United States Patent

[11] 3,632,406

[72] Inventors **Philip J. Clough**
Cape Elizabeth, Maine;
Steve Eisner, Schenectady, N.Y.

[21] Appl. No. **4,340**
[22] Filed **Jan. 20, 1970**
[45] Patented **Jan. 4, 1972**

[73] Assignee **Norton Company**
Worcester, Mass.

[54] **LOW-TEMPERATURE VAPOR DEPOSITS OF THICK FILM COATINGS**
8 Claims, 12 Drawing Figs.

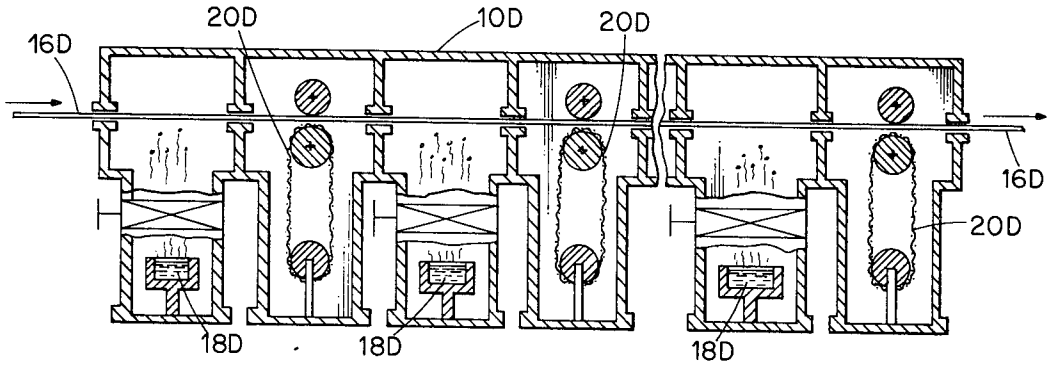
[52] **U.S. Cl.** **117/107.1,** 117/10, 117/49, 117/50, 264/81

[51] **Int. Cl.** **C23c 13/00,** C23c 13/02, C23c 13/04

[50] **Field of Search** 117/107.1, 49, 50, 10; 264/81

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—Kenneth P. Glynn
Attorneys—Hugh E. Smith, Herbert Gatewood, Oliver W. Hayes and Jerry Cohen

ABSTRACT: The application of metal coatings through vapor deposition is improved by activating the coating with an abrasivelike action during the deposition process. The resultant coatings have increased smoothness, ductility and high-density (low-porosity).



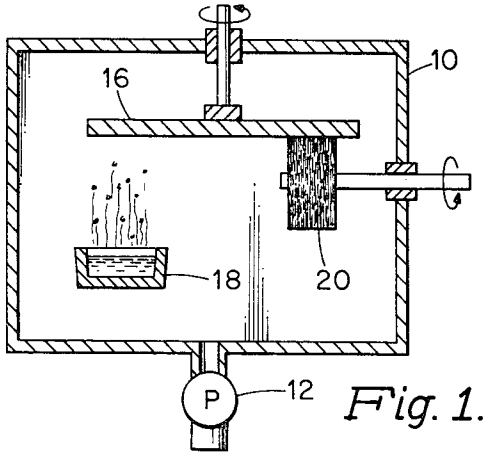


Fig. 1.

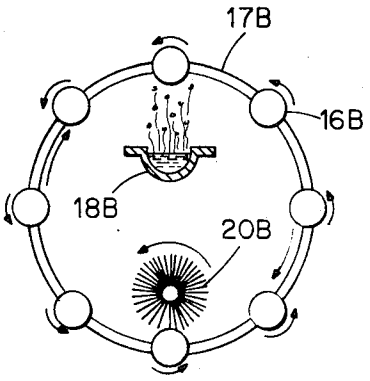


Fig. 1B.

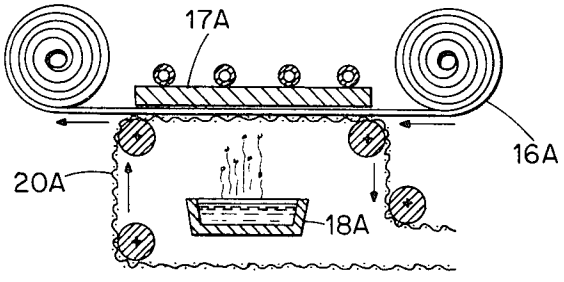


Fig. 1A.

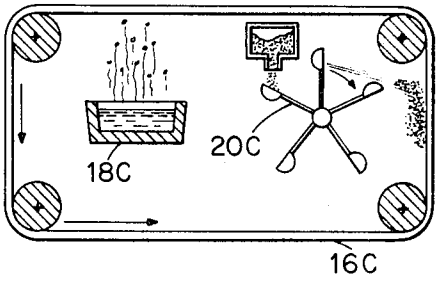


Fig. 1C.

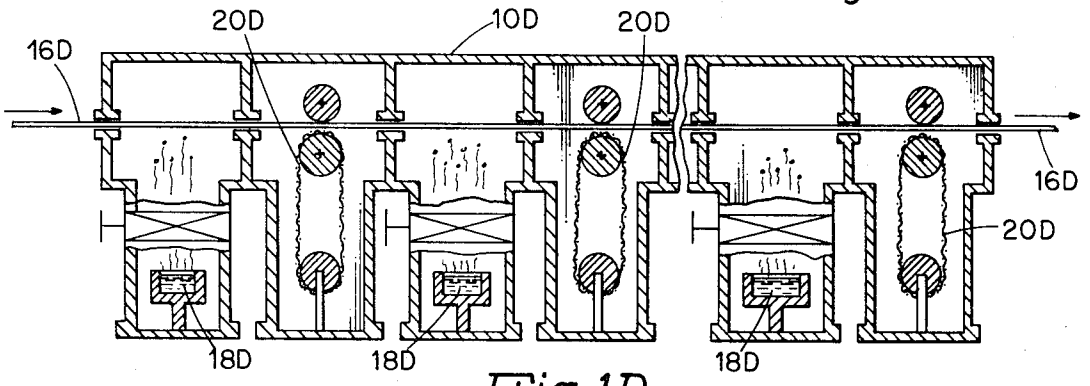


Fig. 1D.

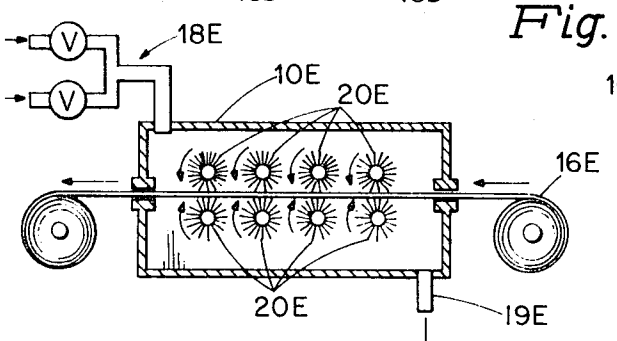


Fig. 1E.

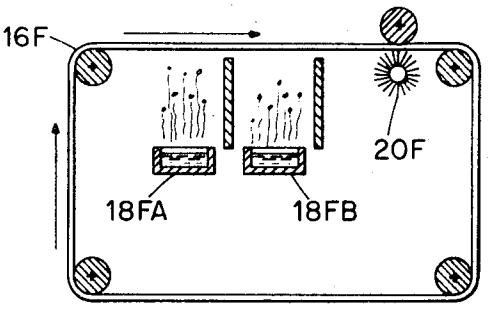


Fig. 1F.



Fig. 2B.

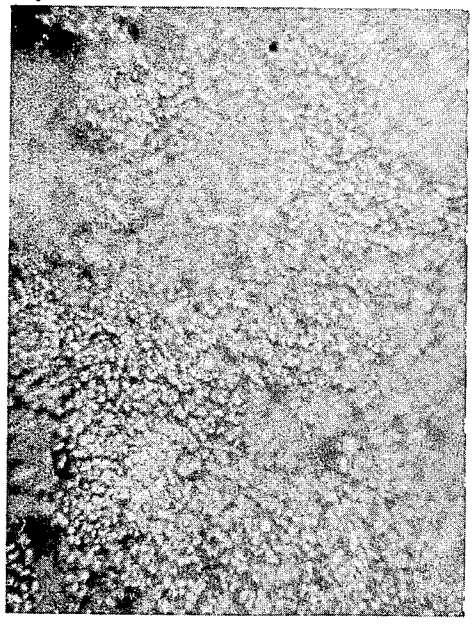


Fig. 2A.

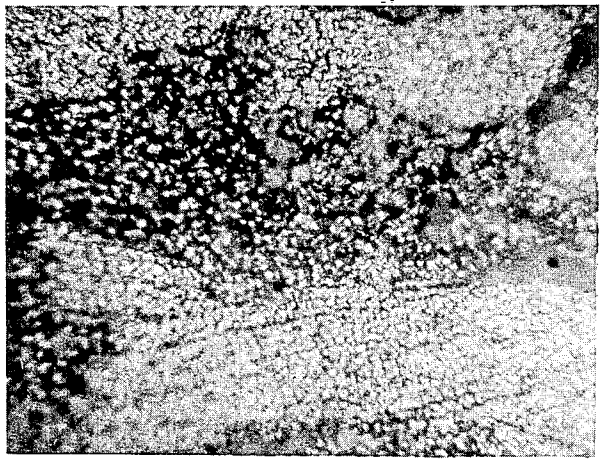


Fig. 2C.



Fig. 2D.

Fig. 3.



LOW-TEMPERATURE VAPOR DEPOSITS OF THICK FILM COATINGS

RELATED APPLICATIONS

Eisner, Ser. No. 718,468, filed Apr. 3, 1968 (now abandoned) and Ser. No. 863,499, filed Oct. 3, 1969, (of common assignment herewith).

OBJECTS

It is the principal object of the invention to provide an improved process of vapor deposition coating.

It is a further object of the invention to provide a new method of vapor deposition making possible the use of vapor deposition, particularly the vacuum evaporation technique of physical vapor deposition, in systems not heretofore deemed suitable (e.g., coating of brass substrates without the prior art drawback of zinc distillation or coating plasticized plastic webs).

Vapor deposition has utility in providing functional and decorative coatings including usage in making mirrors; printed circuit patterns and other electronic devices; conductive and insulating coatings; corrosion-erosion- and oxidation-resistant protection; metallurgical refining and crystal growing. The utility of known vapor deposition processes is more fully indicated in the above references.

It is a further object of the invention to provide a process improvement in chemical and physical vapor deposition processes reducing the temperatures involved in physical and chemical vapor deposition.

It is a further object of the invention to improve the physical properties of vapor deposited coatings.

It is a further object of the invention to provide apparatus for effectively utilizing the foregoing processes in commercial operations.

GENERAL DESCRIPTION

The purposes of the invention are accomplished by carrying out a vapor deposition process, which involves vaporizing a substance to be deposited and moving the vapors to a substrate to be coated and condensing the vapors on the substrate, over a period of time to coat the substrate, and contacting the coated surface of the substrate throughout a major portion of the period of coating with the application of abrasivelike action to deposited nascent sublayers of the coating immediately after deposition of the sublayers and before new sublayers are deposited over them. It has been discovered that the resultant coatings have improved smoothness and ductility and/or tolerate a wider range of processing conditions to achieve these properties, compared to coatings produced through conventional vapor deposition.

Such improvements in properties are desired, per se, and can also lead to improvement in adhesion or decrease the need for, or eliminate in some cases, other treatments normally applied to improve coating adhesion.

The substrate may be a continuous web of metal or plastic or a discrete or batch part of irregular contour such as a metal casting, or plastic molding. Substrate temperature, surface preparation and composition specifications may be lowered in the present invention. For instance vacuum deposition of metal on metal often requires heating the metal substrate and in some cases this may anneal out desired work hardening properties of the substrate or distill out a volatile component of a metal alloy (e.g., zinc from brass). The present invention allows coating at reduced heat inputs to the substrate—in some cases little or no heat input (other than heat transferred by vapor arrival and source radiation and by abrasive action, all of which together are substantially below conventional substrate heat inputs and can be more locally concentrated at the substrate surface with less disturbance to substrate properties). Another degree of freedom introduced by the invention is greater tolerance of substrate outgassing (e.g., plasticizers or water vapor from plastic films) consistent with adequate adhesion of coating to substrate.

The coating vapor may be in elemental or compound form, metal or nonmetal. It may be a sole species in a vacuum background or combined with an inert gas carrier or in chemical combination with a gaseous carrier. The abrasive action is applied to the nascent coating sublayers. The term "nascent" means that the deposited sublayer of material is contacted with the application of abrasive action before it has lost its mobility. The term "sublayer" reflects a theoretical division of a single coating into sublayers which are each contacted with abrasive action to insure that the effects of abrasive action are imparted throughout the gross coating thickness. The actual abrasive action is applied to significantly thin sections (sublayers) of the coating while in a nascent state. The sublayers may be applied at intervals of time or in rapid simultaneous sequence with uninterrupted growth of the coating to full thickness.

The "abrasivelike action" may be applied through any of the conventional techniques of abrasion including grinding, polishing, lapping, honing, brushing and blasting, but it is controlled so that it imparts energy to the "sublayer" of coating at the coating surface without substantial removal of coating material (preferably none, but in any event no more than the amount deposited) but with sufficient energy and dynamic hardness to form embedded strain lines in the coating. These are strain lines that become visible on microscopic examination as the coating is etched to varying depths. In most cases low-power magnification reveals the strain lines. But in some instances magnification to high power (10,000 ×) may be necessary.

The energy imparted to the sublayer material increases mobility of the deposited molecules of the sublayer and increases the free energy of nearby coalescence sites and this increased mobility and free energy, together with mechanical deformation provided by the abrasive action, reorients the crystallographic growth pattern of the coating.

It is preferred and distinctly advantageous, that the abrasive action be applied in a manner to impart shear force to the coating. This is done to achieve a limited physical deformation of the coating and to provide maximum contact time for individual abrasive particles to contact the then exposed surface of the coating sublayer.

The incidence of application of abrasivelike action (hereinafter sometimes referred to as "abrasion steps") to sublayers will typically range on the order of hundreds of sublayers but may hypothetically range to two sublayers abraded. In the interest of definiteness of expression, the limit of sublayers treated within the scope of the invention is stated to be at least 10 adjacent sublayers abraded.

There are two basic approaches to the introduction of abrasive action into the coating process.

First, there can be an alternation of (sublayer) coating steps with abrasion steps. That is, a sublayer is deposited. Then, the coated surface is abraded, then another sublayer is deposited and it is abraded, continuing until the total thickness of sublayers equals the desired coating thickness. This would involve apparatus having a vapor source, substrate, substrate coating station, substrate abrasion station and means for moving the substrate back and forth between stations in repetitive alternation. The alternation should be in regular cyclic fashion and the coating vapor supply should be at constant rate to make the sublayers of equal thickness. The movement can be reciprocating, rotational or of any other kind. The movement is relative; coating and abrasion stations may be moved to and from the same substrate point, rather than vice versa.

The second approach is to have the deposition and abrasion steps occur simultaneously on a macroscopic scale. This can be accomplished by running a porous abrasive-carrying medium over the substrate while depositing vapor deposition involving straight line motion, the porous medium should have clear-through openings so that vapors moving in straight line paths from source to substrate can pass through the carrier. On a microscopic scale, this second approach is the same in principle as the above first approach; i.e., there is an alternation of sublayer deposition and abrasion steps.

In both the "alternating" and "simultaneous" abrasion-deposition combinations, the process should be controlled so that the abrasion affects (i.e., is applied to all sublayers of) the coating throughout at least a continuous major portion of its thickness. The major portion is preferably the entire coating but may be a distinct portion such as a bottom portion to serve as an adhesion promoting prime coat for the balance of the coating, applied without abrasion; a reinforcing midportion; or a top portion having decorative or functional (e.g., erosion resistance, lower porosity) properties differing from those of the balance of the coating. Within such major portion of the coating the abrasive action is applied to a plurality of the sublayers and preferably to at least 10 sublayers which are adjacent to each other (not separated from each other by any sublayers not significantly affected by the abrasive action). The term "affected by" means that the abrasivelike action produces embedded strain lines in a sublayer affected by such action. The maximum thickness of sublayer deposited between abrasion steps should be limited to 1/10 of the total thickness of the coating portion composed of such sublayers and should be no greater than 1 micron (10,000 A.).

A further and distinctly advantageous aspect of the invention is that improved vapor deposition of alloys (including compounds) is realizable through the invention. The abrasion contributes to homogenization of the deposited material.

A particular approach to utilization of the abrasion assisted technique is to deposit components of the alloy as sublayers in sequence, then abrade the sublayers while in nascent state, then deposited additional sublayers, then abrade, and so forth in repetitive alternation, the end result being an alloy coating.

DRAWINGS

FIG. 1 is a schematic view of a vapor deposition apparatus of the vacuum evaporation type providing alternate sublayer deposition and abrasion in repetitive cyclic fashion throughout the coating process.

FIG. 1A is a schematic view of a portion of another vapor deposition and abrasion which is simultaneous on a macroscopic scale.

FIG. 1B shows a portion of a vapor deposition apparatus utilizing a rotary jig work holder for discrete-part substrates.

FIG. 1C shows a portion of a vapor deposition apparatus using blast type of abrasion.

FIG. 1D shows a continuous coating system using the invention.

FIG. 1E shows a chemical vapor deposition system.

FIG. 1F shows an alloy deposition system using the invention.

FIGS. 2A, 2B, 2C, 2D and 3 are copies of photomicrographs taken of coating specimens with and without the abrasion treatment of the present invention, as indicated in the discussion below.

SPECIFIC DESCRIPTION

Referring to FIG. 1 there is shown an apparatus for practice of the invention of a type used in the examples below. The apparatus comprises a vacuum chamber **10**, a high-vacuum pumping system **12**, a substrate **16** and a source **18** of coating vapors. A rotary steel brush **20** of the type normally mounted on a ¼-inch hand drill for cleaning rust off metal surfaces is mounted in the chamber. Driving shafts are provided for the substrate and the brush, preferably operating in counterrotation fashion. Drive motors for each of the substrate and brush may be mounted in the vacuum chamber or mounted outside the chamber with drive shafts passing through rotary vacuum seals in the chamber wall.

Referring to FIG. 1A there is shown a portion of a second embodiment of such apparatus. This embodiment is particularly suitable for coating continuous long lengths of flexible web substrate **16A**—e.g., metal foil, organic plastic film sheet, wire, etc.—which are usually in roll form and unrolled and rerolled in a coating process. A cooled plate **17A** is provided to back up the thin substrate. As an alternative, a cooled rotary drum could be used instead of the plate **17A**.

A source of vapors **18A** contains material to be evaporated. The material is evaporated and moves primarily in straight line paths (with molecular collision causing some zigzag motion) to the substrate where it is condensed. During this coating process an open fabric belt **20A**, (as described in U.S. Pat. No. 3,020,139 to Camp et al., or in the above-cited Related Applications), passes over the substrate. The openness of the belt allows passage of coating vapors. But the packing density of abrasive is sufficiently tight as described in the above-cited Related Applications to insure good coverage of the coating sublayer surface with abrasive action.

The belt may be fed from a supply and taken up for use on a one-shot basis or made in the form of a closed loop for reuse throughout a coating cycle.

Where the coating is vacuum coating the abrasive belt must provide clear-through openings to allow coating vapors moving in a straight line from the source to reach the substrate. Where the coating is done at a higher pressure the openings through the abrasive carrier may be tortuous paths.

FIG. 1B shows a portion of another coating apparatus involving use of a rotary jig **17B** supporting many small substrates **16B**, e.g. in the nature of plastic or metal castings or molded parts. A source of coating material is provided at **18B**. An abrasive flap wheel **20B** is applied to the coated surface of the parts between sublayer depositions. The upper half of the apparatus may be thought of as a coating station, the lower half as an abrasion station. The jig, rotating at constant speed, moves each piece from one station to the other in back-and-forth repetitive, cyclic fashion.

FIG. 1C shows a portion of another coating apparatus wherein a substrate **16C** is spliced into a closed loop form and rotated so that it repetitively passes a coating vapor source **18C** for coating of sublayers of a total coating. An abrasive blasting mechanism is provided at **20C**. However no gas carrier is used for the blasting media as in conventional sand blasting. Rather the abrasive particles should be accelerated by centrifugal force or momentum transfer through impact against rotating paddles or a propeller (not shown).

Instead of a closed loop, the substrate might be a long ribbon or wire passing in a spiral path around a troughlike evaporation source and elongated brush to provide multiple cycles of alternate deposition and abrasion.

FIG. 1D shows a continuous web coater apparatus **10D** of the type now in commercial use for vacuum coating aluminum or steel or glass sheets. The apparatus comprises alternating coating and deposition chambers, *x* and *y* respectively.

Other forms of apparatus which are obviously usable, per se in some instances or with modifications in other instances, in the practice of the presently disclosed process are indicated in U.S. Pat. No. 3,012,904.

Various forms of seals and maintenance accessories suitable for use in such continuous apparatus, allowing replacement of abrasive belts or sources without air-releasing the whole system and which could be used in the FIG. 1D species, are shown in U.S. Pats. No. 2,975,753 (Hayes), No. 2,989,026 (Gardner et al.), No. 2,983,249 (Gardner et al.), No. 3,040,702 (Eng et al.). See also U.S. Pat. No. 3,123,493 (Brick) showing a brush wheel precleaner and continuous vacuum metallizing line.

Continuous or semicontinuous vapor deposition lends itself to use in vapor forming—coating a metal on a substrate with a release coated surface and stripping the metal coating, as shown for instance, in U.S. Pat. No. 3,043,728 (Stauffer) and No. 3,183,563 (Smith). The thick coating involved in vapor forming or the like is especially benefitted by the improved coating provided in the present invention.

FIG. 1E shows another application of the invention. The apparatus shown is a chemical vapor deposition shown at **10E**. A substrate strip **16E** to be coated passes through the chamber, is heated (by passing an electric current through the strip or by an external heater). The coating vapor source comprises an inlet valve system **18E**. A vapor outlet **19E** is also provided. A series of brushes **20E** are spread along the substrate to abrade the coating as it builds up (the increments of coating thickness

built up between brushes being the "sublayers" defined herein).

FIG. 1F illustrates the distinctly advantageous application of the invention to alloy coating. A substrate belt **16F** passes over a source **18FA** of one element of a binary alloy and over a source **18FB** of the other element of the alloy and then runs past an abrasion station **20F** and does so in a repetitive alternation provided by recycling substrate **16F** as an endless belt or by running in a spiral path over elongated sources (see also the discussion of FIGS. 1A and 1C, above). Sublayers "A" and "B" of the alloy components are homogenized into the alloy "A–B" through the action of the abrasive means **20F**.

Preferably baffles are provided between the sources. But the alloy components can be codeposited with vapor crossover (no baffle) or even out of the same crucible. A baffle separating the abrader from the vapors is preferable in any event.

The energy provided through abrasive action allows correction of stoichiometry defects in the coating. The degree of correction desired or achieved will vary with the needs of a particular coating task.

The benefits of the invention are illustrated in part by the following nonlimiting illustration of its practice and various characteristics observed for it.

EXAMPLE 1

A vapor deposition apparatus, of the vacuum coating type, was set up as shown schematically in FIG. 1. The substrate **16** was a round disc of steel plate. The evaporant was molten aluminum contained in graphite crucible source **18** heated by an induction coil; it was evaporated at substantially constant rate. The source to substrate distance was one foot. The substrate was rotated during coating at 25 revolutions per minute. The brush was rotated at 100 revolutions per minute at no load, which speed was reduced to 80 by contact with the stationary substrate and then reduced to about 50 when substrate rotation was started counter to the direction of brush rotation. The coating was carried out in an ambient vacuum of about 10^{-3} torr pressure and for a period of 10 minutes. The substrate was not heated or cooled directly during the coating process. The resultant aluminum film was about 0.005 inch thick. This indicates a nominal sublayer thickness of 20 microinches per pass (rotation), corresponding to about 5,000 A. The coating had an observably different surface appearance and characteristics in the area corresponding to the brushing from the remainder. It was brighter in the brushed area, duller in the unbrushed area. It was cracked in the unbrushed area, uncracked in the brushed area. The coating as a whole had poor adhesion and was separated from the substrate. The unbrushed section cracked when bending was attempted. The brushed section was sufficiently ductible to bend into a U-form with a radius of bend of less than 0.005 inch and the legs of the "U" touching at their ends without cracking the film.

EXAMPLE 2

The procedure of example 1 was repeated with similar results using a glass disk substrate.

EXAMPLE 3

Pieces of aluminum film from example 2 (both from brushed and unbrushed areas) were analyzed by optical microscopy and transmission electron microscopy. The results are illustrated in FIGS. 2A, 2B, 2C, 2D, and FIG. 3.

FIG. 2A is a photograph of a cross section view of unbrushed film observed through an optical microscope at 1,550 × magnification after polishing and etching. FIG. 2B is a similar view of a brushed section. The brushed film has a more dense, void-free cross section than the unbrushed section which is noticeably porous.

FIG. 2C is a transmission electron photomicrograph of the unbrushed film (at 30,500 × magnification) and FIG. 2D is a micrograph of the brushed section (at 25,500×magnification). The grain size of the brushed section is about ¾ the grain size of the grain size of the unbrushed section. The grains in the brushed film are relatively dislocation-free compared to the unbrushed film.

FIG. 3 is a photograph of an optically magnified view (1,550×) of the film surface showing brushed and unbrushed areas. The unbrushed area surface has the globular knobly appearance characteristic of vacuum deposited metals. The brushed area has scratch texture in the direction of brushing and noticeably finer globular features. The globules show substantial alignment in the brushing direction (the line of relative movement between brush and film).

EXAMPLE 4

Aluminum film sections from example 2 were tested for tensile strength, ductility and hardness. The results were

Coating Region	Strength (p.s.i.)	Ductility (% Elongation)	Hardness (Knoop Scale No.)
Brushed	17,600	1.3	43
Unbrushed	6,000	0	40

EXAMPLE 5

A piece of the aluminum film from example 2 containing abraded (brushed) and unabraded areas was polished with a fine grit (400) sandpaper to remove the abrasion lines on its surface. The polishing direction was normal to the direction of the abrasion applied during coating. The sample was then etched by immersion for 4 minutes in a bath made by mixing 10 grams sodium hydroxide in 90 milliliters of water. A line scratch pattern reappeared on the surface of the abraded area. It was also noted that pores developed in the unabraded area, but not in the abraded area of the film. Etching for 2 more minutes increased this trend with the unabraded area developing a spongelike appearance.

The results of example 5 indicate the utilization of the process of the present invention in producing coatings which are more resistant to chemical attack than conventional vapor deposited coatings.

While the mechanism inherent in abrasion during coating which afford the useful improvements described above are not completely understood, the following phenomena appear to be of greatest importance.

Abrasion serves as a source of energy to encourage a greater number of nucleation sites. In this respect the effect is similar to known effects of heating the substrate during coating. The resultant finer grain structure is less likely to result in a porous coating of impaired strength and ductility. The energy input also reduces the likelihood of poisoning of certain growth directions (anisotropy) and thus limits lattice dislocations.

On a gross effects level, the abrasion involves to a certain extent small hard particles pushing against the coating which will tend to back into open spaces or voids. It is believed, however, that local thermal and cleaning effects are more significant than the mechanical effects. Although the abrasion itself produces a depression (embedded strain line) the surface of this depression is one of locally superior free energy and a superior site for grain nucleation.

What is claimed is:

1. An improved method of vapor deposition comprising the steps of:
   a. producing a substance to be deposited in vapor form and moving the vapors to a substrate to be coated;
   b. condensing the vapors on the substrate over a period of time to coat the substrate;
   c. applying, throughout a major portion of the period of coating, an abrasivelike action to deposited nascent sublayers of the coating to impart energy to such sublayers to form embedded strain lines therein,

the abrasivelike action being imparted to each of several sublayers immediately after deposition of the said sublayers and before new sublayers are deposited over them, the coating

portion so treated including at least 10 adjacent sublayers, each having a thickness of no greater than 1 micron.

2. The method of claim 1 wherein the steps of condensing and abrasivelike action are carried out in repetitive alternation during the same gross coating process.

3. The method of claim 1 wherein the steps of condensing and abrasivelike action are carried out simultaneously on a macroscopic scale.

4. The method of claim 1 wherein the steps of the process are carried out in an ambient vacuum zone and gas is removed from the zone during coating and with the deposition of coating being essentially a straight line flow from source to substrate.

5. The process of claim 1 wherein the substrate comprises a plurality of discrete parts.

6. The process of claim 1 wherein the substrate comprises a continuous web in the form of a film, foil, sheet, wire or the like.

7. The process of claim 1 wherein the coating is stripped from its substrate after coating.

8. The process of claim 1 wherein an alloy coating composition is deposited and homogenized through said abrasivelike action.

* * * * *