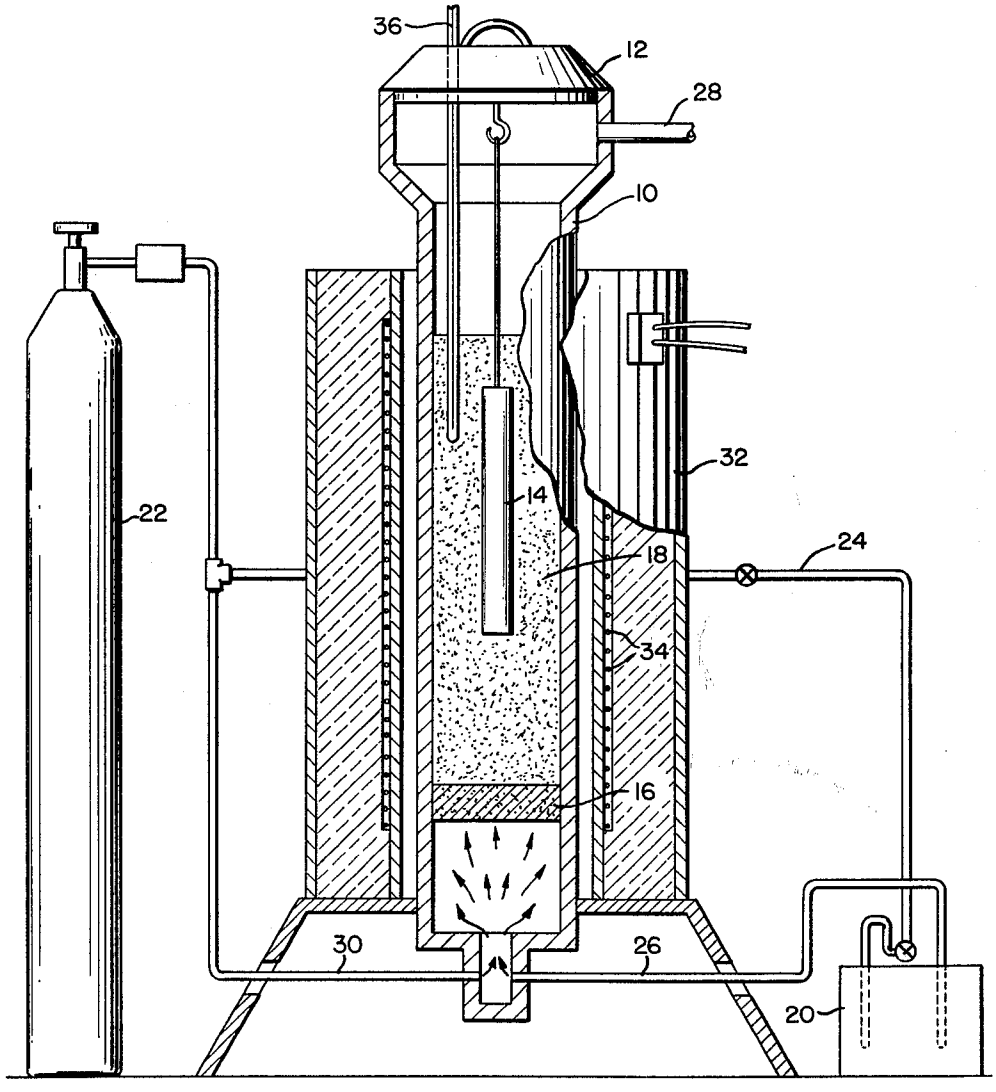
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CHEMICAL VAPOR PLATING PROCESS

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CHEMICAL VAPOR PLATING PROCESS

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This invention relates to an improved chemical vapor plating process for depositing a coating on an object's surface. More particularly, the process comprises contacting the surface being coated with agitated, particulate solids during the deposition of the coating to provide a uniform, adherent, continuous coating.

"Vapor plating," as used in the art, commonly includes both physical and chemical vapor plating processes. Physical vapor plating processes include such processes as evaporation of metals and vacuum metalizing. The terminology "chemical vapor plating," as used throughout the specification and claims, is intended to exclude physical vapor plating. It is intended that "chemical vapor plating" only include deposition of a coating by means of a chemical reaction of a thermally activated chemical vapor plating material in a vaporized state at or near a hot object's surface being coated. Illustrative of chemical vapor plating reactions are thermal reduction, thermal decomposition, and thermal disproportionation reactions. Thermal reduction reactions include hydrogen or metal reductions of a halide and reactions of halides with a gas containing carbon, nitrogen, boron, silicon, or oxygen compounds. Thermal decomposition reactions include decompositions of halides, oxygen-containing compounds, carbonyl compounds, and hydride compounds. Suitable thermal activation temperatures for various vaporized chemical vapor plating materials and other process conditions are known to the art. A recent survey presenting a unified picture of vapor plating is found in Vapor Plating by C. F. Powell, I. E. Campbell, and B. W. Gonser, John Wiley & Son, Inc., New York, New York, 1955. Numerous other publications describe vapor plating and, in particular, the chemical vapor plating processes of the nature with which the present invention is concerned.

The present invention is concerned with an improvement in chemical vapor plating processes to provide superior coatings. The process of the invention is useful for coatings deposited by chemical vapor plating processes and is especially useful for overlay coatings.

Various metals, nonmetals, and metallic and nonmetallic compounds are deposited as coatings by chemical vapor plating from thermally activated plating materials in a vapor state. Pure deposits of many metals are deposited by chemical vapor plating processes to provide dense, massive metal coatings or deposits. Among the various metal coatings deposited are coatings of copper, aluminum, titanium, zirconium, hafnium, thorium, germanium, tin, lead, vanadium, niobium, tantalum, arsenic, antimony, bismuth, chromium, molybdenum, tungsten, uranium, rhenium, iron, cobalt, nickel, ruthenium, rhodium, osmium, iridium, platinum, and various metal alloys of these metals, such as titanium-tantalum, zirconium-tantalum, and chromium-molybdenum alloys. Carbon and carbide coatings also may be deposited. Among the various carbide coatings are coating of boron carbide, silicon carbide, titanium carbide, zirconium carbide, hafnium carbide, thorium carbide, vanadium carbide, niobium carbide, tantalum carbides, chromium carbides, molybdenum carbides, tungsten carbides, uranium carbides, and mixtures, such as tantalum and hafnium carbides, tantalum and zirconium carbides, and tantalum carbide with tantalum nitride. Nitride coatings also may be deposited. Among the deposited nitride coatings are zirconium nitride, titanium nitride, tantalum nitride, niobium nitride, and hafnium nitride. Boron and boride coatings also may be deposited. Among the boride coatings are coatings of aluminum boride, titanium boride, zirconium boride, hafnium boride, thorium boride, vanadium boride, niobium boride, iron borides, and nickel borides. Silicon and silicide coatings also may be deposited. Among the various silicide coatings are coatings of titanium silicides, zirconium silicides, vanadium silicides, niobium silicides, tantalum silicides, molybdenum silicides, tungsten silicides, platinum silicides, iron silicides, cobalt silicides, and nickel silicides. Oxide coatings also may be deposited. Among the various oxide coatings are coatings of aluminum oxide, boron oxide, silicon dioxide, zirconium dioxide, chromic oxide, and mixtures, such as aluminum oxide with zirconium dioxide and silicon dioxide with aluminum oxide.

A large number of objects and surface and substrate materials may be coated by the aforementioned coatings. Among surface and substrate materials coated by overlay coatings are copper, nickel, tantalum, molybdenum, tungsten, iron, steels, graphite, porcelain, alumina, fused silica, "Pyrex" glass, and sintered carbide bodies. The coatings may be deposited on either metallic or nonmetallic materials. Wire, rod, tubing, plate, strip, and fabricated objects, such as electronic tube elements, X-ray tube targets, and the like may be coated.

In all, a wide variety of various metallic and nonmetallic materials may be deposited as coatings from thermally activated plating materials in a vapor state on a wide variety of surfaces and objects. Chemical vapor plated surfaces and articles are useful in many applications with an important usage being in the chemical processing industry. In this industry, such equipment as pipes, valves, vessels, and the like, frequently are made of a strong base material having particularly desirable noncorrosive and chemical-resistant properties. Suitable chemical vapor plating process conditions are taught in the art. Process conditions vary, depending on the thermally activated chemical vapor plating material, the particular coating, and the base material, with from a few mils up to a half inch or more in thickness of coating being deposited in plating times ranging from a few minutes to many hours. Often the chemical vapor plating is carried out as a batch process, although some coatings are deposited by continuous processes. Usually the vapor plating process comprises a reduction or decomposition of a volatilized compound in the feed stream by means of a heated surface of the base material, with a deposition of a coating on this heated surface and with by-products of the reduced or decomposed compound pumped off, flushed off in a stream of carrier gas, or removed by reaction with other materials in the system.

Among the problems encountered in chemical vapor plating of coatings is the obtaining of an adherent, uniform, continuous coating. Care must be used to suitably clean the surface to be coated and in handling the cleaned surface until deposition of the coating to assure good adherence of the coating to the base material or object's surface. Even with extreme care in cleaning and handling, quite frequently coatings are obtained with portions of the coating not adhering to the surface or adhering weakly or adhering so weakly that chipping, flaking, and blistering occur readily upon application of light forces, such as flexing, bending, and pounding. Even with care in cleaning and handling the base material or object's surface, quite frequently the prior-art coatings are discontinuous, porous, crystalline, and nonuniform in thickness. In chemical vapor plating, a coating frequently deposits

initially in scattered centers on the surface with further coating depositing between and bridging these initial centers. In bridging these initial centers of deposited coating, the coating frequently does not bond firmly to the surface therebetween and often encloses voids. For the foregoing and other reasons, coatings deposited by the usual prior-art plating processes are of limited usage and are not completely satisfactory for many purposes and in particular for those applications where adherent, uniform, continuous coatings are required.

It is an object of this invention to provide improved adherent, uniform, continuous coatings by contacting the surface being coated through chemical vapor plating with agitated, particulate solids. It is another object to provide a relatively inexpensive and commercially useful chemical vapor plating process for providing uniform, adherent, continuous coatings capable of use in many applications. It is a further object in a chemical vapor plating process to provide superior adherency of a coating to an object's surface through a contacting of the base material and deposited coating with agitated, particulate solids during the deposition of the coating. These and other objects will become apparent from the following description and the attached drawing.

The drawing is a front elevational view, partly in section, of an apparatus for carrying out the method of this invention by applying coating in a bed of fluidized infusible particles.

The chemical vapor plating process of the invention comprises contacting the object's surface being coated and/or the coating being deposited with finely divided, particulate solids during deposition of the coating.

Individual particles of the particulate solids for the process are of a small size. In order to provide the benefits of the invention for the entire coating deposited on the object's surface, at least a portion of the individual particles of the solids are of a size minute enough to permit ingress to and contact with the smallest accessible area of the object's surface being coated. Generally, particles of a range of sizes are employed. In the embodiments of the process employing a bed of randomly moving finely divided solid particles, the object whose surface is being coated is of a size not permitting a random movement of the object equivalent to the three-dimensional random movement of the solid particles or is maintained in a position preventing equivalent random movement. Usually this is accomplished in these embodiments by employing solid particles of which the largest individual solid particle is smaller in size than the object. In other embodiments of the process the largest individual particle always is smaller in size than the object being coated.

In the process, the hot surface of the object being coated is maintained at a temperature suitable to thermally activate the particular chemical reaction of the vaporized chemical vapor plating material permitting coating material to deposit. For any particular chemical vapor plating material, an activation temperature is a temperature at which there takes place a chemical reaction of the particular material releasing coating material for deposition. Activation temperatures for various chemical vapor plating materials and their reactions are taught in the art. Usually, the surface being coated is maintained at a desired known activation temperature by heating and by controlling by conventional means the temperature of the object's surface and/or the object itself. In the process, desirably, there is maintained a differential in temperature between the surface being coated and the particulate solids. Where the heated surface being coated is at an activation temperature and the particulate solids are of about the same temperature, process efficiency is impaired in that coating material deposits on both the heated surface and the particulate solids. Desirably, only the surface being coated is maintained at an activation temperature or the surface being coated is maintained at an activation temperature more conductive to the thermal activation than the temperature of the particulate solids. For most thermally activated chemical vapor plating materials, this means that the surface being coated is maintained at a higher temperature, that is the surface is hotter than the particulate solids. With some chemical vapor plating materials and chemical reactions thereof, such as aluminum monochloride and its disproportionation reaction and some other materials and their exothermic chemical reactions, processing techniques are facilitated and/or efficiency increases obtained with the surface being coated at a lower temperature, that is, the surface is colder, than the particulate solids. In the practice of the process a temperature differential is maintained usually by heating or cooling, as the case may be, the object's surface and/or the object by conventional means and by introducing the solid particles, vaporized chemical vapor plating material, and other gases at temperatures above or below, as the case may be, the temperature of the object's surface with only the object's surface maintained at an activation temperature or at a more favorable activation temperature. In the embodiments of the process employing a gas stream having solid particles entrained or suspended therein, the average temperatures of the entrained or suspended particles may be about the same as or different than the activation temperature at which the object's surface is maintained. Although coating efficiency of the object's surface in this embodiment is impaired, when the temperatures are about the same, operation is possible. Desirably in the practice of this embodiment with about the same temperatures, exposure of the vaporized chemical vapor plating material to the particulate solids or solid particles is limited or minimized to minimize the decrease in coating efficiency with any such brief contact occurring adjacent to the surface being coated, or just before contact of the solid particles and the vaporized chemical vapor plating material takes place with the surface. In the embodiments of the process employing a bed of randomly moving particulate solids and in the other embodiments of the process the temperature differential between the object's surface being coated and the average temperature of the bed of particulate solids necessarily is maintained to promote a preferential deposition of the coating material on the object's surface. The average temperature of a bed of randomly moving particulate solids or of finely divided solid particles may be obtained by averaging the measurements of temperatures obtained by a plurality of temperature measuring devices uniformly spaced among the solid particles.

In the invention, the contacting bombardment of the article by the solids during deposition of the coating may be accomplished by a number of methods. The particulate solids may be suspended or entrained and transported in a plating stream or in an inert gas or vapor stream. This moving stream containing the particulate solids then may be directed to contact the surface being plated and the coating being deposited during coating deposition. The particulate solids may be placed in a coating apparatus along with the article being plated, and this bed of the solids subjected to mechanical vibration or agitation to cause random movement of the particulate solids and contacting by the randomly moving solids of the surface being plated during coating deposition. A variation of this process is the coating of an interior of a hollow vessel with the hollow vessel serving as the coating apparatus and with rotative movement or vibration of the vessel causing a bed of particulate solids within the vessel to agitate and contact the vessel's interior during the chemical vapor plating. The agitated, finely divided particulate solids also may be in the form of a gas-fluidized bed with an object being plated so placed that fluidized particles contact the object's surface being plated during deposition of the coating. Maintenance of fluidized beds of the particulate solids is by means of the plating feed stream, an inert gas or vapor, or conventional means.

One of the most promising is in a gas fluidized bed of inert infusible particles. Such an apparatus is illustrated in the drawing.

Referring to the drawing, the fluidized bed apparatus comprises a vertically extending cylinder 10 having top closure member 12 from which the object to be coated 14 is suspended. A porous plate 16 is fixed near the lower end of cylinder 10. The cylinder is partially filled with a bed of granular material 18 completely surrounding object 14.

A coating gas generator 20 is provided for generating a reactive gas such as, for example, silicon iodide. A source 22 of an inert gas such as argon is also provided. Means 24 are provided for causing the argon to flow through the reactive gas generator 20 to sweep the reactive gas through a line 26 into the lower portion of cylinder 10. The reactive gas passes up through porous plate 16 through bed 18, where it contacts object 14, and then flows out through an outlet 28 to a condenser or other means of disposal not shown. A line 30 is also provided for causing inert gas to flow directly from source 22 to the lower portion of cylinder 10.

Cylinder 10 is completely surrounded by a source of heat such as an electric muffle furnace 32. Furnace 32 is provided with a winding of resistance wires 34 adapted to raise the temperature of cylinder 10 to the desired value.

In operation, the object to be coated is placed in the granular bed 18, and the entire apparatus is raised to coating temperature by applying an electric current to muffle furnace 32. After the bed has reached the desired temperature as indicated by a thermometer 35, inert gas is allowed to flow through line 30 into the lower portion of cylinder 10. The gas passes upwardly through porous plate 16 and granular bed 18 with sufficient velocity to suspend the particles of granular bed 18 thereby fluidizing the same. The reactive gas is then allowed to flow from generator 20 to line 26 and upwardly through the bed, where it comes in contact with object 14, depositing a coating thereon in the manner well-known in the vapor plating art. However, while this plating is being deposited, the surface of object 14 is being constantly abraded, scoured and scrubbed by the moving particles in the turbulent fluidized bed. This results in a superior coating free from the defects heretofore prevalent in vapor plating coatings.

The contacting of the object's surface being plated with agitated, particulate solids during deposition of a coating by a chemical vapor plating process results in obtaining superior coatings. These superior coatings possess a greater uniformity, superior adherency to the base surface, and are dense coatings noticeably free from voids and pinholes. Coatings of superior smoothness are obtainable. Apparently coatings deposited by the process of the invention tend to smooth over surface roughness and fill tiny voids of the surface being coated. A random contacting action of the particulate solids against the surface exerts a manifold effect. An apparent cleansing of the surface takes place and a dissipation of the impact forces of the particulate solids appears to accelerate formation of nucleating points in large numbers for creation of numerous initial deposition centers. Apparently the contacting with the numerous particles of the particulate solids also serves to assure a uniformity in coating by a breaking up of the concentration gradient of the thermally activated plating material or the intermediates or products of the plating reaction between the surface being plated and the bulk of the plating atmosphere. In addition, the turbulent mixing by the agitated, particulate solids minimizes any bulk concentration gradient, for example, between the inlet and the outlet of that fraction of the plating vessel which contains the particulate solids. During deposition of vapor plated coatings, the contacting by the particulate solids removes loosely adherent overlay coating and allows only coating adhering firmly to remain. The contacting also appears to polish the coating as applied and to remove irregular surface defects, such as whiskers and crystallites, by breaking down such irregular deposits before they build to an appreciable size to destroy uniformity of the coating. Apparently the contacting also compacts and densifies the deposited coating so that voids and pinholes are absent or noticeably reduced in size and number. However, whatever the particular explanation may be, the contacting with agitated, inert, particulate solids of the surface being chemically vapor plated during the coating deposition serves a beneficial purpose, in that coatings superior to those deposited without such a contacting are obtained.

Many particulate materials are suitable particulate solids for use in the process of the invention. Suitable particulate materials desirably are characterized as being substantially free from chemical reaction with the surface or substrate material, the thermally activated plating material, and the plating atmosphere at the temperature of the surface of the object or substrate material being coated. The particles of the particulate solids remain as discrete solid particles and desirably undergo no substantial changes in form and physical state under the particular process conditions employed. Desirably the particles do not disintegrate into smaller particles, do not deform easily, and have no appreciable tendency to become molten and sticky at the process conditions. Preferably the particulate solids are of equal or greater hardness than the coating and the base materials, so as to permit a ready control of cleaning and loose coating removal action, usually through control of the magnitude of the forces of these particles striking against the surface being coated. Metal particulate materials, if of the same metal as the base material or the coating material, or if at least as stable as the base being coated and the coating products at the particular process conditions, are uniquely suitable. Preferred particulate solids are a finely divided solid form of the particular material being deposited as the coating. For example, tantalum metal particles are the preferred particulate material when tantalum pentachloride is vaporized and is mixed with hydrogen to serve as the feed stream to deposit a tantalum overlay coating. Other solids, particulate materials, which are solids and desirably are substantially nonreactive with the base material and feed reactants and gases at the temperature of the surface being coated, are suitable. Aluminum oxide, Al_2O_3, zirconium oxide, ZrO_2, and thorium dioxide, ThO_2, because of relative inertness to halogens and halides, are useful in halide chemical vapor plating processes. Silicon dioxide, SiO_2, is also well suited for various chemical vapor plating processes. These oxides are infusible at the temperatures employed. A wide variety of solid, inert, particulate materials are available and the invention is not limited to a particular particulate solid material.

Particle size of the particulate solids may vary widely. Extremely fine particles, such as those of submicron size and even those as large as several microns, will tend to be embedded and occluded in overlay coatings. Such extremely fine particles preferably are avoided or are included only as a minor proportion of the over-all amount of solid particles being employed. Additionally, the mass of such fine particles presents practical difficulties in obtaining sufficient driving force to knock loosely adherent coating off of the base surface. Extremely large particles are avoided. These extremely large particles present practical difficulties in propelling, and their mass is great enough that by gravity alone they undesirably displace the object from the contacting area or dimple and dent the coating and the surface being coated. In comparison with the object being coated, the individual particles of the particulate solids preferably are of a minute size.

Optimum particle size depends greatly on the particular

coating material, the particular base material and article being coated, and the particular means for contacting, as well as the nature of the particulate material. In practice, solid particles, ranging in size from as large as about one-inch diameter to extremely small irregular or uniformly shaped particles of which less than 50 percent by weight pass through a U.S. No. 325-mesh sieve, are useful. The finer size particles are suitable for suspension; the intermediate size particles are suitable for the fluidized bed contacting means; and the coarser particles are suitable for the tumbling-type contact means. Within this useful particle size range, preferred particles are between 45 microns to ¼ inch in size. In most applications of the process, the particulate solids comprise particles of a range of particle sizes. Generally, where a high rate of coating deposition is used, the particles desirably are of a somewhat larger size than where a lower deposition rate is used to ensure a rebounding of the particles and a freedom from particles embedded in the coating. Through control of the means and manner of causing the particles to contact the surface being plated, a removal of coating having less than a selected amount of adherence to the base surface is possible, with assurance of a coating having a desired adherence being obtained. In practice, coarse particles contacting with gravitational force permit the obtaining of overlay coatings adherently bonded to the base surface.

This invention will now be described further with reference to specific examples for illustratiing that the process of the invention including a contacting by a particulate material during coating deposition provides coatings superior to those coatings obtained without the contacting by the particulate material.

Example I

The plating apparatus comprises a 1.75 inch I.D. by 12 inches long tubular-shaped plating chamber of Vycor. Suspended centrally by wires in this chamber is a cleaned, 1/16-inch thin-wall, steel tube 0.875 inch O.D. by 2.5 inches long. Within the plating chamber are placed loose particles of aluminum oxide, Al_2O_3, of about 60-mesh size in an amount to cover the piece to be plated. After purging the chamber with argon gas, a tantalum pentachloride and argon gaseous mixture is admixed with hydrogen, just prior to entrance into the bottom of the chamber, to provide a feed stream. The feed stream comprising a 255:1 molar ratio of hydrogen to tantalum pentachloride is the result of combining together a 0.8 c.f.m. stream of purified hydrogen gas and a 0.065 c.f.m. stream of 1:20 molar ratio mixture of tantalum pentachloride and argon. The feed stream at atmospheric pressure and a temperature of about 210° C. enters the bottom of the plating apparatus and exits from the top of the chamber to pass through an expanded disentrain unit. In passing through the plating chamber, the feed stream creates movement and fluidization of the Al_2O_3 particles so that the suspended steel tube receives numerous contacts by randomly moving agitated Al_2O_3 particles. The suspended steel tube is heated to a temperature of between 840° and 900° C. by means of an electrical induction coil located around the outside of the Vycor chamber. As the feed stream contacts the heated steel tube, a hydrogen reduction of tantalum pentachloride takes place with a deposition of an overlay coating of tantalum metal on the heated steel tube. After about 2 hours, the heating of the metal tube and introduction of the feed stream are discontinued, and the plating chamber purged with argon gas until the coated steel tube cools to about room temperature (20° C.).

A number of steel tubes are coated with tantalum coatings according to the preceding procedure. A number of steel tubes also are coated with tantalum coatings according to the preceding procedure except for an omission of aluminum oxide particles from the plating chamber. Comparison of the coated steel tubes from both procedures reveals: With the procedure omitting the aluminum oxide particles, the deposited tantalum coatings are dark gray to black, dull and lacking luster, blistered in places, are several mils thick with nonuniformity in thickness with the heaviest coatings at the lowest suspended portion of the tubes, and of a crystalline appearance. Upon scratching these coatings with a fingernail, small flakes of coating are removed and blisters break to expose uncoated areas of the steel tubes. With the process of the invention including agitated aluminum oxide particles contacting the steel tube during deposition of the coating, the deposited tantalum coatings are light gray, shiny and glossy, continuous, apparently free of blisters and occluded voids, are several mils thick and uniform in thickness, and of a decidedly less crystalline appearance. Upon scratching these coatings with a fingernail, no apparent change in the coatings results.

When depositing a tantalum coating on a metal surface by a reduction of either tantalum pentachloride or tantalum pentabromide with hydrogen, by a procedure in substantial accordance with the preceding exemplified process of the invention, suitable process conditions are: a metal surface temperature of 800° to 1000° C.; a hydrogen-to-tantalum pentahalide molar ratio of between 100:1 and 600:1; and a linear gas velocity, calculated at standard pressure and temperature through the cross-sectional area above the fluidized bed, of 15 to 50 feet/minute.

Example II

By combining together a 0.28 c.f.m. stream of purified hydrogen gas and a 0.019 c.f.m. stream of 1:5.8 molar ratio gaseous mixture of niobium pentachloride and argon there is prepared a feed stream having a $NbCl_5$:A:H_2 molar ratio of 1:5.8:102. This feed stream, in place of the feed stream of Example I, is introduced into the same plating apparatus employed in Example I to coat 1/16 inch thick-wall steel tubes by the same procedure of Example I except that the suspended steel tube is heated to a temperature of 840° to 870° C.

A number of steel tubes are coated with niobium overlay coatings for several hours by this procedure with and without the inclusion of aluminum oxide particles in the plating chamber. A comparison of these coated steel tubes reveals: With the procedure omitting the aluminum oxide particles, the deposited niobium coatings are several mils thick, dark gray, dull, partially blistered, nonadherent in portions, crystalline, and fairly porous. With the process of the invention including agitated randomly moving aluminum oxide particles contacting the steel tube during deposition of the overlay coating, the deposited niobium coatings are several mils thick, light gray, shiny and glossy, free from blisters, adherent, and only slightly crystalline and slightly porous.

To deposit a tungsten coating by a procedure in substantial accordance with the preceding exemplified process of the invention and by a reduction of vaporized tungsten hexachloride with hydrogen, suitable process conditions are: a temperature of 600° to 900° C. for the surface being coated; two gas feeds to the fluidized bed, one gas feed consisting essentially of 2 to 50 mole percent of tungsten hexachloride in an inert carrier gas, the other gas feed of hydrogen gas in an amount to provide a hydrogen-to-tungsten hexachloride molar ratio of between 150:1 and 600:1 in the fluidized bed; and a linear gas velocity of the total gas, calculated at standard pressure and temperature through the cross-sectional area above the fluidized bed, of 15 to 50 feet/minute.

Example III

By combining together a 0.28 c.f.m. stream of purified hydrogen gas and a 0.018 c.f.m. stream of a 1:8.1 molar ratio gaseous mixture of molybdenum pentachloride and argon, there is prepared a feed stream having a

$MoCl_5$:A:H_2

molar ratio of 1:8.1:142. This feed stream at atmospheric pressure and a temperature of about 220° C. is introduced into the same plating apparatus employed in Example I with the tubular walls of the Vycor plating chamber at a temperature of about 500° C. The aluminum oxide particles are used in an amount such that, upon fluidization by the feed stream, the particles randomly contact only the lower half of the tubular wall of the Vycor container with the upper half of the tubular wall receiving little or no contacting by the fluidized aluminum oxide particles during the coating deposition.

After several hours, this coating process is discontinued, with the plating chamber purged with argon gas until it cools. At this time, the coated interior walls of the Vycor plating chamber are examined. The upper half of the tubular wall, that wall portion not contacted by inert particulate material during coating deposition, is covered with a dark, dull, nonadherent, molybdenum powder deposit easily removed by light rubbing. The lower half of the tubular wall, that wall portion contacted by the fluidized aluminum oxide particles, is coated with a thin, bright, continuous molybdenum coating adherently bonded to the Vycor chamber and not removed by hard rubbing.

Example IV

A feed stream mixture of chromic chloride and hydrogen gas in the molar ratio of 1:400 of chromic chloride to hydrogen is passed through a one-inch diameter, 12-inch length Vycor tube containing finely divided, pure silicon dioxide of a particle size between −30 to +80 U.S. sieve size. The feed stream enters at a rate of 0.3 c.f.m. and thoroughly agitates the silicon dioxide particles causing the particles to repeatedly contact the entire Vycor tube interior. The feed stream exits through an expanded disentrainment tube so that entrained silicon dioxide particles in the feed stream are separated and returned to the Vycor tube. The Vycor tube is heated to a temperature of about 800–900° C. by an exteriorly located heating means. After several hours the interior of the Vycor tube is found to be coated with a thin, uniform, adherent, continuous, chromium coating.

Example V

Tantalum pentachloride and tungsten hexachloride are formed from chlorine and tantalum and tungsten, respectively, by methods known to the art. A 2-inch diameter, ⅛-inch thick, flat disk of molybdenum metal is mounted inside a bell jar chamber which is surrounded by an exteriorly located induction coil for heating and maintaining the molybdenum sheet at a temperature of 900° C. The bell jar is provided with three orifices for gaseous feed streams at the bottom and with an exit for exhausted feed streams at the top with a means provided for condensing and collecting chlorides and other constituents of the exhausting feed stream. A mixture of tantalum pentachloride and hydrogen in a molar ratio of 1:100 is introduced at a temperature of 200° C. through one feed stream orifice, and a mixture of tungsten hexachloride and hydrogen in a molar ratio of 1:100 is introduced at a temperature of about 225° C. through a second feed stream orifice. A third stream consisting of finely divided tantalum metal particles, about 80 mesh size, suspended in argon gas is introduced through the third orifice so as to impinge chiefly on one side of the mounted disk. The introduced feed streams from the three orifices mix within the bell jar, contact the molybdenum disk, and exit from the bell jar. After several hours with the molybdenum disk at a temperature of 900° C. the introduction of the feed streams and the heating of the disk are discontinued and the molybdenum disk is cooled. Upon examination, the molybdenum disk shows a thin, tantalum-tungsten alloy coating, which is smoother, more continuous, more polished, more uniform, and more strongly adherent to the molybdenum sheet on the side contacted by the impinging tantalum particles than on the side not so contacted.

Example VI

Nickel carbonyl, $Ni(CO)_6$, is prepared by a method known to the art for use in coating the inside of a rotatable, steel autoclave. The steel autoclave, about 1 foot in inside diameter by 2 feet long, contains finely divided (about 6 mesh) steel shot sufficient to fill the autoclave about half full. With the autoclave on its tilted long axis, rotating at several r.p.m., heated to a temperature of about 250° C., and after purging with argon gas, a feed stream at atmospheric pressure and a temperature of 25° C. of a mixture of nickel carbonyl and argon in the molar ratio 1:25 is introduced into the heated, rotating autoclave. After several hours, the rotating and heating of the autoclave, and the introduction of the feed stream are discontinued, and the autoclave cooled. Upon examination of the interior of the autoclave, the interior is found to be coated with a thin, smooth, continuous, polished, nonporous, adherent, nickel overlay coating.

Although the invention has been illustrated in the specific examples with particular materials and particular process conditions, the invention is not limited to the particular materials and conditions illustrated in specific examples. Instead, it is intended to embrace within its scope all such modifications and variations as fall within the meaning, purview, and equivalency of the illustrated examples and foregoing description of the invention. It is believed apparent from the foregoing description and specific embodiments of the invention that the invention may be embodied in other specific forms without departing from the true spirit, scope, and essential characteristics of the invention.

What is claimed is:

1. In a chemical vapor plating process for depositing a coating on a hot surface of an object through a contacting of said surface with a vaporized chemical vapor plating material thermally activated by the surface, the combination therewith of: contacting the surface with the vaporized chemical vapor plating material and with moving finely divided infusible solid particles during deposition of the coating on the surface while maintaining the average temperature of said particles at a value sufficiently remote from the activation temperature of said chemical vapor plating material to prevent substantial deposit of said chemical vapor plating material thereon with the surface of said object at an activation temperature for the chemical vapor plating material.

2. In a chemical vapor plating process for depositing a coating on a hot surface of an object through a contacting of said surface with a vaporized chemical vapor plating material thermally activated by the surface, the combination therewith of: suspending finely divided infusible solid particles of a size capable of suspension and of a smaller size than said object in a gas; and bringing the gas containing said suspended finely divided solid particles, said particles being substantially non-reactive with said object and said chemical vapor plating material, to impinge upon the surface during the contacting of the surface with the vaporized thermally activated chemical vapor plating material.

3. In a chemical vapor plating process for depositing a coating on a hot surface of an object through a contacting of said surface with a vaporized chemical vapor plating material thermally activated by the surface, the combination therewith of: contacting the surface with the vaporized chemical vapor plating material and with finely divided infusible solid particles moving in a gas and impinging upon the surface during the contacting of the surface with the vaporized thermally activated chemical vapor plating material, while maintaining said vaporized chemical vapor plating material out of contact with said particles in any location away from the immediate vicinity of said surface where the temperature of the particles is sufficiently close to the activation temperature of said plating material to cause substantial deposit of said chemical vapor plating material on said particles,

said surface being maintained at an activation temperature for the chemical vapor plating material.

4. In a chemical vapor plating process for depositing a coating on a hot surface of an object through a contacting of said surface with a vaporized chemical vapor plating material thermally activated by the surface, the combination therewith of: contacting the surface with the vaporized chemical vapor plating material and a bed of randomly moving finely divided infusible solid particles during deposition of the coating on the surface with the surface at an activation temperature for the chemical vapor plating material.

5. The process of claim 4 employing the contacting of a gas fluidized bed of said solid particles, said gas fluidized bed comprising vaporized chemical vapor plating material and the finely divided infusible solid particles.

6. The process of claim 4, including the suspending of finely divided solid particles of a size smaller than one-inch diameter of which less than 50 percent by weight pass through a U.S. No. 325-mesh sieve.

7. The process of claim 4, including the suspending of finely divided solid particles of a metal substantially free from reaction with the heated surface and the vaporized chemical vapor plating material at the temperature of the heated surface.

8. The process of claim 4 including the suspending of finely divided solid particles consisting of the material comprising the object's surface.

9. The process of claim 4 including the suspending of finely divided solid particles consisting of the material comprising the coating.

10. In a chemical vapor plating process for depositing a coating on a hot surface of an object through a contacting of said surface with a vaporized chemical vapor plating material thermally activated by the surface, the combination therewith of contacting the surface with the vaporized chemical vapor plating material, and maintaining said surface at an activating temperature for said chemical vapor plating material while agitating finely divided infusible solid particles, to cause said particles to randomly contact the surface during the deposition of the coating thereon.

11. In a chemical vapor plating process for depositing a smooth, continuous, uniform, adherent coating on a heated surface of an object through a contacting of said surface with a vaporized chemical vapor plating material thermally activated by the surface, the combination therewith of: contacting the surface and the coating being deposited on the surface with the vaporized chemical vapor plating material and agitated, randomly moving particles of a bed of inert infusible particulate solids, said solids being substantially non-reactive with said object and said chemical vapor plating material, while maintaining the surface and coating deposited thereon at an activation temperature for the chemical vapor plating material and maintaining the average temperature of said particulate solids at a value which will prevent substantial activation of the vaporized chemical vapor plaing material.

12. The process of claim 11 including a reduction of a vaporized niobium halide with hydrogen to deposit a niobium coating on a metal surface.

13. The process of claim 11 including a reduction of a vaporized molybdenum halide with hydrogen to deposit a molybdenum coating on a metal surface.

14. The process of claim 11 including a pyrolysis of a metal carbonyl compound to deposit the metal on a metal surface.

15. The process of claim 11 including a reduction of vaporized tantalum halide with hydrogen to deposit a tantalum coating on a metal surface.

16. The process of claim 11 including a reduction of a vaporized tungsten halide with hydrogen to deposit a tungsten coating on a metal surface.

17. The process of claim 11 employing particulate solids consisting of the material comprising the object's surface.

18. The process of claim 11 employing particulate solids consisting of the material comprising the coating.

19. The process of claim 11 employing the contacting of a gas fluidized bed of said particulate solids, said gas fluidized bed consisting essentially of a fluidizing gas, vaporized chemical vapor plating material, and said particulate solids.

20. The process of claim 19, including: carrying forth a reduction of vaporized tantalum pentachloride with hydrogen gas at a temperature of 800° to 1000° C. with a hydrogen-to-tantalum pentachloride molar ratio of between 100:1 and 600:1; and maintaining a linear gas velocity, calculated at standard pressure and temperature through the cross-sectional area above the fluidized bed, of 15 to 50 feet per minute; whereby a tantalum coating is deposited on a metal surface.

21. The process of claim 19 including: carrying forth a reduction of vaporized tantalum pentabromide with hydrogen gas a temperature of 800° to 1000° C. with a hydrogen-to-tantalum pentabromide molar ratio of between 100:1 and 600:1; and maintaining a linear gas velocity, calculated at standard pressure and temperature through the cross-sectional area above the fluidized bed, of 15 to 50 feet per minute; whereby a tantalum coating is deposited on a metal surface.

22. The process of claim 19 including: carrying forth a reduction of vaporized tungsten hexachloride with hydrogen gas at a temperature of 600° to 900° C.; supplying two gas feeds to the fluidized bed, one gas feed consisting essentially of 2 to 50 mole percent of tungsten hexachloride in an inert carrier gas, the other gas feed of hydrogen gas in an amount to provide a hydrogen-to-tungsten hexachloride molar ratio of between 150:1 and 600:1 in the fluidized bed; and maintaining a linear gas velocity of the total gas, calculated at standard pressure and temperature through the cross-sectional area above the fluidized bed, of 15 to 50 feet per minute; whereby a tungsten coating is deposited on a metal surface.

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