ABSTRACT OF THE DISCLOSURE

A metallic coating is deposited on a substrate by heating the substrate and contacting the substrate with vaporized metal-organic beta-ketoamine chelates, which react on contact with the hot substrate surface in a gaseous atmosphere to deposit the metal coatings.

BACKGROUND OF THE INVENTION

This invention relates to the vapor phase deposition of metallic substances from certain metal chelates. Chemical vapor-deposition coating methods were developed from techniques employed as early as 1880 by the incandescent lamp industry. A few years later, attention was directed to vapor deposition as a method of preparing high purity metals.

Chemical vapor deposition is a method of plating in which the deposits are produced by heterogeneous gas-solid or gas-liquid chemical reactions at the surface of a substrate. A volatile compound of the element or substance to be deposited is vaporized and the vapor thermally decomposed, or reacted with other gases or vapors, at the substrate to yield nonvolatile reaction products which deposit on the substrate as a coating.

Nickel has most usually been deposited from the vapor phase by the thermal decomposition of nickel tetracarbonyl, Ni(CO)₄. This procedure, through nickel tetracarbonyl decomposes at inconveniently low temperatures for some purposes, seems to be quite satisfactory in terms of the nickel films obtained. Nickel tetracarbonyl is, however, highly toxic-sufficiently so to discourage its use despite its other advantages. It is desirable therefore to find alternative volatile metal compounds, from which satisfactory metallic films or coatings can be obtained, and which avoid this toxicity hazard. Nickel acetylacetonate:

has been tried, but seems to require reduced pressure for optimum results and suffers from premature thermal decomposition. Nickel hexafluoroacetylacetonate and nickel trifluoroacetylacetonate have also been tried, but they are quite expensive to prepare.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide improved and inexpensive plating compounds suitable for vapor phase deposition of various metals.

It is a further object of this invention to provide a new and improved process for the vapor phase deposition of nickel and other metals or combinations of metals from metal organic beta-ketoamine chelates. Briefly, the above objects are accomplished in accordance with the present invention, by (1) vaporizing metal organic beta-ketoamine chelates, for example: nickel acetylacetone imide, copper acetylacetone imide, bisacetylacetoneethylenedimino nickel, and bisacetylacetoneethylenedimino copper, in a porcelain or silica boat container within a cylindrical quartz furnace tube at pressures up to and including atmospheric; (2) causing the vaporized metal chelate to be carried by pure hydrogen gas to a platinum, quartz or a glass fiber target substrate, held at a controlled temperature substantially higher than the vaporization temperature of the metal chelate, so as to deposit a pure metal coating on the substrate through hydrogen reduction of the chelate; (3) exhausting deposition by products for safety, and a possible recycling procedure. The nickel and copper acetylacetone imides have a high degree of volatility, are relatively nontoxic, and comparatively easy and inexpensive to prepare. The nickel and copper acetylacetoneethylenedimides also have definite advantages in terms of cost, ease of preparation and ease of handling these compounds can yield pure, dense, adherent metal coatings for a variety of end uses such as growing films on chosen substrates for molecular electronic devices, or coatings or structures of refractory materials for use in the aerospace industry.

Further objects and advantages of the invention will become apparent as the following description proceeds and features of novelty which characterize the invention will be pointed out in particularity in the claims annexed to and forming a part of this specification.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of our invention, reference may be had to the accompanying drawings, in which:

FIG. 1 shows a simplified schematic drawing of the vapor-deposition process;

FIG. 2 shows a flow diagram for vapor deposition; and

FIG. 3 shows a sectioned view of the deposition apparatus used in the experiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred metal-organic beta-ketoamine chelates for use as suitable volatile starting materials for the chemical vapor deposition of their respective metals, are chelates of the following structures:

(STRUCTURE I)

wherein M can be Ni, Cu, Co, and Cr among other metals, R₁ can be CH₃ or CF₃, R₂ can be CH or CF, R₃ can be H, CH₃ or CF₃ and X can be H or CH₃ and

(STRUCTURE II)

wherein M can be Ni and Cu among other metals, R₁ can be CH₃ or CF₃, R₄ can be CH₃ or CF₃, R₅ can be H, CH₃ or CF₃ and X can be H or CH₃, and

as an example of Structure I, and with copper and nickel acetylacetoneethylenedimides (bisacetylacetoneethylen-
Although Ni, Cu, and Co are the preferred metals, other metals that are also considered within the scope of this invention include Fe, Mn, Cr, Pd, and Pt as well as mixtures of all these metals to form alloys of Fe–Co–Cu–Ni–Cr. These alloys might be deposited by co-deposition of several different metal-organic beta-ketoamine chelates.

The following preferred procedure can be used to yield nickel acetylacetonate imide (bisacetylacetonate imide nickel (II) also bis 4-imino-2-pentanomino-nickel (II)) one of the metal-organic beta-ketoamine chelates which we used as a metal vapor deposition plating compound in this invention (Structure I): to a solution of acetylacetone imide (4-imino-2-pentanone) in ethanol is added a solution of nickel (II) nitrate 6-hydrate in water containing aqueous ammonia. The reaction mixture is shaken vigorously and allowed to stand. The precipitate forms as follows:

$$2C_2H_3NO_2 + Ni(NO_3)_2 + 2H_2O \rightarrow [(C_3H_5NO_2)Ni] + 2H_2NO_2 + 2H_2O$$

Other chelates of Structure I can be formed analogously by mixing an ethanolic solution of the beta-keto imine (beta-imino ketone) with an ammoniacal metal salt solution.

The following preferred procedure can be used to yield nickel acetylacetonethylenediamine (bisacetylacetonethylenediamine nickel (II)) another of the metal-organic beta-ketoamine chelates which we used as a metal vapor deposition plating compound in this invention (Structure II): to a solution of recrystallized bisacetylacetonethylenediamine is added an aqueous solution of nickel acetate tetrahydrate. To that mixture aqueous ammonia is added and the reaction mixture heated nearly to boiling. The precipitate forms after the reaction mixture is cooled. Copper acetylacetonethylenediamine can be prepared by substituting copper acetate monohydrate for nickel acetate tetrahydrate in the method above.

The chemical vapor-deposition processes constitute a highly versatile and flexible means of applying a coating of most of the refractory metals and nonmetals. Coating thickness can be varied, and fairly well controlled over a wide range, and most refractory materials can be obtained in a pure state by vapor-deposition processes, than by conventional metallurgical practices.

One of the most frequently used types of chemical vapor-deposition reaction is hydrogen reduction, at an elevated temperature, of the plating compound vapor. Hydrogen reduction is carried out at elevated temperatures where the reduction reaction is favored because a favorable thermodynamic equilibrium or a suitably rapid reaction rate is attained. Hydrogen reduction may be thought of as a thermal decomposition reaction which is facilitated by breakdown of one of more of the gaseous products of the decomposition. Consequently, the temperature required for a given extent of decomposition or rate of deposition from a given compound is appreciably lowered, usually by several hundred degrees, below that needed in the absence of hydrogen. It is desirable, in the hydrogen-reduction process, that the plating compound used have appreciable volatility at temperatures well below those at which the reduction reaction is thermodynamically or kinetically favored. If this condition cannot be met, the plating compound will have to be vaporized into a stream of inert carrier gas, which is then mixed with hydrogen at the point or region where deposition is desired.

Referring now to FIG. 1 of the drawings, a metal organic compound 1 (represented in block form) is shown in a container 2 at a temperature T. Chemically reactive hydrogen gas atoms 3 are shown as well as impurity nitrogen gas atoms 4. The target substrate 5 at a temperature T" which has metal atoms 6 deposited or plated on it while the other gaseous byproducts of the decomposition are exhausted or removed through opening 8. In the vapor deposition process shown schematically in FIG. 1, the metal organic is vaporized at a temperature T and carried past the target by hydrogen gas. The metal organic vapor and hydrogen gas mixture come in contact with the substrate 5 at a temperature T', which is lower than the melting point of the metal to be plated but higher than T, and at that point, the hydrogen reduces the metal organic to the metal that is deposited on the hot target.

The advantages of vapor-deposition technology should be obvious after considering the details of the process. It is possible to selectively volatilize a feed material, transport it to a desired location, and precipitate it as a controlled structure. Further details of the thermodynamics, evaporation, and transport processes, and nucleation of vapor deposited films can be found in Powell, Vapor Deposition, John Wiley & Sons, 1966 Chapter 1, herein incorporated by reference.

A flow diagram of the experimental apparatus used in Examples 4, 5, 6, 7, 9, 12 and 14 of this specification is shown in FIG. 2. The hydrogen 20 is high purity (99.95%) grade with N2 and O2 as the main impurities. The hydrogen is passed over a palladium deoxy catalyst 22, through a CaSO4 drier 23, then over a molecular sieve and metered at the entrance of the vaporization and plating chamber (deposition apparatus) 24, shown in detail in FIG. 3. The argon gas, if it is to be used, it passed through zincirconium turnings 25 heated to 800 degree C. then metered into the plating chamber. Exhaust gases are passed through a Dry Ice trichloroethylene trap, to condense the reaction vapors. A mechanical vacuum pump 26 is used when operating at low pressure.

A sectioned view of the deposition apparatus or plating chamber 24, used in Examples 4, 5, 6, 7, 9, 12 and 14 of this specification is shown in FIG. 3. An external heater 30 surrounds the glass volatilization chamber 31. An inner glass tube 32 supports the sample boat container 33 and is necked down around the target substrate 34 to collimate the sample vapors, thus increasing compound vapor to substrate contact. The target substrate 34 is in good thermal contact with a Kvarr metal probe 35 which is heated internally with a Chromaloax heater. The metal probe is drilled to accept a thermocouple and is calibrated where the target temperature goes above 700 degrees C. An alternate target is used consisting of a platinum coil heated resistively with the apparent temperature determined by using a Pyrometer Instrument Company micro-optical pyrometer, Model No. 95-EA5.

In the examples, the metal organics, usually solid, were placed in a silica sample boat and placed into the apparatus rapidly to reduce atmospheric contamination. The carrier gas used was hydrogen. The hydrogen gas flow, through gas inlet 36, was metered into the system through a Hoke vacuum needle valve. The hydrogen in the chamber where the target temperature goes above 700 degrees C. An alternate target is used consisting of a platinum coil heated resistively with the apparent temperature determined by using a Pyrometer Instrument Company micro-optical pyrometer, Model No. 95-EA5.

Quartz, glass fibers, tantalum and platinum were tried as target substrate materials. The quartz targets used in the examples were tubular cylinders approximately 3/8” x 1 1/4” and closed at one end. The fit of these cylinders was such that good thermal contact was obtained with the Kvarr metal probe, providing excellent heat transfer to the target surface. The tantalum and platinum targets were made of 0.008 inch wire wound into coil filaments approximately 1/2 inch long with a coil diameter of 1/8 inch. Temperature control of the target probe was
accomplished using a Wheeler controller with a Chromel-alumel thermocouple. The target filaments were held at temperature by passing an alternating current through the wire coil. The volatilization chamber was heated externally by a spiral tub furnace with the temperature controlled using a thermoelectric controller with a Chromel-alumel thermocouple. The internal pressure of the system was determined using a thermocouple vacuum gauge and a Wallace-Tierney direct reading dial gauge. In all the following examples this experimental apparatus was used, in conjunction with the hereinafter described procedure.

The plating process of Examples 4, 5, 6, 7, 9, 12 and 14 of this specification was accomplished by the following procedure. After placing the silica boat containing the metallocanic beta-ketoamine chelate (about 200 mg.) into position in the plating chamber 24 shown in FIG. 3 of the drawings, the system was closed by insertion of the target holding end 38 into the glass volatilization chamber 31. A trap was attached at the exhaust gas outlet 37, (cooled using a Dry ice trichloroethylene bath) then valved to the mechanical pump which evacuated the system. In cases where runs were carried out at atmospheric pressure, the system pressure was then raised and use of the vacuum pump discontinued.

After the system was evacuated, purged and the pressure regulated, the degreased and cleaned target substrate was heated to the desired operating temperature. The hydrogen gas flow was adjusted and the plating chamber heated to the desired temperature of metal plating compound volatilization. The temperature was increased in the final moments of operation to insure the complete volatilization of the sample. The chamber was then cooled while keeping the target at temperature until all the volatile materials were reacted or condensed. The target temperature was then lowered.

After cooling to room temperature, the apparatus was disassembled and the target weight and inspected visually under a microscope to determine the nature of any deposit. An X-ray diffraction powder pattern of the deposit was then obtained using a 114.6 mm. camera and CuKα radiation with a nickel filter. The diffraction unit used was a North American Phillips type 12045/3. In some cases, additional information was obtained by a spectrographic technique using an Associated Electrical Industries MS-702 spark source mass spectrometer. Some film deposits were also examined using an electron diffraction unit with an excitation voltage of 50,000 ev.

The purity of metals deposited from metal-organics and the stoichiometry of compound deposits are influenced by the temperature of the substrate, the vaporizer, system pressure, gas flow, plating compound concentration, and length of time in the deposition zone. Varying these parameters may not only change the appearance of a deposit but completely change its composition. Operation at a reduced pressure to improve uniformity of a deposit may lead to a change in deposit.

EXAMPLE 1

The compound Ni-acetylactoneimide (bis(acetylactoneimide) nickel (II)), for use as a metal-organic beta-ketoamine chelate vapor decomposition plating compound, was prepared as follows. Eleven and two-tenths grams (0.05 mole) of recrystallized bis(acetylactoneimide)imide, as prepared by the method of McCarthy, Hovey, Ueno and Martell in J. Am. Chem. Soc. 77, 5820 (1955), was dissolved in 200 ml. of water by gentle boiling. To the warm solution was added, slowly with stirring, a solution of 12.4 grams (0.05 mole) of nickel acetate tetrahydrate in 200 ml. of water. One hundred ml. of 1M aqueous NH₄ was then added slowly. The resulting mixture was then heated nearly to boiling, maintained at this temperature for a few minutes, and finally cooled in a refrigerator for several hours. The red crystalline product was filtered off, washed several times with water and air dried to give 10.3 grams of crude product.

The chelate was recrystallized twice by the following procedure. Ten grams of the compound was dissolved in 100 ml. of methanol by gentle heating. The warm solution was filtered and 30 ml. of water added. The mixture was cooled several hours in the refrigerator and the product filtered off, air dried and finally dried for 4 hours at 100 degree C. The recovery was 80% of the crude product taken (M.P. 198–199 degrees C).

EXAMPLE 2

The compound Cu-acetylactoneimideimide (bis(acetylactoneimideimide) copper (II)), for use as a metal-organic beta-ketoamine chelate vapor decomposition plating compound, was prepared by essentially the same method as in Example 1. Ten grams (0.05 mole) of copper acetate monohydrate was substituted for the nickel acetate. The yield of crude violet product was 11.1 grams. The product was twice recrystallized by dissolving in methanol (75 ml. for each 11 grams) by gentle warming. The solution was cooled to room temperature and filtered through filter paper. To the filtrate was added, a little at a time, 75 ml. of water. The mixture was cooled for 2 hours in the refrigerator. The product was filtered off, air dried, and finally dried for 4 hours at 100 degree C. The recovery was 60 to 80% of the amount of crude product taken (M.P. 137–138 degree C).

EXAMPLE 3

The compound Ni-acetylactone imide (bisacetylace tone imide nickel (II) or bis 4-imino-2- pentanonoate nickel II), for use as a metal-organic beta-ketoamine chelate vapor deposition plating compound, was prepared as follows. To a solution of 12.0 grams (0.12 mol) of acetylactone imide in 100 ml. of 95% ethanol was added a solution of 20.4 grams (0.07 mol) of nickel (II) nitrate 6-hydrate in 300 ml. of water containing 25 ml. of 15 M aqueous ammonia. The reaction mixture was shaken vigorously until a light orange precipitate formed. This mixture was allowed to stand approximately 10 hours. After filtration, the 12.0 grams of crude product was re-crystallized from 900 ml. of a 1:1 mixture of benzene and petroleum ether (B.P. 90 to 110 degree C.). The first crop of crystals weighed about 8.0 grams. After reducing the volume of the filtrate to 50 ml., of a second crop of 0.60 gram was obtained, (M.P. 349–351 degrees C.).

EXAMPLE 4

The results of chemical vapor deposition tests, using the aforesaid procedure and the apparatus of FIGS. 2 and 3 of this specification, for Ni-acetylactoneimideimide, as prepared in Example 1, are outlined in Table 1:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Target temp., °C</th>
<th>Target material</th>
<th>Volatilization yield, %</th>
<th>Pressure, mm. Hg</th>
<th>Hydrogen flow rates, cc./min.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-acetylactoneimideimide</td>
<td>450 Quartz...</td>
<td>232</td>
<td>750</td>
<td>75 A very light metallic coating was formed, but not enough for X-ray diffraction.</td>
<td>Nickel deposit was readily formed.</td>
<td></td>
</tr>
<tr>
<td>Pt...</td>
<td>550</td>
<td>246</td>
<td>730</td>
<td>80 A nickel deposit was readily formed.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 Pt...</td>
<td>232</td>
<td>730</td>
<td>500 Nickel was readily deposited.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results indicate that nickel metal may be easily deposited from this compound at the temperatures tested. A target substrate temperature of 450 degrees C. gave only a small and scattered coating but at the higher temperatures, a good coating of nickel was readily obtained.

**EXAMPLE 5**

The results of chemical vapor deposition tests, using the aforesaid procedure and the apparatus of FIGS. 2 and 3 of this specification, for Cu-acetylacetonateethyleneimide, as prepared in Example 2, are outlined in Table 2:

<table>
<thead>
<tr>
<th>Compound: Cu-acetylacetonate-ethylenimide (200 mg.)</th>
<th>Target temp., °C.</th>
<th>Target material</th>
<th>Volatilization temp., °C.</th>
<th>Pressure, torr</th>
<th>Hydrogen flow rates, cc./min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>230 Quarts, do.</td>
<td>199</td>
<td>780</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>336 Quarts, do.</td>
<td>232</td>
<td>770</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 Pyrex</td>
<td>250</td>
<td>780</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this experiment copper metal was successfully plated on the quartz target.

**EXAMPLE 6**

The results of chemical vapor deposition tests, using the aforesaid procedure and the apparatus of FIGS. 2 and 3 of this specification, for nickel-acetylacetone imide, as prepared in Example 3, are outlined in Table 3:

At target temperatures of 300 and 400 degrees C., an excellent coating of pure nickel metal was formed. The coating was bright and metallic in nature. At 250 degrees C., a small amount of NiC was also deposited along with nickel metal. When the pressure was reduced and the target temperatures held at 325 degrees C., then the predominant deposit was NiC with small amounts of nickel metal present. All the deposits were smooth and bright. Metal carbide formation would seem to be favored by low pressure and low target temperatures.

In a second set of experiments using an apparatus similar but not exactly identical to that shown in FIG. 3 of the drawings, we were able to determine quantitatively the amount of nickel metal produced from nickel acetylacetonone imide as a function of substrate temperature. It was found, for a carrier gas of pure hydrogen at atmospheric pressure, that the yield of nickel metal was essentially quantitative at substrate temperatures above 300 degrees C.

When fine Pyrex Glass Wool fibers (Fisher Scientific Co.) were used as the target in Example 6, those fibers exposed to the hydrogen and nickel acetylacetone imide vapors were found to be coated with a uniform and adherent nickel metal coating. The coated fibers were electrically conductive and were attracted to a permanent magnet. Nickel plated glass or quartz wool prepared in this way may be useful for such applications as electrodes or in other applications where high surface area of nickel metal is desired.

In the deposition examples above, the hydrogen functioned both as a carrier gas for the chelate vapors and also entered into the deposition reaction. The simplest representation for the reduction involves the straight forward replacement of nickel by hydrogen in the organic portion of the chelate for example, with Ni-acetylacetone imide:

\[
\begin{align*}
\text{Ni} + \text{H}_2 & \rightarrow \text{Ni} + \text{H}_2 \\
\text{Ni} + \text{H}_2 & \rightarrow \text{Ni} + \text{H}_2
\end{align*}
\]

To demonstrate the actual importance of hydrogen in the nickel deposition reaction we carried out an experiment with nickel acetylacetone imide (target temp. 400 degrees C., volatilization temp. about 260 degrees C., pressure 730 torr) in which 150 cc./min. of high purity helium was substituted for the hydrogen normally used. No appreciable deposition of nickel occurred, while nickel deposits quantitatively under these conditions in hydrogen.

The extent to which one of the gaseous products of decomposition, the catalytically active active nickel surface would seem to be ideal for such reaction to occur to produce products such as shown below.

To demonstrate the actual importance of hydrogen in the nickel deposition reaction we carried out an experiment with nickel acetylacetone imide (target temp. 400 degrees C., volatilization temp. about 260 degrees C., pressure 730 torr) in which 150 cc./min. of high purity helium was substituted for the hydrogen normally used. No appreciable deposition of nickel occurred, while nickel deposits quantitatively under these conditions in hydrogen.

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The extent to which one of the gaseous products of decomposition, the catalytically active active nickel surface would seem to be ideal for such reaction to occur to produce products such as shown below.

To demonstrate the actual importance of hydrogen in the nickel deposition reaction we carried out an experiment with nickel acetylacetone imide (target temp. 400 degrees C., volatilization temp. about 260 degrees C., pressure 730 torr) in which 150 cc./min. of high purity helium was substituted for the hydrogen normally used. No appreciable deposition of nickel occurred, while nickel deposits quantitatively under these conditions in hydrogen.
EXAMPLE 9

The compound cobalt (II) acetylacetonate imide (bis-acetylacetone bis cobalt (II) or bis-4-imino-2-pentanonato cobalt (II), for use as a metal organic beta-ketoamine chelate vapor deposition plating compound, was prepared as follows. Acetylacetonate imide (3.30 grams) and 3.61 grams anhydrous CoCl₂ were mixed, as solids, in a flask. The mixture was heated briefly on a hot plate until a blue slurry was obtained. After cooling, 1.85 grams of potassium tert-butoxide was stirred in as a solid. After the initial exothermic reaction had subsided, 35 ml of absolute ethyl alcohol was added and the mixture was heated with stirring until the blue color disappeared and a brown solid formed (about 15 minutes). The mixture was then evaporated to room temperature in a stream of nitrogen. The brown lumpy residue was washed with successive 25 ml portions of water and transferred to a sintered glass crucible. Drying in a vacuum gave 1.25 grams of red product having a melting point of about 235 degree C.

EXAMPLE 10

The results of chemical vapor deposition tests, using the aforedescribed procedure and the apparatus of FIGS. 2 and 3 of this specification for cobalt (II) acetylacetonate imide, as prepared in Example 8, are outlined in Table 5 below:

<table>
<thead>
<tr>
<th>Compound: Cobalt (II) acetylacetonate imide (200 mg.)</th>
<th>Target temp., °C</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target material</td>
<td>Quartz</td>
<td></td>
</tr>
<tr>
<td>Volatilization temp., °C</td>
<td>287</td>
<td></td>
</tr>
<tr>
<td>Pressure torr</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>Hydrogen flow rate cc./min</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

The deposit in this case consisted mainly of a bright, metallic foil, together with some black powdery material. Both deposits were identified as cobalt metal by X-ray diffraction analysis.

EXAMPLE 11

The compound trifluoroacetylacetone imide required in the preparation of the nickel derivative of Example 11, was synthesized as follows. Trifluoroacetylacetone (7.7 grams) was dissolved in 10 ml absolute ethyl alcohol. Five ml of concentrated aqueous NH₄OH and an additional 5 ml ethyl alcohol were added successively. The mixture was heated briefly, nearly to boiling. After cooling, the mixture was then taken to dryness in a stream of nitrogen at room temperature. The residue was heated with 75 ml N-heptane to give partial solution. The hot solution was filtered through filter paper and the insoluble residue remaining on the paper discarded. The filtrate was cooled and reduced to about ½ its original volume in a stream of nitrogen. After further cooling in a refrigerator the yellow crystals were filtered off, washed with cold petroleum ether and air dried at room temperature. Yield was 1.2 grams having a melting point of about 85–87 degree C.

EXAMPLE 12

The results of chemical vapor deposition tests, using the aforedescribed procedure and the apparatus of FIGS. 2 and 3 of this specification for nickel (II) trifluoroacetylacetone imide, as prepared in Example 11, are outlined in Table 6 below:

<table>
<thead>
<tr>
<th>Compound: Nickel trifluoroacetylacetone imide (200 mg.)</th>
<th>Target temp., °C</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target material</td>
<td>Quartz</td>
<td></td>
</tr>
<tr>
<td>Volatilization temp., °C</td>
<td>287</td>
<td></td>
</tr>
<tr>
<td>Pressure torr</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>Hydrogen flow rate cc./min</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

The metallic coating produced was identified as nickel metal by X-ray diffraction analysis.

EXAMPLE 13

The compound nickel acetylacetone-1,2-propylene diimide, for use as a metal-organic beta-ketoamine chelate vapor deposition plating compound was prepared as follows. Propylene diamine (3.7 grams) was added to 10 grams acetylacetone in a flask. After the exothermic reaction had subsided, the mixture was dissolved in 200 ml of water. A solution of 0.05 mole of nickel acetate in 200 ml water was added, followed by 100 ml 1 molar aqueous NH₄OH. Upon heating, the resulting red solution gradually deposited red crystals. After 5 minutes heating, mixture was cooled, first to room temperature and then in a refrigerator. The compound was filtered off and air dried to give 8.1 grams of product. Recrystallization was achieved by dissolving in 50 ml of hot methanol, filtering hot and adding 100 ml water to the filtrate. Two successive recrystallization gave 6.0 grams of air dried red crystals of melting point about 158–159 degree C.

EXAMPLE 14

The results of chemical vapor deposition tests using the aforedescribed procedure and the apparatus of FIGS. 2 and 3 of this specification for nickel acetylacetone-1,2-propylene diimide, as prepared in Example 13 are outlined in Table 7 below:

<table>
<thead>
<tr>
<th>Compound: Nickel acetylacetone-1,2-propylene-diimide (200 mg.)</th>
<th>Target temp., °C</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target material—Quartz</td>
<td>Volatilization temp., °C</td>
<td>287</td>
</tr>
<tr>
<td>Pressure torr</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>Hydrogen flow rate cc./min</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

In this case two bands of bright metallic deposit were formed, one upstream of the other. Both bands of metal foil were identified as pure nickel metal by X-ray diffraction analysis.

We claim as our invention:

1. A process of coating a substrate with metal comprising the steps of vaporizing a metal-organic beta-ketoamine chelate in a gaseous atmosphere and contacting a substrate, heated to a temperature higher than the vaporization temperature of the metal-organic beta-ketoamine chelate, with said vapor for a time sufficient to cause the substrate to be coated with metal.
2. The process of claim 1 wherein the metal-organic beta-ketoamine chelate has the structure

wherein M is selected from the group consisting of Ni, Cr, Cu, Co, Fe, Mn, Pd and Pt, R₁ is selected from the group consisting of CH₃ and CF₃, R₂ is selected from the group consisting of H and CH₂, the gaseous atmosphere contains flowing hydrogen gas and the substrate temperature is between 200 and 700 degrees C.

3. The process of claim 1 wherein the metal-organic beta-ketoamine chelate has the structure

wherein M is selected from the group consisting of Ni, Cr, Cu, Co, Fe, Mn, Pd and Pt, R₄ is selected from the group consisting of CH₃ and CF₃, R₅ is selected from the group consisting of CH₂ and CF₂, X is selected from the group consisting of H, CH₂ and CF₂, X is selected from the group consisting of H and CH₂, the gaseous atmosphere contains flowing hydrogen gas and the substrate temperature is between 200 and 700 degrees C.

4. The process of claim 1 wherein the substrate is a fibrous material.

5. The process of claim 1 wherein the metal-organic beta-ketoamine chelate is selected from the group consisting of bisacetylacetoneimide nickel (II), bisacetylacetoneethylendimino nickel (II) and bisacetylacetoneethylene-dimino copper (II), the gaseous atmosphere contains flowing hydrogen gas and the substrate temperature is between 200 and 700 degrees C.

6. The process of claim 5 wherein the hydrogen gas is flowing at a rate of at least 60 c./min., and gaseous byproducts of vaporization are removed.

References Cited

UNITED STATES PATENTS
3,356,527 12/1967 Mosher et al. ....... 117—107.2
3,242,102 3/1966 Schneckenbecker .... 117—107.2
2,430,520 11/1947 Marboe ............ 117—107.2

ALFRED L. LEAVITT, Primary Examiner
W. E. BALL, Assistant Examiner

U.S. Cl. X.R.

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