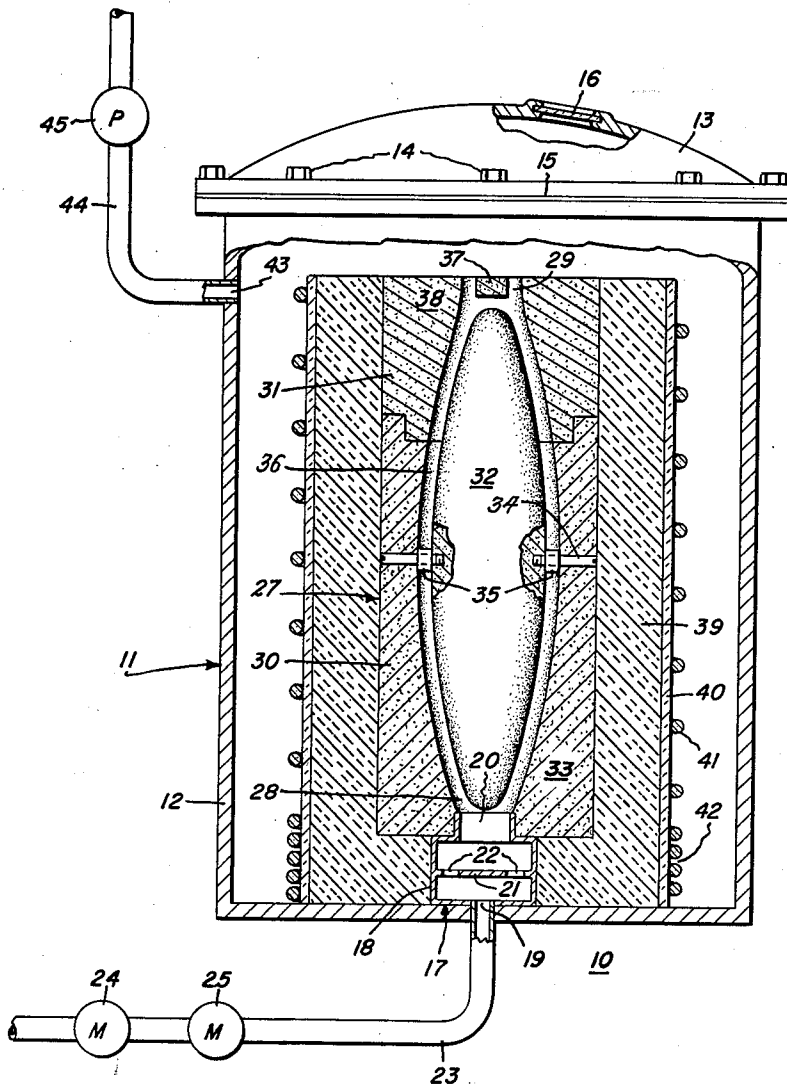


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METHOD FOR DEPOSITING CARBON COATINGS
ON HIGH TEMPERATURE MATERIAL MEMBERS
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METHOD FOR DEPOSITING CARBON COATINGS ON HIGH TEMPERATURE MATERIAL MEMBERS

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This invention relates to methods of forming composite articles and more particularly to methods of forming composite articles having a member with a hard carbon coating thereon.

This application is a continuation in part of application Serial No. 135,657, filed September 1, 1961, now abandoned, and assigned to the same assignee as the present application.

Hard carbon coatings are desirable to provide wear and abrasion resistant surfaces for members. These coatings are defined as having a scratch hardness greater than glass. For example, such coatings would be advantageous for covering members to produce dies and seal rings.

Carbonaceous gases have been thermally decomposed and deposited on a surface to produce pyrolytic graphite. As a result of the decomposition, carbon is removed from the gas and deposits on the surface so that planar graphite crystallites are aligned into a layer structure. It would also be desirable to provide composite articles having a member with an adherent, hard carbon coating which has more randomly oriented crystallites to provide good wear properties. Furthermore, it would be advantageous to provide deposition methods of forming such composite articles.

It is an object of our invention to provide a deposition method of forming adherent, hard carbon coatings on members.

It is another object of our invention to provide a deposition method of forming such hard carbon coatings with more randomly oriented crystallites.

It is a further object of our invention to provide a deposition method of forming adherent, hard carbon coatings on members in which different types of coatings are deposited on separate members.

In carrying out our invention in one form, a deposition method comprises providing an enclosure with two connected portions, positioning at least one member of high temperature material within a first portion of said enclosure, positioning at least one member of high temperature material in a second portion of said chamber, maintaining the pressure of said enclosure between one millimeter of mercury and atmospheric pressure, heating an unsaturated hydrocarbon material to a temperature in the range of 1300° C. to 1700° C. to decompose the material to a carbonaceous vapor, supplying the vapor to the first portion of the enclosure, depositing a portion of the vapor as an adherent hard carbon coating on the member within the first portion of the enclosure, supplying the remaining vapor to the second portion of said enclosure, and depositing said remaining vapor at a temperature of at least 200° C. below the initial temperature of the vapor in the first portion as an adherent harder carbon coating on said member within the second portion of said enclosure.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

The single figure is a sectional view of a deposition apparatus for forming hard carbon coatings in accordance with our invention.

In the single figure, a deposition apparatus is shown

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generally at 10 which comprises a chamber 11 having a lower body portion 12 and a cover 13 which is hinged to the lower body portion by means of bolts 14 and employs an "O" ring 15 therebetween. Viewing window 16 is provided in cover portion 13 to view the operation and to read an optical pyrometer (not shown). A preheater 17 is positioned on the inner surface of the bottom wall of chamber 11 and consists of a container 18 having an inlet 19 and outlet 20. A baffle 21 is positioned within the preheater and is provided with a plurality of openings 22 around the perimeter thereof.

A feed line 23 is connected at the inlet opening 19 of preheater 17 and extends through the bottom wall of chamber 12 to an unsaturated hydrocarbon material source (not shown). Such a material in gaseous, solid or liquid state, is fed from the source through a total consumption meter 24, a rate meter 25 and line 23 to preheater 17.

An enclosure 27 of graphite or other high temperature material having an inlet 28 and an outlet 29 is positioned on preheater 17 by aligning inlet 28 of the enclosure with outlet 20 of preheater 17. Enclosure 27 can be constructed of several pieces, such as a lower part 30 and an upper part 31 joined together. In this manner, a member 32 is placed within a first portion 33 in the enclosure and supported therein in a relatively simple fashion. There is shown a member 32 of graphite or other high temperature material supported concentrically within first portion 33 of enclosure 27 by means of pins 34 and nuts 35. For example, first portion 33 extends from inlet 28 to the end of member 32 adjacent outlet 29.

A narrow passage 36 is formed between the exterior surface of member 32 and the interior surface of first portion 33 of enclosure 27. A member 37 of graphite or other high temperature material is positioned within a second portion 38 of enclosure 27. For example, second portion 38 extends from the end of member 32 through outlet 29. Suitable insulation in the form of carbon black 39 surrounds enclosure 27 and is held in position by a quartz or asbestos paper cylinder 40. Conventional induction heating coils 41 surround cylinder 40 to provide heat for enclosure 27, member 32, and passage 36 during the deposition process. An induction heating coil 42 surrounds cylinder 40 adjacent preheater 17 to provide heat for the preheater. Chamber 12 is also provided with an outlet 43 to which is connected a line 44 associated with a vacuum pump 45 to reduce the pressure in chamber 12.

While it is disclosed that the enclosure is a two-piece structure, a one-piece structure or a plurality of pieces can be employed. If a plurality of pieces are used, the interior surface of the enclosure can be machined to conform to the exterior contour of the member.

We discovered unexpectedly that different types of adherent, hard carbon coatings are produced on separate members of high temperature material within an enclosure having a first portion connected with a second portion. At least one member is positioned within the first portion while at least one member is positioned within the second portion. The pressure of the enclosure is maintained between one millimeter of mercury and atmospheric pressure.

An unsaturated hydrocarbon material, which is heated in a temperature range of 1300° C. to 1700° C. decomposes the material to a carbonaceous vapor which is supplied to the first portion of the enclosure. Such first portion and its associated member can also be heated in this temperature range to decompose the unsaturated hydrocarbon material which has been supplied thereto. Furthermore, the unsaturated hydrocarbon material can be decomposed to a carbonaceous vapor and supplied to the enclosure in which both the first portion and its associated member have been heated to a temperature in the range of

1300° C. to 1700° C. The unsaturated hydrocarbon material, which has been decomposed to a carbonaceous vapor as described above, has a portion of its vapor deposited as an adherent hard carbon coating on the member within the first portion of the enclosure.

A lower temperature range of 1100° C. to 1500° C. is maintained for the remaining carbonaceous vapor which has been supplied to the second portion of the enclosure. This lower temperature range within the second portion of the enclosure prevents excessive carbon-carbon bond scission whereby a hard carbon coating is formed which coating is harder than the coating on the member within the first portion of the enclosure. Other materials appear to be driven off in this lower temperature range with a resulting hard carbon formation. The second portion of the enclosure is maintained in the above lower temperature range. The flow of the vapor from the first portion to the second portion of the enclosure is also used to reduce the temperature. If desired, the second member can be cooled by any suitable means, such as cooling coils, to the lower temperature range. The remaining vapor which has been supplied to the second portion of the enclosure is deposited at a temperature of at least 200° C. below the initial temperature of the vapor in the first portion as an adherent harder carbon coating on the member within the second portion of the enclosure.

It was previously described that members 32 and 37 and enclosure 27 are formed of graphite or other high temperature material. First portion 33 of enclosure 27 and member 32 are subjected to temperatures in the range of 1300° C. to 1700° C. while second portion 38 of enclosure 27 and member 37 are subjected to temperatures in the range of 1100° C. to 1500° C. Such a high temperature material is a material which can be subjected to elevated temperatures without adverse effect to its solid state condition.

Such a material is not usable if it melts, or vaporizes at the operating temperature employed and would not be a high temperature material. Various high temperature materials other than graphite can be employed. For example, in the temperature range of 1300° C. to 1700° C., boron nitride and zirconia are suitable. In the range of 1000° C. to 1500° C., alumina is usable. At 1100° C., silica and quartz may be employed. It will also be appreciated that a material suitable for the higher temperature range may also be employed in the lower temperature range.

In the operation of deposition apparatus 10 shown in the single figure, a member 32 of graphite is positioned within first portion 33 of enclosure 27 by means of pins 34 and nuts 35. Member 32 and enclosure 27 are spaced apart to provide a narrow passage 36 therebetween. Enclosure 27 of graphite is then positioned on preheater 17 with outlet 20 of preheater 17 and inlet 28 of enclosure 27 in alignment. Member 37 of graphite is positioned within second portion 38 of enclosure 27. Cylinder 40 surrounds enclosure 27 and provides a space which is filled with carbon black insulation 39. Induction coils 41 surrounds cylinder 40 for heating enclosure 27, member 32, and passage 36 while an induction coil 42 provides heat for preheater 17. Cover 13 is bolted to lower body portion 12 of chamber 11.

The chamber atmosphere is maintained between 1 millimeter of mercury and atmospheric pressure. An unsaturated hydrocarbon material, such as dicyclopentadiene, is mixed with a methane carrier and is fed through a total consumption meter 24, and a rate meter 25 prior to entering preheater 17 through line 23. Power is supplied to induction coils 41 and 42 to bring the temperature of the first portion 33 of enclosure 27 and preheater 17 up to a temperature in the range of 1300° C. to 1700° C. We have found that this temperature range decomposes the unsaturated hydrocarbon material to a carbonaceous vapor. The unsaturated hydrocarbon material can also be heated in the above temperature range to de-

compose the material to a carbonaceous vapor. Additionally, such carbonaceous vapor can be supplied to passage 36 while the first portion of the chamber and its associated member are heated also in the same temperature range.

A portion of the carbonaceous vapor is deposited as an adherent hard carbon coating on the member within the first portion of the enclosure. The remaining carbonaceous vapor is supplied the second portion of the enclosure and deposited at a temperature of at least 200° C. below the initial temperature of the vapor in the first portion as an adherent harder carbon coating on the member within the second portion of the enclosure. The above process with an unsaturated hydrocarbon material can be carried out over a wide range of pressure conditions such as one millimeter of mercury to atmospheric pressure at gas flow rates, such as 8 to 16 cubic feet per hour.

Several examples of composite articles including a hard carbon coating which were made in accordance with the methods of the present invention are as follows:

Example I

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A commercial graphite member was positioned within the first portion of a commercial graphite enclosure to form a passage therebetween. Another member of commercial graphite was positioned within the second portion of the enclosure. After the cover was bolted to the lower body portion, the chamber atmosphere was evacuated initially to a pressure of 10^{-4} centimeters of mercury by the pump and maintained subsequently at a pressure of about 10 millimeters of mercury. Power was supplied to the induction coils to heat the first portion of the enclosure to a temperature of about 1690° C. A methane carrier which was saturated with dicyclopentadiene was supplied at a rate of 16 cubic feet per hour at a pressure of about 10 millimeters of mercury to the chamber. The dicyclopentadiene was decomposed to a carbonaceous vapor and a portion of the vapor was deposited as an adherent hard carbon coating on the member within the first portion of the enclosure. A portion of the vapor was cooled to about 1200° C. and deposited as a harder carbon coating on the member within the second portion of the enclosure. The deposition was continued for a period of about 236 minutes. The latter member had a coating of about 30 mils thickness.

Example II

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A commercial graphite member was positioned within the first portion of a commercial graphite enclosure to form a passage therebetween. Another member of commercial graphite was positioned within the second portion of the enclosure. After the cover was bolted to the lower body portion, the chamber atmosphere was evacuated initially to a pressure of 10^{-4} centimeters of mercury by the pump and maintained subsequently at a pressure of 10 millimeters of mercury. Power was supplied to the induction coils to heat the first portion of the enclosure to a temperature of about 1315° C. A methane carrier which was saturated with dicyclopentadiene was supplied at a rate of 8 to 12 cubic feet per hour at a pressure of 10 millimeters of mercury to the chamber. The dicyclopentadiene was decomposed to a carbonaceous vapor and a portion of the vapor was deposited as an adherent hard carbon coating on the member within the first portion of the enclosure. A portion of the vapor was cooled to about 1100° C. and deposited as a harder carbon coating on the member within the second portion of the enclosure. The deposition was continued for a period of about 387 minutes. The latter member had a coating of about 20 mils thickness.

Example III

A deposition apparatus was set up generally in accord-

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ance with the single figure of the drawing. A commercial graphite member was positioned within the first portion of a commercial graphite enclosure to form a passage therebetween. Another member of commercial graphite was positioned within the second portion of the enclosure. After the cover was bolted to the lower body portion, the chamber atmosphere was evacuated initially to a pressure of 10^{-4} centimeters of mercury by the pump and maintained subsequently at pressures of 2, 20 and 200 millimeters of mercury. Power was supplied to the induction coils to heat the first portion of the enclosure to a temperature of about 1400°C . A methane carrier which was saturated with dicyclopentadiene was supplied at a rate of 8 cubic feet per hour at pressures of 2, 20 and 200 millimeters of mercury to the chamber for periods of 2, 2 and 1 hours, respectively. The dicyclopentadiene was decomposed to a carbonaceous vapor and a portion of the vapor was deposited as an adherent hard carbon coating on the member within the first portion of the enclosure. A portion of the vapor was cooled to about 1200°C . and deposited as a harder carbon coating on the member within the second portion of the enclosure. The latter member had a coating of 60 mils thickness.

While other modifications of this invention and variations in the method which may be employed within the scope of the invention have not been described, the invention is intended to include such that may be embraced within the following claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A deposition method which comprises providing an enclosure with two connected portions, positioning at least one member of high temperature material within a first portion of said enclosure, positioning at least one member of high temperature material in a second portion of said enclosure, maintaining the pressure of said enclosure between one millimeter of mercury and atmospheric pressure, heating an unsaturated hydrocarbon material to a temperature in the range of 1300°C . to 1700°C . to decompose said material to a carbonaceous vapor, supplying said vapor to the first portion of said enclosure, depositing a portion of said vapor as an adherent hard carbon coating on said member within the first portion of said enclosure, supplying the remaining vapor to the second portion of said enclosure, and depositing said remaining vapor at a temperature of at least 200°C . below the initial temperature of the vapor in said first portion as an adherent harder carbon coating on said member within the second portion of said enclosure.

2. A deposition method which comprises providing an enclosure with two connected portions, positioning at least one member of high temperature material within a first portion of said enclosure, positioning at least one member of high temperature material in a second portion of said enclosure, maintaining the pressure of said enclosure between one millimeter of mercury and atmospheric pressure, supplying an unsaturated hydrocarbon material to the first portion of said enclosure, heating the first portion of said enclosure to a temperature in the range of 1300°C . to 1700°C . to decompose said material to a carbonaceous vapor, depositing a portion of said vapor as an adherent hard carbon coating on said member within the first portion of said enclosure, supplying the remaining vapor to the second portion of said enclosure, and depositing said remaining vapor at a temperature of at least 200°C . below the initial temperature of the vapor in said first portion as an adherent harder carbon coating on said member within the second portion of said enclosure.

3. A deposition method which comprises providing an

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enclosure with two connected portions, positioning at least one member of high temperature material within a first portion of said enclosure, positioning at least one member of high temperature material in a second portion of said enclosure, maintaining the pressure of said enclosure between one millimeter of mercury and atmospheric pressure, heating an unsaturated hydrocarbon material to a temperature in the range of 1300°C . to 1700°C . to decompose said material to a carbonaceous vapor, supplying said vapor to the first portion of said enclosure, heating the first portion of said enclosure to a temperature in the range of 1300°C . to 1700°C ., depositing a portion of said vapor as an adherent hard carbon coating on said member within the first portion of said enclosure, supplying the remaining vapor to the second portion of said enclosure, and depositing said remaining vapor at a temperature of at least 200°C . below the initial temperature of the vapor in said first portion as an adherent harder carbon coating on said member within the second portion of said enclosure.

4. A deposition method which comprises providing an enclosure with two connected portions, positioning at least one member of high temperature material within a first portion of said enclosure, positioning at least one member of high temperature material in a second portion of said enclosure, maintaining the pressure of said enclosure between one millimeter of mercury and atmospheric pressure, heating an unsaturated hydrocarbon material to a temperature in the range of 1300°C . to 1700°C . to decompose said material to a carbonaceous vapor, supplying said vapor to the first portion of said enclosure, depositing a portion of said vapor as an adherent hard carbon coating on said member within the first portion of said enclosure, supplying the remaining vapor to the second portion of said enclosure, maintaining the second portion of said enclosure at a temperature of at least 200°C . below the initial temperature of the vapor in said first portion, and depositing said vapor as an adherent harder carbon coating on said member within the second portion of said enclosure.

5. A deposition method which comprises providing an enclosure with two connected portions, positioning at least one member of high temperature material within a first portion of said enclosure, positioning at least one member of high temperature material in a second portion of said enclosure, maintaining the pressure of said enclosure between one millimeter of mercury and atmospheric pressure, supplying an unsaturated hydrocarbon material to the first portion of said enclosure, heating the first portion of said enclosure to a temperature in the range of 1300°C . to 1700°C . to decompose said material to a carbonaceous vapor, depositing a portion of said vapor as an adherent hard carbon coating on said member within the first portion of said enclosure, supplying the remaining vapor to the second portion of said enclosure, maintaining the second portion of said enclosure at a temperature of at least 200°C . below the initial temperature of the vapor in said first portion, and depositing said vapor as an adherent harder carbon coating on said member within the second portion of said enclosure.

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