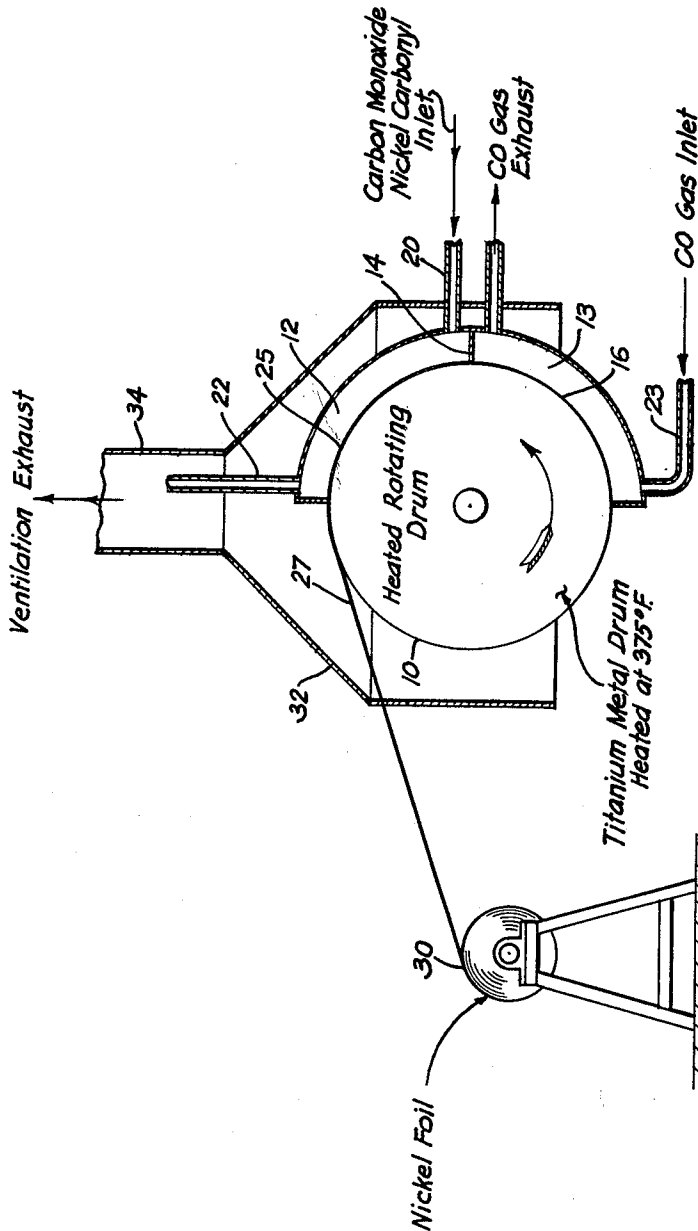


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METHOD AND APPARATUS FOR OBTAINING RELEASE OF GAS PLATED
METAL DEPOSITS FROM SUBSTRATE SURFACES
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METHOD AND APPARATUS FOR OBTAINING RELEASE OF GAS PLATED METAL DEPOSITS FROM SUBSTRATE SURFACES

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1 Claim. (Cl. 22—57.3)

This invention relates to a method and apparatus for the production of strippable gas plated deposits. The invention is more particularly concerned with gas plating, and subsequent stripping of the deposit from the substrate surface to provide a self-supporting film, strip, sheet or the like of such deposits.

The invention provides a method for obtaining easy release of deposits of metals, metal carbides, metal oxides, and the like metallic and non-metallic deposits from substrates, when such deposits are formed by thermal decomposition of gaseous compounds of the same. The dry plating method, as employed to produce such deposits, is referred to as "gas plating."

In accordance with my invention, it has been unexpectedly discovered that by initially treating the substrate to be gas plated with a gas which is adsorbed on the surface of the substrate, the resultant gas plated deposit of metallic or non-metallic substance is readily stripped away from the substrate.

The terms "metal" and "metallic" gas plated deposits as hereinafter used are intended to include metal, as well as non-metallic deposits, e.g. oxides and carbides of metals, and exemplified in the examples.

It is known that air and the like gas is adsorbed on the surface of a substrate material, and attempts have been made heretofore to remove such adsorbed gases prior to gas plating deposits on the substrate. I have discovered, however, after considerable experimentation, that by selecting a particular gas or combination of adsorbable gaseous mixture and a substrate material which absorbs the gas, strippable gas plated deposits are produced. By such selection and control of the gas plating, the adsorbent gas is caused to be released substantially immediately subsequent to formation of the deposit. The release of the adsorbed gas must take place concurrently with or immediately after initial deposition of the deposit whereby a barrier is formed which prevents the deposit from tenaciously adhering to the substrate surface. As a result, the adhesion of the metal deposited is weakened sufficiently to permit the deposit to be readily stripped away from the surface of the substrate.

It is essential that the adsorbent gas or combination of gases be carefully chosen and that such gas or gaseous mixture used be only moderately adsorbed. Where the adsorbent gas is highly or strongly adsorbed its release takes place too copiously and causes the metal deposit to blister. Hydrocarbon vapors, e.g., ethylene, propylene and the like cannot be satisfactorily used full strength as adsorbent gases on a titanium substrate for this reason, since they are so highly adsorbed that a blistered metal deposit results.

The invention is particularly useful in the production of metal foil, strips and sheets of pure metal, e.g., copper, nickel, chromium, etc. Strippable non-metallic deposits such as the oxides, carbides and the like are also readily produced by my process.

One embodiment of the invention is illustrated in the accompanying drawing which depicts diagrammatically an apparatus for making nickel metal foil employing the gas plating stripping method of my invention.

Referring to the drawing in detail, a drum 10 which is heated by suitable means, e.g. steam, heating elements,

or the like, not shown, is disposed in airtight or hermetically sealed chambers 12 and 13, the chambers being formed by the dividing partition 14. The drum 10 is rotated in the direction indicated on the drawings. Suitable rotating means such as an electrical motor, not shown, may be used for this purpose. One half-portion of the drum surface, as indicated generally at 16, is exposed to an atmosphere containing the adsorbent gas which functions to lower the adhesion of the deposited metal whereby the same can be stripped or peeled away from the substrate surface.

In the apparatus illustrated, nickel foil is produced employing a thermally decomposable gaseous mixture of nickel carbonyl and carbon monoxide. The gas plating mixture is introduced into the chamber through an inlet conduit 20 and waste gases exhausted through an exit pipe 22. Carbon monoxide gas, which is used as the adsorbent metal-release gas is introduced into the chamber 13 through an inlet conduit 23.

The substrate surface of drum 10 is composed of titanium metal which adsorbs carbon monoxide to provide a metal release surface for receiving the gas plated nickel deposit, as indicated generally at 25. As the drum 10 rotates, the deposited metal is continuously gas plated onto the moving surface of the drum, the metal deposited is thus stripped therefrom, as illustrated at 27, and rolled up on a storage roll 30. The drum 10 and associated elements is enclosed in an outer jacket 32 which is provided with a ventilation exhaust or chimney 34 into which the waste gas exhaust conduit 22 discharges.

An important use of this invention is in the making of metal foil. A heated drum is suitably disposed in an airtight chamber, as illustrated and described, the drum being rotated while its surface is exposed to an atmosphere containing an adsorbent gas or gases and vapors of a metal compound. The selected gas has the property of ready adsorption on the surface of the drum and which gas is gradually released as the metal deposits on the drum surface by thermal decomposition of the circulated vapors in contact with the heated surface of the drum. The deposited metal is continuously stripped away and recovered as metal foil.

Another use for the invention is for making complex shapes or forms by thermal deposition of a metal on a master or pattern substrate surface from which the metal deposited is freed to recover an exact replica in pure metal of the pattern or shape.

For example, in making phonograph record molds, metals such as nickel or iron are deposited on a nickel or silver surface to make a "mother" matrix or a "stamper" matrix. By use of an adsorbent gas or gases which are adsorbed on the substrate surface in the plating atmosphere, separation of the deposit is made easy. Where no adsorbent gas is used the metal deposit can be peeled away from the substrate surface only with difficulty, damaging the surfaces in the process.

The gas or mixture employed, however, must not be too strongly adsorbed and copiously released during gas plating, otherwise blistering results as aforementioned. Nitrogen for example cannot be used by itself on a nickel surface, because this gas is so strongly adsorbed that pockets of the gas are created which push the deposit away, giving an appearance resembling a blister. To avoid this a mixture of the strongly adsorbed gas is employed with less strongly adsorbent gases, e.g. a mixture of nitrogen and carbon dioxide in 1:10 ratio by volume may be used.

In making metal shell forms to be used as molds, patterns, dies, or repetitively identical shapes useful as components in mechanical devices, the same may be made by thermal deposition of metal bearing compounds, e.g. gas

plating metal on heated forms. In particular, where the heated form is non-permeable, and usually made of a common metal, e.g. iron and steel, the use of an adsorbent gas, for example carbon dioxide in the plating atmosphere will produce a metal deposit which is easily separated to provide a deposited metal shell. Use of carbon monoxide, on the other hand, makes separation difficult from many common metals, but works very well with titanium, columbium and similar metals.

The substrate metal surface of the drum is obviously important from the foregoing. Metals found especially suitable are titanium and columbium for making metal foils as described. Drum surfaces composed of these metals adsorb nearly all gases and release them during gas plating and as deposition of metal starts. Stainless steel alloys are also particularly suitable and are employable with a variety of gases. When depositing aluminum metal on titanium by thermal decomposition of tri-isobutyl aluminum vapors, however, the presence of even moderate amounts of hydrocarbon gases such as propylene and isobutylene must be avoided since they are strongly adsorbed and released too copiously, as aforementioned, so that the deposit blisters. On the other hand, argon is a suitable adsorbent gas to use.

It has further been found that strippable depositions of nickel on nickel molds and patterns by thermal decomposition of nickel carbonyl cannot be prepared using nitrogen gas as an adsorbent gas by itself. The nitrogen gas is too strongly adsorbed and causes the deposit to blister. Carbon monoxide is suitable but argon works better.

When depositing nickel on a silver substrate surface by gas plating with nickel carbonyl, any oxygen present is strongly adsorbed causing blistering. A suitable adsorbent gas, however, is carbon dioxide.

When depositing nickel on steel from nickel carbonyl, hydrogen is so strongly adsorbed that blistering occurs. On the other hand, when depositing iron on a substrate by thermal decomposition of iron carbonyl, the gas plating is carried out at a relatively higher temperature than in the case of nickel carbonyl, so that hydrogen may be used as the adsorbent gas. Hydrogen, or a large percentage thereof, is less adsorbed and therefore a good adsorbent and carrier gas for achieving easy release of deposits from steel without blistering. Using carbon monoxide, or ammonia, it is more difficult to separate the metal deposit from the substrate surface.

The following examples are given which are descriptive but not limitative of my invention.

Example 1

Nickel foil is made by gas plating by carrying out thermal decomposition of vapors of nickel carbonyl on a heated, continuously rotating drum. The drum surface is composed of titanium metal, and as the nickel metal deposit forms it is continuously stripped away from the surface of the drum. Carbon monoxide is used as the adsorbent and carrier gas and conveys nickel carbonyl vapors to the plating area. The drum is covered for $\frac{1}{2}$ of its periphery by a hood-like chamber that retains the vapors and gases, as illustrated by the apparatus shown by the drawing.

Example 2

In the making of a stamper metal copy from a "mother" matrix metal copy of a phonograph record, the mother matrix is gas plated with nickel to a thickness of 0.010 inch by thermal decomposition of nickel carbonyl vapors. In this instance, the previously cleaned mother matrix is placed on a platen in an airtight chamber. The air is purged from the chamber with argon containing 10% nitrogen. Suitable electrical resistance heaters attached to the platen are turned on which raise the temperature to 350° F. Nickel carbonyl vapors are admitted to the chamber and deposition of nickel occurs. After 0.010 inch thickness is deposited, the nickel carbonyl vapors

are discontinued and the chamber purged with argon. The mother and deposit are removed, the edge trimmed, and the deposit separated by mechanically stripping the same away from its substrate surface. Because of the use of the 10% nitrogen, a portion of which is adsorbed on the nickel "mother," separation of the deposit is easy and eliminates mechanical damage that can otherwise occur.

Example 3

An aluminum concave mirror is made by depositing 0.020 inch thickness of aluminum on a highly polished optically accurate convex form made of titanium and then stripping away the aluminum metal deposit. The surface next to the titanium is the reflecting surface. The deposition is carried out by heating the titanium metal substrate form to 500° F. in a gas vapor mixture containing 20% isobutylene, 20% tri-isobutyl aluminum vapors, 0.25% oxygen, balance argon. Controlled separation is secured by using only 4% isobutylene during the initial stage and gradually increasing this amount to 20%. This gas is adsorbed by the titanium metal substrate and then released as gas plating progresses so that blistering is not encountered.

Where the plating gas contained as high as 20% by volume of isobutylene at the start or during the initial stages of gas plating deposition of metal, blistering of the deposit was observed. Using a gaseous mixture containing only about 4% of the hydrocarbon, however, as described, the principle of the invention was employed, and the adsorption was in the correct range to achieve separation without blistering.

Example 4

In this instance iron is deposited on a steel pattern heated to 450° F. by gas plating with iron carbonyl vapors and then stripping away the iron metal deposit. The process is repeated successively to mass produce iron shell reverse replicas of the said pattern. A plating gas mixture consisting, by volume, of 20% iron carbonyl vapor, 40% argon, and 40% hydrogen, is used. Hydrogen is employed as the adsorbed stripper gas on the steel surface and is released immediately subsequent to the start of plating, providing a barrier to prevent the metal deposit from integrally uniting with its substrate surface. The iron shell deposit is thus easily stripped away from the substrate. The adsorption of hydrogen gas in this case is in a correct range, whereas when nickel gas plating by thermal decomposition of nickel carbonyl at 350° F. adsorption of hydrogen is so much stronger and greater that blistering of the deposit occurs.

Example 5

A high temperature diffraction grating of chromium carbide is made by thermal decomposition of vapors of chromium hexacarbonyl on a grating ruled on a block of zirconium. The piece is disposed in an airtight chamber which is purged with nitrogen, and heated to 500° F. Vapors of chromium hexacarbonyl are then introduced to produce a gas plated deposit of chromium carbide. Zirconium strongly adsorbs the nitrogen and releases it as deposition of chromium carbide is initiated. The deposit is built up to $\frac{1}{16}$ " thickness and is then readily stripped from the zirconium substrate surface.

Example 6

A complex shell of pure refractory beryllium oxide which is free of binders or fluxes is made by thermal deposition of beryllium diethyl vapors in the presence of ethyl alcohol vapor. A titanium substrate machined to the contour to be duplicated is heated in a purged airtight chamber. Ethylene is admitted and is adsorbed on the surface at 600° F. Vapors of the beryllium diethyl and ethyl alcohol are then admitted and deposition of beryllium oxide takes place on the heated substrate. After $\frac{1}{32}$ " deposit is built up, the chamber is purged or evacuated,

and the gas plated substrate cooled and the deposit stripped. The ethylene gas used before plating was adsorbed and then released at the start of gas plating, thus permitting separation of the beryllium oxide deposit.

A modification of my method of making concave mirrors comprises the use of polished glass for the substrate surface form and carbon dioxide as the adsorbent carrier gas. This gas is adsorbed on glass and released just subsequent to the start of deposition of aluminum whereby easy separation of the deposit is obtained. Mirrors made utilizing the gas plating and adsorbent gas stripping methods as hereinbefore described, need no polishing or finishing treatment. A significant saving of labor is thus achieved over conventional processes which generally require a polishing treatment.

In the foregoing, reference has been made to deposition of metals; however, my invention is equally applicable to non-metallic deposits made by thermal decomposition of vaporized compounds, provided such deposits are non-porous. Aluminum oxide, metal carbides and carbon, e.g. graphite, are examples.

It will be understood that various changes and modifications of my invention may be made by those skilled in the art to suit various conditions and uses to which the invention may be put. It is accordingly contemplated that such changes may be made within the spirit and scope of this invention and which is more particularly set forth in the appended claim.

What is claimed is:

Apparatus for making a self-supporting metal foil shape comprising a rotatable drum substrate surface for receiving a gas plated deposit, said substrate surface comprising titanium metal, means enclosing a portion of said substrate surface of the drum, and means introducing an adsorbent gas into said enclosure, a second enclosure means adjacent said first enclosure means enclosing an adjacent portion of said substrate surface of the drum, and means introducing a thermally decomposable metal bearing gas into said second enclosure means, means for heating said substrate surface to a temperature to cause thermal decomposition of said metal bearing gas and deposition of metal on said substrate surface, and means for stripping said deposition of metal from said substrate surface to recover a self-supporting metal foil.

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