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CATHODIC PROTECTION OF TITANIUM SURFACES

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ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, the process of this invention for protecting titanium from etching while immersed in an aqueous acid solution characterized by ability to etch a bare titanium-containing metal surface comprises placing said titanium in intimate electrical contact with a low hydrogen overvoltage metal, and maintaining on said titanium a low cathodic current density with respect to an anode in said solution for a time period greater than that required to etch said bare titanium-containing surface without application of said cathodic current.

This invention relates to a novel process for preventing etching of titanium surfaces.

Because of its resistance to chemical attack, titanium metal has been used in the fabrication of equipment which is exposed, during use, to corrosive materials. For example, titanium is used in heating elements, heat exchangers, racks, etc. which may be employed in metal-plating processes. However, it has been found that even corrosion-resistant titanium may be strongly etched by solutions containing halide ions, particularly when the solution is acidic and contains an oxidizing agent. Such solutions may be used in chromium plating, nickel plating, acid copper plating, acid tin plating, acid zinc plating, etc. Chromium plating baths are typical of the acid, oxidizing halide-containing baths and will hereinafter be referred to for purpose of illustration.

Chromium plating baths typically contain high concentrations of chromic acid, e.g. about 150–500 g./l. These baths may be catalyzed by fluoride ion, including simple fluoride and complex fluorides such as silicofluoride, fluoaluminate, fluoborate, fluotitanate, etc. Plating is generally carried out at elevated temperatures, say 34–72° C. Under these conditions, titanium heat exchangers, coils, heating elements or the like which may be present in the bath are rapidly attacked and etched. The service life of such equipment is thereby reduced, resulting in excessive replacement and maintenance costs. No satisfactory technique for preventing this corrosion has heretofore been found. Lacquers, coatings, tapes and the like flake off or fall off in the bath and also drastically reduce heat transfer which, of course, is highly undesirable.

It is an object of this invention to provide a novel process for protecting titanium from etching when in contact with corrosive baths. It is a further object to provide a process for preventing etching of titanium metal in contact with chromium plating baths. Other objects will be apparent to those skilled in the art upon reading the following description.

In accordance with certain of its aspects, the process of this invention for protecting titanium from etching while immersed in an aqueous acid solution comprises placing said titanium in intimate electrical contact with a low hydrogen overvoltage metal, and maintaining on said titanium a low cathodic current density with respect to an anode in said solution.

The process of this invention is effective for the protection of titanium, typically in the form of exposed ti-

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tanium surfaces. Typically, the surface to be protected may be the surface of plating equipment such as heating coils, heating elements, heat exchangers, partitions, stirrers, or the like. The equipment may be fabricated from titanium sheets, rods, titanium-clad sheets, etc. The titanium may be commercially pure titanium or high-titanium alloys, typically containing at least 90% titanium.

During use, the titanium equipment may be immersed in an aqueous acidic solution, including plating baths, cleaning baths, stripping baths, etc. The acid solution may typically contain dissolved halide ion, such as chloride, simple fluoride, complex fluoride, etc. The process of this invention may be particularly useful where the aqueous acid solution is a chromium plating solution containing chromic acid and fluoride, either as simple fluoride or as complex fluoride such as silicofluoride, fluoaluminate, fluotitanate, fluoborate, etc.

In accordance with this invention, the titanium surface to be protected may be placed in intimate electrical contact with a low hydrogen overvoltage metal. Hydrogen overvoltage is a measurement of the amount of work required to liberate hydrogen at the cathode. Thus, it is conventionally expressed as the difference in E.M.F. between the potential of the electrode when hydrogen is liberated during electrolysis and the potential of the reversible hydrogen electrode, both potentials being referred to the same electrolyte. A cathode having a lower hydrogen overvoltage will, therefore, generate hydrogen at a lower voltage than a cathode having a higher hydrogen overvoltage. Low hydrogen overvoltage metals, as the term is used in this application, are those metals which have a hydrogen or activation overvoltage less than that of the well known intermediate hydrogen overvoltage metals, such as copper. Typically, the metals which may be used in practice of this invention may have an overvoltage equal to or less than the overvoltage of clean, massive nickel. These low overvoltage metals may have an overvoltage of less than about 0.3 volts at a current density of 0.1 ampere per square decimeter, as defined, for example, in The Corrosion Handbook by H. Uhlig (John Wiley 1948) page 1144. As will be apparent to those skilled in the art, the hydrogen overvoltage of a metal may be modified by the method of treating the metal surface.

Typical low hydrogen overvoltage metals of this invention may include platinum, palladium, rhodium, gold, iridium, and nickel, including black nickel and electrodeless nickel, preferably in a finely-divided or active, catalytic form.

These metals, in a form suitable to provide a low hydrogen overvoltage, may be placed in intimate electrical contact with the titanium surface to be protected. They may be employed in connection with the titanium surface in a number of ways. One highly convenient method for applying the low hydrogen overvoltage metal is by depositing it electrolytically from a solution containing an ion of the low hydrogen overvoltage metal. Preferably, the solution may be an aqueous solution of a water-soluble compound which gives, in solution, an ion of the low hydrogen overvoltage metal.

These compounds of the low hydrogen overvoltage metals may include salts, acids, etc. They may provide ions of the low hydrogen overvoltage metal in the form of simple ions or complex ions. For example, chloroplatinic acid solutions may be employed as a source of platinum ions; and chloroauric acid may be employed as a source of gold ions. Complex ions of the metals may also be used, e.g. the halide and cyanide complexes of gold, the AuO_2^- (aurate) ion, etc. Similar equivalent metal compounds may be employed. When the low hydrogen overvoltage metal may exist in more than one oxidation or valence state, any of these may be employed for the plating bath.

Typical water-soluble compounds of the low hydrogen overvoltage metals which may be used include palladium dichloride, chloroplatinic acid, platinum chloride, platinum diamine dinitrite, potassium chloroplatinate, potassium chloroplatinite, tetramine platinous chloride, tetramine platinous fluoride, palladium nitrate, rhodium chloride, iridium tetrachloride, chloroiridic acid, gold chloride, gold cyanide, etc. The preferred compounds may include palladium chloride, gold chloride, and chloroplatinic acid and preferably these may be employed in aqueous solution.

The titanium surface to be protected may be placed in intimate electrical contact with the low hydrogen overvoltage metal by electrodepositing the low hydrogen overvoltage metal onto the titanium surface. Typically, this may be effected by immersing the titanium surface as cathode in a solution containing ions of the low hydrogen overvoltage metal, and passing electric current between said titanium surface and an anode in said solution.

Preferably, the low hydrogen overvoltage metal may be electrodeposited from an aqueous solution. Typically, the aqueous solution may contain about 0.5–20 g./l., preferably 2–10 g./l., say 5 g./l. of low hydrogen overvoltage metal ion, calculated as metal. Compatible acids, e.g. hydrochloric acid, or salts of complex-forming ions, e.g. sodium cyanide, may be added to maintain the low hydrogen overvoltage metal in solution, by maintaining the desired pH or excess of complex-forming ion.

The aqueous solutions may typically be maintained at a temperature of about 20–90° C., preferably 25–60° C., say 40° C. during electrodeposition of the low hydrogen overvoltage metal. Typically, the electrodeposition may be carried out at a cathode current density of about 0.5–5 a.s.d., preferably 0.8–2 a.s.d., say 1 a.s.d. for about 0.2–5 minutes, preferably 0.5–2 minutes, say one minute. The thickness of the low hydrogen overvoltage metal deposit may typically be of the order of about 0.05–0.50 micron, preferably 0.1–0.2 micron, say 0.15 micron. Thicker deposits may be employed if desired, but no substantial additional advantages may be realized thereby.

Other techniques may be employed for placing the titanium in intimate electrical contact with the low hydrogen overvoltage metal. For example, the titanium may be overlaid with a foil of the low hydrogen overvoltage metal. It may be coated by hot-melt dipping, by dusting with low hydrogen overvoltage metal powder, followed by fusing, by immersion plating, etc. The low hydrogen overvoltage metal may be provided as a thin foraminous sheet, including mesh, expanded metal, perforated metal, etc., in intimate electrical contact with, and preferably positioned immediately adjacent to and electrically connected with the titanium surface to be protected. The foraminous sheet may be made of the low hydrogen overvoltage metal or it may be metal, e.g. steel, coated with a low hydrogen overvoltage metal such as platinum or palladium in the manner noted supra. The titanium surface to be protected from etching may preferably be overlaid with and contiguous to the thin foraminous sheet.

The quantity of low hydrogen overvoltage metal required to effectively protect the titanium may be very small. Larger amounts may be employed, but it may be found that such larger amounts, i.e. thicker layers, will not be appreciably better for the prevention of undesir-

able etching. Although the preferred amount of low hydrogen overvoltage metal may be approximately the amount required to form a monomolecular layer thereof on the area treated, it may be found that a continuous monomolecular layer may not be formed. Instead, the low hydrogen overvoltage metal may be present in the form of discrete "islands," and a considerable percentage of the treated surface may be apparently exposed to contact with the plating solution. It would be expected that such exposed areas would not be protected and would be etched in the same manner as a totally untreated surface. Surprisingly, it has been found that even these relatively non-uniform treatments are highly effective in substantially eliminating the undesirable etching of the entire treated surface of the titanium article, when used under corrosive conditions in the manner described below.

During the period that the titanium surface in intimate electrical contact with the low hydrogen overvoltage metal is immersed in the aqueous acid solution, a low current density cathodic potential is maintained thereon with respect to an anode in said solution. Thus, the titanium surface in intimate electrical contact with the low hydrogen overvoltage metal is maintained cathodic to an anode in the solution by passage therebetween of a current at a low current density. The low current density which may be employed is typically 0.1–2 amperes per square decimeter (a.s.d.) and preferably 0.5–1 say 0.8 a.s.d.

The anode with respect to which the cathodic potential is maintained may, when the aqueous acid solution is a plating solution, be the anode or anodes normally employed in the plating operation. Other portions of the equipment, e.g. partitions, tank walls, etc. may also function as the anode. The desired current density may be provided from a relatively low output source of direct current which is electrically connected to both the anode and the titanium object.

Practice of specific embodiments of this invention may be observed from the following illustrative examples.

Five test strips measuring 2.54 x 7.62 x 0.08 cm. were cut from a sheet of titanium alloy having the composition 98% Ti and 2% Pd. Three of the strips were plated with a 0.15 micron deposit of platinum by electrolyzing them as cathode for one minute in an aqueous solution containing 6 g./l. of platinum, (16 g./l. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and 300 ml. per liter of aqueous HCl, a specific gravity of 1.19, at a current density of about 1 a.s.d. The remaining two strips were not plated.

Each strip was cleaned, weighed, and immersed in a chromic acid plating bath having the following composition at 55° C.

Component	Concentration (g./l.)
CrO_3 -----	225
SiF_6^- (added as K_2SiF_6) -----	2.3
SO_4^- (added as SrSO_4) -----	1.2

One plated and one unplated strip were simply immersed, without current, in the solution. Two plated strips and one unplated strip were made cathodic at 0.8 a.s.d. (0.05 a.s.i.) during immersion. At the end of the test, the strips were again weighed and the amount of titanium dissolved was determined and calculated as loss of weight in grams per square centimeter of surface per hour (gm./cm.²/hr.). The results of this comparison are shown in Table I.

TABLE I

Example	Surface	Conditions	Duration of Immersion (hrs.)	Weight Before Immersion (gms.)	Weight after Immersion (gms.)	Weight Difference	Weight change, gm./cm. ² /hr.
1-----	Pt electroplate-----	Cathodic-----	40	7.3344	7.3343	-0.0001	(1)
2-----	do-----	do-----	63	7.5570	7.5573	+0.0003	(1)
3-----	do-----	No Current-----	40	7.5728	7.5410	-0.0318	-0.000031
4-----	No electroplate-----	do-----	40	7.2738	7.2578	-0.0160	-0.000016
5-----	do-----	Cathodic-----	40	7.1564	6.5478	-0.6086	-0.00059

¹ Negligible.

As may be seen from Table I, Examples 1 and 2, which represent practice of this invention, showed substantially no change in weight during the test. Titanium surfaces protected by this novel technique would, therefore, remain free of corrosion and etching even after long periods of use. In contrast, the strips of Examples 3, 4, and 5 were badly etched by the chromium plating solution. It is noteworthy that the platinum electroplate in Example 3 did not protect the titanium but actually increased the corrosion to double compared to bare titanium with no plate in Example 4. It is also noteworthy that the bare titanium in Example 5 is not protected by the cathodic treatment alone, but instead corrodes about 38 times as fast as bare titanium which is simply immersed in the solution (Example 4).

Although this invention has been illustrated by reference to specific embodiments, various modifications thereof which clearly fall within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. The process for protecting titanium from etching while immersed in an aqueous acid solution which is characterized by ability to etch a bare titanium-containing metal surface which comprises placing said titanium in intimate electrical contact with a low hydrogen overvoltage metal, and maintaining on said titanium a low cathodic current density with respect to an anode in said solution for a time period greater than that required to etch said bare titanium-containing surface without application of said cathodic current.

2. The process of claim 1 wherein said aqueous acid solution contains dissolved halide ion.

3. The process of claim 1 wherein said aqueous acid solution is a chromium plating solution containing chromic acid and fluoride.

4. The process of claim 1 wherein said low hydrogen overvoltage metal is electrodeposited on said titanium.

5. The process of claim 1 wherein said low hydrogen overvoltage metal is selected from the group consisting of platinum, palladium, rhodium, gold, iridium and nickel.

6. The process of claim 1 wherein said low hydrogen overvoltage metal has a hydrogen overvoltage of less than about 0.3 volt at a current density of 0.1 ampere per square decimeter.

7. The process of claim 1 wherein said low cathodic current density is about 0.1-2 amperes per square decimeter.

8. The process of claim 1 wherein said low hydrogen overvoltage metal is platinum.

9. The process for protecting titanium from etching while immersed in an aqueous chromium plating solution containing chromic acid and fluoride which comprises placing said titanium in intimate electrical contact with a low hydrogen overvoltage metal selected from the group consisting of platinum, palladium, rhodium, gold, iridium and nickel; and maintaining on said titanium a low cathodic current density of about 0.1-2 amperes per square decimeter with respect to an anode in said solution.

10. The process of claim 9 wherein said low hydrogen overvoltage metal is electrodeposited on said titanium.

11. The process of claim 9 wherein said low hydrogen overvoltage metal is platinum.

12. The process of claim 9 wherein said low cathodic current density is about 0.5-1 ampere per square decimeter.

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