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TREATMENT OF TITANIUM SURFACES

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ABSTRACT OF THE DISCLOSURE

A method of electroplating titanium with copper or nickel including cleaning the surface in an etchant, then rinsing the etched surface in rinse water containing a small amount of a titanium complexing agent and then electroplating while the surface is still wet. Anions of cyanide, tartrate, citrate and acetate are disclosed as suitable chelating or complexing ions for the titanium. Subsequent nickel and chromium layers can be applied and then heat treated at above 400° C. The etchant can be HCl containing a minimum amount of a noble metal salt such as platinic chloride.

The present invention relates to the treatment of titanium surfaces, that is to say, surfaces made of titanium or titanium-base alloys.

Although titanium alloys have many desirable properties the use of these alloys for some engineering purposes has been restricted by their poor surface properties and various processes which have aimed at improving the surface properties have only had limited success in practice.

The invention is concerned with a treatment for a titanium surface which prevents it rapidly acquiring a coating of oxide and enables the surface to be successfully further treated. An unprotected titanium surface, either in the etched or unetched state, very rapidly acquires an oxide film either by direct atmospheric oxidation or by hydrolysis of titanium salts if immersed in an aqueous solution. This film of oxide frequently renders further successful treatment of the surface difficult or impossible.

In particular, the formation of an oxide coating on titanium surfaces has defeated attempts to secure consistently adherent electrodeposited coatings and a particular object of the present invention is to provide a process by which adherent metallic coatings can be electrodeposited on titanium surfaces, in order, for example, to increase the surface hardness or reduce their notorious tendency to gall.

In accordance with the invention, a process which substantially prevents the formation of an oxide film on a titanium surface comprises etching the surface, rinsing the surface immediately after it has been etched with a rinsing solution, and immediately placing the rinsed titanium surface with a film of rinsing solution retained on it in a plating solution and depositing a film of a metal, for example copper or nickel, on the surface by electrolytic action, the rinsing solution containing complexing anions with which titanium forms a soluble complex which always remains soluble in the rinsing and plating solutions.

Examples of complexing anions which may be used are cyanide and organic anions such as tartrate, citrate and ethylene diamine tetra-acetate anions.

The complexing anions must not be hydrolysed when passed into more dilute plating solutions or react in alkaline plating solutions to form in either case a precipitate which would interfere with the deposition of an adherent metal layer.

In carrying out the process it is important for the etched titanium surface to be placed immediately in the rinsing solution and to be transferred as rapidly as possible from the rinsing solution to the electrolytic solution as it is essential, in order to prevent the formation of an oxide film, for the titanium surface to be effectively covered with the rinsing solution containing complexing anions between the moment that it is freed from the etching solution to the moment that a film of metal begins to form on the titanium surface in the electrolytic solution.

Advantageously the electrolytic plating solution is, for example, a copper tartrate or copper cyanide plating solution, which already contains complexing anions before the introduction of rinsing solution on a titanium surface. In these circumstances, the rinsing and plating solutions would normally be provided with the same complexing anions but this is not mandatory.

Titanium surfaces are normally etched prior to electroplating treatment in order to remove oxide and any work-hardened layer. Titanium, however, can be etched only with difficulty; etching for example, with concentrated hydrochloric acid (S.G. 1.16) is a protracted process unless carried out at near boiling point. In accordance with a feature of the invention, etching is carried out by using more concentrated hydrochloric acid (e.g. S.G. about 1.18) whereby titanium surfaces can be effectively etched in a few hours (or even less for certain alloys) at a moderately elevated temperature (i.e. about 30° C.).

In accordance with a further feature of the invention, the effectiveness of this etching process is generally enhanced and in particular the period required for satisfactory results is reduced (in a typical case from about three hours to about one hour) by the introduction of a noble metal such as platium into the etching solution. This may be done by inserting an electrode of the noble metal, e.g. a platinum wire, in the etching bath and connecting it electrically to the titanium surface being etched, but more consistent results are generally achieved by adding to the bath a solution of a noble metal salt, e.g. platinic chloride. Only a small concentration is required, e.g. a 2% solution of chloroplatinic acid is effective if one part (or even less) is added to a bath containing 300 parts by volume.

The process as described, in accordance with the invention, is particularly useful as a preparatory stage in the formation of adherent coating of metals, for example chromium or nickel overlaid with chromium, electrodeposited on titanum surfaces to improve their surface properties, for example, to increase surface hardness and/or reduce the tendency to gall.

In accordance with an important feature of the invention, a process for providing a titanium surface with an adherent metallic layer comprises treating the titanium surface in accordance with the invention as above described, electrodepositing on the treated surface one or more further metal layers if desired, and finally subjecting the plated surface to heat treatment at a temperature of the order of 400–450° C. The further metal layers can be electrodeposited by conventional methods. Heat treatment is essential to produce adherent coating with a high order of consistency; treatment for the order of one hour has been found to produce consistently strong adhesion. If the initial film is of copper this should be a thin flash to avoid the formation of a layer of brittle intermetallic compounds with the titanium as a result of the heat treatment.

By carrying out this plating, electrodeposition and heat treatment process in accordance with the invention, ad-

herent coatings have been laid down on a variety of titanium alloy surfaces containing various alloying elements. Examples of these alloys with the percentage of alloying elements and the structure of the titanium alloys are as follows:

(1) 2.3 Al, 10.7 Sn, 4.1 Mo, 0.2 Si, 0.07 Fe; structure—($\alpha+\beta$)
(2) 4 Al, 4 Mn; structure—($\alpha+\beta$)
(3) 5 Al, 2.5 Sn; structure—(α)
(4) 2 Cu; structure—(α)
(5) 3 Al, 11 Cr, 13 V; structure—(β)

By way of example, there will now be described a process for laying down an initial metal film of copper on an article made of a typical titanium-base alloy containing 4% Al, 4% Mn, structure—($\alpha+\beta$). The article is first washed with carbon tetrachloride and is thoroughly scoured with pumice powder and alkali. After rinsing to remove pumice, the article is inspected for water-break and excess water is removed, e.g. by shaking.

The article is then immersed in hydrochloric acid of S.G. 1.18 at 30° C. for 3 hours. This removes a depth of approximately 0.001 in. of metal. The article is then transferred directly from the etching acid to a cold aqueous solution at room temperature containing 5% w./v. of Rochelle salt and is agitated for a few seconds.

After this rapid rinse the article is copper plated without delay. A suitable copper tartrate plating bath has the following composition:

	G.
Copper sulphate (crystals)	60
Sodium hydroxide	50
Rochelle salt (sodium potassium tartrate)	160

Water to 1 litre.

Cathodic connection is made before immersion. Current is applied for about 5 minutes at room temperature to give a current density of about 4 amps/sq. ft.

Alternatively, the etched article may be rinsed in a 5% w./v. sodium cyanide solution and the copper plating can be carried out in a conventional copper cyanide bath which may have the following composition:

	G.
Copper cyanide	22.5
Sodium cyanide	34
Sodium carbonate	15
Sodium thiosulphate	2

Water to 1 litre.

The pH value of the bath should be 11.5—12.5.

A Rochelle-type cyanide bath may also be used, a typical composition being as follows:

	G.
Copper cyanide	26
Sodium cyanide	35
Sodium carbonate	30
Rochelle salt	45

Water to 1 litre.

The pH value of the bath should be about 12.5.

Current is applied to either cyanide bath as for the copper tartrate bath.

Adherent layers of nickel and chromium can then be laid down on the copper-plated titanium surface, by way of example, by the following process.

The copper-plated titanium article is rinsed in water acidified with 1% v./v. of sulphuric acid and is then plated in a conventional Watts-type nickel bath with a layer of nickel, normally about 0.0005 in. thick. The electrical connection is again preferably made before immersion.

The nickel-plated article is rinsed in water and then chromium-plated to the required depth in a conventional chromium-plating bath, the electrical connection being again preferably made before immersion.

The article is then finally rinsed and dried and placed in a furnace at about 450° C. for one hour. It should be noted that the heat treatment may affect the properties of certain titanium alloys.

Tests show that titanium articles having features such as grooves and corners are consistently provided with adherent surface coatings by this procedure. Impacts of 1 ft.-lb. delivered by a sharp tungsten carbide punch failed in all but exceptional cases to cause any flaking (i.e. local detachment) of the deposited layers even when six or more impacts were delivered close together within a confined area.

Adherent coatings of chromium may be laid down directly on a copper flash without the intermediate nickel layer, for example, by missing out the nickel plating step from the process described above.

Adherent nickel coatings (overlaid with chromium if desired) may be laid down direct on an etched titanium surface which has been rinsed in Rochelle salt solution by immersing it directly in a nickel bath and then proceeding as described above. Although the nickel bath does not itself contain complexing anions, complexing anions in the rinsing solution are able to protect the titanium until nickel is deposited, particularly when this is rapid through the electrical connection being made before immersion. As used in the foregoing description and in the claims hereof, the term "titanium surface" includes surfaces of titanium base alloys as well as surfaces of titanium metal.

I claim:

1. A process for plating a titanium surface with another metal by electrodeposition from an electrolytic plating bath containing a salt of the metal to be deposited on said surface, comprising the steps, in sequence, of etching the surface to remove oxide therefrom, immediately thereafter rinsing the etched surface in an aqueous solution containing anions selected from the group consisting of cyanide, tartrate, citrate and acetate which form a complex with titanium soluble in said rinsing solution and in the electrolytic plating bath immediately after said rinsing step, immersing said surface while still wet with said rinsing solution in said plating bath containing a salt of the metal to be plated, and electroplating said metal on said surface.

2. A titanium surface electroplated according to the process of claim **1** with a layer of a metal from the group consisting of copper, nickel and chromium, said surface being substantially free of oxide and other impurities whereby the adherence of said layer to said surface is substantially increased.

3. A process according to claim **1** in which the metal deposited on the titanium surface is either copper or nickel.

4. A process according to claim **1** in which the plating solution already contains complexing anions before the introduction of the titanium surface.

5. A process according to claim **1** in which the said complexing anions are either tartrate or cyanide anions.

6. A process according to claim **1** in which the titanium surface is etched in concentrated hydrochloric acid having a specific gravity of about 1.18.

7. A process according to claim **1** in which at least one additional metal layer is then electrodeposited on the treated titanium surface, and the plated surface is finally subjected to a heat treatment at about 400–450° C.

8. A process for plating a titanium surface with another metal by electrodeposition from an electrolytic plating bath containing a salt of the metal to be deposited on said surface, comprising the steps, in sequence, of etching the surface with concentrated HCl having a specific gravity of about 1.18, in the presence of a noble metal such as platinum to remove oxide therefrom, immediately thereafter rinsing the etched surface in an aqueous solution containing anions which form a complex with titanium soluble in said rinsing solution and in the electrolytic plating bath immediately after said rinsing step, immersing said surface while still wet with said rinsing solution

in said plating bath containing a salt of the metal to be plated, and electroplating said metal on said surface.

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