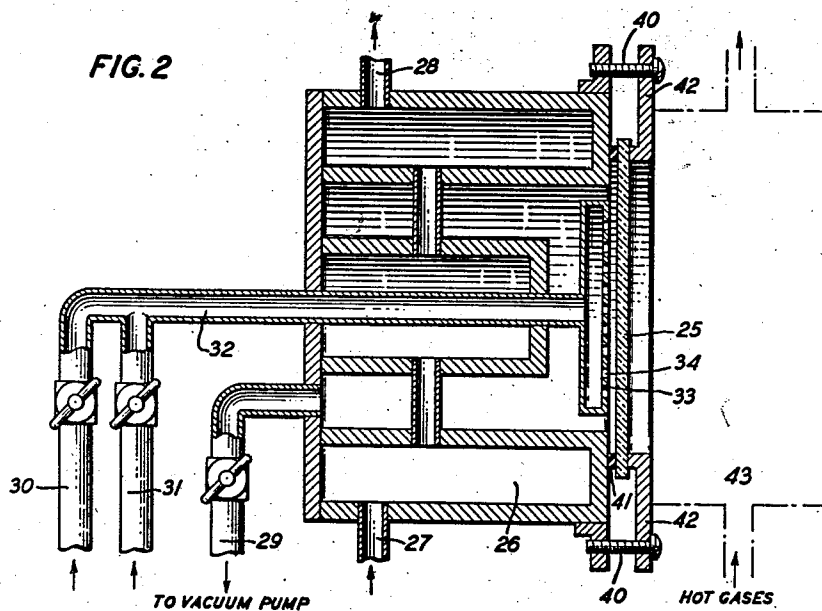
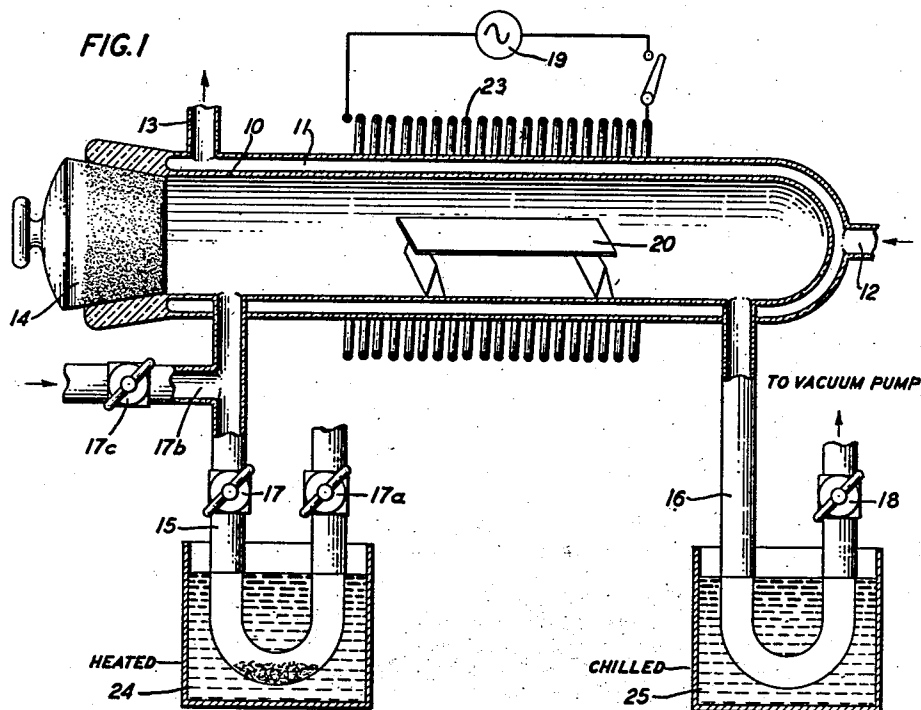


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54 J. J. LANDER
PLATING WITH SULFIDES, SELENIDES, AND TELLURIDES
OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN
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PLATING WITH SULFIDES, SELENIDES, AND
TELLURIDES OF CHROMIUM, MOLYB-
DENUM, AND TUNGSTENJames J. Lander, Millington, N. J., assignor to
Bell Telephone Laboratories, Incorporated, New
York, N. Y., a corporation of New YorkContinuation of abandoned application Serial No.
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5 Claims. (Cl. 117—106)

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This invention relates to processes for coating objects with sulphides, selenides and tellurides of one of the metals chromium, molybdenum or tungsten or with mixtures of such substances.

This application is a continuation of my application Serial No. 547,910, filed August 3, 1944, and now abandoned, and all benefits legally flowing from its copendency therewith are claimed.

The invention relates, more particularly, to coating solid metals or metallic alloys with tightly adhering coatings of such substances but the invention is not restricted to coating metals and may be employed for coating other objects of a nature which may be brought to a proper high temperature condition necessary to apply the coating.

Objects may be coated for various purposes, for example ornamentation, to render them weather resistant, to render their surfaces non-conducting or, in some instances, to make them photoelectric. Pointed or other objects may be coated to give them rectifying properties. Thin magnetic sheet material may be coated for the purpose of producing thereon an electrically resistant layer which may be uniform and thin, for example, from 0.001 to 0.0001 inch in thickness.

In a general way, plating may be accomplished by first removing impurities or other substances from the surface to be coated, especially those impurities or substances which would tend to prevent the production of a tightly adherent coating.

It may be desirable to coat the object to be plated first with a thin layer of metallic chromium, molybdenum and tungsten and then continue the plating with an oxide, sulphide, selenide or telluride. In general, the process is carried out by placing the object to be plated in a vessel in which a low gas pressure may be obtained and introducing a carbonyl of the metal chromium, molybdenum or tungsten along with some gas which will supply the proper amount of oxygen, sulphur, selenium or tellurium and maintaining the object to be plated at a suitably high temperature which will vary under different conditions and with different substances but, in general, may range from 200° C. in certain cases up to 800° C. or even higher in other cases.

Among the features of the invention are adaptability of the invention to the plating of inaccessible surfaces, depressions or grooves of objects; the removal of foreign bodies from the surface to be plated in order to promote the reproduction of a tightly adherent plate; the process of beginning plating with a metal or substantially

pure metal covering it with one of the various metallic compounds of an adherent layer; maintaining a low pressure in the plating chamber; utilization of proper temperatures in combination with suitable gas pressures to produce the desired plating, and other features which will appear hereinafter.

For illustration of apparatus useful in carrying out the invention, reference is made to the accompanying drawings.

Fig. 1 is a diagram partly in cross-section of apparatus capable of being used for the purposes of the invention for plating a metallic sheet, for example, a thin sheet of magnetic material; and

Fig. 2 is a cross-sectional diagram of an arrangement for plating a surface of glass or similar vitreous material of any kind which can be raised to a sufficiently high temperature to be plated.

Not only flat surfaces but concave, convex or surfaces of any other shape may be plated by utilizing properly modified apparatus.

Referring now to Fig. 1 and mode of operating it to plate an object, there is provided a ceramic or glass vessel 10 which possesses a cooling water jacket 11 having a water inlet 12 leading to a suitable source of water supply and a water outlet 13. The inlet and the outlet may be located at any suitable portion or portions of the glass or ceramic vessel 10. The vessel as illustrated is tubular in form and is provided with a large tightly fitting stopper 14 which may be made gas-tight by means of ground glass surfaces or otherwise and has connected to it two other tubes 15 and 16 which are U-shaped. Tube 15 is provided with valves 17 and 17a and a side inlet tube 17b with a valve 17c. Tube 16 is provided with a valve 18. A winding or coil 23 adapted to be traversed by high frequency current supplied from suitable high frequency source 19 is hung, mounted or otherwise disposed about the central portion of the tube 10. An object 20 consisting of metal to be plated is represented as a thin sheet of magnetic material, for example, a ferromagnetic alloy consisting of 78½ per cent nickel and 22½ per cent iron. The object 20 typifies any one or more objects to be placed in the vessel 10 to be coated and is mounted on wedge-shaped supports of glass mica or ceramic material or is otherwise hung, supported or disposed within the vessel 10. In some instances it may be merely sufficient to lay the object 20 or a group of objects 20 within the vessel 10. The object 20 may consist of any type of metal or metallic alloy which can be raised

to the desired plating temperature hereinafter specified without becoming too soft or melting. In the operation of the device tube 16 is connected to a vacuum pump through a valve 19, which may be of any convenient type, and the U tube part of the tube 16 may be chilled in a vessel 25 containing a cooling fluid to entrap and thereby save undecomposed carbonyl. Tube 17b may be utilized to supply suitable gas such as oxygen, hydrogen sulphide, sulphur vapor, hydrogen selenide, or hydrogen telluride. These gases may be oxygen, sulphur, selenium, tellurium, their hydrides and mixtures thereof. Metallic carbonyls may be introduced directly through a tube 15 through the series of valves 17 and 17a or alternatively the metallic carbonyl may be placed in the U tube in solid form and vaporized by immersing the U tube 15 in a vessel 24 with a heated fluid. The vaporized metallic carbonyl may be carried into the plating vessel by conducting a stream of gas through the U tube 15.

For utilizing the equipment of Fig. 2 to plate one surface of a ceramic sheet 25 the sheet is placed adjacent to a structure which includes a water cooled jacket 26 supplied with cold water from inlet 27 leading to an outlet 28. The tube 29 is provided with suitable valves leading to a vacuum pump and the tubes 30 and 31 also are provided with suitable valves serving to supply metallic carbonyl and such gases as are used in accordance with the examples set forth or equivalent or similar examples. The carbonyl gas along with other gases supplied pass through a space 32 which is kept cool by the water jacket and into a perforated head 33 which has a number of small perforations 34 for supplying the carbonyl vapor and other gases to the surface of the plate 25. The plate 25 is firmly secured by means of screws 40 and a heat resistant gasket 41 which may be composed of a substance such as copper. The flanges 42 are integral with or otherwise secured in a gas-tight manner to a heating chamber 43 into which hot gases may be supplied from a furnace to heat the plate 25 by heat conduction to a desired plating temperature as will hereinafter be specified.

The following examples will be considered to apply equally well to the arrangement of Fig. 1 for plating a metallic sheet or to Fig. 2 for plating one side of a vitreous sheet as well as to plating other objects with suitable modifications of the equipment.

Example 1

An object may be plated with green chromium oxide having the formula Cr_2O_3 . For this purpose chromium carbonyl is supplied to the plating chamber during the time when the vacuum pump is operating to maintain the pressure in the plating chamber at around 1 millimeter of mercury or lower. If the pressure is allowed to rise, the pressure of the carbonyl vapor must be reduced to reduce the decomposition of carbonyl in the plating chamber at points other than the surface of the object to be plated. The object to be plated is raised to a temperature of 200° up to 600° or 800° C. by high frequency induction or otherwise. In addition to metallic carbonyl, oxygen is introduced in approximately stoichiometric proportions, that is, oxygen and chromium in the proportions represented by the formula Cr_2O_3 . If the temperature is low, around 200° C., an excess of oxygen, CO_2 , or H_2O should be introduced, but at higher temperatures of around 400° C. and upward, the excess of oxygen should be reduced to no excess or a very slight

excess. Plating or coating objects at the lower part of the range of temperatures allows a more rapid plating rate in that less decomposition in the gas phase will take place. It is to be understood that the object to be plated is rendered free of foreign substances. One method of accomplishing this would be to treat the metal with acid and wash off the adherent acid with a substance such as alcohol immediately before placing the object in the plating vessel and immediately subjecting the object to applied vacuum after it has been introduced into the plating vessel. This removes the residual alcohol by evaporation. Another way of cleaning the surface of the object to be plated is to introduce it into the plating vessel and heating it by electromagnetic induction to a temperature such as 600° C., while maintaining a flow of H_2 or other suitable gas in the plating chamber. This is done before introducing any carbonyl gas or other gases which are to be used in plating operation.

Example 2

In order to plate an object with one or the other of the chromium sulphides, CrS or Cr_2S_3 , chromium carbonyl is introduced into the plating chamber along with hydrogen sulphide (H_2S) or sulphur vapor. The carbonyl gas may be introduced through one of the inlet pipes and hydrogen sulphide or sulphur vapor through the other inlet pipe. A suitable plating temperature is around 400° C. to 600° C. and the gases should be supplied in amounts equal to the stoichiometric ratios of sulphur and chromium for producing the desired compound.

Example 3

Compounds of chromium with selenium, such as CrSe and Cr_2Se_3 , may be plated by introducing hydrogen selenide H_2Se together with chromium carbonyl in stoichiometric ratios appropriate to plate the desired compounds. A plating temperature around 400° C. to 600° C. and a pressure of 1 millimeter of mercury may be employed.

Example 4

Compounds of tellurium and chromium, such as CrTe and Cr_2Te_3 may be plated by introducing chromium carbonyl and hydrogen telluride in stoichiometric ratios of chromium and tellurium suitable to produce the desired compound. The object to be plated may be heated to between 400° C. and 600° C. and a pressure of 1 millimeter of mercury maintained in the plating chamber.

Example 5

Molybdenum oxides, such as purple molybdenum oxides Mo_2O_3 , brownish purple molybdenum oxide Mo_3O_8 and a white molybdenum oxide MoO_3 or mixtures thereof may be plated. Along with the molybdenum carbonyl there may be introduced air, pure oxygen, CO_2 , or H_2O . Stoichiometric amounts of the gases introduced with respect to the molybdenum and oxygen content may be employed if high plating temperatures above 400° C. are used. At lower temperatures an excess of oxidizing agent will be necessary to counteract the reducing tendency of the carbon monoxide, a tendency which is dependent upon the pressure. Gas pressures in the plating chamber of 1 millimeter of mercury or less may be employed.

Example 6

Sulphides of molybdenum, such as Mo_2S_3 , MoS

and MoS_3 may be plated by introducing molybdenum carbonyl along with hydrogen sulphide or sulphur vapor in a manner analogous to the preparation of the oxides when introducing H_2O . Plating temperatures of 400°C . or somewhat higher and gas pressures in the plating chamber of 1 millimeter of mercury or less may be employed.

Example 7

Selenides of molybdenum, such as MoSe_2 and Mo_2Se_3 , or mixtures thereof may be plated. Along with the molybdenum carbonyl hydrogen selenide H_2Se may be introduced and a plating temperature of 400°C . to 600°C . and a pressure of 1 millimeter of mercury or less may be employed.

Example 8

Molybdenum tellurides, such as MoTe and MoTe_2 may be plated by introducing hydrogen telluride H_2Te along with molybdenum carbonyl in stoichiometric ratios to produce the desired substance. Mixtures of these tellurides in a solid solution of one in the other may also tend to be produced. Temperatures of 400°C . to 500°C . and gas pressures in the plating chamber of 1 millimeter of mercury or less may be employed.

Example 9

Tungsten oxide, such as W_2O_5 which has a bluish-violet color, WO_2 which has a brownish color, and WO_3 which has a light yellow color, may be plated by introducing water, oxygen or CO_2 . Stoichiometric ratios with respect to the tungsten and oxygen of tungsten carbonyl and the oxygen containing gas may be employed, except at relatively low temperatures, in which case an excess of oxygen containing material should be employed. Plating temperatures of the surface to be plated may range from 400°C . to 800°C ., and pressures of 1 millimeter of mercury or less should be mounted in the plating chamber.

Example 10

Tungsten sulphide, such as WS_2 and WS_3 , or mixtures thereof, may be plated by introducing tungsten carbonyl and hydrogen sulphide in suitable ratios with plating temperatures of 400°C . or somewhat higher and gas pressures of 1 millimeter of mercury or less.

Example 11

Tungsten selenide, such as WSe_2 and WSe_3 , may be plated by introducing tungsten carbonyl along with hydrogen selenide in suitable stoichiometric ratios of tungsten and selenium for the particular compound desired with plating temperatures of 400°C . or upward and gas pressures in the chamber of 1 millimeter of mercury or lower.

Example 12

Tungsten tellurides, such as WTe and WTe_2 , may be plated by introducing tungsten carbonyl and hydrogen telluride H_2Te under conditions similar to those set forth with respect to the selenides of Example 11.

In every case set forth above, the plating operation may begin by introducing the metallic carbonyl alone or more preferably with an excess of hydrogen. A thin metallic plate of the metal chromium, molybdenum or tungsten may thus be deposited, which layer may be, if desired, very thin, perhaps no more than a thickness corresponding to a few molecules of the metal. Then by introducing the other gas, such

as the oxygen, sulphur gas, hydrogen sulphide, selenium gas, hydrogen selenide, tellurium gas, or hydrogen telluride, the desired compound may be plated over the metal. This will promote adherence because it has already been disclosed by me that tightly adhering platings of such metals may be produced under suitable conditions if the surface of the base metal to be plated is chemically free from impurities, such as oxides or other substances which would tend to impair the adhesion.

In plating or coating according to the present specification the highest permissible temperature of the surface to be plated would ordinarily not exceed 800°C ., but may be somewhat less or somewhat more dependent upon the particular substances which are used in plating and the particular compositions to be deposited. In every case the maximum temperature must be well below the softening or decomposition point of the object to be plated and also below the melting or vaporization point of the substance to be deposited as a plating or coating. Consequently, each and every one of applicant's claims is to be construed, regardless of the specific language used therein, as having an upper temperature limit conforming to each and every one of the foregoing conditions.

What is claimed is:

1. The method of plating a surface of an object, which will withstand heating, which comprises maintaining the surface to be plated at a temperature in the range of from 200° to 800°C ., continuously bringing in contact with the surface to be coated the gaseous carbonyl of an element selected from the group consisting of molybdenum, tungsten and chromium together with at least one gaseous substance selected from the group consisting of sulphur, selenium, tellurium and their hydrides, continuously withdrawing therefrom decomposition products and maintaining the total gas pressure at up to 5 millimeters of mercury.

2. The method of plating a surface of an object, which will withstand heating, which comprises maintaining the surface to be plated at a temperature in the range of from 400° to 800°C ., continuously bringing in contact with the surface to be coated the gaseous carbonyl of an element selected from the group consisting of molybdenum, tungsten and chromium together with at least one gaseous substance selected from the group consisting of sulphur, selenium, tellurium and their hydrides, continuously withdrawing therefrom decomposition products and maintaining the total gas pressure at up to 5 millimeters of mercury.

3. The method of plating a surface of an object, which will withstand heating, which comprises maintaining the surface to be plated at a temperature in the range of from 400° to 800°C ., continuously bringing in contact with the surface to be coated the gaseous carbonyl of an element selected from the group consisting of molybdenum, tungsten and chromium together with gaseous hydrogen sulphide, continuously withdrawing therefrom decomposition products and maintaining the total gas pressure at up to 5 millimeters of mercury.

4. The method of plating a surface of an object, which will withstand heating, with a molybdenum sulphide, which comprises maintaining the surface to be plated at a temperature in the range of from 400° to 800°C ., continuously bringing in contact with the surface to be coated

the gaseous carbonyl of molybdenum, together with gaseous hydrogen sulphide, continuously withdrawing therefrom decomposition products and maintaining the total gas pressure at up to 5 millimeters of mercury.

5. The method of plating a surface of an object, which will withstand heating, with a molybdenum sulphide, which comprises maintaining the surface to be plated in a hermetically sealed enclosure, at a temperature in the range of from 400° to 800° C., continuously bringing in contact with the surface to be coated gaseous molybdenum carbonyl, together with gaseous hydrogen sulphide, continuously withdrawing therefrom decomposition products and maintaining the to-

tal gas pressure at up to 5 millimeters of mercury.

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