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METAL DIENYL GAS PLATING

Jack J. Bulloff, Columbus, Ohio, assignor to The Commonwealth Engineering Company of Ohio, Dayton, Ohio

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This invention relates to the art of deposition of metals, and more particularly to the plating of objects by the deposition of metal from readily decomposable volatile metal bearing compounds and commonly referred to as "gas plating."

Heretofore deposition of metals has been accomplished utilizing a heat-decomposable volatile compound of the metal to be deposited. Gas plating of metals which form carbonyls, alkyls, aryls and aralkyls has thus been carried out employing these metal bearing compounds.

The plating of metals which do not readily form carbonyls, alkyls or aryls as aforementioned, has been difficult to accomplish. Furthermore, the use of gaseous decomposable metal alkyls or aryls requires careful handling and exacting controls to avoid explosion, especially when gas plating in the presence of air, oxygen, water vapor or oxygenic gases often used for conditioning deposits. In addition, it is desirable to employ metal bearing compounds which are intrinsically less poisonous in use than the gaseous carbonyls. The present invention overcomes these disadvantages by the use of dienyl metal bearing compounds for gas plating.

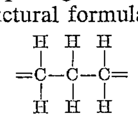
It is accordingly an object of the present invention to deposit metal, metal carbide or carbide metal phases on suitably heated substrates by the use of a relatively cool vapor of a metal diene compound.

It is a further object of the invention to provide a method of gas plating metals which do not readily form organo alkyl and aryl compounds or metal carbonyls such as titanium, vanadium, and the like.

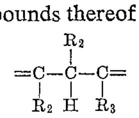
It is a further object of the invention to provide a method and apparatus for gas plating metals using dienyl heat decomposable metal bearing compounds which are decomposable at relatively low temperatures and which dissociate to deposit the metal constituent on substrates.

These and other objects and advantages will become more apparent in view of the following description.

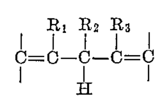
Briefly, the invention comprises carrying out gas plating wherein the workpiece or substrate to be plated with metal is heated to a temperature sufficient to cause decomposition of a volatile metal bearing dienyl compound brought in contact therewith. The invention broadly concerns the use in gas plating of compounds of the class illustrated by the structural formula



and substitution compounds thereof such as



where the double bond linkage can be of any type such as



where R_1, R_2 and R_3 may be hydrogen or an alkyl group or a combination thereof.

Further the invention contemplates the use of metal bearing compounds which possess at least three carbons and contain diene structure.

Examples of such compounds are the metal dicyclopentadienides, the metalloid polycyclopentadienyl compounds, and the tri- and tetra-cyclopentadienides, and their indenide and other congeners.

In carrying out the process the article or substrate to be gas plated is preferably placed in an enclosure and the air removed therefrom as by the use of a vacuum pump, and the article heated to a temperature sufficient to cause decomposition of the gaseous metal bearing dienyl compound introduced into the enclosure and brought in contact with the heated article.

The following examples are illustrative but not limitative of how the process of the invention may be carried out.

Example I

An iron wire is heated to red heat (500–700° C.) in a bell jar with the air removed by vacuum, to a pressure of 3 millimeters mercury and the atmosphere of the bell jar replaced with gaseous manganese cyclopentadienyl. Upon subjecting the heated wire for 3 minutes to the plating atmosphere it was found that the wire was coated with a film of manganese metal and Mn_3C.

Example II

In a bell jar as in Example I, there is inserted a steatite rod which is suitably connected to an electrical circuit and dielectrically heated to a bright red heat (500–700° C.). Thereafter titanium biscyclopentadienyl vapor is admitted to the evacuated jar and in contact with the heated rod. A coating of titanium carbide is found to be formed on the steatite rod.

Example III

Copper wire was heated by electrical induction similarly as in Example II to red heat (500–700° C.) and the heated copper rod subjected to gaseous titanium biscyclopentadienyl whereby the same is coated with titanium metal and titanium carbide.

Example IV

The article comprises a rod of thorium metal which is heated to approximately 800° F. and contacted with magnesium dicyclopentadienide to deposit a thin film of magnesium metal thereon.

The metal bearing compounds found useful are the metals which form cyclopentadienides, especially the metals of group II and III of the periodic table, e.g., Be, Al, La, Lu.

Example V

In this instance the gas plating is carried out as described in Example I, using gaseous vanadium biscyclopentadienyl to deposit vanadium.

Also metals which form biscyclopentadienyls such as those found in groups IV, V, VI, VII and VIII of the periodic table, such as Ti, V, Cr, Re, Fe, Co, Ni, Ru. Manganese forms the biscyclopentadiene. Also metals of group Ia, IIa, IIIa, IVa and Va, the metalloids of those groups which form polypentadienyls, for example $M(C_5H_5)_x$ where x is the valence for example of Si, Ge and Sb.

In accordance with my invention, a process is provided for gas plating of metals by employing metal bearing compounds which do not contain oxygen, use being made of poly-enyl compounds of both open-chain and cyclic molecular structures. The metal-organic compounds best suited for gas plating contain at least three carbon atoms and up to five in the basic molecular structure with at least two unsaturated (C═C) groupings in the molecule. Vaporized metal bearing compounds selected from the group consisting of cyclopentadienides, biscyclopentadienyls, biscyclopentadienides, and polypentadienyls being utilized as the gas plating medium. The metal plating gas may be used with or without carrier gas, e.g., argon, nitrogen, as is conventional in this art.

When it is desired carrier gas may be utilized together with the dienyl metal bearing gaseous compounds, particularly where the metal vapors are to be passed through a system as when gas plating a continuously moving strip, filament or sheet. Each substrate or material which is to be plated will be heated to the proper temperature, which temperature depends upon the metal bearing dienyl compound used. Each of such metal compounds has a temperature at which it decomposes. This varies over a range, but in general temperatures between 300–1000° C. may be utilized to effect the gas plating with the dienyl metal bearing compounds.

Mixtures of these dienyl metal bearing compounds may be used to deposit a combination of the metals or alloys as desired. Further, after coating the substrate the resultant metal coated product may be annealed or heat treated as may be desired. Such annealing may also be carried out in an inert atmosphere where oxidation of the newly deposited metal coating is undesirable.

It will be understood that while the method and apparatus disclosed and described herein illustrate a preferred form of the invention and how it can be carried out, modifications obviously may be made by those skilled in the art without departing from the spirit and scope of this invention and all such modifications that fall wtihin the disclosure and scope of the appended claims are intended to be included herein.

What is claimed is:

1. In a process of gas plating wherein the substrate to be plated is heated to a temperature sufficient to cause decomposition of a volatile metal compound brought in contact therewith, the step of bringing a gaseous metal bearing poly-enyl compound in contact with said substrate while the latter is heated above the decomposition temperature of said compound and under a non-oxidizing atmosphere to cause decomposition of the gaseous metal compound and deposition of metal onto the surface of the substrate.

2. In a process of gas plating wherein the substrate to be plated is heated to a temperature sufficient to cause decomposition of a volatile metal compound brought in contact therewith, the step of bringing a gaseous metal bearing dienyl compound containing at least three carbons in its molecular structure in contact with said substrate while the latter is heated above the decomposition temperature of said compound and under a non-oxidizing atmosphere to cause decomposition of the gaseous metal compound and deposition of metal onto the surface of the substrate.

3. In a process of gas plating wherein the substrate to be plated is heated to a temperature sufficient to cause decomposition of a volatile metal compound brought in contact therewith, the step of bringing a gaseous metal bearing poly-enyl compound in contact with said substrate while the latter is heated above the decomposition temperature of said compound and under a non-oxidizing

atmosphere to cause decomposition of the gaseous metal compound and deposition of metal onto the surface of the substrate, said poly-enyl compound being selected from the group consisting of cyclopentadienides, biscyclopentadienyls, biscyclopentadienides and polypentadienyls.

4. A process of gas plating substrate as in claim 1, wherein said metal bearing compound consists of a metal dienyl compound containing at least two carbons in the molecule.

5. A process of gas plating substrate as in claim 1, wherein said metal bearing compound consists of a metal dienyl compound containing a poly-enyl molecular structure.

6. A process of gas plating substrate as in claim 1, wherein said metal bearing compound consists of a metal diene of the metals of group Ia, IIa, IIIa, IVa, and Va.

7. A process of gas plating manganese onto a substrate which comprises heating the substrate to 500–700° C. under a non-oxidizing atmosphere, and subjecting the thus heated substrate to gaseous manganese cyclopentadienyl to cause decomposition of the manganese diene and deposition of manganese onto the surface of said substrate.

8. A process of gas plating titanium onto a substrate which comprises heating the substrate to 500–700° C. under a non-oxidizing atmosphere, and subjecting the thus heated substrate to gaseous titanium biscyclopentadienyl to cause decomposition of the titanium diene and deposition of titanium onto the surface of said substrate.

9. A process of gas plating magnesium onto a substrate which comprises heating the substrate to 500–700° C. under a non-oxidizing atmosphere, and subjecting the thus heated substrate to gaseous magnesium dicyclopentadienide to cause decomposition of the magnesium diene and deposition of magnesium onto the surface of said substrate.

10. A process of gas plating vanadium onto a substrate which comprises heating the substrate to 500–700° C. under a non-oxidizing atmosphere, and subjecting the thus heated substrate to gaseous vanadium biscyclopentadienyl to cause decomposition of the vanadium diene and deposition of vanadium onto the surface of said substrate.

11. A process of gas plating a substrate to deposit a layer of metal carbide thereon consisting of heating the substrate to 500–700° C. in a non-oxidizing atmosphere and thereafter bringing vaporous metal cyclopentadienyl in contact therewith to deposit a coating of metal carbide thereon.

12. A process of gas plating a substrate to deposit a layer of metal carbide of titanium thereon consisting of heating the substrate to 500–700° C. in a non-oxidizing atmosphere and thereafter bringing vaporous metal titanium biscyclopentadienyl vapor in contact therewith to deposit titanium carbide onto the substrate.

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