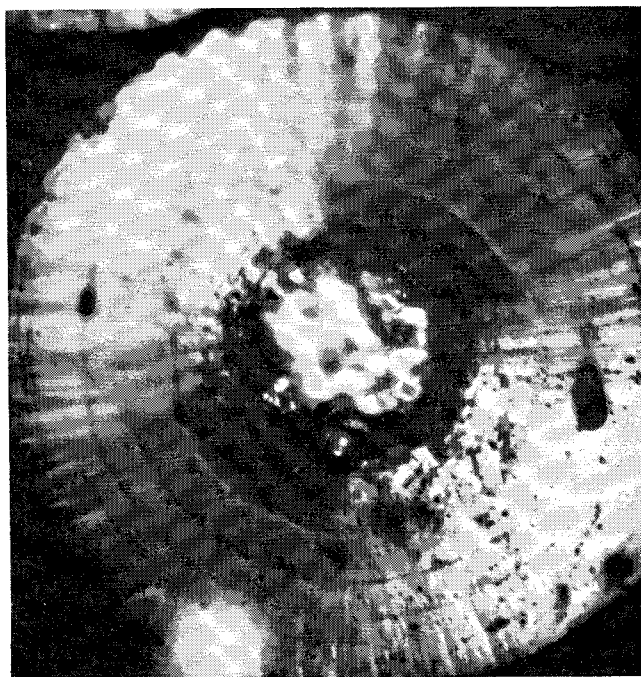


Fig. 6 Fine grained pyrolytic graphite structure.

graphite synthesis was dependent upon the functional structure of the preliminary hydrocarbon molecule. Figures 3 and 4 show the wide latitude of surface structures and deposition rates encountered under otherwise similar conditions. Some compounds as isopentane produced major soot inclusions and highly defected pyrolytic graphite (Fig. 5). Other compounds such as the bromides, iodides, and amines were found to be excellent precursory materials. Ethyl bromide, ethyl iodide, and triethyl amine were chosen as the preferred sources of pyrolytic graphite for continuous fiber research. These materials produced very smooth, high density, pyrolytic graphite fibers, as shown in Fig. 6, having ultimate tensile



Fig. 5 Defect structures caused by soot inclusions.

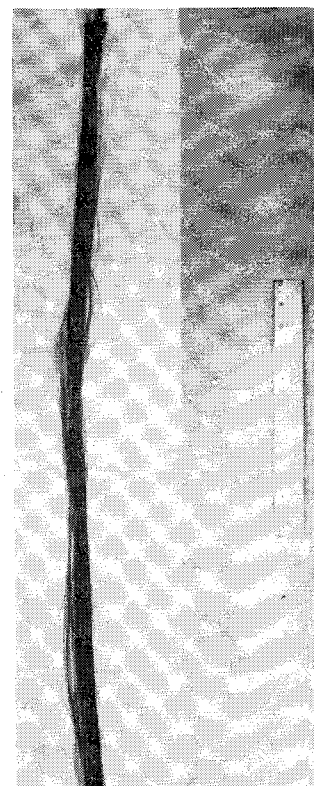


Fig. 7 Pyrolytic graphite yarn (1000 fibers,  $90\text{-}\mu$  diam).

**Table 1 Tensile strength of continuous pyrolytic graphite fibers<sup>a</sup>**

Test no.	Diam, mils	Core, mils	Strength, psi	% by vol. P.G.
54	2.02	1.0	52,400	76
50	2.55	1.0	51,200	85
44	1.70	1.0	53,200	65
42	4.04	1.0	66,400	94
58	1.03	0.5	76,250	77
59	0.8	0.5	118,200	61
60	0.8	0.5	145,300	61

<sup>a</sup> Gage length, 2.0 in.; loading rate, 0.02 in./min.

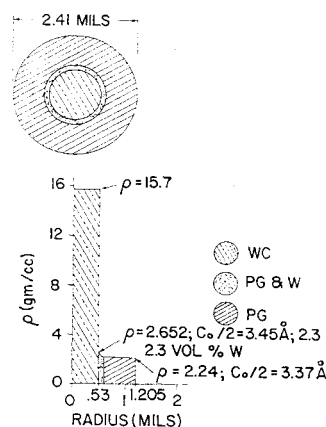
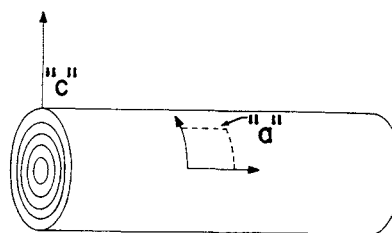
strengths higher than similar fibers produced from other compounds.

## V. Continuous Pyrolytic Graphite Filaments

Pyrolytic graphite fibers were formed in continuous monofilament and filament form. The monofilaments were 3.5 mils in total diameter with a 1-mil tungsten (Fig. 7) substrate. Filaments with lengths to 2600 ft were obtained. Multiple filament pyrolytic graphite fibers were synthesized with individual filaments of 1-mil total diameter on a 0.5-mil tungsten substrate. These fibers were produced by simultaneously plating six tungsten wire substrates.

## VI. Filament Properties

The graphite in the pyrolytic graphite filaments is not single crystal structure. However, it approaches the orderliness of single crystals and can be formed easily. In the pyrolytic process, carbon crystallites are built up atom-by-atom on a suitable substrate. A preferred orientation of these crystallites is obtained parallel to the substrate. Hundreds of such crystallites in platelet form may assume this position for every crystallite normal to the substrate. A model of such a

**Fig. 8 Pyrolytic graphite crystallite order (model).****Fig. 9 x-ray density profile of continuous pyrolytic graphite fiber.****Fig. 10 Pyrolytic graphite crystal order.**

preferred orientation is shown in Fig. 8. Such a unique structure results in highly anisotropic fiber properties. Specific filament properties are as follows.

### Density Profile

The x-ray density profile of an early experimental continuous fiber is shown in Fig. 9. The tungsten core has been completely converted to tungsten carbide with a density of 15.7 g/cm<sup>3</sup>. A narrow undefined band of pyrolytic graphite surrounds this core. The C<sub>0</sub>/2 distance is expanded to 3.45 Å as a result of 2.3 volume percent tungsten. The density is 2.65 g/cm<sup>3</sup>. The remaining portion is composed of pyrolytic graphite, which represents 83 volume percent of the fiber. The graphite has an x-ray density of 2.20 to 2.24 g/cm<sup>3</sup>.

### Strength

Room temperature tensile strength of the continuous graphite filaments are not particularly attractive when compared to the values of commercially available oxide and metallic filaments. At the present time, tensile breaking strengths for the continuous graphitic filaments range from about 50,000 to 145,000 psi (see Table 1). Average tensile strengths of 350,000 psi are obtained with "E" glass, and values of 457,000 psi are measured for tungsten microwires.

**Fig. 11 Pyrolytic graphite whiskers 8-to 9-μ diam.**

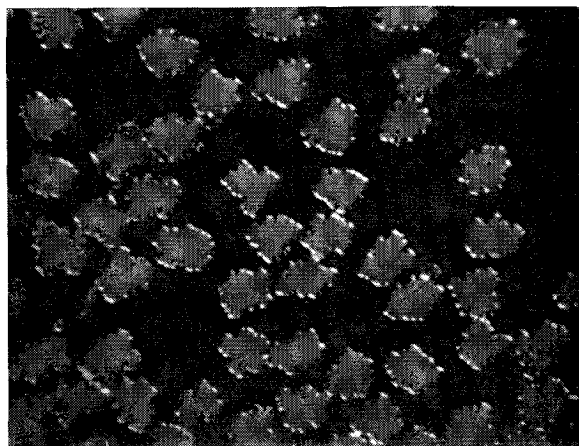


Fig. 12 Pyrolyzed rayon cloth with pyrolytic graphite coating, 600X.

The room-temperature tensile properties of continuous graphite filaments become more interesting when compared to other types of graphitic filaments. This results from the anisotropic nature of pyrolytic graphite. Figure 10 shows the crystal orientation of pyrolytic graphite continuous fibers. Radially in the *c* direction, the graphite fiber is held together by relatively weak Van der Waals' forces. Longitudinally and circumferentially, however, the fiber is very strong because of chemical bonding in the *a* direction. Pure pyrolytic graphite filaments have been reported (Fig. 11) with *a* directional tensile strengths ranging between 52,000 and over 600,000 psi (Table 2), thus attesting to the high strength chemical bond.<sup>11</sup>

Graphite filaments prepared from pyrolyzed rayon yarns have considerably lower strength properties, as noted in Table 3. Tensile strength values for these materials range between 13,200 to 19,800 psi. Significant improvements in tensile strength were obtained, however, by coating the pyrolyzed rayon filaments with various pyrolytic materials. Tensile strengths up to 63,300 psi have been obtained with only micron thicknesses of pyrolytic graphite and alloys thereof (Fig. 12).

Unlike all other fiber compositions, graphitic filaments exhibit a characteristic increase in strength with temperature. This effect is illustrated in Fig. 13, which is a plot of percent strength change with increasing temperature. Only the pyrolytic graphite is shown to increase in strength with elevated temperatures.

#### Oxidation Resistance

Pyrolytic graphite filaments are susceptible to oxidizing atmospheres and fluids because of their elemental chemical composition. The relative degree of oxidation resistance is shown in Fig. 14 with comparative data given for other carbonaceous and graphite filaments. This comparison was

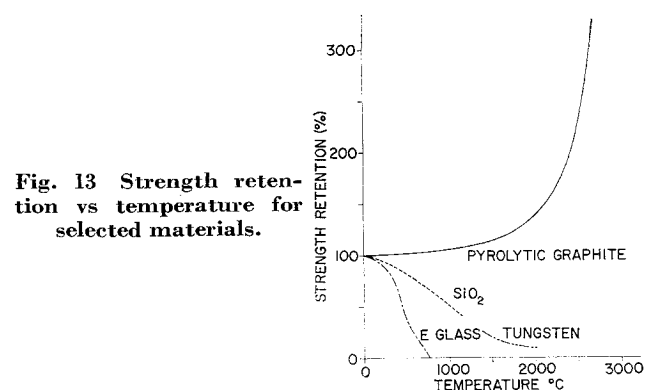


Fig. 13 Strength retention vs temperature for selected materials.

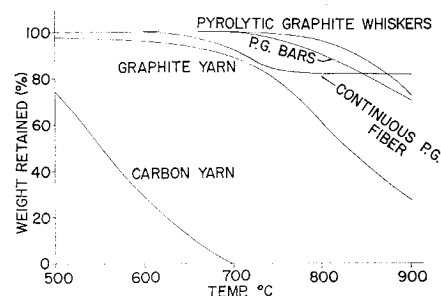


Fig. 14 Oxidation resistance of graphite fibers (TGA).

obtained using approximately 100 mg samples in still air in a Thermo Gravimetric Analysis (TGA) apparatus heated from room temperature to 1000°C at the rate of 5°C/min. All filaments were in 1 in. lengths, but had varying diameters. The pyrolytic graphite whiskers were 30 to 100  $\mu$ , the continuous pyrolytic graphite fibers were 61  $\mu$ , and the pyrolytic graphite bars were 200  $\mu$  in width and thickness. The graphite and carbon yarns were commercial materials with individual fibers 8  $\mu$  in diameter.

#### Other Properties

The pyrolytic graphite fibers were found to possess unique properties not obtainable heretofore in other filamentous materials. These desirable attributes included flexibility, high thermal stability, nonmelting, lightweight, chemical inertness, thermal shock resistant, nontoxic, high surface emittance, continuous lengths, low vapor pressure, dimensional stability, and anisotropic properties.

Current state-of-the-art materials possess certain limitations. These are concerned with oxidation susceptibility,

Table 2 Preliminary tensile properties of pyrolytic graphite whiskers<sup>a</sup>

Diameter, $\mu$	Tensile strength, psi
2.59	641,000
12.5	60,000
15.3	69,000
16.8	52,100
23.8	342,000
37.9	128,000
38.2	113,000
39.0	123,000
92.6	59,000

<sup>a</sup> Unpublished data, R. G. Bourdeau, High Temperature Materials, Inc., May 1964.

Table 3 Tensile strength of graphite yarn, single filament<sup>a</sup>

Diameter, $\mu$	Coating	Coating thickness, $\mu$	Tensile strength, psi
9	...	...	13,200
8.5	...	...	15,400
8.5	...	...	19,800
8	Pyrolytic graphite	26	72,000
8	Pyrolytic graphite	21	63,000
8	Pyrolytic graphite	6	42,000
8	Pyrolytic graphite	9.2	38,800
8	Pyrolytic graphite + 1% boron	2.9	49,800
8	Pyrolytic graphite + 1% boron	0.45	19,800
8	Pyrolytic graphite + 1% boron	46.7	63,000

<sup>a</sup> Unpublished data, R. G. Bourdeau, High Temperature Materials, Inc., May 1964.



moderately low strength, and in some cases, limited availability.

## VII. Conclusions

1) The development of a vapor plating apparatus has led to the first successful synthesis of continuous pyrolytic graphite fibers.

2) These continuous filaments represent an important new physical form of graphite. As such, they bridge the limited availability gap between very high strength graphitic whiskers and relatively low strength pyrolyzed rayon cloths.

3) The pyrolysis of certain substituted alkane hydrocarbons produce more finely grained, higher strength, and more uniform pyrolytic graphite than other conventional hydrocarbon compounds.

4) The graphitic fibers are a first generation materials. Further research is required to improve the unique properties of these fibers and to evaluate them in composites.

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# Investigation of the Charge-to-Mass Ratio of Electrically Sprayed Liquid Particles

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An analysis of the charge-to-mass ratios (specific charges) of particles generated by the electrical atomization process is presented. The study involves the surface energy of the dispersed system of particles, the effects of space charge on the source, and the effects of conductivity on the atomization process. Experimental data are presented in support of these theories. Further, a colloidal suspension in glycerine is experimentally shown to produce particles of high specific charge (400 coul/kg) when electrically dispersed under appropriate conditions.

## I. Introduction

THE electrical spraying of liquids or the electrical atomization of liquids is, basically, a process by which a liquid volume is broken up into small, charged particles as a result of electrostatic pressures overcoming surface tension pressures. According to Drozin,<sup>1</sup> the electrical atomization of liquids was first observed by George Bose in 1745. Rayleigh<sup>2</sup> determined an instability criterion for charged, liquid droplets in 1882. In 1917, Zeleny<sup>3</sup> established a criterion for the instability of an electrified liquid at the end of a capillary tube. Drozin,<sup>1</sup> in 1955, considered the electrical forces causing instability of liquid surfaces as arising from dielectric stresses in the liquid. He does not explain, however, how charged particles can form as the result of dielectric stresses.

In 1952, Thomas<sup>4</sup> advanced the idea of the electrical acceleration of charged colloidal particles to produce thrust for space vehicles. Particles having specific-charges in the range 200 to 10<sup>4</sup> coul/kg would be very useful for propulsion purposes and would tend to bridge the mission capability gap between arcjet thrusters and cesium ion thrusters.<sup>5</sup> Some of the first research on electrical spraying of liquids in application to space-vehicle propulsion was reported by Shultz and Branson<sup>6</sup> and by Hendricks.<sup>7</sup> Other contributions have been submitted by Krohn<sup>8</sup> and Cohen.<sup>9</sup> These studies established the statistical nature of the charge and mass distributions of emitted particles and showed the general shape of current distributions of specific charge for some liquids.

This paper presents a study of the fundamental mechanisms involved in the electrical dispersion of liquids from the tip of capillary tubes. In this process, charged colloidal-size particles are generated by allowing a liquid to flow through a small, metal capillary tube maintained at a high electric potential. Theoretical treatments and experimental results are presented concerning the following aspects of the problem: 1) surface energy minimization of the dispersed system of particles produced from unstable liquids that disperse into

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