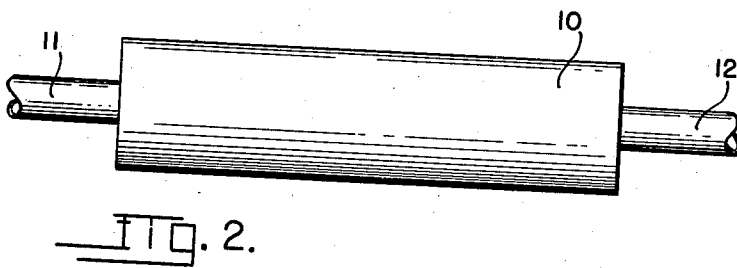
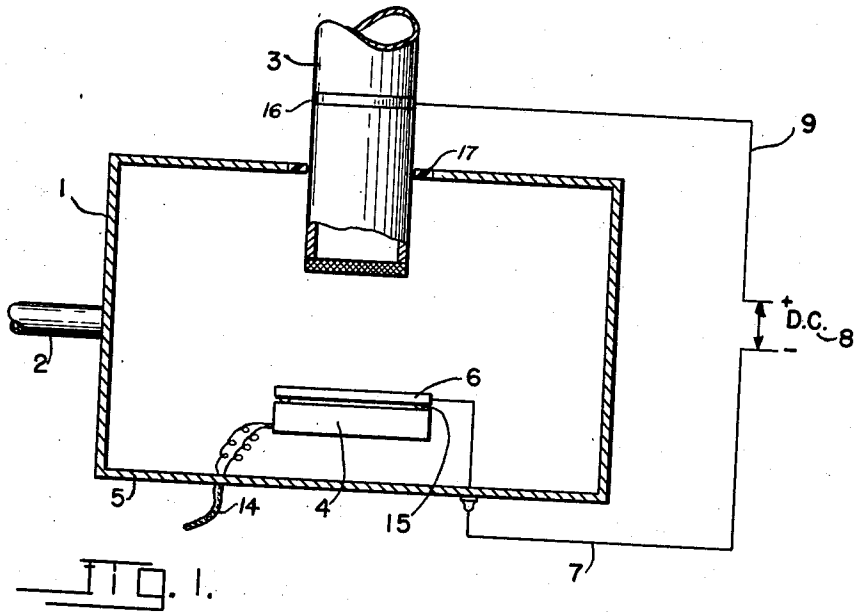


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METHOD AND APPARATUS FOR DEPOSITION OF
MATERIALS BY THERMAL DECOMPOSITION
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METHOD AND APPARATUS FOR DEPOSITION
OF MATERIALS BY THERMAL DECOMPOSITION

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This invention relates to the art of deposition of metals. More particularly, it relates to the plating of metals from the gaseous state, and to the apparatus for carrying out the said process.

The deposition of thin films of protective metal, such as nickel, cobalt, tungsten and molybdenum, or their alloys, on metallic bases has been accomplished by enclosing an object to be plated in a chamber, filling the chamber with decomposable metal-bearing gas, heating the object to be plated to the decomposition temperature of the said gas, and allowing the metal-bearing gas to contact the heated plate and be deposited thereon.

Considerable difficulty has been experienced in securing dense film deposits with such a method and various expedients have been devised to overcome the inherent limitations of the structure of this apparatus. These limitations stem from two primary causes. The first of these is that the gaseous decomposition may take place prematurely, that is, before the gas contacts the article to be plated, thus permitting metal particles to fall upon the surface to be plated resulting in roughness of the plate coating.

Secondly, an interfacial resistance between the advancing wave of plating gas and the surface of the object to be plated opposes the decomposition directly on the free surface of the object.

The result of these effects of uncontrolled decomposition is the production of thin, porous, irregular coatings of deposited metal. While, as noted above, means to effect the control of these undesirable phenomena have been accomplished they require expert workmanship and specialized apparatus.

It is an object of this invention to provide a method by which the above mentioned disadvantages are overcome.

It is an important object of this invention to provide a novel method for gas plating by which a firmly adhering metal coating is obtained.

It is a principal object of this invention to provide a method of gas plating which yields coatings of increased density.

It is also an object of this invention to provide a metal coating which will withstand elevated temperatures without blistering.

It is another object of this invention to provide apparatus for carrying out the process of invention.

These and other objects of the invention are achieved by effecting ionization of the plating gases and their carrier gases and subjecting the same to the action of an electrostatic field having the workpiece to be plated as one electrode thereof.

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More specifically, in the process of invention the application of an electrostatic field which has the workpiece as one electrode thereof causes ionized gases to be directed to the workpiece at great velocity. While in heated gases the collisions between molecules give rise to ionization to some degree, it is desirable to increase this velocity of collision by means of the electrostatic field and the presence of charged gases in the plating chamber by exposing the gases, both carrier and plating gas, to radioactive substances prior to their entry to the chamber.

It should also be noted that it is preferable to secure the second electrode of the electrostatic field to a conductive outlet portion of the chamber whereby the negatively charged gases of decomposition will be attracted thereto and rapidly swept from the chamber. This mode of operation results in decreasing the resistance to the flow of metal-bearing vapors to the surface of the metal to be plated and thus provides for intimate contact of the metal-bearing component with the surface and gives rise to dense uniform non-porous deposits.

The nature and purpose of this invention has been indicated in a general way and there follows a more detailed description of the preferred embodiments of the invention with reference to the accompanying drawing in which:

Figure 1 is a view partly in section of the apparatus of invention; and

Figure 2 is a view of apparatus utilized in carrying out one embodiment of the invention.

Referring to Figure 1, there is shown a chamber 1 having a gas inlet 2 and an outlet 3 electrically insulated from the chamber. Mounted in the chamber is a heating unit 4 connected to a source of energy (not shown) by an insulated lead 14 extending through the wall 5 of the chamber 1. Supported on the heating unit 4 by electrically insulating support members 15 is a workpiece 6 to which there is electrically secured an electrically conductive lead 7 passing through the wall 5 in electrically insulated relation therewith.

The connection between the workpiece 6 and the lead 7 may be through means of any suitable contact arrangement, such as clamps, sockets, or the like. Electrically connected to the opposing end of the lead 7 is the negative pole of a source of direct current, generally indicated at 8. The positive pole of the source 8 is connected by a lead 9 to a conductive portion of outlet 3, thereby setting up an electrostatic field between the inner end of the outlet 3 and the workpiece 6. The outer end of the outlet 3 is

preferably of insulating material but in some instances may be conductive and in such a case is insulated from ground.

In operation metal-bearing gases together with a carrier gas are fed to the chamber 1 through the inlet 2 from suitable containers or mixing chambers which are not shown since they are well known to the art and form no part of the present invention.

The entering gases due to their velocities and frequent collisions may be ionized to a very slight extent and are attracted to the workpiece or cathode 6. The negatively charged cathode will receive the positively charged molecules, causing decomposition of the metal-bearing gases into metallic ions and negatively charged ions of the gases of decomposition. The metallic ions lose their charge to the cathode, resulting in a firm metal deposit, while negatively charged decomposition products will be repelled with great force and at high velocity from the area of the plated surface.

These repelled ions move under the influence of the electrostatic field to the positively charged outlet of the chamber, and in so doing strike or collide with un-ionized gases thereby contributing to the overall ionization of the gas in the chamber. Accordingly when in full operation the chamber will contain large quantities of positively charged metallic ions, and negatively charged gases of decomposition which may be in the ionized state or as charged molecules of carbon monoxide, carbon dioxide, and so forth. The charged metallic ions moving at high velocity towards the cathodic workpiece will deposit thereon in a fine, uniform dense coating, thus overcoming the defect noted hereinbefore of particles settling slowly and forming a rough surface.

It is clear from the foregoing that while it is preferable to have the electrostatic field applied between the workpiece and the outlet of the chamber that the only requirement for impinging the metallic positively charged ions on the workpiece is that the workpiece be the cathode. The positive plate of the electrostatic field may be any other suitable conductive portion of the apparatus.

The electrostatic voltage necessary to effect the novel plating process set forth will be a variable factor dependent upon the distance between the plates of the field, the nature of the plating gas, the pressure and temperature of this gas, and so forth. Other conditions being equal the field strength will decrease as the distance from an electrode increases, and an electrostatic potential of 1000 volts applied to the plates will be decidedly effective at a distance of $\frac{1}{8}$ " between plates. Where the anode and cathodic workpiece are separated by as much as 2 feet approximately 200,000 volts may be required for maximum effectiveness. However, as has been noted, the gas pressure and the nature of the gas may require alteration in these conditions.

The heater unit 4 is utilized to raise the temperature of the cathode workpiece to accomplish complete decomposition of the metal bearing gas at the workpiece surface. This temperature is a variable factor dependent upon the plating gas used, and in the case of nickel carbonyl gas should be in excess of 180° C.

Base materials which may be plated in the foregoing manner are steel, copper, aluminum, cast iron, brass, magnesium, and the like.

The process and apparatus of invention are

applicable for plating with all metals which form gaseous carbonyls, such as chromium, iron, tungsten, cobalt, molybdenum, tellurium, rhenium and nickel. The carbonyl of each of these metals has a temperature at which decomposition is complete, although some decomposition takes place at lower temperatures. The adverse effects of such low temperature decomposition are overcome by the high velocity attained by the particles in the electrostatic field.

In the case of tungsten, nickel, chromium and iron carbonyls it is preferred to maintain the temperature of the workpiece in the range of 350° F. to 425° F., although temperatures below and above this range may be utilized and good plating accomplished. The use of the electrostatic field with the attendant high velocity of the particles permits a reduction in the temperature of the workpiece if other conditions require it.

In Figure 2 there is shown a tubular member 10 having an inlet 11 and outlet 12 and containing radioactive material, such as uranium or radium. The function of the member 10 is to effect a preliminary ionization of either the carrier gas which enters the plating chamber with the metal carbonyl, or to effect preliminary ionization of both the carrier gas and the carbonyl. For this latter purpose outlet 12 of member 10 may be connected directly to inlet 2 of chamber 1.

The effect of the action of the radioactive material is to cause a splitting of the carbonyl molecule M (CO_4) into positively charged M ions and negatively charged (CO_4) ions. Since the metallic ions are now dissociated from the heavier (CO_4) ions the velocity imparted to them by the electrostatic field, before striking the workpiece, will be considerably greater than had dissociation taken place closer to the object to be plated.

The charged carrier gas serves to effectively attract the gases of decomposition from the area of the plating surface, thus further tending to break down the interfacial resistance between the wave of plating gas and the surface of the cathodic workpiece.

Carrier gases useful for the above purpose are nitrogen, helium, hydrogen, carbon dioxide and other inert media. Hydrogen it may be noted is particularly useful since it effects a reducing action and may accordingly be advantageously used under conditions where iron rust might develop and inhibit the process.

While the above embodiments of the invention have particularly set forth the use of carbonyls, it will be understood that other metal bearing gaseous compounds such as metal hydrides, metal alkyls, metal halides and the nitroxyls such as that of copper, the nitroxyl carbonyls and the carbonyl halogens fall within the scope of this invention and may be used with equal facility.

Cleaning of the workpiece preparatory to coating may be effected by any of the means well known to the art, such as acid, alkali, or electrochemical treatment, the only requirement being that a clean metal surface be provided for the reception of the deposited metal to attain the maximum benefit from the novel method of deposition.

It will be understood that this invention is susceptible to modification in order to adapt 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.

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I claim:

1. An apparatus for coating an electrically conductive workpiece comprising a chamber having an inlet and an outlet, a support for said workpiece in said chamber, means for creating a high voltage electrical field within said chamber and having anode and cathode terminals disposed therein, said cathode being arranged for connection to said workpiece on said support, said anode being arranged at said outlet, and means comprising a tubular member having an inlet and outlet and containing radioactive material, said outlet of the tubular member being connected to the inlet of said chamber, means for heating said workpiece and means to supply a stream of gaseous metal carbonyl to the inlet of said tubular member.

2. An apparatus as called for in claim 1 wherein the radioactive material is selected from the group consisting of radium and uranium.

3. A method of coating an electrically conductive workpiece comprising the steps of supporting the workpiece within a chamber, creating an elec-

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trostatic field within said chamber and having said workpiece connected as the cathode, conducting a gaseous metal carbonyl in contact with radioactive material and thereafter conducting said gaseous metal carbonyl through said chamber and in contact with said workpiece.

4. A method of coating electrically conductive workpieces as called for in claim 3 wherein the radioactive material is selected from the group consisting of radium and uranium.

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