EXTRACTION:

**Title:** Electroplating of Metals Using Pulsed Reverse Current for Control of Hydrogen Evolution

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**Abstract:**
Excessive evolution of hydrogen in electrolytic deposition of metals on a cathode substrate can be controlled by using a pulsed reverse current. Reverse current pulses interposed between the forward current pulses consume at least some of the nascent hydrogen and prevent the local pH at the cathode surface from becoming excessively alkaline. Control of hydroxide ion concentration by pulsed reverse current alleviates problems caused by reaction of metal-bearing ions with hydroxide ions generated near the cathode by evolution of hydrogen. The method is useful in depositing functional chromium coatings on electrically conductive substrates from plating baths comprising aqueous solutions of trivalent chromium salts. In such a method the current comprises forward pulses having a duty cycle of from about 50% to about 90% and reverse pulses having a duty cycle of from about 5% to about 30%, and a frequency of from about 5 Hz to about 700 Hz.

**Diagram:**
A diagram showing cathodic and anodic pulses with time durations and current values.
ELECTROPLATING OF METALS USING PULSED REVERSE CURRENT FOR CONTROL OF HYDROGEN EVOLUTION

ORIGIN OF THE INVENTION

[0001] The experimental work leading to this invention was funded in part by the U.S. Government Environmental Protection Agency Contract No. 68D440033.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] This invention relates to methods of electroplating metals onto a substrate and more particularly to electrodeposition of metals using pulsed reverse current for controlling evolution of hydrogen.

[0004] 2. Brief Description of the Prior Art

[0005] Electrodeposition of metal coatings onto a substrate is a process that is widely used in modern industry. Such electrodeposited coatings are usually applied to metallic substrates and are generally intended to provide enhanced surface properties to the base metal. For example, metal coating layers are applied to a base metal to prevent corrosion, enhance surface hardness, provide a smooth surface having a relatively low coefficient of friction, and the like.

[0006] Metal coatings are ordinarily deposited by providing a plating bath which is an aqueous solution of metal-bearing ions, typically simple ions such as Cr^{6+}, Zn^{2+}, Au^{3+}, Cd^{2+}, which are generally present as aquo complexes, or complex ions containing the metal, such as CrO_{4}^{2-}. The metals are present in these ions in a positive oxidation state, e.g. Cr(III) or Cr(VI). The substrate to be plated is immersed in the plating bath and made the cathode of an electrolytic cell. The metal ions are reduced at the surface of the cathode and deposited thereon as a layer of metal.

[0007] The actual mechanism of the cathodic reduction and deposition can be complex, and is not well understood for many practical systems. Because the plating baths are aqueous solutions, electrolysis of water with evolution of hydrogen is usually a competing reaction at the cathode. The hydrogen formed may itself present problems, such as hydrogen embrittlement of the deposited metal coating or interference with the metal deposition caused by bubbles. The removal of hydrogen, with concomitant formation of OH^- ions, also increases the pH of the plating solution adjacent to the surface of the cathode. A high pH in the plating layer may also produce problems such as formation of insoluble metal hydroxide layers on the cathode surface which also interfere with the transportation of the metal-bearing ions and the deposition of metal atoms on the surface.

[0008] In order to prevent the problems associated with hydrogen evolution at cathodic plating surfaces, the plating industry has adopted a number of expedients. The metal-bearing ions that are commonly used in industrial electroplating have been found to minimize the effects of hydrogen evolution. For example, chromium is conventionally plated from a chromate bath in which the metal is present in the hexavalent state (Cr(VI)), and gold is generally plated as the cyanide salt.

[0009] Moreover, certain metals present problems in depositing layers having satisfactory properties such as uniformity, luster and hardness, especially at useful plating rates. To overcome these problems the plating industry has developed plating baths that contain various additives that enhance the rate or ease of electrodeposition and the properties of the coatings.

[0010] Some of these expedients have resulted in the use of plating baths that are hazardous to use and difficult to dispose of by environmentally benign procedures. For example, it is has been found that the best results in gold electroplating are achieved using cyanide solutions which are evidently hazardous to use and difficult to remediate for disposal. Similarly, it is customary to plate chromium layers, particularly functional chromium layers, from solutions wherein the chromium is in the hexavalent state, typically as chromic or dichromate ions, a hazardous and carcinogenic form of the metal.

[0011] The workplace and environmental problems experienced with chromium plating are especially pressing because of the very extensive use of electroplated chromium coatings in industry.

[0012] Chromium coatings on a base metal are widely used in automotive, aerospace and other industries to provide a finished article with surface properties that are not inherent in the base metal itself or are attainable only by using expensive alloys. Such coatings are usually deposited on the base metal by electroplating. Two types of chromium coatings are used, conventionally identified as functional coatings and decorative coatings. Functional coatings consist of a relatively thick layer of chromium (typically 1.3 to 760 micrometers thick) to provide a surface with functional properties such as hardness, corrosion resistance, wear resistance, and low coefficient of friction. Such functional coatings are used on automotive struts and shock absorber rods, hydraulic cylinders, crankshafts, and industrial rolls. Carbon steel, cast iron, stainless steel, copper, aluminum, and zinc are substrates commonly used with functional chromium layers.

[0013] Decorative coatings consist of a thin layer of chromium (typically 0.003 to 2.5 micrometers, plated over a nickel layer) to provide a bright surface with wear and tarnish resistance. Such coatings are used on automobile bumpers and trim, bath fixtures, and small appliances.

[0014] Chromium is generally plated from an aqueous solution containing soluble chromium species wherein the chromium is in the hexavalent state (Cr(VI)). Such a hexavalent chromium plating bath is a chromic acid solution containing various chromate ions, dichromate ions, dichromate and trichromate. Sulfuric acid has been recognized as an essential ingredient of Cr(VI) plating baths.

[0015] Although plating from Cr(VI) baths has been the dominant commercial procedure for a long time, the process has certain disadvantages. A Cr(VI) plating bath is typically operated at a temperature significantly above room temperature and produces a mist of chromic acid. Consequently, measures to protect the workers from exposure to the toxic fumes are required by safety rules and by law. Exhaust/scrubber systems must be installed to keep the chromium concentration in the workplace atmosphere no greater than the prescribed limit of 0.01 mg/m^3. The amount of chro-
mium that can be emitted to the air and water of the environment is also strictly regulated by federal and local law. Some deposition of decorative chromium plating is done from trivalent chromium (Cr(III)) baths. Plating from Cr(III) baths instead of Cr(VI) baths has several environmental advantages.

1. Cr(III) is non-toxic, non-hazardous and is not an oxidizing agent. Therefore, meeting air quality regulations is easier and working conditions are greatly improved. The exposure limit for Cr(III) is an order of magnitude higher than for Cr(VI).

2. Waste disposal costs for Cr(III) plating are significantly less than for Cr(VI) plating. Hydroxide sludge generation is reduced ten to twenty times because a Cr(III) bath generally contains only about 4-20 g/liter of chromium, as opposed to 150-300 g/liter for a Cr(VI) bath.

3. A Cr(III) bath may be used without additives, which permits the rinse water from the plating operation to be recycled readily.

Plating from a Cr(III) bath also has certain technical advantages.

1. Current interruptions have little effect on the plating.

2. A Cr(III) bath is not affected by drag-in of chloride and sulfate from any previous nickel plating operations. In contract, chloride and sulfate drag-in upset the catalyst balance in Cr(VI) baths.

3. The throwing power of a Cr(III) bath, i.e., the ability to provide a uniform coating of chromium to recesses on the surface of the object to be plated, is greater than that of a Cr(VII) bath.

The effect of the plating bath chemistry, i.e., the composition of the solution, on the plating thickness, brightness, hardness, and corrosion resistance of chromium layers deposited from a Cr(III) bath have been studied by several authors. The effect of the waveform of the plating current on the structure of the chromium deposit, and its distribution, brightness and hardness have also been studied. Commercial Cr(III) baths are available that incorporate certain proprietary organic compounds as additives in order to provide baths for decorative chromium coating applications. However, the concentration of the additives is difficult to control because they are present in very small amounts. Furthermore, the additives react and break down with the passage of time to form contaminants. Consequently, the used Cr(III) bath and the rinse water from such plating operations cannot be replenished and/or recycled because the concentration of the contaminants would build up to unsatisfactory levels. Finally, decorative plating from a Cr(III) bath suffers from low current efficiency.

Currently, functional chromium coating from a Cr(III) bath is not commercially practical because it is difficult to plate thick chromium coatings with appropriate properties. Furthermore, the low current efficiency and low plating rate of Cr(III) baths lead to unfavorable economics.

Attempts to plate gold from non-cyanide solutions have also experienced difficulties. Gold plating baths that do not employ cyanide usually contain sulfite. Gold is deposited from the sulfite complex according to the equation:

\[ \text{M}_{x} \text{Au(SO}_{3})_{y} + \text{H}_{2}\text{O} + e^{-} \rightarrow \text{M}_{x} \text{SO}_{4} + \text{MSO}_{4} \rightarrow \text{OH} \]

where M is an alkali metal or ammonium ion. The sulfite ion is itself in equilibrium with sulfur dioxide according to the equation:

\[ \text{SO}_{3}^{2-} + \text{H}_{2}\text{O} \rightarrow \text{SO}_{4}^{2-} + 2\text{OH}^{-} \]

Because this reaction forms hydroxyl ions, the equilibrium is pH-dependent, and the sulfite ion is ordinarily stable only at alkaline pH. Because the plating reaction generates OH*, the pH near the plated surface (cathode) is usually very high. At alkaline pH, sulfite ions accumulate as gold is consumed and the specific gravity of the solution tends to increase continuously as the bath is operated. This is undesirable for high speed operation, or for applications requiring selectivity. It would clearly be desirable to operate a sulfite gold plating bath under conditions such that sulfur dioxide is volatilized at approximately the same rate at which gold is plated out. In such a case, the process tends to be self-regulating, and would operate in a fashion analogous to that of the cyanide gold plating solutions.

Another electroplating application wherein it is desirable to control hydrogen evolution and the local pH in the region of the cathode is the developing attempts to substitute zinc-nickel or zinc-tin plating for anti-corrosion coatings of cadmium in order to eliminate the use of that toxic metal. Zinc-based alloys, such as Zn—Ni and Zn—Sn are strong candidates to replace cadmium. However the current electroplating process for zinc alloy coatings suffers from two main difficulties:

1. It requires a hydrogen-relief bake post-treatment to eliminate hydrogen embrittlement.

2. It is difficult to control the composition of the alloy as deposited.

Zinc alloy plating suffers from what is known in the plating industry as anomalous deposition. The anomaly involved is the tendency in such systems for the less noble metal to be deposited preferentially. In the case of the zinc-based alloys the result is a coating that contains more zinc and less nickel or tin than desired. According to one of the leading proposed mechanisms the problem is caused by the formation of a zinc hydroxide film within the double layer adjacent to the cathode surface that inhibits the electrodeposition of the more noble metal. Attempts have been made to correct the anomalous deposition by adjusting the composition of the plating bath, but the results have not permitted zinc alloys to replace cadmium extensively.

Still another industrial use of hexavalent chromium compounds in coating applications is the formation of anti-corrosive chromate conversion coatings on aluminum. A recent process developed for replacing chromium in such coatings is the formation of a cerium-molybdenum alloy coating on aluminum. This "Ce+Mo" process involves a chemical treatment of an aluminum alloy surface with Cr(NO₃)₃ solution for several hours, followed by an electrochemical treatment (anodic polarization) in Na₂MoO₄ solution and finally a chemical treatment in CeCl₃ solution. The treatment process requires about six hours to complete and it is difficult to control the chemical treatment step. In addition it is difficult to control the Ce—Mo composition.
and coating distribution due to the chemical treatment process. A cerium coating can be electrodeposited on aluminum. However, the conventional electrolytic method, which uses direct current (DC), involves a large amount of hydrogen evolution due to the very negative reduction potential of Ce\textsuperscript{3+} (≈−2.335 V vs Standard Hydrogen Electrode (SHE)). The evolved hydrogen produces hydrogen embrittlement of the aluminum, stress corrosion cracking (SCC) and corrosion fatigue of aluminum alloys.

Accordingly, a need has continued to exist for a method of controlling the deleterious effects of hydrogen evolution in electroplating processes and, in particular, for plating functional chromium coatings from a Cr(III) plating bath that does not suffer from the disadvantages of current processes.

SUMMARY OF THE INVENTION

The problems of controlling evolution of hydrogen and its direct and indirect effects on the properties of the electroplated coatings and the adverse interaction of hydroxide ion with metal-bearing ions in the plating solution have now been alleviated by the process of the present invention wherein metal layers are deposited from a plating bath onto a cathode substrate using a pulsed reverse current (PRC). The process is especially applicable to electrodeposition of functional chromium coatings from a Cr(III) plating bath.

Accordingly, it is an object of the invention to provide a method of controlling the evolution of hydrogen in electrodeposition of metals at a cathode.

A further object is to control the pH in the vicinity of a cathode at which metals are being deposited electrolytically.

A further object is to provide a functional chromium layer on a substrate.

A further object is to provide a method for depositing a functional chromium layer on a substrate using a Cr(III) plating bath.

A further object is to provide a method of depositing a functional chromium layer using a pulsed reverse current waveform.

A further object is to provide a method for depositing gold on a substrate.

A further object is to provide a method for depositing gold on a substrate from a plating bath containing sulfite.

A further object is to provide a method for depositing Zn—Ni and Zn—Sn alloy layers on a substrate.

A further object is to provide a method of depositing a cerium-molybdenum anticorrosive layer on aluminum and aluminum alloys.

Further objects of the invention will become apparent from the description of the invention that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

The sole FIGURE illustrates a pulsed reverse current waveform of the type used in the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The method of the invention for controlling hydrogen evolution and the deleterious effects thereof in electrodeposition of metals at a cathodic substrate will be discussed in detail in connection with the application of the process to electrodeposition of a functional chromium metal layer on a substrate using a plating bath containing trivalent chromium (Cr(III)) and using pulsed reverse current.

In electroplating from aqueous solutions, the electric current flowing to the cathode is carried by the metal-bearing ions and the hydrogen ions. The hydrogen ions frequently carry a substantial fraction, often more than half, of the current. When the hydrogen ions are discharged at the cathode to form hydrogen gas which is evolved, the concentration of hydroxide (OH\textsuperscript{−}) ions in the vicinity of the cathode is proportionately increased according to the well-known equilibrium reaction of water, and the pH increases. Thus the discharge of hydrogen ions at the cathode effectively generates hydroxide ions at the cathode. The exact distance from the cathode surface to which the increased hydroxide ion concentration, i.e., higher pH, exists will vary depending on the conditions of the particular electroplating process such as total current, agitation of the bath and the like. In any case the increased hydroxide concentration occurs in the vicinity of the cathode where the hydroxide ions can interact with any metal-bearing ions approaching the cathode if such ions are susceptible to reaction with hydroxide ions, the skilled practitioner will recognize that certain metal-bearing ions do not interact directly with hydroxide ions. For example, the dichromate ions (Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}) that are commonly used in plating with Cr(VI) bear a negative charge, and do not react with hydroxide ions. Similarly, gold cyanide ions are not affected by hydroxide ions at the concentrations usually produced in electroplating because of the great stability of the gold-cyanide complex. However, other ions, e.g., Cr\textsuperscript{3+}, Zn\textsuperscript{2+}, and the like, are capable of reacting with hydroxide ions to form insoluble precipitates at the cathode surface. When such ions are used for electroplating the deposition of the metal is inhibited by formation of reaction products with hydroxide ion, such as precipitates.

According to the process of this invention, the use of pulsed reverse current greatly reduces the evolution of hydrogen at the cathode and thereby prevents the large increase in hydroxide ion concentration in the vicinity of the cathode that occurs when DC current is used.

Chromium (III) ions are typical of those ions that can react with hydroxide ions produced in the vicinity of the cathode as a result of the discharge of the complementary hydrogen ions and their removal from the solution by evolution of hydrogen gas.

According to the invention, chromium plating of sufficient thickness to provide the properties of a functional chromium layer can be efficiently and rapidly deposited on a substrate from a Cr(III) plating bath using a pulsed reverse current waveform. It will be understood by those skilled in the art that the pulsed reversed current through the plating bath will be produced by a pulsed reverse voltage applied to the electrodes of the electrolytic cell. Accordingly, the process of the invention may be described in terms of pulsed
reverse current or pulsed reverse voltage. Hereinafter the process of the invention will be discussed in terms of pulsed reverse current.

[0051] Plating of functional chromium layers from Cr(III) baths using the conventional direct-current procedure is not practical because the current efficiency is low and the rate of electrodeposition is relatively slow. Due to the rapid drop in current efficiency, the practical limit for plating from a Cr(III) bath is about 2.5 micrometers. Although the plating thickness increases rapidly when the current is first applied, the deposition rate soon diminishes and eventually becomes very small. The reason for this behavior may be seen from a consideration of the chemistry involved in the electroplating process.

[0052] The object to be plated is made the cathode of the electrolytic cell. At the cathode, chromium is deposited and hydrogen is evolved as represented in the following reactions, which include their standard potentials relative to the standard hydrogen electrode (SHE):

$$\text{Cr}^{2+} + 3e^- \rightarrow \text{Cr(s)} \quad E_{\text{Cr}} = -0.74 \text{ V vs SHE}$$

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \quad E_{\text{H}_2} = 0 \text{ V vs SHE}$$

[0053] Because the evolution of hydrogen at the cathode removes H\(^+\) ions from the solution, the pH near the cathode surfaces increases dramatically and chromic hydroxide (solubility product \(K_{sp} = 5.4 \times 10^{-30}\)) precipitates in the high pH layer at the cathode. The sedimentation of chromic hydroxide covers the cathode surface and its thickness increases as the plating time and pH increase. This promotes an increase of cathode polarization, a further decrease of chromium plating efficiency (i.e., an increase in the amount of hydrogen evolution reaction), and the increase of impurities in the plating film. All these factors retard the normal growth of crystals in the plating film, leading to the prevention of further plating of chromium. Finally, the evolution of hydrogen continues as the only reaction. The precipitation of chromic hydroxide at the cathode also results in surface cracks in the plated layer and reduces the hardness and brightness of the chromium coating.

[0054] These deleterious effects are reduced by the use of a pulsed reverse current in the electrolytic cell.

[0055] A schematic diagram of a pulse reverse current (PRC) waveform is shown in FIG. 1. Each cycle of the waveform comprises a cathodic (forward) current pulse followed by an anodic (reverse) pulse and, optionally, a relaxation period. As will be understood from the following discussion, a reverse pulse need not be present in every cycle to achieve the benefits of the invention, but it is preferred that there be one reverse pulse in each cycle. The cathodic peak current is represented as \(i_1\), and the cathodic on-time is \(t_1\). The anodic current is represented as \(i_2\), and the anodic on-time is \(t_2\). The relaxation time is \(t_r\). The sum of the cathodic on-time, anodic on-time, and relaxation time is the period of the pulse \((T = t_1 + t_2 + t_r)\), and the inverse of the period is defined as the frequency of the pulsed current. The ratio of the cathodic on-time to the period \((t_1/T)\) is the cathodic duty cycle \((D_1)\), and the ratio of the anodic on time to the period \((t_2/T)\) is the anodic duty cycle \((D_2)\). The current density during the cathodic on-time and anodic on-time is known as the cathodic peak current density and anodic peak current density, respectively. The average current density \((i_{ave})\) is the average cathodic current density \((D_1i_1)\) minus the average anodic current density \((D_2i_2)\).

[0056] Once the average current density \((i_{ave})\), pulse frequency \((f)\), cathodic duty cycle \((D_1)\), anodic duty cycle \((D_2)\), and the cathodic to anodic charge ratio \((Q_1/Q_2)\) are given, the cathodic and anodic on-time and relaxation time \((t_1, t_2,\) and \(t_r)\) and cathodic and anodic peak current density \((i_1\) and \(i_2)\) are determined from the following equations:

\[
T = \frac{1}{f}
\]

\[
D_1 = \frac{t_1}{T}
\]

\[
D_2 = \frac{t_2}{T}
\]

\[
Q_1 = \frac{i_1}{f}
\]

\[
Q_2 = \frac{i_2}{f}
\]

\[
i_{ave} = i_1D_1 - i_2D_2
\]

\[
T = t_1 + t_2 + t_r
\]

[0057] Another condition is:

\[
D_1 + D_2 \leq 1
\]

[0058] It should be noted that the cathodic on-time, anodic on-time, and relaxation time, and the cathodic and anodic peak pulse current density are additional parameters available to control the electroplating process compared to conventionally used DC plating wherein the cathodic current flows for the entire duration of the plating process. Furthermore, the higher peak current in the forward cathodic phase of the pulsed reverse current cycle produces a finer grained deposit than that produced by DC of the same average current, thereby yielding a harder chromium layer. The reverse current portion of the cycle consumes nascent hydrogen, thereby keeping the local pH relatively low and prevents the formation of chromic hydroxide which adversely affects the hardness of the deposit. The consumption of nascent hydrogen also helps to avoid hydrogen embrittlement of the deposit. The relaxation period of the current cycle contributes to enhanced current efficiency and plating rate by allowing time for the chromium ions to diffuse to the cathode surface, thereby increasing the local concentration of chromium ions during the forward, plating portion of the cycle.

[0059] For chromium plating from a Cr(III) bath, a cathodic pulse is used having either a long duty cycle or a large pulse current to deposit chromium, followed by an anodic pulse with either a short duty cycle or a small pulse current to convert the nascent hydrogen gas formed during the cathodic cycle to \(H_2\), and a relaxation period to allow the Cr(III) ions to diffuse to the cathode surface and be available for subsequent deposition. During the cathodic portion of the pulse, chromium is deposited and hydrogen is evolved, analogous to the conventional chromic plating. During the anodic portion of the pulse the nascent hydrogen is consumed according to the following reaction:

\[\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-\]
In this manner, a low pH is maintained and chromic hydroxide precipitation is avoided. By properly adjusting the anodic and cathodic peak currents, the anodic and cathodic duty cycles, and the PRC frequency, nascent hydrogen can be consumed. Furthermore, the parameters can also be adjusted to provide that the net plating rate from the Cr(III) plating bath is equivalent to that achieved in current practice using Cr(VI) baths.

In DC plating, chemical additives are used to produce the desired properties of metal coatings. The additives influence a number of properties of deposits, including 1) brightness, 2) hardness, 3) corrosion resistance, and 4) mechanical characteristics, such as strength and ductility. In PRC plating the grain size and coating morphology can be adjusted by modifying the PRC wave forms. Therefore, desired coating properties can be obtained with PRC plating from an additive-free plating bath. If the bath is additive-free, the used solution can be replenished and recycled to the plating tank without contaminated drag-in and zero discharge will be obtained. This will eliminate the disposal of toxic chromium compounds and reduce the environmental impact.

The trivalent chromium bath used for functional chromium plating according to the process of the invention may contain any salt of trivalent chromium that is sufficiently soluble to achieve a practical concentration of trivalent chromium ions in the solution. Suitable bath formulations containing trivalent chromium are disclosed in U.S. Pat. No. 5,415,763, the entire disclosure of which is incorporated herein by reference. Preferred salts are CrCl₃ and KCr(SO₄)₂. The bath may contain one or more suitable salts. The amount of trivalent chromium salt in the plating bath may range from about 0.6 g/L to about 40 g/L, preferably from about 22 g/L to about 28 g/L, calculated as the weight of trivalent chromium ions in the solution, that is from about 0.01 mole/liter to about 0.07 mole/liter, preferably from about 0.42 mole/liter to about 0.54 mole/liter of trivalent chromium. The pH of the plating bath may range from about 1.5 to about 3.5, preferably from about 1.9 to 2.6.

The trivalent chromium plating bath may contain other materials to assist in the plating process and improve the properties of the coated deposit. Preferred bath compositions are those given in the example below.

The frequency of the pulsed reverse current may be from about 5 Hz to about 10 Hz, preferably from about 10 Hz to about 200 Hz. The duty cycle of the forward pulses may range from about 50% to about 90%, preferably from about 80% to about 90%. The duty cycle of the reverse pulses may range from about 5% to about 30%, preferably from about 5% to about 15%. The ratio of current carried by the forward pulses to that carried by the reverse pulses may range from about 5:1 to about 80:1. The reverse pulses may be interposed between some or all of the forward pulses or a plurality of reverse pulses may be interposed between some or all of the forward pulses. It is preferred that the forward and reverse pulses alternate so that one reverse pulse is interposed between each pair of forward pulses, providing a pulse cycle as shown in FIG. 1. It will also be recognized by those skilled in the art that the pulses need not have the square waveform shown in FIG. 1. Any waveform that provides a forward pulse of current and a reverse pulse of current is suitable. Thus the wave forms may be, for example, square, trapezoidal sinusoidal, or even irregular or the like, so long as they provide for a forward cathodic duty cycle and a reverse anodic duty cycle. An asymmetrical sine wave would also be a suitable wave form. The actual shape of the waveform used in a particular application will be determined by practical considerations of electrical current supply equipment.

The invention will be illustrated by the following example, which is intended to be illustrative and not limiting.

**EXAMPLE**

**This example illustrates deposition of a functional chromium layer on a steel substrate.**

A steel rod 1.2 cm in diameter by 28 cm in length, of the type generally used in automotive shock absorbers, was measured with a micrometer and then prepared for electroplating by a conventional three-step treatment comprising an alkaline soak cleaning, electrocleaning, and an acid etch. Between each step of the preparation process the rod was thoroughly rinsed with water.

The rod was then mounted in a laboratory-scale electrolytic cell holding about 3 liters of electrolyte. The rod was configured as the cathode and the anode was an inert electrode.

Experiments were conducted using two different plating bath solutions. The first plating bath (bath A) was an aqueous solution containing the following ingredients in the listed concentrations.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrCl₃·6H₂O</td>
<td>125 g/L</td>
</tr>
<tr>
<td>Cr(SO₄)₂·12H₂O</td>
<td>25 g/L</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>178 g/L</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>80 g/L</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>31 g/L</td>
</tr>
<tr>
<td>HCOOH</td>
<td>60 mL/L</td>
</tr>
</tbody>
</table>

The pH of plating bath A was adjusted with potassium hydroxide to a value of 2.5. The specific gravity of the solution was 1.2. In bath B, the amount of formic acid was decreased to 30 mL/L, and the bath was used at its unadjusted pH of 2.0, as prepared. The electroplating was conducted at a temperature in the range of 20-60°C, to simulate commercial plating conditions in which the bath temperature is not closely controlled.

Test samples were plated using direct current and pulse reverse current (PRC) at various frequencies, average currents (Iave), cathodic and anodic duty cycles (Dc and Da) and charge transfer ratios (Qc/Qa).

After plating the rods were rinsed and dried and their diameters were measured with a micrometer to determine the thickness of the plating. The results are summarized in Table 1 below.
<table>
<thead>
<tr>
<th>Test</th>
<th>$I_{rev} (A)$</th>
<th>$f$ (Hz)</th>
<th>$D_{f}$ (%)</th>
<th>$D_{s}$ (%)</th>
<th>$Q_f/Q_s$</th>
<th>Bath</th>
<th>Plating Thickness (µm)</th>
<th>Plating Time (min)</th>
<th>Plating Rate (µm/min)</th>
<th>Current Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 DC</td>
<td></td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>15.7</td>
<td>30</td>
<td>0.76</td>
<td>18.5</td>
</tr>
<tr>
<td>2</td>
<td>30 100</td>
<td>80</td>
<td>5 10:1 A</td>
<td></td>
<td></td>
<td></td>
<td>40.6</td>
<td>30</td>
<td>1.35</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>30 100 90</td>
<td>8</td>
<td>10:1 A</td>
<td></td>
<td></td>
<td></td>
<td>40.6</td>
<td>30</td>
<td>1.35</td>
<td>33</td>
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<tr>
<td>4</td>
<td>30 100 90</td>
<td>5 20:1 A</td>
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<td></td>
<td>43.2</td>
<td>30</td>
<td>1.44</td>
<td>35</td>
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<td>25 10:1 A</td>
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For comparison purposes, a similar rod plated with a functional chromium layer from a conventional Cr(VI) bath exhibited a plating thickness of 8.9 - 12.7 µm, at a plating time of 10 min, a plating rate of 0.76-1.27 µm/min, and a current efficiency of 24%.

The best results with the process of the invention using bath A were those of tests 2 and 3 which achieved a plating rate of 1.35 µm/min and a current efficiency of 33%. The best overall result was achieved in test 12 wherein the plating rate was 1.85 µm/min and the current efficiency was 34%. This sample also had the best hardness and lowest porosity of the test samples. In test 13 a higher average current produced a greater plating rate. However, the coating had a greater porosity and lower hardness that the sample of test 12.

The results also show that the process of the invention is superior to the conventional process for electroplating decorative chromium layers from a Cr(III) bath using direct current wherein the deposition of chromium metal essentially ceases after a layer about 2.5 µm thick has been plated because of the precipitation of a layer of chromium hydroxide.

The data establish that functional chromium layers can be deposited from a Cr(III) bath with a plating rate and current efficiency comparable to those achieved with a conventional hexavalent chromium bath. Furthermore, the plating rate data show that pulsed reverse current can achieve a plating rate substantially greater than that obtained using direct current. The current efficiency of plating with pulsed reverse current is significantly greater than that of DC plating and comparable with that of conventional chromium plating. The hardness of the chromium layer deposited using pulsed reverse current under optimum conditions was equivalent to that of chromium coatings prepared by conventional plating from a hexavalent chromium bath.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:
1. A method for electrolytic deposition of metals on a cathode substrate comprising immersing an electrically conductive anode and an electrically conductive cathode in an aqueous plating bath containing metal-bearing ions, hydrogen ions, and hydroxide ions, said metal-bearing ions being capable of migrating to said cathode and being discharged at said cathode and depositing metal thereon, said hydrogen ions being capable of migrating to said cathode and being discharged at said cathode to form hydrogen gas, whereby the concentration of said hydroxide ions in the vicinity of said cathode is increased, said metal-bearing ions being capable of reacting with said hydroxide ions in the vicinity of said cathode whereby deposition of said metal on said cathode is inhibited;
2. The method of claim 1 wherein said pulsed reverse current has a frequency of about 5 Hz to about 700 Hz;
3. The method of claim 1 wherein said pulsed reverse current has a frequency of about 10 Hz to about 200 Hz;
4. The method of claim 1 wherein said forward pulses of said pulsed reverse current have a duty cycle of from about 50% to about 90%.
5. The method of claim 6 wherein said forward pulses of said pulsed reverse current have a duty cycle of from about 80% to about 90%.
6. The method of claim 1 wherein said reverse pulses of said pulsed reverse current have a duty cycle of from about 5% to about 30%.

7. The method of claim 1 wherein said reverse pulses of said pulsed reverse current have a duty cycle of from about 5% to about 15%.

8. The method of claim 1 wherein a reverse pulse is interposed between at least some of said forward pulses.

9. The method of claim 1 wherein a reverse pulse is interposed between each pair of forward pulses.

10. The method of claim 1 wherein the ratio of electric charge carried by said forward pulses to electric charge carried by said reverse pulses is from about 5:1 to about 80:1.

11. The method of claim 1 wherein a relaxation period of no current flow is interposed between a reverse pulse and a following forward pulse.

12. The method of claim 1 wherein said metal-bearing ions contain trivalent chromium.

13. The method of claim 1 wherein said metal-bearing ions contain gold.

14. The method of claim 1 wherein said metal-bearing ions comprise ions containing zinc and ions containing nickel.

15. The method of claim 1 wherein said metal-bearing ions comprise ions containing zinc and ions containing tin.

16. The method of claim 1 wherein said metal-bearing ions comprise ions containing cerium and ions containing cobalt.

17. In a method for electrolytic deposition of metals on a cathode substrate by immersing an anode and a cathode in an aqueous plating bath containing metal-bearing ions and passing an electric current between said anode and said cathode, wherein said metal-bearing ions are capable of migrating to said cathode and being discharged at said cathode, and are capable of reacting with hydroxide ions generated in the vicinity of said cathode by evolution of hydrogen at said cathode, the improvement comprising controlling excessive evolution of hydrogen at said cathode by using as said electric current a pulsed reverse current.

18. A method of depositing a layer of chromium metal on a substrate comprising

   providing an aqueous plating bath containing a water-soluble salt of trivalent chromium;

   immersing in said plating bath a cathode comprising an electrically conducting substrate and an anode;

   passing an electric current between said anode and said cathode wherein said current is a pulsed reverse current having a frequency of from about 5 Hz to about 700 Hz, said pulsed current comprising forward pulses having a duty cycle of from about 25% to about 95%, and reverse pulses having a duty cycle of from about 50% to about 5%, said reverse pulses being interposed between at least some of said forward pulses.

19. The method of claim 18 wherein said bath contains one or more water-soluble salts of trivalent chromium and the total concentration of trivalent chromium in said bath is from about 3 g/L to about 200 g/L.

20. The method of claim 18 wherein said bath contains one or more water-soluble salts of trivalent chromium and the total concentration of trivalent chromium in said bath is from about 3 g/L to about 200 g/L.

21. The method of claim 18 wherein said total concentration of trivalent chromium salt in said bath is from about 110 g/L to about 140 g/L.

22. The method of claim 18 wherein said plating bath has a pH of from about 1.5 to about 3.5.

23. The method of claim 22 wherein said plating bath has a pH of from about 1.9 to about 2.6.

24. The method of claim 23 wherein said plating bath has a pH of about 2.5.

25. The method of claim 18 wherein said water-soluble salt of trivalent chromium is selected from the group consisting of CrCl₃ and K₂Cr₂O₇.

26. The method of claim 18 wherein said pulsed current has a frequency of about 10 Hz to about 200 Hz.

27. The method of claim 18 wherein said forward pulses of said pulsed current have a duty cycle of from about 50% to about 90%.

28. The method of claim 18 wherein said forward pulses of said pulsed current have a duty cycle of from about 80% to about 90%.

29. The method of claim 18 wherein said reverse pulses of said pulsed reverse current have a duty cycle of from about 30% to about 5%.

30. The method of claim 18 wherein said reverse pulses of said pulsed reverse current have a duty cycle of from about 15% to about 5%.

31. The method of claim 18 wherein the ratio of electric charge carried by said forward pulses to electric charge carried by said reverse pulses is from about 5:1 to about 80:1.

32. The method of claim 18 wherein a reverse pulse is interposed between at least some of said forward pulses.

33. The method of claim 18 wherein a reverse pulse is interposed between each pair of forward pulses.

34. The method of claim 18 wherein a relaxation period of no current flow is interposed between a reverse pulse and a following forward pulse.