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M. TURKAT
CONTINUOUS METHOD OF MANUFACTURING ABLATIVE
AND REFRACTORY MATERIALS
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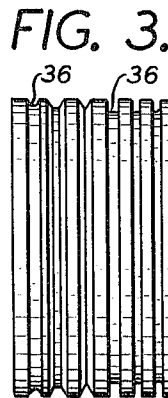
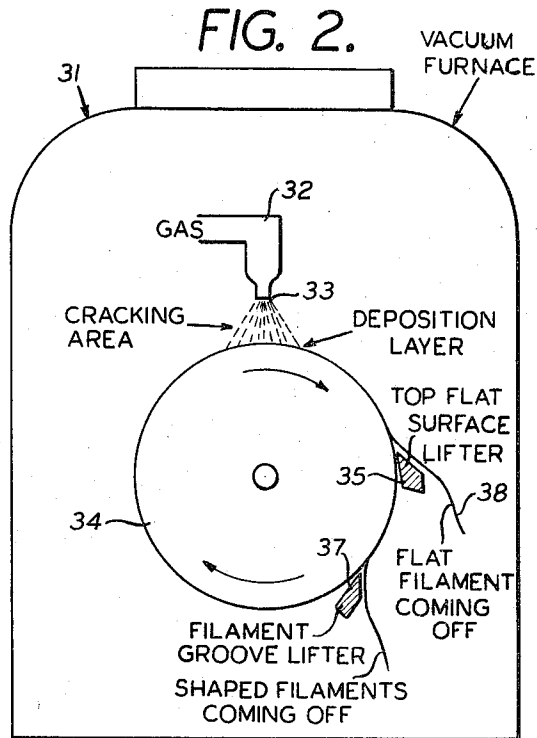
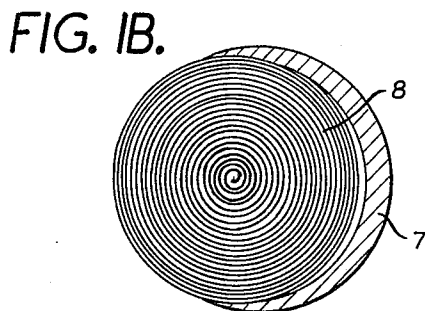
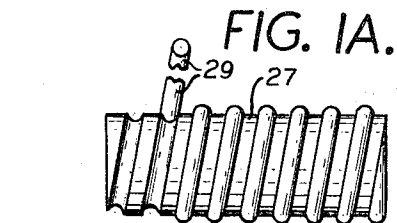
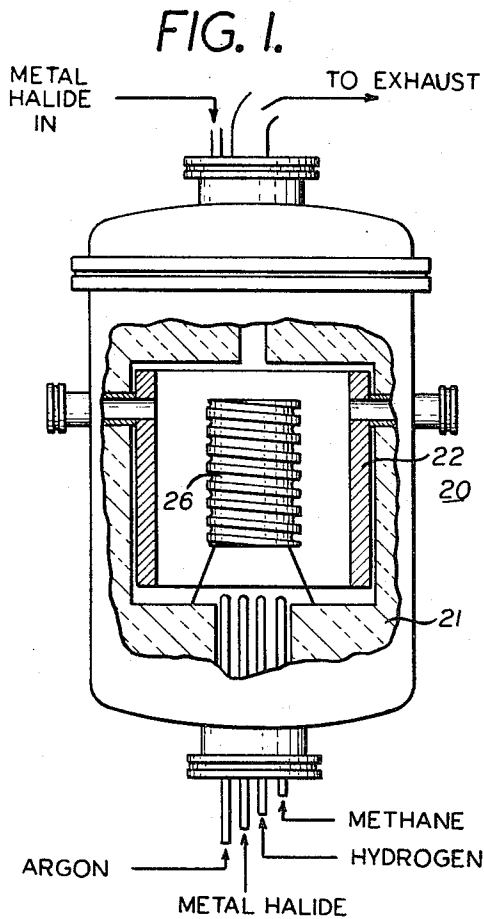


FIG. 3A.

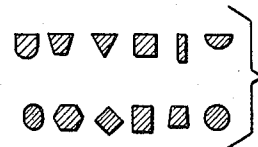
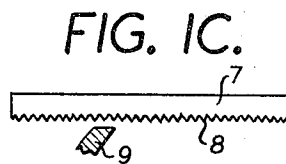


FIG. 4.



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**CONTINUOUS METHOD OF MANUFACTURING
ABLATIVE AND REFRACTORY MATERIALS**

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6 Claims. (Cl. 264-29)

The present application is a continuation-in-part of applicant's co-pending U.S. patent application, Serial No. 130,153, filed August 8, 1961 and entitled High Purity and Non-melting Ablative Filaments; applicant's co-pending U.S. patent application, Serial No. 143,634, filed October 9, 1961, and entitled Apparatus and Continuous Method of Manufacturing Ablative and Refractory Metal Filaments; and applicant's co-pending U.S. patent application, Serial No. 361,492 filed April 21, 1964, and entitled Method of Making High Purity and Non-Melting Filaments; and applicant's co-pending U.S. patent application, Serial No. 361,480, filed April 21, 1964 and entitled High Purity and Non-Melting Filaments.

This invention relates to filaments and, more particularly, to an apparatus and method of manufacturing ablative and refractory filaments.

An object of the present invention is to manufacture high temperature resistant, high strength filaments in lengths of 1 to 1000 feet or more from refractory or ablative materials by means of a continuous process in a high vacuum furnace.

Another object of the invention is to manufacture refractory or ablative filaments of varied shapes and cross-sections by a continuous process in contradistinction to a batch process.

An object of the invention is a continuous method of manufacturing refractory and ablative materials by means of a rotating mandrel in a high vacuum furnace to provide unlimited filament lengths of controlled thickness and uniformity.

A feature of the invention is a filament formed of the class of ablative materials including pyrolytic graphite, carbides, and combinations of these with refractory metals and alloys thereof, in continuous lengths by a continuously operating process in a high vacuum furnace.

Another feature of the invention is the fabrication of high purity non-melting crystalline filaments of ablative materials by the process of cracking or decomposing suitable gases or mixtures of gases under extremely high temperatures in a high vacuum furnace, and depositing the same on a continually rotating mandrel or wheel.

Another feature of the invention is the fabrication of high purity, non-melting, non-porous refractory filaments of appreciable length by the process of cracking or decomposing suitable gases or mixtures of gases under extremely high temperatures and depositing carbon and carbides on continually rotating mandrels having multi-shaped grooves therein.

In accordance with the invention, high temperature, high strength ablative refractory materials such as pyrolytic graphite by hydrocarbon gas cracking techniques, or for example, to provide by metallic vapor decomposition pure crystalline refractory metals, carbides, silicides and borides, in a variety of shapes, cross-sections and coatings by a continuous process involving a rotating mandrel with threads and filament lifters for scooping up the filaments from the mandrel during its rotation.

A variety of filament shapes and cross-sections are fabricated thereby from ablative refractory materials con-

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tinually deposited on the rotating mandrel or wheel in a continuous process. The resulting filaments are characterized by high purity, unlimited lengths, controlled uniform thickness, non-porosity, crystallinity and operability at superhigh temperatures in the range from 5000° to 10,000° F.

For example, starting with a hydrocarbon gas such as methane, predetermined amounts of refractory metal halide vapors can be mixed therewith, along with hydrogen carrier gas, in a vacuum furnace to produce a composite material of pyrolytic graphite with refractory metal carbide. An alternative procedure would end with a mixture of refractory metal halide and hydrogen, yielding a coating of pure metal. Further heat treatment would yield an adherent coating by diffusion bonding to the graphite composite substrate through the formation of an intermediate carbide layer.

The various materials provided in accordance with the invention have special properties, among which are that they will not melt at superhigh temperatures in the range of 5000-7000° Fahrenheit, that heat is dissipated therefrom primarily by radiation and by evaporation of material through sublimation.

Pyrolytic carbon and refractory metal carbides with their high strength at superhigh temperatures, can be used in combination with a ceramic or glass filament for high strength at low temperatures and provides an ideal high strength, light weight missile component.

The materials provided in accordance with the invention have properties and characteristics suitable for application to missile cones, rocket nozzles, missile body sections, extremely high temperature furnace linings and for high temperature piping, filament wound containers for solid fuel in missiles and the like.

Other objects and features will become apparent to those skilled in the art when the following disclosure is read in connection with the accompanying drawings, wherein:

FIGURE 1 is an elevational view partially broken away of a high temperature furnace and a stationery threaded mandrel therein.

FIGURE 1A is a perspective view of the threaded mandrel shown in FIGURE 1.

FIGURE 1B shows an elevational view of a modified mandrel having the form of a flat surface or disc with spiral grooves machined therein.

FIGURE 1C is a side view of the disc mandrel shown in FIGURE 1B.

FIGURE 2 is an elevational view of a modification of a high vacuum furnace with a continuously rotating mandrel therein in accordance with the invention.

FIGURE 3 is a front view of the rotatable mandrel illustrated in FIGURE 2 showing a variety of shaped grooves therein.

FIGURE 3A shows cross-sections of varied shaped filaments derived from the rotatable mandrel illustrated in FIGURE 3.

FIGURE 4 is an elevational view of a filament lifter or scoop utilized in conjunction with the rotating mandrel of FIGURE 3.

Referring to FIGURE 1, a hydrocarbon gas, such as methane, propane, benzene, butane, acetylene, ethane or toluene and hydrogen are mixed with a metered amount of refractory metal halide in a high vacuum furnace 20. The furnace 20, which is water cooled has its inner walls 21 coated with or insulated with ceramic material. It is electrically heated by a graphite resistance element 22 to a high temperature, sufficient to crack

the various gas vapors, such as refractory metal halide, methane and the like, which enter the furnace 20 under controlled heat.

Pure refractory metal and ablative carbide material deposits on the threads of the stationary mandrel 26 from the original decomposed gases, which provide the metallic and/or carbon vapors for deposition in the threads 27 of the mandrel base.

As the decomposed gases and vapors are deposited on the stationary mandrel 26, the helical threads thereof are built up and filled with ablative or refractory deposits, until a smooth, uniform coating over the entire mandrel 26 is produced.

After a smooth coating has been laid down in the threads 27 of the mandrel 26, the vacuum furnace 20 is shut down, the mandrel 26 is removed therefrom and machined by a sharp cutting tool down to the top surface of the mandrel thread 27. Then the wire filament 29, as illustrated in FIGURE 1A, which is embedded in the mandrel threads 27, is removed freely therefrom to be subsequently utilized for any desired purpose.

Referring to FIGURES 1B and 1C, an alternative form of mandrel is shown, wherein a flat disc 7 is provided with a spiral groove 8 machined in its bottom surface, starting from the center of the disc and continuously expanding in diameter until it reaches the outer edge. The size of the flat disc 7 can be varied as desired, namely, its external optimal diameter being limited only by the size of the furnace 20. With the disc mandrel 7, a simpler furnace feed is feasible, and a more uniform deposition of ablative materials and coating of the mandrel for forming the filament, is provided. The filaments of ablative materials can be removed from the disc 7 by a suitable machining tool 9.

Pure crystalline filaments of materials formed by the process described in connection with FIGURES 1, 1B, as well as filaments formed from a combination of pure refractory metals, pyrolytic graphite, refractory metal carbides or silica, may be manufactured in accordance with the aforementioned processes for depositing ablative materials from metallic vapors and hydrocarbon gases cracked in high temperature vacuum furnaces. The length, diameter, shape and combination of refractory and ablative materials may be proportioned in accordance with a particular use desired and may encompass coiled lengths of a thousand feet or more, although the various filaments per se, or combined with various binders as described herein may be utilized for spiral winding to form rocket body structures as well as various intricate shapes capable of withstanding very high temperatures and pressures.

The data for an actual run, in this case to produce pure pyrolytic graphite filaments, is illustrated by the following charts:

Chart I shows filament density as a function of deposition temperature wherein, the chamber pressure was 4 mm. Hg and the gas flow which was adjusted to maintain this pressure was 6 l.p.m. (liters per minute). The hydrocarbon source gas used was chemically pure methane.

Chart I

Density (gm./cc.):	Temperature, ° C.
1.95	1900
2.15	2000
2.24	2100
2.24	2200
2.24	2300

Chart II shows the deposition rate, of the pyrolytic graphite filaments, as a function of deposition temperature; the chamber pressure being 4 mm. Hg and the gas flow being 6 l.p.m. The hydrocarbon source gas used was chemically pure methane.

Chart II

Deposition rate (mils/hour):	Temperature, ° C.
10	1900
15	2000
18	2100
21	2200
23	2300

Although hydrocarbon gas dilution with hydrogen or argon can be used, as previously described, the preferred method is to use only chemically pure hydrocarbon gases.

When it is desired to produce a filament containing refractory metals, metallic vapor is introduced into the process as hereinbefore described. The proportion of metallic vapor to hydrocarbon gas can be varied from 0 to 10 or more; the more parts of metallic vapor employed, the more closely the filament will approach that of a pure refractory metal. The amount of hydrogen gas used can be varied from zero to one part and the pressure can be varied from 2 mm.-10 mm. Hg. The preferred relationship of the gases used can be expressed as follows:

	Parts
25 Metallic vapor	0-10
Hydrocarbon	1
Hydrogen	0-1

Utilizing the foregoing ablative filament manufacturing processes, various types of refractory and refractory alloy filament combinations can be produced. For example, a pyrolytic carbon filament can be made incorporating boron or other refractory materials such as tungsten, tantalum, niobium, molybdenum, zirconium, vanadium, titanium, thorium and chromium. The metals are obtained by vaporizing various decomposable compounds containing said metals; for example, halides, oxides and various organo-metallic materials, such as carbonyls and dicumene compounds. Typical of refractory alloy filament combinations would be, tantalum-niobium, titanium-tantalum and molybdenum-tungsten.

A pyrolytic carbon filament incorporating boron or other refractory materials offers the characteristic properties of higher strength at low temperatures, as well as at high temperatures. For example, additions of boron in the vapor phase during the deposition process in the fabrication of bulk pyrolytic carbon will increase the room temperature tensile strength of this material from 18,000 p.s.i. to 30,000 p.s.i. In the deposition process, various metal and known metal combinations may be produced, such as boron carbide, niobium carbide, tantalum carbide, tungsten carbide, and the like.

Referring to the schematic diagram of FIGURE 2, a high vacuum furnace 31 corresponding to the furnace shown in FIGURE 1 is similarly provided with an inlet source 32 of methane, hydrogen and metal halide. These gases in various combinations are heated to a high temperature sufficient to crack the various gas vapors. At such high temperatures, the cracked gases and decomposition products provide a variety of controllable media in the cracking area 33, from which novel refractory metals and ablative filament materials will deposit therefrom on a continuously rotating mandrel 34. The rotating mandrel 34 is provided with a variety of grooves of different shapes cut thereinto (like threads) as illustrated in FIGURE 3. The deposited filaments will correspond in shape and cross-section with the contours of the grooves in the rotating mandrel 34, coated by refractory metal and ablative material deposited thereon from the original decomposition products containing metallic and/or carbon vapors.

As the mandrel 34 rotates and the grooves thereof are filled with filamentary material, a filament lifter 35 engages that flat surface of the mandrel 34. The flat lifter

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35 lifts off or shaves away the filaments from the surface coating on the mandrel 34. Peeled, flat filaments 38 come off the mandrel 34 as it rotates under the lifter 35. Further along in the rotation of the mandrel 34, as illustrated in FIGURE 2, groove lifters 37 operate on the mandrel by means of fingers 37, have varying shapes conforming to the shapes of the grooves 36 illustrated in FIGURE 3. The filament lifters 37 ride within the grooves 36 and in turn lift out the filaments, which continue to pass down and away from the rotating mandrel 34 to settle on the bottom of the furnace 31.

Thereby a continuous process of forming ablative and refractory metal filaments is provided by the rotating mandrel 34 in contradistinction to the batch process characteristic of the stationary mandrels 26 and 7 shown in FIGURES 1 and 1C respectively.

Pyrolytic graphite, carbide, refractory or carbide refractory alloy filaments are feasible with this continuous rotating method of manufacturing ablative filaments. These basic ablative type filaments can be later processed by various means of bonding in order to make structures useful in missile applications and the like. Basic filaments in continuous long lengths, in accordance with the present invention, can be protectively coated with ceramics, silicides or refractory metals by means of a flame spray technique. Such filaments can be subjected to the flame spray because of their superhigh temperature resistance properties. The basic ablative materials contemplated or provided herein will not melt at 5000° F. and higher and can thus be subjected to the most severe environmental high temperatures for preprocessing the filamentary materials for subsequent production techniques. Uniform coatings of the aforementioned protective materials in extremely long filamentary lengths are made feasible in the aforementioned processes.

With respect to the arc type flame spray technique, it should be understood that gases under high pressure are ignited in a spray gun to drive metal, glass, plastics or ceramics fed into the gun in powdered form. The high pressure flame from the gun immediately melts these powdered materials and spurts them out in a manner similar to an air spray gun. In the present utilization of the arc flame technique, the basic ablative materials coated have to be able to withstand the heat and pressure developed in the spray gun, as well as to offer excellent bonding properties for the desired coating.

In order to coat carbides, it is desirable to have a metallic bonding agent within the carbide that will bind to the arc flame sprayed metal. Fine filaments of carbide can be controlled so as to have the bonding materials formed therewithin. The aforementioned vapor deposition technique may also be utilized to deposit a metal coating externally around the carbide filaments, which will permit the arc flame spraying of metals and refractories thereon, thereby resulting in a stronger and more positive bond throughout the filament structure.

For example, tantalum carbide filaments can be manufactured with a tantalum vapor coating deposited thereon. This filament in turn can be wound onto a spool as in the filament wire technique of applicant's compending application Serial No. 130,153, filed August 8, 1961, and can then have an overall spray of tantalum, providing a uniform bonded coating between filaments and layers of filaments. In this connection, a structure of carbide within, and tantalum without, would result. Such a combination of carbide, tantalum layer laminate has the desirable property of offering a high stress to weight ratio as compared to solid tantalum. In missile design where weight is of extreme importance, such a material, is most desirable inasmuch as it is able to withstand extreme temperatures beyond 5000° F., superhigh pressure and heat, but is extremely light in weight. The value of such a material can be appreciated when it is realized that enormous quantities of fuel can be saved in the operation of missiles. A similar arc flame spraying technique can

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be still further applied in similar respects utilizing ceramics as the overall coating or silica glass formed as an outer shell or surface of the laminate structure.

Various carbide refractory alloys and refractory materials can be thus combined in various proportions and structures to permit superior body structures for applications to fields requiring extreme ranges of physical and thermal properties and specifications.

It should be apparent to those skilled in the art that various modifications may be made in the process and methods disclosed herein or in the resultant products thereof without departing from the spirit and scope of the invention.

What is claimed is:

1. A method of forming continuous lengths of a pure crystalline filament of pyrolytic graphite, pyrolytic carbides and combinations thereof, comprising the steps of cracking hydrocarbon gases in a vacuum furnace at temperatures in the range of about 1900°–2300° C., depositing the decomposition products thereof on a rotating mandrel having filament peeling means in engagement therewith and continuously peeling said decomposition products from said rotating mandrel in the form of a continuous filament said mandrel having helical grooves formed thereon.

2. A method of forming continuous lengths of a pure crystalline filament of refractory metals and alloys, and combinations thereof with pyrolytic graphite and pyrolytic carbides, comprising the steps of cracking hydrocarbon gas and decomposable metallic compounds in a vacuum furnace at temperatures in the range of about 1900°–2300° C., depositing the decomposition products thereof on a rotating mandrel having filament peeling means in engagement therewith and continuously peeling said decomposition products from said rotating mandrel in the form of a continuous filament said mandrel having helical grooves formed thereon.

3. A method of forming continuous lengths of a pure crystalline filament of pyrolytic graphite, pyrolytic carbides and combinations thereof, comprising the steps of cracking hydrocarbon gases in a vacuum furnace at temperatures in the range of about 1900°–2300° C., depositing the decomposition products thereof on a rotating mandrel having a helical groove formed therein and further having peeling means disposed within said groove, thereby forming a continuous coating of said decomposition products on said mandrel, removing, by cutting means, so much of said coating as was deposited outside of said helical groove, thereby leaving a helical filament of said coating material on said mandrel, and finally peeling said coating material from said groove, by said peeling means, in the form of a continuous filament.

4. A method of forming continuous lengths of a pure crystalline filament of refractory metals and alloys, and combinations thereof with pyrolytic graphite and pyrolytic carbides, comprising the steps of cracking hydrocarbon gas and decomposable metallic compounds in a vacuum furnace at temperatures in the range of about 1900°–2300° C., depositing the decomposition products thereof on a rotating mandrel having a helical groove formed therein and further having peeling means disposed within said groove, thereby forming a continuous coating of said decomposition products on said mandrel, removing, by cutting means, so much of said coating as was deposited outside of said helical groove, thereby leaving a helical filament of said coating material on said mandrel, and finally peeling said coating material from said groove, by said peeling means, in the form of a continuous filament.

5. A method of forming continuous lengths of a pure crystalline filament of pyrolytic graphite, pyrolytic carbides and combinations thereof, comprising the steps of cracking hydrocarbon gases in a vacuum furnace at temperatures in the range of about 1900°–2300° C., deposit-

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ing the decomposition products thereof on a rotating mandrel having a spiral groove formed therein and further having peeling means disposed within said groove, thereby forming a continuous coating of said decomposition products on said mandrel, removing by cutting means, so much of said coating as was deposited outside of said spiral groove, thereby leaving a spiral filament of said material on said mandrel, and finally peeling said coating material from said groove, by said peeling means, in the form of a continuous filament.

6. A method of forming continuous lengths of a pure crystalline filament of refractory metals and alloys, and combinations thereof with pyrolytic graphite and pyrolytic carbides, comprising the steps of cracking hydrocarbon gas and decomposable metallic compounds in a vacuum furnace at temperatures in the range of about 1900°-2300° C., depositing the decomposition products thereof on a rotating mandrel having a spiral groove formed therein and further having peeling means disposed within said groove, thereby forming a continuous coating of said decomposition products on said mandrel, removing, by cutting means, so much of said coating as was deposited outside of said spiral groove, thereby leaving a spiral filament of said material on said mandrel, and finally peeling said coating material from said groove, by said peeling means, in the form of a continuous filament.

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