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**PROCESS FOR PRODUCING COATINGS ON
CARBON AND GRAPHITE FILAMENTS**

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The present invention is concerned with improved processes for applying pyrolytic coatings to carbon and graphite filaments and more particularly with improved processes for applying coatings of pyrolytic graphite, pyrolytic graphite-alloys, pyrolytic carbides, and pyrolytic borides to carbon and graphite filaments.

Generally such pyrolytic coatings are applied by decomposing the source gases (e.g., hydrocarbons for pyrolytic graphite, elemental halides for pyrolytic borides, and mixtures of hydrocarbons and halides for pyrolytic carbides and pyrolytic graphite alloys) on the heated surfaces of the filaments. It has been usually found that it is quite difficult to provide uniform coatings. Often the diameter of the coatings will vary from location to location and sometimes areas of the filament charge will not be coated at all.

One object of the present invention is to provide improved processes for applying pyrolytic coatings.

Another object of the present invention is to provide processes for applying pyrolytic coatings to carbon and graphite filaments or fibers so as to improve the tensile strength and oxidation resistance of said materials.

Still another object of the present invention is to provide processes for producing high temperature resistant filamentary reinforcements for end uses such as erosion resistant ablative heat shields.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products possessing the features, properties, and the relation of elements which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

It has been found in the present invention that a substantial improvement in the uniformity of the pyrolytic coatings may be brought about by carrying out the pyrolytic decomposition at reduced pressure (i.e., less than atmospheric pressure), within a temperature range of about 1300 to about 2100° C. and by using about 10 to 400 parts by volume of a diluent gas per part by volume of the source gas.

As stated above, the processes of the present invention may be used for applying coatings of pyrolytic graphite, pyrolytic graphite-alloys, pyrolytic carbides and pyrolytic borides. As examples of elements which may be used to form the pyrolytic carbides, borides, and pyrolytic graphite-alloys mention may be made of hafnium, tantalum, zirconium, niobium, titanium, tungsten, silicon, and boron.

Hydrocarbons and elemental halides for use in the processes of the present invention may be selected from

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the various materials of this nature available. As examples of useful hydrocarbons mention may be made of alkanes such as methane, ethane, and propane; cycloalkanes such as cyclopropane, cyclobutane, and cyclohexane; and aromatics such as benzene, toluene and xylene. Particularly useful results have been obtained using methane. As examples of useful halides mention may be made of boron trichloride, silicon tetrachloride and the refractory metal halides such as zirconium tetrachloride, tantalum pentachloride, niobium pentachloride, hafnium tetrachloride, titanium tetrachloride and tungsten pentachloride.

In the processes of the present invention, as stated above, about 10 to 400 parts by volume of a diluent gas is used per part by volume of the source gas. Especially useful results were obtained by using about 25 to 50 parts of the diluent gas per part of the source gas. Generally the diluent gas may be selected from hydrogen, nitrogen, and the inert gases such as helium and argon. In preparing the pyrolytic carbides, borides and the pyrolytic graphite-alloys using halides, it has been found preferable to use an inert gas such as argon.

The processes of the present invention may be carried out in any closed, pressure-proof chamber which is equipped with means for reducing the pressure and heating the filaments to the desired temperatures. The chamber should also be equipped with means for holding the filaments. In coating the filaments, cloths, fabrics, or the like with pyrolytic graphite and pyrolytic graphite-alloys, more uniform and improved coatings were obtained by passing the source gases directly against the filaments and through the fabric or cloth. This was achieved by wrapping the filament structure around the perforated side walls of a cylindrical gas injector and feeding the source gas out through the perforations. In coating fabrics or cloths with pyrolytic carbides and borides, best results were obtained by having the source gas pass over as well as through the filament structure. This was accomplished by placing perforations in the end walls of the gas injectors as well as the side walls. Fibers or filaments such as, for example, staples, wool or the like are coated while held in an annular container around the cylindrical gas injector.

As stated above, the processes of the present invention are carried out at temperatures ranging between about 1300 to 2100° C. Usually the preferred temperatures within this range will depend on the coating being deposited. For pyrolytic graphite and pyrolytic graphite-alloys, best results were obtained at temperatures between about 1400 to 1600° C. and more particularly at 1500° C. For pyrolytic carbide and boride coatings, the preferred temperature lies between about 1500 to 2100° C. and more particularly between 1500 to 1800° C.

The pressures, at which the processes of the present invention are carried out, will usually be less than 100 mm. of mercury and more particularly less than 20 mm. Preferably the reactions are carried out at pressures of less than 10 mm. and more preferably at pressures of less than 5 mm.

The carbon and graphite filaments, fabrics, cloths or the like upon which the processes of the present invention are carried out are the pyrolysis products of yarns, wool, felts, cloth, etc. Generally such carbon and graphite materials are quite readily oxidized. The coatings applied by the processes of the present invention bring about a sub-

stantial improvement in the oxidation resistance of these materials, especially at temperatures of 600° to 800° C. The processes of the present invention also improve the tensile strength of the filaments and the warp strengths of the fabric or cloth. Usually the tensile strengths of the filaments increase from about 3000 to 50,000 p.s.i., to about 15,000 to 85,000 p.s.i. and the warp strengths of the fabrics of cloths show increases from about 17% to over 100%.

Although the processes of the present invention improve the strength of the filaments and fabric, it is often found that the coatings have an adverse effect of the brittleness of the materials. For this reason it is preferable that the coatings be less than 8 microns and more particularly less than 2 microns. Coatings of 1 micron or less have been found particularly useful.

It has also been found in the present invention that the brittleness brought about by the coatings of the present invention may be substantially reduced by heating the filaments and cloth subsequent to coating, to at least 3000° C. and more particularly between about 3000° and 3250° C. Usually treatment at this temperature for about one half to one hour will provide satisfactory results.

The preferred pyrolytic graphite-alloys within the present invention are those which comprise about 1 to 2% of the material which is to be alloyed with the graphite, e.g., zirconium, silicon, boron, hafnium, titanium, tantalum, etc. Alloys of the graphite with zirconium, boron, and titanium were found particularly useful.

The following nonlimiting examples illustrate the processes of the present invention.

Example 1

Carbon wool filaments were placed on a mandrel in a closed chamber which was then brought to a temperature of about 2000° C. and a pressure of about 1 mm. A mixture of methane, being fed at a rate of 0.02 liters per minute were passed through the apparatus for about 30 minutes. The ratio by volume of argon to methane was thus about 400 to 1. A 1 micron uniform coating of pyrolytic graphite was deposited on the filaments.

Example 2

Graphite yarn filaments were placed on a mandrel in a closed chamber which was then brought to a temperature of about 1400° C. and a pressure of about 0.7 mm. A mixture of methane, at a feed rate of 0.06 liters per minute, and hydrogen, at a feed rate of 6 liters per minute, were fed into the chamber. The ratio by volume of hydrogen to methane was about 100 to 1. The filaments were uniformly coated and had tensile strengths of about 58,400 p.s.i.

Example 3

Carbon cloth was wrapped around the cylindrical perforated walls of a mandrel in a closed chamber which was then brought to a pressure of 10 mm. and a temperature of about 1550° C. Methane at a flow rate of 0.75 liters per minute and hydrogen at a flow rate of 23.4 liters per minute were fed through the mandrel for about 4 hours. The ratio by volume of hydrogen to methane was thus about 31 to 1. The cloth was uniformly covered with a coating having a thickness of 1.0 to 1.4 microns.

Example 4

In a manner similar to Example 3, carbon cloth at a temperature of 1500° C. and at a pressure of 3.2 mm. was treated for six hours with a mixture comprising methane, at a flow rate of 0.4 liters per minute, boron trichloride at a flow rate of 0.007 liters per minute, and argon at a flow rate of 9.5 liters per minute. The ratio by volume of argon to the source gases, methane and boron trichloride was thus about 23 to 1. A uniform pyrolytic

graphite-boron alloy coating, having a thickness of 1.2 to 1.4 microns was deposited. The alloy contained by weight about 1.8% of boron.

Example 5

The process was carried out for about 2 hours in a manner similar to Example 4 except that zirconium tetrachloride at a flow rate of about 0.009 liters per minute was used in place of the boron trichloride. The ratio by volume of argon to the source gas, methane and zirconium tetrachloride was about 12 to 1. A uniform coating of pyrolytic graphite-zirconium alloy, having a thickness of about 1 micron was obtained. The alloy contained by weight about 1.0% zirconium.

Example 6

The process of Example 5 was repeated in substantially the same manner except hafnium tetrachloride was used in place of the zirconium tetrachloride. The ratio by volume of argon to source gas, methane and hafnium tetrachloride was about 22 to 1. A uniform coating of the pyrolytic graphite-hafnium alloy, having a thickness of about 1 micron, was obtained. The alloy contained by weight about 1.0% hafnium.

Example 7

Carbon cloth was heated to a temperature of 1500° C. at a pressure of 4.7 mm. A gas comprising tantalum pentachloride at a flow rate of 0.06 liters per minute and argon at a flow rate of 1.25 liters per minute was passed through the cloth for three hours. The ratio by volume of argon to tantalum pentachloride was thus about 21 to 1. The cloth took on a good tantalum carbide appearance.

Example 8

The process was carried out in a manner similar to Example 7 except zirconium tetrachloride was used in place of the tantalum pentachloride. In this case, the cloth was heated to a temperature of about 1450° C. at a pressure of about 3.7 mm. A gaseous mixture of tantalum pentachloride and argon were passed through the cloth for about 45 minutes. The flow rate of the halide was about 0.3 liters per minute while the argon flow rate was about 6.5 liters per minute. The ratio by volume of argon to halide was thus about 22 to 1. A uniform surface deposit of zirconium carbide was obtained.

Example 9

The process was carried out in a manner similar to Example 7 for 2 hours at a pressure of 0.7 mm. using niobium pentachloride in place of the tantalum pentachloride. The ratio by volume of argon to halide in this run was maintained at about 25 to 1. A substantial portion of the cloth had a niobium carbide coating.

Example 10

Carbon cloth was wrapped around the cylindrical perforated walls of a mandrel in a closed chamber which was then brought to a pressure of about 1.3 mm. and a temperature of about 1200° C. Zirconium tetrachloride and boron trichloride each at a flow rate of about 0.15 liters per minute and hydrogen at a flow rate of about 3.86 liters per minute were fed through the mandrel for about 2 hours. The ratio by volume of hydrogen to halide was about 13 to 1. A thin coating of zirconium diboride was obtained on the cloth.

Samples of various coated carbon and graphite cloths were heated to elevated temperature in the presence of air to determine the oxidation resistance thereof. The air flow rate was about 0.06 feet per second. Each test was about 5 minutes duration. The results of the oxidation tests are set forth in the following table.

TABLE I

Substrate Material	Coating Material	Coating Thickness (microns)	Percent Weight Loss		
			600° C.	800° C.	1,200° C.
Carbon Cloth.....	As received.....	Uncoated	91.50	93.70	100.00
Do.....	Pyrolytic Graphite.....	1.4	0.15	22.14	93.90
Do.....	Pyrolytic Graphite =2% boron alloy...	1.4	0.25	2.03	73.34
Do.....	Pyrolytic Graphite =1% zirconium alloy.	1.0	0.63	10.20	86.90
Do.....	Pyrolytic Graphite =1% hafnium alloy.	1.0	0.36	42.40	85.90
Do.....	Pyrolytic tantalum carbide.....	0.5	0.35	59.40	65.60
Do.....	Pyrolytic Graphite=1% titanium alloy	1.2	0.26	1.27	88.30
Do.....	Pyrolytic Graphite =1% silicon alloy...	1.0	0.39	4.34	94.30
Do.....	Pyrolytic Graphite-total 2% zirconium and boron alloy.	1.0	0.39	0.88	91.56
Do.....	As received.....	Uncoated	0.40	53.00	85.00
Do.....	Pyrolytic Graphite.....	1.9	0.17	1.61	79.80
Do.....	Pyrolytic Graphite =2% boron alloy...	1.0	0.27	2.35	84.36
Do.....	Pyrolytic Graphite =1% zirconium alloy.	1.2	0.54	3.10	86.90
Do.....	Pyrolytic Graphite =1% hafnium alloy.	1.0	0.29	5.18	85.30
Do.....	Pyrolytic tantalum carbide.....	0.5	0.24	1.44	78.40
Do.....	Pyrolytic Graphite =1% titanium alloy	1.0	0.26	1.27	88.30
Do.....	Pyrolytic Graphite =1% silicon alloy...	1.0	0.39	4.34	94.30
Do.....	Pyrolytic Graphite =2% zirconium and boron alloy.	1.0	0.39	0.88	91.60

Although the above examples particularly illustrate only some of the alloys, borides, and carbides which may be deposited by the processes of the present invention, it should be understood that those not particularly shown have properties similar to the ones shown and the principles of the present invention will be equally applicable.

Since certain changes may be made in the above processes and products without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for depositing pyrolytic coatings on carbon and graphite filaments, which comprises depositing said coatings at a temperature between about 1300° C. and 2100° C. and at a pressure of less than 100 mm. of mercury, using about 10 to 400 parts by volume of a diluent gas to 1 part by volume of a source gas, said source gas comprising at least one material selected from the group consisting of hydrocarbons and halides of tantalum, zirconium, niobium, hafnium, titanium, tungsten, silicon, and boron.

2. A process as defined in claim 1 wherein the pressure is less than 20 mm. of mercury and 25 to 50 parts by volume of said diluent gas is used per part by volume of the source gas.

3. A process as defined in claim 1 wherein said diluent gas is selected from the group consisting of hydrogen, nitrogen, and the inert gases.

4. A process as defined in claim 1 wherein said coated filaments are heated to at least 3000° C.

5. A process for depositing pyrolytic graphite coatings on carbon and graphite filaments which comprises depositing said coatings at a temperature between about 1300° C. and 2100° C. and at a pressure of less than 100 mm. of mercury using about 10 to 400 parts by volume of a diluent gas selected from the group consisting of hydrogen, nitrogen, and the inert gases to 1 part by volume of a hydrocarbon gas.

6. A process as defined in claim 5 wherein said temperature is between about 1400 and 1600° C., said pressure is less than 20 mm. of mercury, and about 25 to 50 parts by volume of said diluent gas is used per part by volume of said hydrocarbon gas.

7. A process as defined in claim 4, wherein said hydrocarbon gas is methane.

8. A process as defined in claim 4 wherein said filaments subsequent to being coated with pyrolytic graphite are heated to a temperature of at least 3000° C.

9. A process for depositing pyrolytic graphite-alloy coatings on carbon and graphite filaments which comprise depositing said coatings at a temperature between about 1300° C. and 2100° C. and at a pressure of less than 100 mm. of mercury, using about 10 to 400 parts by

volume of an inert gas to 1 part by volume of a source gas, said source gas comprising a hydrocarbon and at least one halide of an element selected from the group consisting of tantalum, zirconium, niobium, hafnium, titanium, tungsten, silicon, and boron.

10. A process as defined in claim 9 wherein said temperature is between about 1400 and 1600° C., the pressure is less than 20 mm. and 25 to 50 parts by volume of said inert gas is used per part by volume of said source gas.

11. A process as defined in claim 9 wherein said halide is zirconium tetrachloride.

12. A process as defined in claim 9 wherein said halide is boron trichloride.

13. A process as defined in claim 9 wherein said halide is hafnium tetrachloride.

14. A process for depositing pyrolytic carbides on carbon and graphite filaments which comprises depositing said coatings at a temperature between about 1500° C. and 2100° C. and at a pressure of less than 100 mm. of mercury using about 10 to 400 parts by volume of at least one of the inert gases to 1 part by volume of a source gas, said source gas comprising a halide of an element selected from the group consisting of tantalum, zirconium, niobium, hafnium, titanium, tungsten, silicon, and boron.

15. A process as defined in claim 14 wherein said temperature is between about 1500° C. and 1800° C., the pressure is below about 20 mm. and 25 to 50 parts by volume of said inert gas is used per part by volume of said source gas.

16. A process for depositing pyrolytic borides on carbon and graphite filaments which comprises depositing said coatings at a temperature between about 1500° C. and 2100° C., and at a pressure below about 100 mm. of mercury, using about 10 to 400 parts by volume of an inert gas to 1 part by volume of a source gas comprising a boron halide and a halide of an element selected from the group consisting of tantalum, zirconium, niobium, hafnium, titanium, tungsten, and silicon.

17. A process as defined in claim 16 wherein said boron halide comprises boron trichloride, said temperature is between about 1500° C. and 1800° C., the pressure is below about 20 mm., and 25 to 50 parts by volume of said inert gas is used per part by volume of said source gas.

18. Carbon and graphite filaments having a coating thereon to improve the tensile strength and oxidation resistance thereof, said coated filaments being produced by depositing on said filaments a coating selected from the group consisting of pyrolytic graphite, pyrolytic graphite alloys, pyrolytic carbides, and pyrolytic borides, said coating having a thickness of less than about 2 microns being deposited at a temperature between about 1300° C. and 2100° C. and at a pressure of less than

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about 100 mm. of mercury using about 10 to 400 parts by volume of a diluent gas to 1 part by volume of a source gas comprising at least one material selected from the group consisting of hydrocarbons and halides of tantalum, zirconium, niobium, hafnium, titanium, tungsten, silicon and boron.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,369,920 Dated February 20, 1968

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 66 and column 5, line 68, the claimed reference number "4" should read -- 5 --.

Signed and sealed this 23rd day of June 1970.

(SEAL)

Attest:

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