A process for plating aluminum, magnesium or zinc with an adherent nickel coating is provided. The process comprises contacting the surface of the metal to be treated with an aqueous solution of hydrofluoric acid or a material which releases hydrofluoric acid, such as ammonium bifluoride, a soluble, catalytic metal salt of a metal such as nickel, iron or silver, and subsequently applying a nickel coating which is stress-free to said treated metal surface, preferably 0.2 to 1 mil in thickness, from an amine borane reductive plating solution maintained at a pH of about 6 to 7 and containing an organic monovalent or divalent sulfur compound. A thicker nickel overcoating may be subsequently applied to the nickel coating using either hypophosphite or borohydride reductive plating baths, or electrodeposited nickel. Further, adhesion and wear resistance can be improved by post heat-treating.

BACKGROUND OF THE INVENTION

Field of invention

This invention relates to processes for plating metals and more particularly to processes for nickel plating aluminum, magnesium, zinc or alloys therebetween.

Prior art

Aluminum, magnesium and zinc are metals which are relatively soft and require a hard coating to upgrade their wear resistance and corrosion resistance, or to a coating to improve their solderability. Heretofore, the metals have been coated with a thin conversion coating such as chromate, which was adequate for metal-to-plastic wear contact but quickly broke down in metal-to-metal wear contact.

In U.S. Pat. 3,472,742, issued Oct. 14, 1969, to the National Aeronautics and Space Administration, the upgrading of aluminum surfaces is described. The prior art at that time is described as treating the aluminum surface with the usual etching bath, electroplating nickel onto the surface and then, to achieve satisfactory adhesion of the nickel to aluminum, the plated aluminum was baked at an elevated temperature as high as 500°C. Variations of this process have been in the etching bath or electroplating bath.

The claimed invention of the above-mentioned patent involves (1) etching the aluminum with a solution containing nitric acid and, optionally, hydrofluoric acid when the aluminum contains silicon, (2) applying a sodium silicate solution and then baking it on the aluminum, (3) nickel plating the treated aluminum with a hypophosphite electroless nickel plating solution, (4) applying an acidic rinse, and (5) applying an electroplated nickel. It is stated that such a process fills irregularities such as pits and voids which are present in the surface of the aluminum. Such elaborate processes produce nickel plates coated on the aluminum which exhibit only marginal adhesion performance and breakdown in metal-metal wear situations.

SUMMARY OF THE INVENTION

According to the present invention there is provided a process for plating a metal selected from the group consisting of aluminum, magnesium, zinc and alloys thereof, comprising: contacting the surface of said metal with an aqueous solution containing hydrofluoric acid and a soluble metal salt, the metal of said metal salt being a metal which is displaced by aluminum, magnesium or zinc and which is catalytic to the plating of nickel by chemical reduction, and reductively plating the treated metal surface with a nickel coating from an amine borane reductive plating solution maintained at a pH of about 6 to 7 and containing an organic monovalent or divalent sulfur compound.

DETAILED DESCRIPTION OF THE INVENTION

The present process for nickel plating aluminum, magnesium or zinc employs a specific pretreatment and a specific electroless plating bath to produce a nickel coating which does not delaminate under severe wear service conditions.

Initially, the metal article to be plated is contacted with an aqueous solution containing hydrofluoric acid, which can be derived from a material which releases hydrofluoric acid such as ammonium bifluoride or an alkali metal fluoride, and a soluble metal salt, from which the metal of the salt is deposited on the surface of the metal article as a thin, semicontinuous layer which is preferably catalytic to the subsequent electroless nickel step. The temperature of the solution is generally maintained below about 45°C, usually between 25 and 45°C, and preferably between 30 and 40°C. At temperatures much above 45°C the solution can eat away the article to be plated, leaving the surface pitted and less desirable for the subsequent electroless nickel plating operation; however, higher temperatures can be used if the treating solution is quite dilute and/or the contact time is quite short. An important consideration in the treatment is that the metal surface roughness will be within the range of 15 to 50 microinches.

The concentration of hydrofluoric acid in the aqueous solution is between about 1 and 25 percent by weight of the solution, and preferably will be between about 3 and 15 percent by weight. While the concentration of the metal salt will vary with the amount of hydrofluoric acid present, the upper limit will be the solubility of a particular metal salt in the solution and the lower limit will be the concentration at which pitting of the article to be plated occurs, i.e., the hydrofluoric acid is corroding or pitting the article's surface faster than the metal of the metal salt is being deposited. Generally, the concentration of the metal salt will be between 5 and 50 percent by weight of the solution.

The metal salt used in the solution must fulfill three requirements: (1) It must be soluble in the hydrofluoric acid solution (2) the metal of the salt must be displaced by aluminum, magnesium or zinc, as the case may be, when the solution is contacted with the metal article to be plated, and (3) the metal as deposited on the surface of the metal article to be plated must present a catalytic surface for the subsequent electroless nickel plating. Preferred salts are metal salts of acids such as the mineral acids and monobasic acids and oxides while the preferred metals of the salts are nickel, copper and silver. However, other metals which will fulfill the three requirements are aluminum, platinum, brass, manganese, chromi- um, titanium, molybdenum, tungsten, gold, platinum, cobalt and copper. The term "catalytic surface" as used in reductive plating refers to a surface which contains, either in whole or in part, a material which promotes on its surface the reduction of nickel ions.

The metal to be plated is treated with the above-described aqueous solution at the desired temperature with or without the application of a cathodic electric current to the part. The time of contact will depend on whether an electric current is applied. Generally, the time should

ABSTRACT OF THE DISCLOSURE

A process for plating aluminum, magnesium or zinc with an adherent nickel coating is provided. The process comprises contacting the surface of the metal to be treated with an aqueous solution of hydrofluoric acid or a material which releases hydrofluoric acid, such as ammonium bifluoride, and a soluble, catalytic metal salt of a metal such as nickel, iron or silver, and subsequently applying a nickel coating which is stress-free to said treated metal surface, preferably 0.2 to 1 mil in thickness, from an amine borane reductive plating solution maintained at a pH of about 6 to 7 and containing an organic monovalent or divalent sulfur compound. A thicker nickel overcoating may be subsequently applied to the nickel coating using either hypophosphite or borohydride reductive plating baths, or electrodeposited nickel. Further, adhesion and wear resistance can be improved by post heat-treating.

Claims

1. A process for plating a metal selected from the group consisting of aluminum, magnesium, zinc and alloys therebetween comprising: contacting the surface of said metal with an aqueous solution containing hydrofluoric acid and a soluble metal salt, the metal of said metal salt being a metal which is displaced by aluminum, magnesium or zinc and which is catalytic to the plating of nickel by chemical reduction, and reductively plating the treated metal surface with a nickel coating from an amine borane reductive plating solution maintained at a pH of about 6 to 7 and containing an organic monovalent or divalent sulfur compound.

2. The process of claim 1 wherein the material utilized in the aqueous solution containing hydrofluoric acid is ammonium bifluoride or an alkali metal fluoride, and the soluble metal salt is such a metal salt of a metal which is catalytic to the plating of nickel by chemical reduction.
be as short as possible to avoid corroding the surface of the article but still deposit a layer of metal from the metal salt. If an electric current is used, the contact time will be from about 1 to 10 seconds, while about 0.5 to 10 minutes will be used if no electric current is applied. In the latter case, an optimum time is about 1 minute.

After treatment with the above-described aqueous solution, the treated article is nickel plated from an amine borane chemical plating bath maintained at a pH of 6 to 7 which contains an organic monovalent or divalent sulfur compound. Such a bath yields a ductile coating with low stress, i.e., when the coating is self-supporting, it is free from distortion caused by tensile or compressive forces. Amine borane plating baths are known to those skilled in the art. U.S. Pat. 3,062,666 issued to Henry G. McLeod on Nov. 6, 1962; U.S. Pat. 3,338,726 issued to Talivaldis Berzins on Aug. 29, 1967; and U.S. Pat. 3,234,031 issued to Eberhard Zirngiebl and Heinz Günter on Feb. 8, 1966, describe amine borane nickel plating baths and processes for chemically plating nickel from such baths onto catalytic surfaces. The disclosures of these patents are hereby incorporated by reference. The plating bath pH is maintained between pH 6 and 7. At a pH above 7, the metal article tends to dissolve and at a pH below 6, the nickel coating will tend to have stresses which will cause the coating to delaminate. The stress level is dependent upon the presence of sulfur stabilizer and its concentration in the bath. Generally, the sulfur compound is at a concentration of 0.001 to 5 g./l and a concentration of 0.01 to 1 g./l is usually sufficient. Useful sulfur compounds are known to those skilled in the art.

The thickness of the nickel coating depends to some extent on subsequent treatments. For example, if the electrolecet plate nickel coating is to be overcoated with electroplated nickel or nickel applied from a standard sodium borohydride bath or sodium hypophosphite chemical plating bath, the thickness should be at least 0.1 mil, preferably from 0.2 to 1 mil. If no overcoat is to be applied, the thickness can be whatever is desired. Generally, however, 0.2 to 2 mils will be sufficient for most end-use applications.

To improve the adhesion, hardness and wear resistance of the nickel coating, the coating can be heat-treated at a temperature within the range of about 150°C to 300°C either after plating or after the nickel overcoat is applied.

One of the nickel plated aluminum sheets was heat-treated at 200°C in a forced air oven without damage. The coating adhesion was increased in that a smaller diameter bulge of greater severity was produced before delamination of the coating occurred. When an approximately 3 inch x 4 inch zinc panel was substituted for the aluminum in Example 1, similar results were obtained.

Using the dimethylamine borane plating bath of Example 1 and various aqueous treating solutions, the aluminum pieces of Example 1 were treated, plated and the plated pieces tested. The results are shown in Table II.

### Table II

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Treating solution (oz/gal)</th>
<th>Temp. °C</th>
<th>Time</th>
<th>Coated</th>
<th>Adherent</th>
<th>Continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl (90)-NaClO (10%)</td>
<td>77</td>
<td>1 min</td>
<td>Yes</td>
<td>Fail</td>
<td>Fail</td>
</tr>
<tr>
<td>2</td>
<td>NaCl (90)-NaClO (5%)</td>
<td>77</td>
<td>1 min</td>
<td>Yes</td>
<td>Fail</td>
<td>Fail</td>
</tr>
<tr>
<td>3</td>
<td>NaCl (90)-NaClO (1%)</td>
<td>77</td>
<td>1 min</td>
<td>Yes</td>
<td>Fail</td>
<td>Fail</td>
</tr>
<tr>
<td>4</td>
<td>NaCl (90)-NaClO (0.5%)</td>
<td>77</td>
<td>1 min</td>
<td>Yes</td>
<td>Fail</td>
<td>Fail</td>
</tr>
<tr>
<td>5</td>
<td>AgNO₃ (30)-H₂O (70%)</td>
<td>77</td>
<td>1 min</td>
<td>Yes</td>
<td>Fail</td>
<td>Fail</td>
</tr>
<tr>
<td>6</td>
<td>CuCl₂ (30)-H₂O (70%)</td>
<td>77</td>
<td>1 min</td>
<td>Yes</td>
<td>Fail</td>
<td>Fail</td>
</tr>
</tbody>
</table>

**Example 7**

Example 1 was repeated except other sulfur compounds were substituted for thioglycolic acid with essentially equivalent results. These sulfur compounds were mercapto acetic acid, dithioglycolic acid, and...
2-mercaptobenzothiazine. Without sulfur in the bath the coatings were cracked and nonadherent.

**EXAMPLE 8**

Using the baths and procedure of Example 1, an aluminum alpha block used to test wear resistance in the ASTM Test D 2714 using the LFW-1 wear testing device was nickel plated to a thickness of 1.5 mils. The coating after 25,000 cycles had a scar in lubricated wear at 300 lbs. load of 15 mils.

As a control, an aluminum alpha block was treated with a standard zinicate solution (Control 2 in Example 1) and nickel plated in a standard sodium hypophosphite nickel plating bath at 90° C. to a nickel thickness of 1.5 mils. This nickel coating had a scar volume in the lubricated wear test of 1250 mils.

**EXAMPLE 9**

Example 1 was repeated to give a nickel coating on the pieces of aluminum 0.2 mil in thickness. A portion of the plated pieces was placed in a standard sodium borohydride nickel plating bath at 92° C. and a portion was placed in a standard sodium hypophosphite nickel plating bath at 90° C. until the coating increased in thickness to 1 mil. Both coatings were adherent and there was no evidence of undercutting of the coatings despite a highly alkaline bath in the case of the sodium borohydride bath.

What is claimed is:

1. A process for plating nickel by chemical reduction on a metal selected from the group consisting of aluminum, magnesium, zinc and alloys therebetween comprising: contacting the surface of said metal with an aqueous solution containing hydrofluoric acid and a soluble metal salt, the metal of said metal salt being a metal which is displaced by aluminum, magnesium or zinc and which is catalytic to the plating of nickel by chemical reduction, and reductively plating the treated metal surface with a nickel coating from an amine borohydride reductive plating solution maintained at a pH of about 6 to 7 containing an organic monovalent or divalent sulfur compound.
2. The process of claim 1 wherein the temperature for contacting is below about 45° C. and the soluble metal salt is selected from the group consisting of salts of nickel, copper, iron and silver and is at a concentration in the solution ranging from the point at which hydrofluoric acid dissolves the metal surface faster than the metal from the metal salt is deposited, to the solubility limit of the metal salt in the solution.

3. The process of claim 2 wherein the hydrofluoric acid concentration in the solution is from about 1 to 25 percent by weight.
4. The process of claim 3 wherein the metal surface is immersed in the aqueous solution maintained at a temperature of about 30 to 40° C.
5. The process of claim 3 wherein the nickel coating is from about 0.2 to 1 mil in thickness.
6. The process of claim 5 wherein the nickel coating is overcoated with a coating of electroplated nickel, nickel reductively plated from a sodium borohydride plating bath or nickel reductively plated from a sodium hypophosphite plating bath.
7. The process of claim 6 wherein the nickel plated metal is heat-treated at a temperature within the range of about 150 to 300° C.
8. The process of claim 5 wherein the nickel plated metal is heat-treated at a temperature within the range of about 150 to 300° C.
9. A process for nickel plating a metal selected from the group consisting of aluminum, magnesium, zinc and alloys therebetween comprising: applying to the surface of said metal an aqueous solution of about 1 to 25 percent by weight hydrofluoric acid and 5 to 50 percent by weight of a nickel salt selected from the group consisting of nickel acetate, nickel oxide and a nickel salt of a mineral acid at a temperature within the range of about 25 to 45° C. and applying a nickel coating about 0.2 to 1 mil in thickness to the metal surface from an amine borohydride reductive plating solution maintained at a pH of about 6 to 7 and containing an organic monovalent or divalent sulfur compound.
10. The process of claim 9 wherein the nickel plated metal is heat-treated at a temperature within the range of about 150 to 300° C.

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U.S. Cl. X.R.

117—50, 71 M; 204—32 R, 37 R, 38 B, 38 S