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3,676,179 COATED ARTICLE AND METHOD FOR MAKING SAME

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ABSTRACT OF THE DISCLOSURE

A method of coating with pyrolytic carbon to provide a coated article having high strength characteristics. Deposition of pyrolytic carbon is effected on an article from a carbonaceous atmosphere at a preselected temperature under conditions that result in formation of carbon having a preselected coefficient of thermal expansion which is less than that of the article. During cooling of the coated article to ambient temperature, the difference between the coefficients of thermal expansion of the article and the pyrolytic carbon causes the pyrolytic carbon coating to be placed under substantial compressive tangential stress. Deposition is usually carried out at a temperature of about 1500° C. or below to deposit fairly dense isotropic or laminar carbon. The coefficient of thermal expansion of the article being coated is usually between about 6 to $9 \times 10^{-6}/^{\circ}\text{C.}$, with the preferred material being graphite.

The present invention relates generally to the coating of articles and, more particularly, it relates to methods of coating articles with pyrolytic carbon and to the products of such methods.

Coating articles with pyrolytic carbon is a known coating operation. Generally, it is carried out by deposition onto the articles of pyrolytic carbon formed by high temperature decomposition (pyrolysis) of carbonaceous substances, such as volatile or gaseous hydrocarbons. In U.S. Letters Patent No. 3,298,921, there are disclosed various specific examples of effecting such deposition and the types of crystalline pyrolytic carbon formed are defined. The disclosure of this patent is incorporated herein by reference. A preferred method of coating disclosed in that patent involves a fluidized bed process in which the hydrocarbon gas, or a mixture of the hydrocarbon gas with a carrier gas, is utilized to levitate a bed of the articles being coated.

In fluidized bed coating, and in other known alternative methods for depositing pyrolytic carbon, elevated temperatures are used to produce decomposition of the hydrocarbon gas. Such decomposition temperatures vary between, for example, 800° C. and 2300° C. At such elevated temperatures the hydrocarbon gas decomposes and elemental carbon is deposited on the articles.

By suitable selection of temperature, carbonaceous substance and other operating variables, various different types of pyrolytic carbon are obtained. As set forth in the foregoing patent, at least three different carbon structures may be obtained, namely, laminar carbon, isotropic carbon and granular carbon. The strengths of these types of pyrolytic carbon vary, and when it is desired to obtain high strength characteristics in the pyrolytic carbon deposited, the stronger carbon types, i.e., isotropic and laminar carbon, are used.

It is an object of the present invention to provide a method of depositing pyrolytic carbon wherein high structural strength is obtained. A further object is to provide strong pyrolytic carbon-coated articles.

Generally, in accordance with the present invention,

the conditions of pyrolytic carbon deposition are carefully controlled to deposit pyrolytic carbon having a coefficient of thermal expansion less than the coefficient of thermal expansion of the article to be coated so that, after the coated article cools to room temperature, the pyrolytic carbon is under compressive tangential stress. It is believed that any substantial compressive tangential stress that is created increases the structural strength of the coated article and that the greater the magnitude of the tangential compressive stress, the greater is the resultant strength of the coated article, until an upper limit is reached as discussed hereinafter. The carbons of primary interest are isotropic carbons deposited at temperatures of about 1500° C. or below, which carbons have a modulus of rupture in the range of 30,000 to 70,000 p.s.i. and are thus well capable of withstanding these tangential compressive stresses.

More particularly, pyrolytic carbon has greater structural strength under compressive stress than under tensile stress. It is possible to take advantage of its higher compressive strength to provide a coated article having high structural strength. The use of these relatively high temperatures necessary to obtain pyrolysis of the hydrocarbon gas and consequent deposition on the article being coated facilitates the obtaining of this objective because of the significant temperature differential available.

Because of the high temperatures at which pyrolysis is carried out, the materials of which the articles to be coated may be made are somewhat limited. Such material, sometimes referred to herein as the substrate, should not lose substantial strength at pyrolysis temperatures and should not chemically react with the substances in the pyrolysis zone. Examples of suitable substrate materials include carbon (graphite in particular), tantalum, tungsten, molybdenum, alloys thereof, and refractory materials in general, such as mullite. The coefficient of thermal expansion of potential substrate materials is usually known, or if not known can readily be determined. For purposes of the present applications, substrates are usually chosen having coefficients of thermal expansion between about 6 to $9 \times 10^{-6}/^{\circ}\text{C.}$

The article to be coated is disposed in the zone wherein pyrolysis is to be carried out and is heated therein to a preselected temperature. This temperature, as subsequently set forth, is functionally related to the type of carbon to be deposited, to the desired coefficient of thermal expansion of the deposited carbon, and to the magnitude of the final compressive tangential stress that is attained in the cool coated article. The temperature and the other coating conditions are accordingly chosen to provide the particular crystalline type of carbon desired and to provide a preselected coefficient of thermal expansion of the carbon which is less than the coefficient of thermal expansion of the substrate material.

Because one of the objectives of the coating operation is to provide a product having high structural strength, the pyrolytic carbon employed should complement this objective. Generally, the density of the pyrolytic carbon deposited should be at least about 1.5 gm./cm.³ because porous carbons do not exhibit as high resistance to compression as do more dense carbons. Likewise, because good structural strength is a criterion of the resultant product, the pyrolytic carbon coating should be thick enough to provide such strength. Accordingly, the pyrolytic carbon coating will be at least about 25 microns thick and usually will have a thickness of 100 microns or more. Although both laminar and isotropic carbons can be employed to produce coated articles having good structural strength, isotropic carbon is preferred because it exhibits no tendency to delaminate and because stresses due to anisotropic expansion do not arise in isotropic coatings

on irregular shapes at locations where small radii of curvature are encountered. Isotropic carbon having an apparent crystallite size of about 50 A. or less and which is deposited at between about 1200° C. and 1500° C. is generally preferred.

Cooling of the coated article from the elevated deposition temperature results in shrinkage or contraction of both the substrate material and the coating. To obtain the desired compressive tangential stress, the bond between the carbon coating and the substrate must be sufficiently strong and the coefficient of thermal expansion of the pyrolytic carbon coating should not be so much different than the coefficient of thermal expansion of the substrate as to break or rupture the bond. On the other hand however, the coefficient of thermal expansion of the carbon should certainly not be greater than the coefficient of thermal expansion of the substrate material least the coating be placed in tension upon cooling, rendering it more susceptible to fracture. The coefficient of thermal expansion of the pyrolytic carbon coating is selectively less than that of the substrate material so that, upon cooling of the coated article, the substrate material contracts more than the coating and places the coating under compressive tangential stress. However, the difference in coefficients should not be so great that, upon cooling, the compressive fracture stress of the coating is reached (which would result in failure of the coating) or the substrate separates from the coating at the interface therebetween.

The magnitude of the compressive tangential stress in the coating material after cooling is dependent not only on the difference in coefficients of thermal expansion of the respective material, but also upon the temperature differential between deposition temperature and ambient temperature. The prospective temperature difference is therefore taken into consideration in determining the desired coefficient of thermal expansion for the pyrolytic carbon to be deposited. Because of the different inter-related variable to be considered, no set numerical value can be definitively stated; however, usually the thermal coefficient of expansion of the substrate will not be more than about 50 percent greater than that of the carbon coating.

If the coated article will be used at temperatures other than ambient temperature, then the temperature of intended use is also taken into consideration. Preferably, the coating should be under tangential compressive stress both at ambient temperature and at the temperature of use, if they are different.

The modulus of rupture of pyrolytic carbon deposited at about 1500° C. or below should exceed 30,000 p.s.i. tangential compressive stress has been obtained in pyrolytic carbon coatings between about 5000 and 30,000 p.s.i. with the resultant coated articles exhibiting high structural strengths. Tangential compressive stress at least as high as 20,000 p.s.i., may be obtained using a substrate made of graphite to which the pyrolytic carbon forms an excellent bond. An actual upper limit of the tangential compressive strength has not been determined and will presumably be dependent at least in part upon the substrate material and how strong a bond is obtained thereto. In general when this upper limit is exceeded, if the carbon layer is relatively thick, debonding occurs, and if the carbon coating is thin, compressive failure of the carbon layer occurs.

Articles of various geometric configurations may be coated in accordance with the present invention. Usually the coated articles will have a largest dimension at least equal to one-half inch inasmuch as the strength of the article is a desired advantage. However, for some specific purposes, smaller articles might be desirable. Spheres, rods and even tubes are examples of such articles that may be fabricated having good structural strength.

The following examples show two illustrative processes for making strong articles coated with pyrolytic carbon.

Both examples employ the generally preferred methods of depositing isotropic carbon at temperatures below about 1500° C. For purpose of further explanation, when employing a pyrolytic deposition process, it is generally not substantially more difficult to deposit isotropic carbon at temperatures below about 1500° C. than to deposit laminar carbon or higher temperature isotropic carbon. Accordingly, because such lower temperature isotropic carbons can be deposited having a BAF of 1.1 or less, apparent crystallite sizes of 50 A. or less and a density up to about 2.0 g./cm.³, they are usually employed because they have greater strength and greater wearability. However, isotropic carbon deposited at temperatures above about 1500° C., as from methane or propane or the like, might be used for many applications. Likewise, Laminar carbon, which as deposited from methane at temperatures below 1500° C. has a apparent crystallite size of about 50 A. or less and has a density greater or equal to about 1.5 g./cc., may adequately fill the requirements of many applications.

EXAMPLE I

A generally spherical article is chosen made of graphite having a coefficient of thermal expansion of about $8 \times 10^{-6}/^{\circ}\text{C}$. The spheroid, approximately $\frac{3}{4}$ inch in diameter, is lightly sandblasted to remove any loose particles and is placed in a vertical graphite reaction tube. The tube is about 6.3 centimeters in diameter and is heated to a temperature of about 1400° C. while a flow of helium gas therethrough is maintained. When coating is ready to begin, the spheroid plus an ancillary charge of 100 grams of zirconium dioxide particles (to provide additional available deposition surface area as explained in U.S. Pat. 3,399,969) having an average particle size of about 400 microns are loaded into the reaction tube. Propane gas is admixed with the helium to provide a partial pressure of propane of about 0.3 atm. (total pressure of 1 atm.). The total flow of gas is held at about 4000 cc. per minute. The propane undergoes pyrolysis and deposits carbon. Carbon is deposited on the spheroid in the form of isotropic pyrolytic carbon having a coefficient of thermal expansion of about $5 \times 10^{-6}/^{\circ}\text{C}$. Subsequent examination also shows the carbon has a BAF of about 1.1, an apparent crystallite size of about 40 A. and a density of about 1.7 grams per cm.³. Deposition is continued until an isotropic pyrolytic carbon coating about 6 mils (150 microns) thick is obtained, a time of about an hour.

The resultant coated sphere is allowed to cool to ambient temperature and is removed from the reaction tube. The change in temperature of nearly 1400° C. between the deposition temperature and ambient temperature effects a sufficiently greater contraction of the substrate carbon spheroid than of the isotropic carbon coating to set up a circumferential compressive stress in the coating of about 15,000 p.s.i. This stress is well below the estimated compressive fracture stress of the coating.

The resultant coated article is considered to have high structural strength. For example, a control article which is similarly coated with pyrolytic isotropic carbon which has a greater coefficient of thermal expansion than the carbon substrate, so that its circumference is under tensile strength, will fracture upon being dropped from a height of about three feet. The coated article described above having its outer coating in compressive stress may be dropped repeatedly from the same height without damage. Other tests show the coated spheroid exhibits not only good resistance to fracture, but also good wear-resistance.

EXAMPLE II

A graphite spheroid similar to that coated in Example I is introduced into the same reaction tube which is heated to a temperature of about 1350° C. while maintaining a flow of helium gas through it. When coating is

ready to begin, a similar ancillary charge of 100 grams of ZrO_2 particles is loaded into the reaction tube. Propane gas is admixed with the helium to provide a gas flow of about 8000 cc. per minute having a partial pressure of propane of about 0.4 atm. (total pressure of 1 atm.). All of the helium is bubbled through methyltrichlorosilane. The propane and the methyltrichlorosilane pyrolyze to deposit a mixture of isotropic carbon and silicon carbide on the spheroid. Deposition is continued until a coating about 8 mils (200 microns) thick is obtained, a time of about an hour.

The resultant coated sphere is allowed to cool to ambient temperature and is removed from the reaction tube. Examination of the isotropic carbon-silicon carbide coating shows it has a coefficient of thermal expansion of about $6 \times 10^{-6}/^\circ C.$ and a density of about 2 grams per $cm.^3$. The coating contains about 10 weight percent silicon, in the form of silicon carbide. The isotropic carbon has a BAF of about 1.1 and an apparent crystallite size of about 35 A. The change in temperature effects a sufficiently greater contraction of the substrate spheroid than of the coating to set up a circumferential compressive stress in the coating of about 10,000 p.s.i. This stress is well below the estimated compressive fracture stress of the coating.

The resultant coated article is considered to have excellent structural strength. The coated spheroid may be dropped repeatedly from about three feet without damage. Other tests show the coated spheroid exhibits not only good resistance to fracture, but also good wear-resistance. The isotropic carbon-silicon carbide coating is considered to have all the advantages from the standpoint of strength and wearability as the completely carbon coating produced in Example I. Moreover, with other coating variables being maintained generally equal, it is considered that an isotropic carbon coating that is deposited with a silicon carbide additive will have greater strength than the same isotropic carbon without the additive. In general, it is considered that up to about 15 percent by weight of silicon, or an equivalent amount of a similar carbide-forming additive, may be included without detracting from the desirable properties of the pyrolytic carbon coatings as described hereinbefore.

Various modifications and alternative embodiments of the present invention will be suggested to those having skill in the art and are intended to be within the spirit and scope of the present invention.

Various of the features of the present invention are set forth in the following claims.

What is claimed is:

1. A coated article having high strength characteristics, which comprises an article made of graphite having a coefficient of thermal expansion between 6 to $9 \times 10^{-6}/^\circ C.$ and a coating of pyrolytic carbon surrounding said graphite article which pyrolytic carbon was deposited thereupon at a temperature well above ambient and which has a strong bond to said underlying graphite article, said pyrolytic carbon having a density of at least 1.5 g./cc. and having a coefficient of thermal expansion which is less than that of the graphite article and being under substantial compressive tangential stress as a result of the thermal contraction occurring during cooling of the coated graphite article from deposition temperature to ambient temperature.

2. The coated article in accordance with claim 1 where-

in said compressive tangential stress is at least about 5000 p.s.i.

3. The coated article in accordance with claim 1 wherein the thickness of said pyrolytic carbon coating is at least about 25 microns.

4. The coated article in accordance with claim 1 wherein said pyrolytic carbon is isotropic carbon.

5. The coated article in accordance with claim 4 wherein said isotropic carbon has an apparent crystallite size of about 50 A. or less.

6. The coated article in accordance with claim 5 wherein said isotropic carbon has a BAF of about 1.1 or less.

7. The coated article in accordance with claim 1 wherein said pyrolytic carbon coating contains an additive carbide dispersed therethroughout.

8. The coated article in accordance with claim 7 wherein said additive carbide is silicon carbide.

9. A method of forming an article having high strength characteristics, which method comprises heating a graphite article having a coefficient of thermal expansion between 6 and $9 \times 10^{-6}/^\circ C.$ to a preselected deposition temperature of at least about $1200^\circ C.$, effecting deposition of pyrolytic carbon on said graphite article from a carbonaceous atmosphere at said preselected temperature under conditions that result in formulation of carbon having a density of at least 1.5 g./cc. and having a coefficient of thermal expansion which is less than that of said graphite article, and cooling the coated graphite article to ambient temperature, the difference between the coefficients of expansion of said graphite article and of said pyrolytic carbon being such and the bond therebetween being sufficiently strong that in cooling from deposition temperature to ambient temperature said pyrolytic carbon coating is placed under substantial compressive tangential stress.

10. A method in accordance with claim 9 wherein said deposition temperature is not greater than about $1500^\circ C.$

11. A method in accordance with claim 9 wherein the compressive tangential stress is at least about 5000 p.s.i.

12. A method in accordance with claim 9 wherein the thickness of said pyrolytic carbon coating is at least about 25 microns.

13. A method in accordance with claim 9 wherein said carbonaceous atmosphere contains a hydrocarbon, an inert gas and a volatile compound containing a carbide-forming element.

14. A method in accordance with claim 13 wherein said volatile compound contains silicon.

15. A method in accordance with claim 9 wherein said pyrolytic carbon coating is isotropic carbon having an apparent crystallite size of about 50 A. or less.

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