Aug. 12, 1958 P. R. MARVIN 2,847,319

GAS PLATING OF AGGREGATES

Filed April 26, 1954 2 Sheets-Sheet 1

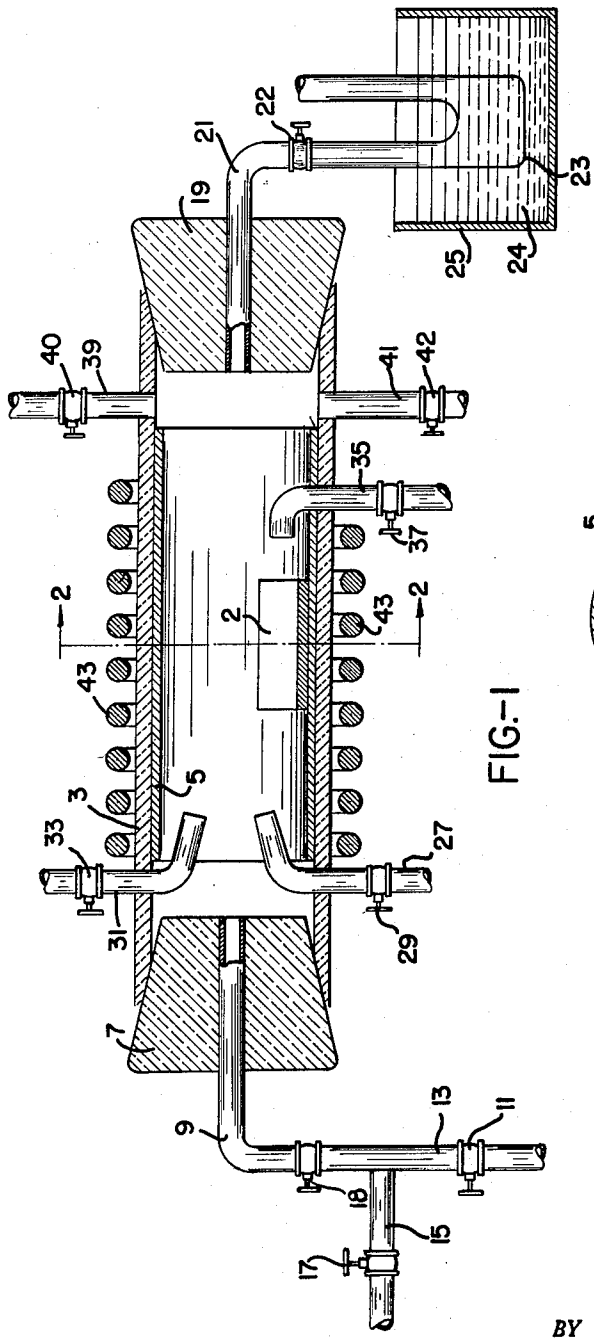



FIG.-1

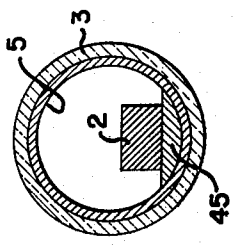



FIG.-2

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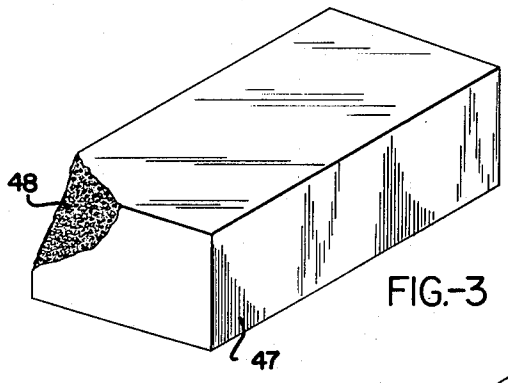



FIG.-3

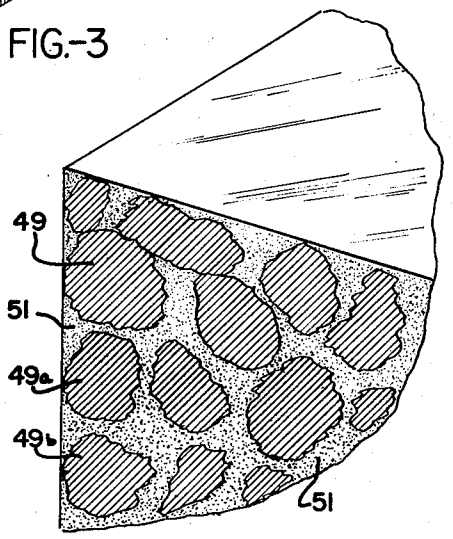



FIG.-4

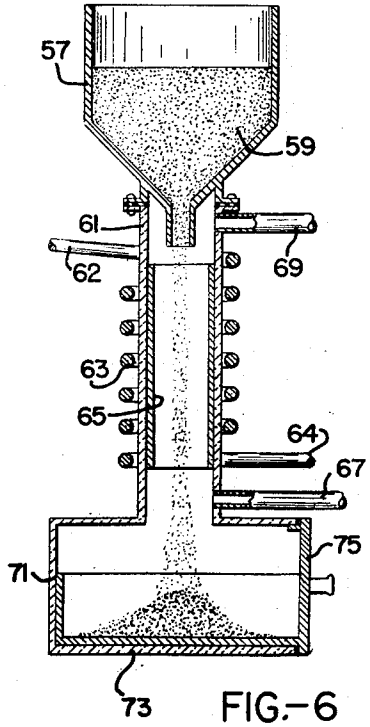



FIG.-6

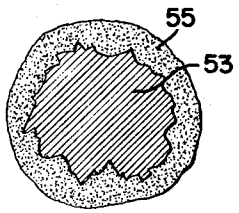



FIG.-5

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2,847,319

# GAS PLATING OF AGGREGATES

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15 Claims. (Cl. 117—47)

This invention relates to aggregates and particularly to aggregates formed of particles of very hard material which when compressed together comprise a rigid body having extremely minute interstices between particles or portions thereof. More particularly the invention relates to the provision within the interstices of such bodies of metal deposited from heat decomposable gaseous metal bearing compounds, the function of the metal deposit being to modify physical, chemical, electrical and other properties of the aggregate.

The invention particularly contemplates filling the interstices of aggregates, such as those of the carbides, silicides and powdered metals; the carbides and silicides are normally hard and while the particles adhere after compression small interstices exist which affect the material and particularly the electrical properties thereof. Powdered metals, the particles of which are extremely hard, may be advantageously treated in accordance with the invention, with a softer metal, for example, filling the interstices.

Referring to a particular aggregate which is useful in electric furnaces silicon carbide in particle form is readily compressed under high pressures; however, interstices exist between the particles which because of their hard nature and irregular contour do not contact each other uniformly over the particle surface. These interstices exist even though the powdered carbide is provided with a little binder to assist the molding action and to assist the retention of the particles during the usual firing operation after compression.

It is particularly within the contemplation of this invention to provide means for filling the interstices of such aggregates with metal to materially modify in a desirable way the physical, electrical and mechanical properties of aggregates.

It is a primary object of this invention to provide normal aggregate materials into which metal is integrated into the structure of the aggregate.

It is an important object of the invention to describe a novel process for the incorporation of metal into an aggregate structure.

One embodiment of the invention contemplates forming an aggregate of small particles, heating the aggregate and then depositing from the vapor state a metal of a heat decomposable compound by contact of the compound with the aggregate or a portion thereof, at a temperature sufficient to effect metallic deposition. The vapors bearing the metals have a capacity for entering the interstices or spacings between the particles and no decomposition of the vapor occurs until the gas strikes a portion of the aggregate which is heated to at least the thermal decomposition point of the vapor.

Regulation of the temperature across the aggregate body permits the regulation of the metal deposition and the metal deposit may be extended to a complete body or to only a portion thereof as desired. For example, deposition of metal may be limited to an interior portion



of a body by providing only the interior with sufficient heat to occasion vapor decomposition.

The characteristics of the aggregate may be altered in a most suitable manner for many applications by the metal deposit. For example, the electrical conductivity of a body of silicon carbide may be altered as a whole without materially changing other characteristics of the metal itself; this is occasioned because normaly the silicon carbide structure has interstices or voids therein which narrow the effective path for electrical current flow to just the area where the silicon carbide crystals are in contact—the spacings or voids contribute to an overall electrical resistance requiring increased voltages, but the spacings do not contribute to, for example, the heat developed by the passage of current. Metal in the interstices improves the area of the conductive path, permits some voltage reduction for the same heating effect, which heating effect is not materially altered by the presence of the metal.

Physical and chemical properties are also affected by the presence of the metal, depending upon the nature of the aggregate itself as well as the deposited metal. The deposited metal adheres well to the material of most aggregates and the metal also accordingly serves a desirable bonding function. In connection with the physical properties it is to be noted that absorption properties of the aggregates are controlled as are catalytic properties by limiting the position and the extent of the metal deposited.

A further embodiment of the invention is particularly suitable for extremely hard materials, the particles of which do not bond readily together even under extreme pressures. In accordance with this embodiment of the invention the particles forming the aggregate are themselves first coated wtih a metal which is somewhat softer than the material of the aggregate, and which metal under compression will fuse to itself; the metal coating thus serves not only to modify the normal characteristics of the aggregates, but to provide improved adherence of the particles, and in some cases to eliminate other bonding materials.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings wherein:

Figure 1 is a schematic view of apparatus useful in the metallizing of aggregates;

Figure 2 is a sectional view taken on line 2—2 of Figure 1;

Figure 3 is a perspective view of a portion broken away of an aggregate produced in accordance with the invention;

Figure 4 is a perspective view partially in section, greatly enlarged, with a somewhat exaggerated compressed crystal structure illustrating the product of invention;

Figure 5 is a greatly enlarged view of a single crystal coated with metal, a plurality of which crystals are useful in the formation of aggregates;

Figure 6 is a view partially in section illustrating apparatus useful in the production of coated metal crystals shown in Figure 5.

Referring to the drawings, there is shown generally at 1 in Figure 1 apparatus for the deposition of metal throughout the body of an aggregate comprised of silicon carbide crystals indicated at 2. The aggregate is formed of crystals having the usual irregular shape, the same having been compressed together under high pressure. Despite the pressure employed very small interstices exist between the particles, as may be noted from Figures 3 and 4, and where the carbide is to be used, for example, as an electrical resistance element, to effect heating as

referred to hereinbefore, the porosity or interstices requires an increased voltage to be applied to the aggregate without materially contributing to the heat developed by the aggregate in its useful function. Accordingly it is desirable to fill the spacings between the crystals with an electrically conductive metal which in the present case may be nickel.

In Figures 1 and 2 the numeral 3 designates a tube of glass which is non-magnetic material and the tube or tubular member is provided internally with a coating of metal 5 over a portion of the interior surface substantially centrally of the length. The left hand end of the tubular member (Figure 1) is provided with a glass stopper 7 which is suitably coated with a thin film of a lubricant and inserted against the glass end of the tube to provide an air-tight seal. The stopper 7 is bored centrally and communicates with a glass conduit 9 which is provided with a valve 11 in the arm 13 thereof and through which a carrier gas such as carbon dioxide may be passed to the member 3.

While it is normally preferred to employ carbon dioxide as the carrier gas nitrogen, hydrogen, argon or other inert gases may be utilized.

Arm 15 of conduit 9 is provided with a valve 17 to control the flow of a metal bearing heat decomposable gaseous compound, in the present case nickel carbonyl, to the chamber defined by the member 3. Other gases may be substituted for the nickel carbonyl and will require only a moderate change in the plating conditions, as will be noted more particularly hereinafter; such gases may include copper acetylacetonate, chromium hexacarbonyl, and the carbonyls of tungsten and molybdenum. However, nickel is preferred where the interstices of the aggregate are extremely small, as the carbonyl of nickel permeates such bodies readily.

The member 3 at the right hand end thereof (Figure 1) is provided with a glass stopper 19 which is lubricated and sealed against the interior glass of the member; stopper 19 is provided with a bore which connects with conduit 21 having a valve 22 therein. The remote lower end 23 of the conduit 21 is enlarged and immersed in a cold mixture of Dry-Ice and acetone 24 contained in the tank 25. The portion 23 serves to condense out undecomposed metal bearing gases which may pass through the system during the course of the metallizing operation.

Secured just within the positioned stopper 7 and extending through the glass tube 3 and metal body 5 is a conduit 27 having a valve 29 and a conduit 31 having a valve 33 for the admission of cold gases to the plating chamber of the member 3. At the right hand end adjacent the stopper 19 is a similar conduit for the admission of cold gases indicated by the numeral 35 and having a valve 37. Also passing through the member 3 are outlet conduits indicated at 39, 41, the former having a valve 40 therein and the latter being provided with a valve 42.

Surrounding the tubular member 3 is an inductive heating coil 43 supplied from a source (not shown) and which is effective when energized to heat inductively the metal film 5 within the tube which may suitably be of powdered iron deposited on the interior wall of the tube from the gaseous state. To provide an abundance of inductively heated metal within the plating chamber defined by the member 3 there is provided, as shown more clearly in Figure 2, a solid body 45 of iron which is also heated by the coil 43 when the same is energized.

The body 45 may be of any suitable dimension to effect heating of an aggregate quickly or slowly as desired and will itself in the course of the plating operation, as will also the metal body 5, be subjected to the deposition of metal, and accordingly the same will build up slowly over a period of time. Such is normally not detrimental to the operation, and in fact, may be beneficial, for as the metal wall builds up, the tubular member may be used in applications requiring more intense heat from, for example, the surface 5.

To provide a compacted body the silicon carbide crystals with metal throughout the body is first brought to uniform temperature, above that at which nickel carbonyl decomposes, for example, the body may be heated uniformly to a temperature of about 500° F. The body is then placed within the member 3, the ends thereof are closed with the stoppers and with all valves except the vacuum line valves 40, 42 closed, vacuum is applied to the interior of the plating chamber to withdraw all air therefrom. Substantially at the same time valves 11 and 18 may be opened to permit a flow of carbon dioxide gas to the interior of the tube and valve 22 is opened to permit of exhaustion of the apparatus. The carbon dioxide will tend to cool the surface of the silicon carbide body 2 (Figure 1) but such cooling will normally not be sufficient to reduce the surface temperature quickly, and accordingly while an atmosphere of carbon dioxide prevails within the plating chamber, cold gas at low temperature such as argon, nitrogen or hydrogen, is introduced through valves 29, 31 to sweep over the aggregate, and is rapidly withdrawn through valves 40, 42 to a recovery operation if desired.

This operation requires only a matter of seconds to materially reduce the temperature of the body 2 at the surface thereof to below the decomposition point (325–450° F.) of nickel carbonyl, while the interior of the body remains above the decomposition point. Valve 22 may remain open or not as desired during the cooling operation. Immediately after the temperature of the outer portions of the body 2 has been lowered below the decomposition point the valves 29, 33, 40 and 42 are closed off and with valve 22 open, valve 17 is opened to permit metal bearing gas to flow through valve 18 and conduit 9 to the plating chamber.

Metal bearing gas contacting the body 2 permeates the interstices thereof and when the gas reaches the interior portion of the body which is above the thermal decomposition point of the carbonyl, the gas decomposes depositing nickel in the interstices. Vacuum is applied to withdraw gases of decomposition through conduit 21 and valve 22, and some decomposed gas will also pass the conduit to be condensed at 23; the undecomposed material may of course be reused in the operation.

The decomposition of the nickel carbonyl is an exothermic process and accordingly the interior temperature of the aggregate body 2 tends to be maintained, thus encouraging the deposition of increasing amounts of metal; however, the metal within the body 2 is also subject, to some degree, to being heated inductively, and energization of the coil 43 after the initial metallic deposition also tends to maintain the temperature internally of the body high. Accordingly plating takes place from the interior towards the surface.

Energization of the coil 43 also provides heat to the thin iron film on the interior of the glass member and the body 2 is heated by radiation as well as conduction from the metallic body 45. Accordingly there is a progressive heating of the body from the interior outwardly in the atmosphere of the carbonyl and the body 2 has the interstices thereof completely filled with metal as indicated particularly in Figure 4.

The body 2 upon completion of the operation is removed from the plating chamber after the same has been exhausted of all gases, other than carbon dioxide, by the subjection of the apparatus to vacuum conditions, with only valves 11, 17 and 22 open. The apparatus is readily openable at the stoppers 7 and 19 simply by closing valve 22 to build up a pressure of carbon dioxide in the chamber which is substantially equal to that of the atmosphere. The apparatus is then ready for another plating operation and will be found to have only a very slight deposition of nickel on the metallic bodies within the plating chamber.

The specific conditions of operation will vary with the nature of the aggregate to some extent and will vary more specifically with the nature of the plating gas. The aggregate of course must be of a material which will permit it to withstand the temperature at which the plating gas used decomposes, and the metal bearing gas must of course be selected with a view to the end use of the aggregate.

Suitable materials for the plating of silicon carbide, aluminum carbide and most metals are indicated in the following table, together with the operating temperatures therefor:

| Plating Material | System Pressure, mm. of Hg | Temperature Range of Plating, ° F. |
|---|---|---|
| $Ni(CO)_4$ | 0.5–1.0 | 350–450 |
| $Cr(CO)_6$ | 0.5–1.8 | 375–450 |
| $Mo(CO)_6$ | 0.5–1.8 | 450–650 |
| $W(CO)_6$ | 0.5–1.8 | 525–775 |
| $Cu(C_5H_7O_2)_2$ | 0.5–1.8 | 400–750 |
| $(C_4Hg)_3$ PAuCl | 0.5–1.0 | 200–350 |
| $(C_4Hg)_3$ PAuCl | 1.0–3.0 | 250–400 |

The use of carrier gases with the plating gases is optional, but in general hydrogen is preferred as it both permeates the aggregates well and has the reducing action which tends to prevent the formation of any oxides of the metals which would tend to be brittle.

In a further embodiment of the invention the particles which are to form the aggregate may be coated with metal prior to compression thereof and such a particle is indicated at **53** in Figure 5 with a coating of metal **55** thereon. The apparatus for effecting the metallic coating of these small crystals is shown in Figure 6 wherein a hopper **57** glled with crystals **59** has secured thereto vertically therebelow a tubular member of non-magnetizable material **61**. The member **61** is surrounded by an induction heating coil **63** having leads **62, 64** connected to a source of energy (not shown). Interiorily the tube is provided with a film of magnetic iron, preferably deposited on the interior of the tube by the thermal decomposition of iron pentacarbonyl, and the film extends completely around the interior of the member **61** to define therewith a central passage through which the particles **59** will pass as shown.

An inlet conduit **67** is provided for the flow of plating gases, such as those already described, upwardly through the tubular member to an outlet **69**. The particles as they course the passage are heated by radiation from the iron film **65** and decompose the metal bearing gas and the particles accordingly become coated with the nickel, when the gas is nickel carbonyl, and are collected in a receiver **71** which is formed of a partition **73** integral with the tube and a metal portion **75** which may be removed with the particles therein. The metal coated particles are then subjected to pressure to form the aggregate and the relatively soft metal coatings fuse together to form a body having substantially interstitial spacings. This procedure is useful for particles such as silicon carbide, as well as powdered metals, where the metal particles themselves are very hard, harder than the coating thereon.

With either method of formation of the aggregate the metal fills the spacing which would normally be present between the irregularly shaped and often jagged aggregate particles; the addition of the metal of course increases the weight of the aggregate as well as changing the electrically conductive nature thereof, and the metal should be selected with a view to a balance between the various factors required in the ultimate product.

Abrasive materials, such as emery, Alundum and corundum, are particularly suitable for the practice of the invention.

It will be understood that this invention is susceptible to modification in order to adopt it to different usages



and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. The process which comprises permeating the interstices of an aggregate solid body with a heat decomposable metal bearing compound and thermally depositing metal therefrom only on interior portions of the body by maintaining exterior portions of the body sufficiently below the temperature of the interior that substantially no decomposition and no deposition occurs as the decomposable gas travels the exterior to the interior of the body.

2. The process which comprises providing a porous solid body with an internal temperature which is above that of the decomposition temperature of a heat decomposable metal bearing compound, maintaining the external body temperature being that of the decomposition temperature, immersing the body in an atmosphere containing a metal bearing gas decomposable at the internal temperature to permit the same to permeate the porous body while maintaining the external temperature below that of the decomposition point whereby deposition of metal from the heat decomposable compound occurs internally of the body.

3. The process for depositing metal from heat decomposable gaseous metal bearing compounds to fill with metal the interstices of a compacted aggregate solid body of particles which comprises surrounding the body with a gaseous atmosphere of the decomposable compound while only the interior thereof is above the decomposition point to deposit metal interiorly only, heating the deposited metal inductively while maintaining the gaseous atmosphere to cause additional metal to plate out on that first deposited, and continuing the heating while maintaining the atmosphere until the interstices are substantially completely filled.

4. The process for depositing metal from heat decomposable gaseous metal bearing compounds to fill with metal the interstices of a compacted aggregate solid body of particles which comprises surrounding the body with a gaseous atmosphere of the decomposable compound while only the interior thereof is above the decomposition point whereby the gaseous atmosphere penetrates the interstices to deposit metal interiorly, heating the body surface and the deposited metal while maintaining the gaseous atmosphere to cause additional metal to plate out on that first deposited, and continuing the heating while maintaining the atmosphere until the interstices are substantially completely filled with metal deposited from the decomposable compound.

5. Apparatus for the deposition of metals from heat decomposable metal bearing compounds comprising: a tubular member of electrically non-conductive and non-magnetizable material in which the gas thermally decomposes to deposit metal on an object, said tubular member having a closable opening through which objects to be plated may be introduced into the tubular member; a hollow magnetically responsive body supported interiorly of the member and extending therealong; an induction heating coil surrounding the member externally for inductive heating of the conductive body; means to pass the heat decomposable gas through the member; and means to remove gases of decomposition from the member.

6. An apparatus arrangement for the plating of objects with metal deposited by the thermal decomposition of heat decomposable metal bearing gaseous compounds comprising: a tubular member closable at the ends; means to introduce the gaseous compound into the tubular member; means to evacuate the member; means for introducing a cooling gas into said tubular member; a body of magnetizable metal secured to the wall internally of the tubular member; and induction heating means externally of the tube for inductively heating the metal body and the interior of the tubular member.

7. Apparatus for the plating of objects with metal deposited by the thermal decomposition of heat decomposable metal bearing gaseous compounds comprising: a hopper for particles on which metal is to be deposited; a tubular member of nonmagnetizable material secured to the hopper substantially vertically therebelow; a body of magnetizable metal secured to the tube wall interiorly thereof, the metal body and member defining a central vertical passage therethrough; an induction heating coil surrounding the member externally and arranged to heat the metal body inductively; means to receive particles passing from the hopper through the passage; and means to flow the decomposable metal bearing gas countercurrent to the stream of particles passing downwardly through the passage.

8. The process for depositing metal from heat decomposable gaseous metal bearing compounds to fill with metal the interstices of a compacted aggregate solid body of particles, which method comprises heating the body to a temperature above that of the thermal decomposition point of a metal bearing gas, cooling the exterior of the body below the said thermal decomposition point and while the interior of the body is still above the said thermal decomposition point permeating the interstices of the body with an atmosphere containing a metal bearing gas decomposable at the interior temperature but not at the exterior temperature to deposit metal interiorly of the body.

9. The process for depositing metal from heat decomposable gaseous metal bearing compounds to fill with metal the interstices of a compacted aggregate solid body of particles, which method comprises heating the body to a temperature above that of the thermal decomposition point of a metal bearing gas, passing a stream of a cold gas over the body to cool the exterior of the body below the temperature of the interior and below that of the said thermal decomposition point of a metal bearing compound, providing about the body an atmosphere of a heat decomposable metal bearing gas which is thermally decomposable at the temperature of the interior of the body to cause the gas to permeate the body and deposit metal on the interior, heating the metal deposited interiorly inductively to maintain the interior temperature above the said thermal decomposition point, and maintaining the metal bearing gas atmosphere to cause said metal to build up from the interior outwardly.

10. The process for making a silicon carbide article of manufacture, which comprises the steps of providing an aggregate solid body of silicon carbide having interstices therein, permeating the interstices of the solid body with a heat decomposable metal bearing compound, and thermally depositing metal from the heat decomposable compound only on the interior portions of the body of silicon carbide by maintaining the exterior portions of the body sufficiently below the temperature of the interior that substantially no decomposition and deposition occurs as the decomposable gas travels from the exterior to the interior of the body.

11. The process of claim 1 in which the heat decomposable metal bearing compound is nickel carbonyl.

12. The process of claim 1 in which the heat decomposable metal bearing compound is copper acetylacetonate.

13. The process of claim 1 in which the heat decomposable metal bearing compound is chromium hexacarbonyl.

14. The process of claim 1 in which the heat decomposable metal bearing compound is tungsten carbonyl.

15. The process of claim 1 in which the heat decomposable metal bearing compound is molybdenum carbonyl.

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