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Carmichael et al.

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[54] **COATING APPARATUS**

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[51] **Int. Cl.** **C23c 13/12**

[58] **Field of Search** ..... 118/49.1, 49.5; 219/121 EB

[56] **References Cited**

UNITED STATES PATENTS

2,685,535	8/1954	Nack	118/49.5 X
2,746,420	5/1956	Steigerwald	118/8
3,134,695	5/1964	Henker et al.	118/49.5
3,192,892	7/1965	Hanson et al.	118/49.1
3,488,426	1/1970	Dietzel	118/49.5 UX
3,528,387	9/1970	Hamilton	118/49.1

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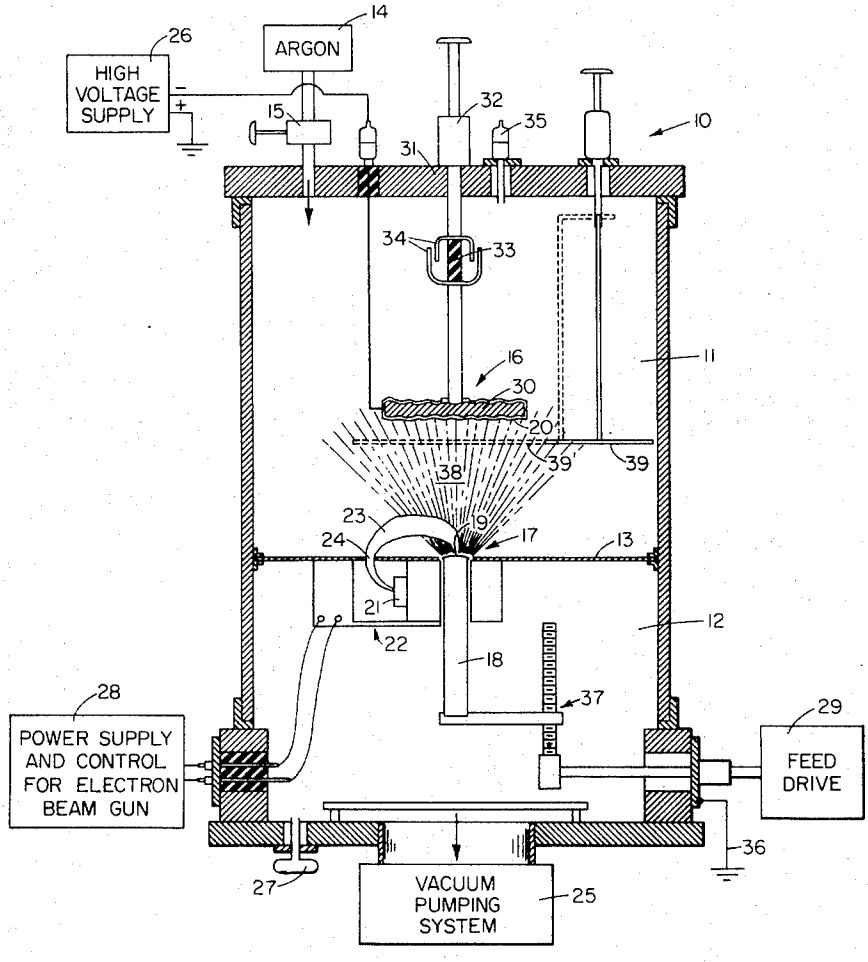
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[57] **ABSTRACT**

Apparatus for providing a tightly adherent coating on a substrate comprising a first chamber, means for providing an ionizable gas such as argon to the first chamber, a cathode comprising the substrate in the first chamber, a second chamber adjacent to the first chamber, a wall between the first chamber and the second chamber, an anode comprising a supply of the coating material, an exposed surface portion of the material (approximately planar and parallel to the wall) being in the first chamber and spaced from the cathode, a source of electrons in the second chamber, means for directing electrons from the source in a beam through an opening in the wall and on to the exposed surface portion of the anode, means for substantially evacuating the second chamber, and means for providing the cathode with a negative electric potential relative to the anode.

The electron directing means comprises an electron beam gun that directs the electron beam initially in a direction approximately parallel to the wall and away from the exposed anode surface portion, bends the beam through approximately one right angle to pass through the opening, and then bends it through approximately two more right angles to strike the exposed anode surface portion in a direction approximately perpendicular to the exposed anode surface portion.

13 Claims, 4 Drawing Figures



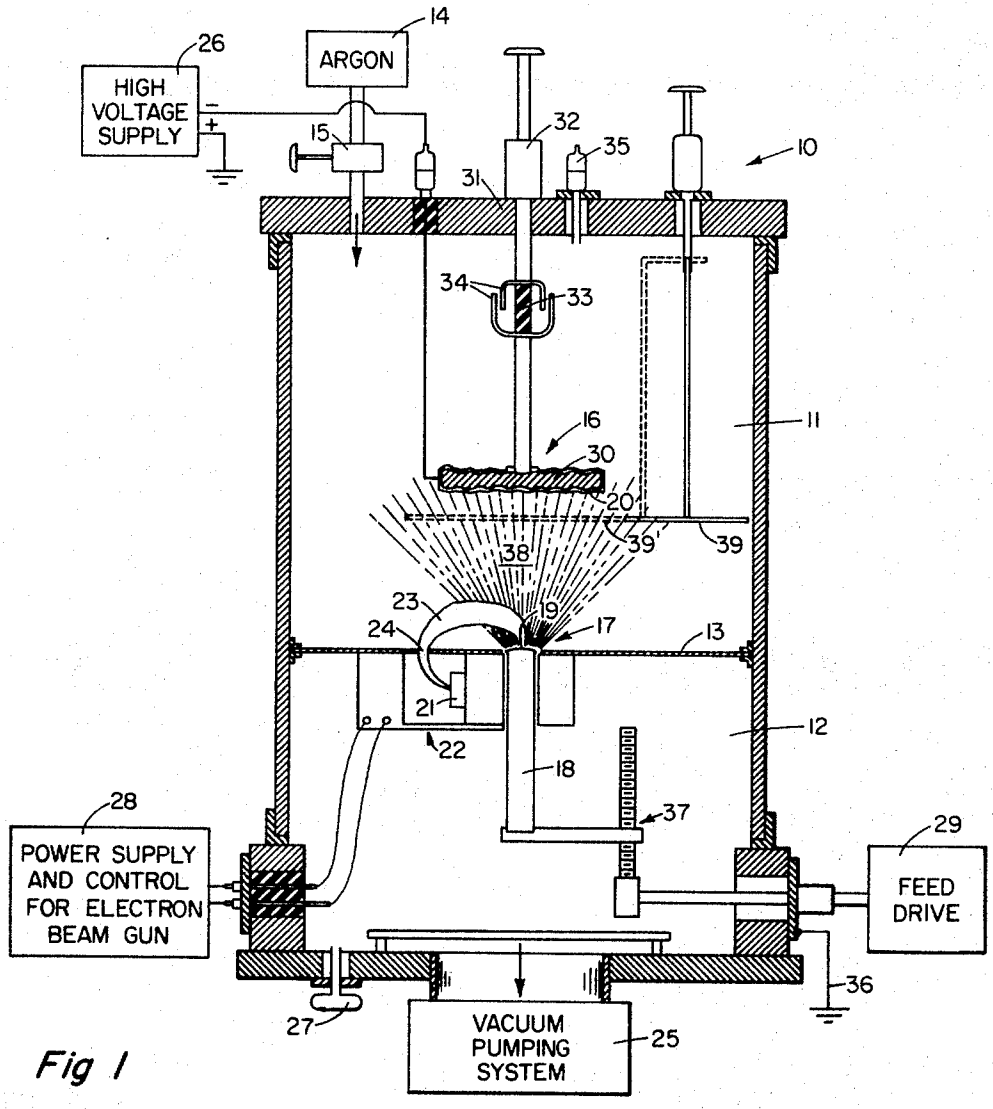


Fig 1

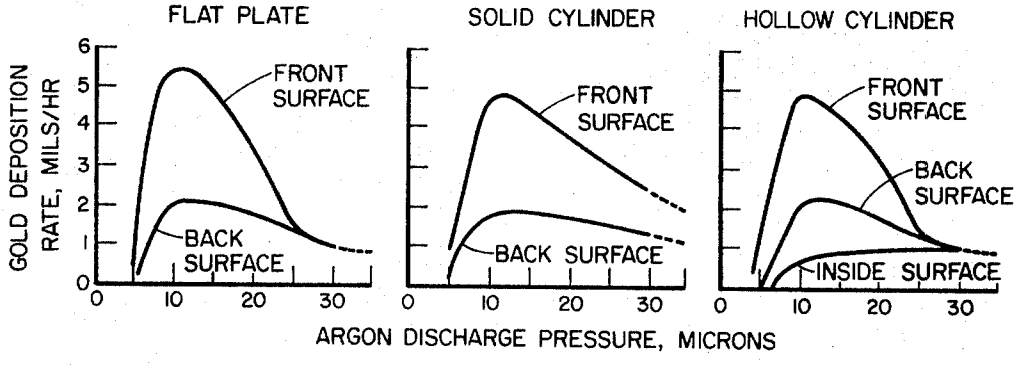


Fig 2 Fig 3 Fig 4

COATING APPARATUS

BACKGROUND OF THE INVENTION

Ion plating is a technique of vacuum coating, newer than vacuum evaporation (metallizing) and sputtering. In ion plating, the part to be coated is made the negative electrode or is placed in a low-pressure (vacuum) dc glow discharge, usually of argon. The positive ions from the discharge are accelerated by an electric field and bombard the surface of the part, continuously cleaning it before and during deposition. The coating material is then evaporated into the gaseous discharge, where it is ionized. The coating-material ions in the glow discharge region, which surrounds the part, are accelerated to all surfaces of the part across the cathode (Crookes) dark space (between the glow discharge region and the part). Because the dark space has across it most of the field gradient (voltage drop) of the discharge, the ions deposit on the surfaces of the part with high energy, typically forming a very adherent coating.

Thus two competing phenomena are simultaneously occurring at the surface of the part: one, the deposition of the coating-material ions; the other, the sputtering of the deposit by the argon and coating-material ions. The effective rate of deposition is determined by the relative rates of these two phenomena, and the material deposition rate must exceed the sputtering rate to obtain a deposit. The cleaning action of the sputtering by the ions is important in establishing the adhesion of the structure of the deposit.

The foregoing process characteristics give ion plating the following key advantages:

A. Exposure of the part to be coated to reactive gases or liquids is avoided. For example, hydrogen embrittlement is not encountered.

B. The part to be coated can be maintained at room temperature, or can be heated or cooled. Temperature-sensitive materials, such as aged or hardened alloys, salts, rubbers and plastics, can be coated.

C. Excellent adherence is usually obtained even between combinations of materials that normally do not form adherent interfaces. The careful cleaning, pretreatment, and handling steps often required for other coating methods are usually not necessary for ion plating.

D. Because the coating-material ions are created throughout the glow discharge surrounding the part, the method has very good throwing power, and quite uniform coatings can be deposited by ion plating without rotating the part. Build-up at corners of parts also is not encountered in this process.

The first two advantages are typical of all vacuum deposition processes to some extent. The latter two advantages, unique to ion plating, point the way to important future applications of this technique. Disadvantages are that masking to block coating of certain areas of some parts is difficult in ion plating because of its great throwing power, and that direct deposit-thickness monitoring during deposition has not been developed. Major obstacles to increased applications of the process, however, have been the lack of development of processing parameters and their interrelationships and of practical source-evaporation systems for ion plating a wider variety of materials.

The ion plating process was first reported in Mattox, D. M., Film Deposition Using Accelerated Ions, Report No. SC-DR281-63, Sandia Corporation, Nov. 1963. It

is the subject of Mattox's U.S. Pat. No. 3,329,601, issued July 4, 1967. Investigations of the process were concerned with gold, aluminum, and chromium coatings applied to both metal and ceramic parts as reported in Mattox, D. M., Ion Plating, Report No. SC-R-68-1865, Sandia Corporation, November, 1968. To obtain coatings on ceramics to which a negative potential cannot be directly applied, a screen wire cage arrangement having a negative voltage is used around the parts to accelerate the ions to the parts to be coated. One of the principal early applications was the coating of a uranium reactor core with aluminum for corrosion protection.

An interesting application of ion plating for coating high-strength steel, titanium, and aluminum alloy fasteners with pure aluminum alloy fasteners with pure aluminum for corrosion protection in marine environments is described in McCrary, L. E., Carpenter, J. F., and Klein, A. A., Specialized Application of Vapor-Deposited Films, Transactions of the International Vacuum Metallurgy Conference - 1968, American Vacuum Society, New York, N. Y., 1968. This work included demonstration of the deposition of uniform and adherent film on screw threads, without any build-up at the thread crown. Spalvins, et al, have reported some useful descriptions of ion-plated coatings on complex shapes and of ion-plated coatings of several alloys deposited using flash evaporation in Spalvins, T., Przybyszewski, J. S., and Buckley, D. W., Deposition of Thin Films by Ion Plating on Surfaces Having Various Configurations, Report No. NASA-TN-D-3707, July 26, 1966; and in Spalvins, T., Deposition of Alloy Films on Complex Surfaces by Ion Plating With Flash Evaporation, Report No. N70-32006, June, 1970. Gold coatings 1300 to 1500 Angstroms thick were deposited on components of a ball bearing and several other complex shapes. Strong bonding of the coatings to the substrates and excellent uniformity were obtained. The alloy coatings which were ion plated using flash evaporation to vaporize the materials into the glow discharge were lead-tin and copper-gold compositions. The original compositions of the alloys were closely maintained in the deposit using this technique and very good adherence and uniformity were achieved. In these and other references on the process, it is noted, however, that the range of materials that have been ion plated is rather limited and relatively little information is reported on the relationship of the processing variables involved in ion plating.

The present invention overcomes most of the disadvantages mentioned above. It also provides higher coating rates, and coatings of materials having higher melting points, various alloys, ceramics, glasses, quartz, alumina, beryllia, and other materials not satisfactory deposited heretofore by ion plating.

SUMMARY OF THE INVENTION

Typical apparatus according to the present invention for providing a tightly adherent coating on a substrate comprises a first chanber, means for providing an ionizable gas to the first chamber, a cathode comprising the substrate in the first chamber, a second chamber adjacent to the first chamber, a wall between the first chamber and the second chamber, an anode comprising a supply of the coating material, an exposed surface portion of the material being in the first chamber and spaced from the cathode, a source of electrons in the

second chamber, means for directing electrons from the source in a beam through an opening in the wall and on to the exposed surface portion of the anode, means for substantially evacuating the second chamber, and means for providing the cathode with a negative electric potential relative to the anode.

The electron directing means typically comprises an electron beam gun that directs the electron beam initially in a direction approximately parallel to the wall and away from the exposed anode surface portion, bends the beam through approximately one right angle to pass through the opening, and then bends it through approximately two more right angles to strike the exposed anode surface portion in a direction approximately perpendicular to the wall and to the exposed anode surface portion, which typically is approximately planar and generally parallel to the wall. The apparatus typically comprises also deflection means for causing the electron beam to scan a substantial area of the exposed anode surface portion in a predetermined manner. The substrate preferably is positioned substantially opposite the exposed anode surface portion.

The pressure in the second chamber preferably is maintained at less than about 10^{-3} torr during operation of the electron gun, and the second chamber is fluid-tight except at the opening in the wall, the opening being only substantially equal to the cross section of the beam of electrons passing through it.

The apparatus typically includes means for maintaining the exposed anode surface portion at a predetermined location as material is evaporated therefrom during coating of the substrate. The substrate typically is supported by a portion of the housing of the first chamber, the support including an insulative connecting member and a conductive barrier substantially surrounding the insulative member to prevent any substantial deposition of coating material on the insulative member.

The gas provided to the first chamber may be nitrogen or an inert gas. A preferred gas is argon, and the pressure in the first chamber typically is maintained at about 5 to 50 microns of mercury during coating of the substrate. The negative electric potential provided at the cathode typically is about 1 to 5 kilovolts.

The substrate typically comprises copper, steel, a refractory metal, nickel or an alloy thereof, cobalt or an alloy thereof, alumina, beryllia, or glass; and the coating material typically comprises gold, copper, nickel, aluminum, stainless steel; an alloy of iron, cobalt, or nickel with chromium and aluminum, such an alloy containing also yttrium; glass, or quartz.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially schematic vertical sectional view of typical apparatus according to the present invention.

FIG. 2 is a graph of coating deposition rate against gas discharge pressure for ion plating of a flat plate using apparatus as in FIG. 1.

FIG. 3 is a similar graph for ion plating of a solid cylinder.

FIG. 4 is a similar graph for ion plating of a hollow cylinder.

DESCRIPTION OF A PREFERRED EMBODIMENT

Referring to FIG. 1, typical apparatus 10 according to the present invention for providing a tightly adherent coating 20 on a substrate 30 comprises a first chamber 11, a second chamber 12 adjacent thereto, and a wall 13 between the first chamber 11 and the second chamber 12. Means such as a supply of argon 14 and a variable opening valve 15 provide an ionizable gas to the first chamber 11. A cathode 16 comprising the substrate 30 is located in the first chamber 11, as shown.

An anode 17 comprises a supply such as a rod 18 of the coating material, an exposed surface portion 19 of the material being in the first chamber 11 and spaced from the cathode 30.

A source of electrons 21 is provided in the second chamber 12, with means 22 for directing electrons from the source 21 in a beam 23 through an opening 24 in the wall 13 and on to the exposed surface portion 19 of the anode 17. The electron directing means typically comprises an electron beam gun 22 that directs the electron beam 23 initially in a direction approximately parallel to the wall 13 and away from the exposed anode surface portion 19, bends the beam smoothly through approximately one right angle to pass through the opening 24, and then bends it smoothly through approximately two more right angles to strike the exposed anode surface portion 19 in a direction approximately perpendicular to the wall 13 and to the exposed anode surface portion 19, which is approximately planar and generally parallel to the wall 13. The substrate 30 preferably is positioned substantially opposite the exposed anode surface portion 19.

Means such as a vacuum pumping system 25 is provided for substantially evacuating the second chamber 12, the pressure in the second chamber 12 preferably being maintained at less than about 10^{-3} torr during operation of the electron beam gun 22. This pressure can be monitored by a vacuum gage 27. The second chamber 12 is fluid-tight except at the opening 24 in the wall 13, and the opening 24 is only substantially equal to the cross section of the beam of electrons 23 passing through it. A high voltage supply 26 provides the cathode 16 with a negative electric potential of about 1 to 5 kilovolts relative to the anode 17, which is grounded, as indicated at 36, through the housing of the apparatus 10.

A power supply and control 28 for the electron beam gun 22 includes voltages for deflection coils in the gun 22 for causing the electron beam 23 to scan a substantial area of the exposed anode surface portion 19 in a predetermined manner. Feed drive means 29 are provided for maintaining the exposed anode surface portion 19 of the rod 18 at a predetermined location as material is evaporated therefrom as the coating 20 is deposited on the substrate 30. The substrate 30 is supported by the roof portion 31 of the housing of the first chamber 11, as by an adjustable support 32 including an insulative connecting member 33 and a conductive barrier comprising a pair of spaced cup-like members 34 substantially surrounding the insulative member 33 to prevent any substantial deposition of coating material on the insulative member 33.

The gas provided to the first chamber may be nitrogen; an inert gas such as helium, neon, argon, or krypton; or other suitable vapor. A preferred gas is argon, and the pressure in the first chamber 11 is maintained at about 5 to 50 microns of mercury during coating of the substrate 30 by the variable opening valve 15 from the argon supply 14. This pressure can be monitored by a vacuum gage 35.

The substrate **30** typically comprises copper, steel, a refractory metal, nickel or an alloy thereof, cobalt or an alloy thereof, alumina (Al_2O_3), beryllia (BeO), or glass, and the coating material **20** typically comprises gold, copper, nickel, aluminum, stainless steel; an alloy of iron, cobalt, or nickel with chromium and aluminum (FeCrAl, CoCrAl, or NiCrAl), such an alloy containing also yttrium (FeCrAlY, CoCrAlY, or NiCrAlY); glass, or quartz. These substrate and coating materials have been used with excellent results. Many other materials can also be used very satisfactorily.

EXAMPLES

To characterize and evaluate process conditions and parameters, we used equipment **10** as shown in FIG. **1.**

The electron-beam gun **22** was a rod-fed, **10** kw, single position, 270° beam source (Airco Temescal Model RIH-270). This gun utilizes X and Y water-cooled deflection coils with flush magnetic poles, a 270° deflected beam for increased filament life, a water-cooled copper hearth, and rod feeding (as indicated at **18, 37, 29**) to the source. It employs a six-turn, 0.030-in.-diameter, tungsten filament and produces an arrow head spot (generally triangular) 3/16 to ¼ in. long, depending on the filament-to-beam-former spacing and on the size of the orifice **24** in the wall or conductance baffle **13** where the beam **23** enters the glow discharge region **38** in the first chamber **11.** For process coating applications, the rod-fed type of mechanism **37** was chosen to feed the electron beam evaporating source rod **18.** The rod feeder **37** is mechanically driven by the feed drive **29** and contains the source material **18** (for the coating **20**) which is nominally 1 in. diameter and 10 in. long. This method provides a large inventory of evaporant for continuous operation and provides precise control of the height of the melting pool **19.**

The power supply **28** was a constant voltage, 30-kw unit. The power output provides dc voltage at a constant 10 kv at a total maximum electron beam current of 3 amp. Using this supply, one 30 kw or three 10 kw guns may be operated independently of each other, in the same or in different vacuum chambers **12.** In many process coating applications, more than one source is desired.

To operate an electron beam source in this type of application, the electron emitting source **22** must be isolated from the high pressure discharge region **11** of the system. In the development study, a conductance baffle **13** was used. After the baffle **13** was assembled into position the system was evacuated and the electron beam **23** turned on. As the electron beam current was increased, the electrons "burned" an orifice **24** into the baffle, which resulted in an orifice the same diameter as the electron beam at the highest beam current that could be used for this type of gun. Once this orifice **24** was made, a vacuum-discharge pressure range could be maintained and controlled in the system from 8.5×10^{-5} torr to 1×10^{-3} torr on the electron beam gun side **12,** and from 5 to 35 microns of mercury ($5-35\times10^{-3}$ torr) on the discharge side **11.** An ion gage **27** was used to measure the vacuum, and a Pirani gage **35** was used to measure the discharge pressure. In this range of operational pressures the electron beam gun **22** operated well in excess of 50 hours without any effect on the tungsten filament.

In the initial experiments, the two regions of the system were evacuated below 1×10^{-6} torr and the discharge region backfilled with argon to 30 microns. The electron beam source region of the system was maintained at 8.9×10^{-4} torr. The substrates were cleaned at 2000 volts and 0.5 ma for 15 minutes. The discharge pressure was then decreased to the desired coating pressure. The electron beam source was initiated and the desired power level obtained. At this time, the electron beam power and the discharge pressure were held constant and the shutter **39** was opened to commence ion plating; these conditions were then held constant during the period of deposition. (The open position of the shutter is shown shown at **39.** Dashed lines indicate its closed position at **39'**).

To achieve a coating with the desired characteristics, five parameters require control: glow discharge pressure; evaporant flux (electron beam power); substrate voltage and current; source-to-substrate distance; and substrate geometry. The glow discharge pressure and the evaporant flux are the foremost parameters to be considered for the ion plating process. They affect both the ion deposition efficiency and the uniformity of the coating. The discharge pressure was invetigated from 1 to 30 microns under various conditions. The evaporant flux was measured in terms of the electron beam power applied to the vapor source and was investigated from 1 to 10 kw.

To study the effects of substrate geometry, a flat rectangular plate 0.045 in. thick × 0.7 in. × 2 in., a solid cylinder 0.75 in. in diameter × 1 in. long, and a hollow cylinder 0.69 in. I.D. × 0.75 in. O.D. × 0.65 in. long, were chosen because these basic configurations are usually found in most coating applications. Each has a surface area 3 square inches.

The substrate-to-source distance was held constant at 6.5 inches normal to the source. The substrate voltage generally was 2000 volts dc; but was varied from 800 to 2000 volts in some experiments as shown in the appropriate data. The substrate current density depended on the glow discharge pressure that was used in each experiment and was in the range of from 0.4 to 0.6 ma/cm².

TABLE.—UNIFORMITY OF COATINGS DEPOSITED BY ION PLATING AS A FUNCTION OF DISCHARGE PRESSURE, EVAPORANT FLUX, AND PART GEOMETRY

Argon discharge pressure, microns	EB power to source (evaporant), kw.	Thickness of coating deposited, mils (10^{-3} in.)							
		Plate substrate geometry		Tube substrate geometry				Substrate rod geometry	
		Bottom*	Top	Bottom	Top	Inside bottom	Inside top	Bottom	Top
5	7.2	0.08	0	0.08	0	0	0	0.08	0
10	4.2	0.25	0.15	0.25	0.12	0.09	0.09	0.25	0.15
10	4.5	0.40	0.20	0.32	0.16	0.09	0.09	0.32	0.15
10	6.5							0.72	0.27
10	7.2	0.88	0.35	0.80	0.40	0.16	0.16	0.77	0.32
25	7.8	0.25	0.25	0.25	0.25	0.17	0.17	0.50	0.25

*Bottom is in direct line-of-sight of source.

NOTE.—Coating time was 10 min.

Gold was used as the reference evaporant material because it is quite sensitive to process changes. Other materials investigated were aluminum, quartz, type 304 stainless steel, and FeCrAlY alloy.

How variations in processing parameters affect uniformity of coating is shown in the table above and in FIGS. **2, 3,** and **4.** FIG. **2** shows processing parameters for the flat plate obtained with 7.2 kw electron beam source power, 2000 volts on the substrate 6.5 inches from the source. In FIG. **3** the same type of curves were obtained for the solid cylinder under the same conditions. But pressure over 30 microns would be needed if uniform coating were to be achieved at the particular additions. FIG. **4** shows similar curves for the hollow cylinder under the same conditions, uniform coating was achieved at about 30 microns. Where uniformity is not ciritical, higher deposition rates can be used. In general, uniformity increases as discharge pressure increases and decreases as coating rate increases. For example, with a discharge pressure of 10 microns, coating thickness on the back of the flat plate was **40** percent of that on the front with 7 kw of electron-beam power providing a coating rate of 5.2 mils per hour. At 25 microns (and 7 kw), the rate was 1.5 mils per hour, and uniformity was 100 percent.

The typical structure of gold deposited on copper shows a clean interface that gives strong adherence that withstands a typical tape test. Micrographs show excellent coating uniformity around corners, with no build-up at corners, in contrast with coatings from other processes. The microstructure of stainless steel on copper shows a clean interface and a high-density deposit. Excellent adhesion was obtained with deposition at 12 mils per hour at 20 microns and substrate at 2000 volts. Micrographs show also that a FeCrAlY alloy adheres well on a TD nickel substrate. Deposition at 4.5 mils per hour at 20 microns produces a fine grain structure, even finer structures can be obtained at different rates or by heating substrate. Other examples of ion plated parts include turbine blades with 3 to 15 mils of FeCrAlY alloy, copper hemispheres with 1 mil 304 stainless steel, titanium honeycombs with ½ to 1 of gold and aluminum, and *rf* conduits and pulleys with 1 mil of stainless steel. Insulators ion plated in a wire cage include porcelain, Al_2O_3, and BeO, all coated with stainless steel. The cage forms an electric field around the insulators during deposition to accelerate coating ions to the surface of each part. Glow discharge cleaning before the ion plating yields excellent coating adherence.

In these and various other examples of coating applications for coating parts as an industrial type of process we characterized the ion plating process for stainless steel(Type **304**), FeCrAlY alloy, aluminum, glass, and quartz coatings. The characterization curves in the figures shown for gold are typical for these materials. The amplitudes and crossover points vary slightly for each material, but the coating results are of the same order of magnitude.

X-ray fluorescence analysis of the coatings and the stainless steel source material gave 17.6 weight percent coating of Cr from 20 weight percent source, 7.5 versus 8.5 for Ni, 0.44 versus 0.75 for Mn, 0.03 versus 0.62 for Si and 0.005 versus 0.04 for P. For the FeCrAlY alloy, the comparable figures were 24.5 versus 27.6 for Cr, 4.8 versus 6.8 for Al, and 0.58 versus 1.95 for Y.

The curves in FIGS. **2, 3,** and **4** are for specific materials, shapes, voltages, etc. Gas discharge pressures ranging from about 0.5 to 100 microns have also been shown to be useful in various applications.

Further details, including pictures and micrographs are included in the article "Electron Beam Techniques for Ion Plating" by D. L. Chambers and D. C. Carmichael, Columbus Laboratories, Battelle Memorial Institute, in Research/Development, May, 1971, Volume 22, Number 5, pages 32–35.

While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is to be understood that the terms used herein are merely descriptive rather than limiting, and that various changes may be made without departing from the spirit or scope of the invention.

We claim:

1. Apparatus for providing a tightly adherent coating on a substrate comprising

a first chamber,

means for providing an ionizable gas to the first chamber,

a cathode comprising the substrate in the first chamber,

a second chamber adjacent to the first chamber,

a wall between the first chamber and the second chamber,

an anode comprising a supply of the coating material, an exposed surface portion of the material being in the first chamber and spaced from the cathode,

a source of electrons in the second chamber,

means for directing electrons from the source in a beam through an opening in the wall and on to the exposed surface portion of the anode,

said second chamber being fluid-tight except at the opening in the wall, said opening closely conforming to the cross section of the beam of electrons passing through it.

means for substantially evacuating the second chamber, and

means for providing the cathode with a negative electric potential relative to the anode.

2. Apparatus as in claim **1,** wherein the electron directing means comprises an electron beam gun.

3. Apparatus as in claim **2,** wherein the gun directs the electron beam initially in a direction approximately parallel to the wall and away from the exposed anode surface portion, bends the beam through approximately one right angle to pass through the opening, and then bends it through approximately two more right angles to strike the exposed anode surface portion in a direction approximately perpendicular to the wall.

4. Apparatus as in claim **3,** wherein the exposed anode surface portion is approximately planar and generally parallel to the wall.

5. Apparatus as in claim **4,** comprising also deflection means for causing the electron beam to scan a substantial area of the exposed anode surface portion in a predetermined manner.

6. Apparatus as in claim **4,** wherein the substrate is positioned substantially opposite the exposed anode surface portion.

7. Apparatus as in claim **2,** wherein the pressure in the second chamber is maintained at less than about 10^{-3} torr during operation of the electron gun.

8. Apparatus as in claim **4,** comprising also means for maintaining the exposed anode surface portion at a

predetermined location as material is evaporated therefrom during coating of the substrate.

9. Apparatus as in claim 1, wherein the substrate is supported by a portion of the housing of the first chamber, the support including an insulative connecting member and a conductive barrier substantially surrounding the insulative member to prevent any substantial deposition of coating material on the insulative member.

10. Apparatus as in claim 1, wherein the gas provided to the first chamber is nitrogen or an inert gas.

11. Apparatus as in claim 1, wherein the gas provided to the first chamber is argon.

12. Apparatus as in claim 1, wherein including means to maintain the pressure in the first chamber at about 5 to 50 microns of mercury during coating of the substrate.

13. Apparatus as in claim 1, wherein the negative electric potential provided at the cathode is about 1 to 5 kilovolts.

* * * * *