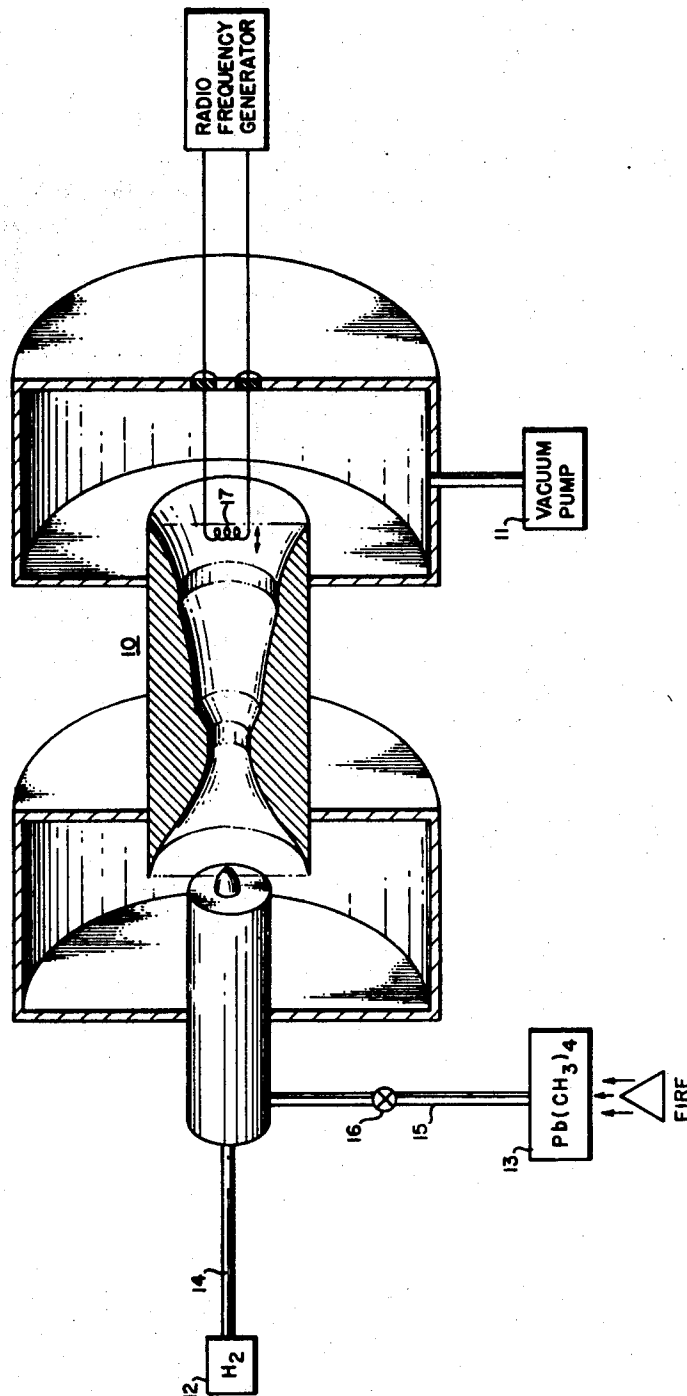


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METHOD FOR CONTROLLED DEPOSITION OF ELEMENTS
ON STRUCTURES OF COMPLEX SHAPES
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**METHOD FOR CONTROLLED DEPOSITION OF
ELEMENTS ON STRUCTURES OF COMPLEX
SHAPES**

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10 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to a method of depositing metallic elements onto physical structures of complex shapes under carefully controlled conditions. A radio frequency probe is inserted into the structure to be coated and the structure is evacuated. A radio frequency is applied to the inner cavity of the structure for induction heating thereof, then a gaseous metallic compound such as lead tetramethyl is admitted into the cavity and carried through the cavity by a carrier gas such as hydrogen. The radio frequency heats the structure and the gaseous metallic compound directed into the cavity decomposes with the result that the lead ions deposit onto the surface of the cavity. The method is carried out sufficiently to deposit a coating of a desired thickness. The probe may be moved axially through the cavity and the radio frequency decreased which will reverse the chemical reaction to smooth out the deposited coating.

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to the deposition of metal onto a surface and more particularly to a process for depositing metallic elements on the inner surface of physical structures of complex shape under carefully controlled conditions of depositing the metals.

BACKGROUND OF THE INVENTION

Heretofore, a method for detecting free radicals has been carried out by removal of metallic mirrors; in these experiments a stream of gas was used as a carrier of the compound which decomposed upon entering a heated hard-glass tube yielding a metallic element and free radicals. The metallic element was deposited as a mirror on the heated surface of the hard-glass tube. By moving the furnace to an upstream position from the first mirror deposited onto the glass tube and heating, a second mirror was deposited with a gradual disappearance of the first mirror. The removal of the first mirror was found to be caused by the free radicals produced at the position of the second heating and reacting with the metallic deposit by the reversal of the chemical reaction. This technique for detection of free radicals by the removal of metallic mirrors proved to be successful for compounds which deposit lead, zinc, antimony, mercury, tin, arsenic, bismuth, selenium, and tellurium. In the prior art system the metallic element was deposited as a mirror at the place along the device which was heated and as the heater element was moved to a different place along the length of the device, the first mirror disappeared and a second mirror was deposited at the position of the heater.

Other vapor deposition processes involve the use of a radio frequency generator in combination with a metal bearing vapor and a carrier gas. In this prior art device the radio frequency generator is connected to a wave guide

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through which a mixture of metal bearing vapor and a reducing gas is directed wherein the application of microwave excitation renders the mixture in a normally stable condition to an unstable condition. The metal of the mixture is deposited onto a sheet of kraft paper which is advanced along the end of the wave guide tube. In this prior art device the metals are deposited onto an element which is passed along the end of the wave guide opposite from the end through which the gases are introduced.

BRIEF SUMMARY OF THE INVENTION

In carrying out the process of the present invention, a radio frequency is applied to the structure to be coated on the inside thereof. This may be in the form of radio frequency power channeled into and filling the entire structure or cavity or as a movable radio frequency power probed inside the structure or cavity. The radio frequency energy heats the inner surface of the structure to be coated by induction heating and the structure is baked-out and evacuated. Compounds in the vapor phase are carried into the heated cavity by a carrier gas. The gaseous mixture flows through the cavity due to the pulling action of a high speed vacuum pump connected to the downstream end of the cavity. The heated cavity causes decomposition of the compounds into metallic elements and free radicals. As the metallic elements are carried through the structure to be coated, the metallic elements attach to the surface of the structure to form a coating thereon. Once the inner surface of the structure has been coated, smooth and uniform surface deposition may be accomplished by varying either the radio frequency power input, the position of the radio frequency power probe, the composition of the gaseous mixture, or the pumping speed. This operation controls the rate and direction of the chemical reaction of the metallic compound undergoing thermal decomposition in the heated cavity. This operation in effect controls the metallic coating on any part of the cavity surface to any desired thickness.

It is therefore an object of the present invention to provide a process of coating the inner surface of a structure which may be of complex shape.

Another object of the invention is to provide a process in which the inner surface of a complex shape, which may contain rough surfaces, may be coated with a smooth surface of a desired thickness.

Still another object is to provide a process which may be carried out by personnel of limited knowledge in the surface coating art.

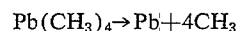
The nature of this invention as well as other objects and advantages thereof will be readily apparent from consideration of the following specification relating to the annexed drawing.

BRIEF DESCRIPTION OF THE DRAWING

The drawing illustrates diagrammatically a device having a complex inner surface which is being coated by the process of the present invention.

DETAILED DESCRIPTION

The deposition process of the present invention is based on the employment of chemical-free radicals and radio frequency inductance heating. A metallic compound such as lead tetramethyl in the vapor phase is carried into a RF induction heated cavity by a carrier gas such as hydrogen or helium under the action of a high-speed vacuum pump. The lead tetramethyl decomposes into lead and methyl radicals according to the reaction:



As the products of the reaction are carried through the structure to be coated, the lead is coated onto the surface of the cavity. Any irregular or rough surfaces on the

inner face of the cavity will be filled in by the lead coating due to the radio frequency energy which will effectively smooth over the entire surface of the cavity. The compound of lead tetramethyl is directed into the cavity until the coating is of a desired thickness. Once the cavity has obtained the desired coating thickness, finer control and smoothness of the surface may be accomplished by varying either the radio frequency power input into the cavity, the position of the radio frequency power probe, the composition of the gaseous mixture or the pumping speed of the vacuum pump.

FIG. 1 illustrates diagrammatically a cavity having elements therein in which the cavity is to be coated. As shown, the cavity 10 is provided with a high vacuum pump 11 at the downstream end which pumps the mixture of carrier gas and the metallic compound vapor through the cavity. The carrier gas 12 and the metallic compound vapor 13 are supplied through tubes 14 and 15 at the end opposite from the vacuum pump. The metallic vapor may be controlled by a valve 16 and the hydrogen may be controlled by a valve on the hydrogen tank. A radio frequency probe 17 is inserted in the cavity and may be movable along the axis thereof as shown by the arrow wherein the cavity is heated by radio frequency induction. For fine control, the position and/or radio frequency power or both are varied to control the rate and direction of the chemical reaction of the metallic compound inside the cavity. By this operation one can effectively reverse the chemical reaction and thus control the removal of the metallic element by the recombination of the free radicals with the metallic elements at the surface.

The following example illuminates the principle of this invention. It is known that the radio frequency conductivity of copper is much greater than that of lead at room temperature. At superconducting temperatures, however, the radio frequency conductivity of lead may be as much as a hundred thousand times greater than the room temperature value of copper. Therefore, for operation at superconducting temperatures, it is desired that a copper wave guide be coated with a lead coating such that the wave guide will obtain the radio frequency conductivity value for lead. The copper wave guide is placed into a vacuum system with the vacuum pump connected to the downstream end. A radio frequency generator of the radio frequency to correspond to the physical dimensions of the cavity is connected as shown in the drawing. Range of operation may be from 1 millimeter to the ultra-high frequency region around 3,000 megacycles. A radio frequency power probe is inserted in the cavity from the downstream end of the wave guide and programmed to move either upstream or downstream discretely or continuously. At the lower frequencies, the probe may be dispensed with, while employing the technique of introducing radio frequency energy directly into the wave guide to be plated. The vacuum pump is placed into operation and the system baked out with local heating and evacuated to a pressure of about 10^{-6} to about 10^{-7} millimeters of mercury. After this operation, a gaseous mixture containing a carrier gas such as hydrogen at a pressure of from about 1 to 2 millimeters of mercury and the gaseous phase of a metallic compound such as tetramethyl lead is directed into the wave guide. The concentration of hydrogen and the tetramethyl lead in the gaseous mixture are independently controlled external to the wave guide as shown in the drawing. The tetramethyl lead vapor is formed by heating liquid tetramethyl lead at room temperature. Initially, the radio frequency probe is programmed to heat the upstream end of the wave guide and move downstream as the lead mirror is formed on the inside surface area of the wave guide. As the gaseous mixture enters the wave guide, it is under the influence of a variable high speed vacuum pump. The tetramethyl lead undergoes thermal decomposition in the locally heated region of the radio frequency probe and yields products of metallic lead and a methyl radical. As the lead deposits on the

local heated surfaces to the thickness desired, the radio frequency probe is moved downstream to repeat this process until the entire inside surface area is coated. When the coating thickness of lead is equal to the depth of radio frequency penetration for lead, the composite conductor (lead on copper) takes on the radio frequency conductivity properties of lead. Once the cavity wall has attained the radio frequency conductivity value for lead, finer control and a smooth, uniform surface deposition may be accomplished by varying the radio frequency power input and/or the position of the radio frequency probe or both together with the pumping speed and composition of the gaseous mixture. For example, one could remove an excess coating of lead from the walls at a downstream position by moving the radio frequency probe to a point upstream of this position. This operation increases the concentration of methyl radical interacting with the walls in the downstream position and effectively removes the lead from the walls by recombination.

It can be seen from the above process that coatings of other metallic elements may be deposited onto a surface from compounds wherein the metallic elements may be of the group comprising the following: zinc, antimony, mercury, tin, arsenic, bismuth, selenium, niobium, and tellurium.

The radio frequency probe may be moved axially along the structure to be coated. In addition, the carrier gas and gaseous metallic compound outlet may be converted with the radio frequency probe and moved through the structure simultaneous with the probe. Any other suitable method of directing the carrier gas and metallic elements into the structure may be used.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. A process for depositing a metallic coating on the inner surface of a structure having a passage therethrough, which comprises:

baking out and evacuating said structure to be coated, continually evacuating said structure to maintain a constant pressure by use of a vacuum pump, inserting an axially movable radio frequency probe into one end of said structure, securing a carrier gas feed and a gaseous metallic compound feed line to one end of said structure, directing a carrier gas and a gaseous metallic compound through said feed lines into said structure, moving said radio frequency probe axially through said structure thereby heating said structure by induction heating, whereby metallic elements deposit onto the inner surface of said structure due to said radio frequency energy and movement of said metallic elements by said vacuum pump.

2. A process for depositing a metallic coating on the inner surface of a structure having a passage therethrough, which comprises:

baking out and evacuating the structure to be coated by an evacuation means, continually evacuating said structure at a uniform pumping rate, channeling a radio frequency energy into one end of said cavity along the axis thereof filling said cavity with said radio energy to heat said structure over its entire length by induction heating, directing a carrier gas into said structure through the end opposite from the evacuation means, and directing a gaseous metallic compound into said structure with said carrier gas until a desired coating thickness has been obtained.

3. A process as claimed in claim 2, wherein:

the carrier gas is selected from a group consisting of hydrogen, helium, argon and krypton.

4. A process as claimed in claim 2, wherein:

said metallic compound directed through said structure is selected from a group of metallic compounds in

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which the metallic elements of each separate compound is selected from a group consisting of lead, zinc, antimony, mercury, tin, arsenic, bismuth, selenium, niobium, and tellurium.

5. A process as claimed in claim 2, wherein:
the structure is evacuated initially to a pressure of at least 10^{-6} millimeters of mercury. 5
6. A process as claimed in claim 5, wherein:
the radio frequency applied for heating said structure is from about 1 mm. to about 3000 megacycles. 10
7. A process as claimed in claim 2, wherein:
the radio frequency applied for heating said structure is from about 1 mm. to about 3000 megacycles.
8. A process as claimed in claim 7, wherein:
the carrier gas is selected from a group consisting of hydrogen, helium, argon and krypton. 15
9. A process as claimed in claim 8, wherein:
the metallic elements forming said metallic compounds directed through said structure is selected from a group of metallic elements consisting of lead, zinc, antimony, mercury, tin, arsenic, bismuth, selenium, niobium, and tellurium. 20

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10. A process as claimed in claim 9, wherein:
the carrier gas is hydrogen,
the gaseous metallic compound is lead tetramethyl,
whereby the lead is deposited onto the surface of said structure.

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