GOVERNMENT OF INDIA: THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

Specification No. 114418. Application No. 114418 Dated 8th February, 1968. Complete Specification left on 28th November, 1968. (Application accepted 6th February, 1969)

Index at acceptance—70C4[LVIII(5)]

PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO THE DIRECT DEPOSITION OF PLATINUM OVER TITANIUM AND TITANIUM-BASED ALLOYS"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following Specification particularly describes the nature of this invention :—

This is an invention by PROF. KADARUNDALIGE SITARAMA GURURAJA DOSS, 1/2 Venkatarama Iyer Street, T. Nagar, MADRAS 17, SRINIVASA SAMPATH, Scientist, Central Electrochemical Research Institute, Karaikudi-3 and Miss KARAIKUDI SANKARANARAYANA SASTRI INDIRA, Scientist, Central Electrochemical Research Institute, Karaikudi-3, all Indian citizens.

This invention relates to improvements in or relating to plating of platinum directly over titanium.

Hitherto it has been proposed to plate platinum over precleaned titanium by spark welding, arc welding, vacuum deposition or electroplating followed by heat treatment. In all these processes, heat treatment is essential to allow interdiffusion of platinum on to titanium so as to render good adhesion possible.

This is open to the objection that—

(a) the hitherto known processes are laborious leading to platinum plates of limited thickness and of poor adhesion to the titanium due to the innate difficulty of removing the persistent oxide layer on the substrate,

(b) the conditions of heat treatment, which is indispensable are critical,

(c) the loss of platinum is higher, and

(d) the stabilities of the reported plating baths are too low.

The object of this invention is to obviate these disadvantages by devising a suitable method for electroplating platinum directly on titanium without need for subsequent heat treatment.

To these ends, the invention broadly consists in:—

(i) degreasing the titanium with an organic solvent like acetone, benzene or trichloroethylene,

(ii) dipping in a mixture containing alkali metal halides (such as sodium oir potassium fluoride 2% - 10%) in the presence of mineral acids (such as hydrochloric acid - 10%),

(iii) anodic and/or cathodic cleaning in an acid solution containing metal fluorides (25—100 g/l), hydrochloric acid (10—70 g/l) and an inhibitor of the type of tetraalkyl ammonium salt e.g. Cetyl trimethyl ammonium bromide, CTAB, (2-10g/l) at a temperature of 30 - 70°C at a current density of 0.1 to 0.5 A/cm² for 2 to 5 minutes.

(iv) electroplating platinum on to titanium treated as above from an alkaline solution containing hexahydroxyplatinate (in concentration ranging from 5-30 gl/Pt), alkali metal acetate (20-50 g/l), alkali metal hydroxide (20-100 g/l) and inhibitor like CTAB (1 to 10 g/l) at a current density of 5 mA-100 mA/cm² for a duration of 2 sec to 3 hours at a temperature of 30-90°C and a pH of 10-14 followed by rinsing.

The following typical examples are given to illustrate the invention.

Example 1

Pretreatment of titanium:

1. Degreasing in acetone.
2. Dip cleaning in the following solution for 2 minutes.

Sodium fluoride	20 gp/
Hydrochloric acid	50 gp/

3. Cathodic cleaning in the following solution for 2 minutes at 30°C at a current density of 0.2 A/cm²

Sodium floride	50 g/l
Hydrochloric acid	40 g/l
CTAB	4 g/l

Electroplating of platinum on titanium treated as above:

4. Platinum as potasium hexahydroxyplatinate : 20 g/l

Potassium acetate	20 g/l
Potassium hydroxide	50 g/l
CTAB	2 g/l
Current density	30 mA/cm²
Time of plating	60 min
Timperature	80°C
pH	12— 13
Current efficiency	90%
Thickness of platinum plating	5

The following are among the main advantages of the invention:

(i) The pretreatment bath developed and described is stable and helps to clean the titanium surface free of oxide film with little metal loss, which is a prerequisite for obtaining an adherent electroplate.

(ii) The plating bath developed and described is capable of being operated between wide limits of bath composition and other conditions.

(iii) The plating efficiency (cathode current efficiency) of the bath is high, nearly 80-90%, and the deposits are smooth and crack-free, ductile or hard.

(iv) The plating bath developed is stable, can be easily controlled and is readily regenerable.

The platinised titanium electrodes made as described above are robust and stand mechanical operations without the platinum being chipped off or peeled from titanium substrate.

(v) The platinum plating which is very adherent can be built to a considerable thickness of upto 10 microns.

(vi) The platinum plated titanium can be employed, without further heat treatment, as inert anode material in corrosive electrolytes as in the electrolytic production of chlorine, hypochlorites, chlorates, perchlorates etc.

Dated this 3rd day of February, 1968.

Sd./-

PATENTS OFFICER,

Council of Scientific & Industrial Research.

COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO THE DIRECT DEPOSITION OF PLATINUM OVER TITANIUM AND TITANIUM-BASED ALLOYS"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

This is an invention by Prof. KADARUNDALIGE SITARAMA GURURAJA DOSS 1/2 Venkatarama Iyer Street, T. Nagar, Madras-17, SRINIVASA SAMPATH, Scientist, formerly of the Central Electrochemical Research Institute, Karaikudi-3 and Miss KARAIKUDI SANKARANARAYANA SASTRI INDIRA, Scientist, of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to improvements in or relating to electroplating of platinum over titanium or titanium-based alloys.

Hitherto it has been proposed to plate platinum over precleaned titanium by spark welding, arc welding, vacuum deposition or electroplating followed by heat treatment. In all these processes heat treatment is essential to allow inter-diffusion of platinum on to titanium so as to make good adhesion possible.

The following are the drawbacks of the hitherto known processes:—

(a) The processes mentioned earlier are laborious leading to plates of platinum of limited thickness ($\sim 1\ \mu$) and of poor adhesion to the titanium due to the innate difficulty of removing the persistent oxide layer on the substrate.

(b) The conditions of heat treatment, an essential step, are critical.

(c) The platinum loss is higher.

(d) The stabilities of the reported platinum plating baths are too low.

The main object of the present invention is to obviate the disadvantages enumerated above by devising a suitable method for electroplating platinum directly on titanium, without the need for subsequent heat treatment.

The main findings underlying the invention are the electrolytic pretreatment of titanium to remove the oxide layer thereon and the electrodeposition of platinum on the surface of titanium so cleaned. The addition of a suitable inhibitor in the cleaning step and the incorporation of an addition agent in the plating bath are novelties leading to an adherent plate of platinum of adequate thickness.

The merit of the invention stems from the finding that adherent plates of platinum of thickness up to 10 microns on titanium is made possible by making use of the procedure described herein. The methods used earlier for cleaning the titanium to remove the oxide film were too drastic and usually resulted in reformation of the oxide (on exposure to air or water) which interferes with the adherence of the plating. The inhibitor made use of helps in removing the oxide and keeping an active metal surface. The addition agent in the plating bath helps to obtain smooth, uinform, adherent and thick deposits of platinum which do not need further heat treatment.

The other findings pertaining to the invention are that the platinum plating on titanium obtained is besides being adherent, bright and free from pores.

The present invention consists of a process for the electroplating of platinum directly on titanium or titanium-based alloys which comprises the precleaning of the surface to be plated free of the oxide film followed by the electro-deposition of platinum. The titanium base is first degreased using an organic solvent like acetone, benzene or trichloro-ethylene and is next subjected to a chemical cleaning step using a mixture containing alkali metal halides such as sodium and potassium fluorides in the presence of mineral acids. This is followed by anodic and/or cathodic cleaning at a current density of 0.2 amp per sq. cm. at room temperature in an acid solution containing alkali metal fluorides, hydrochloric acid and an inhibitor such as CTAB (Cetyl trimethyl ammonium bromide) in concentrations ranging from 25-100 gpl. 10-70 gpl and 2-10 gpl respectively. The final step in the process consists in the plating of platinum on titanium base thus treated making use of an alkaline bath containing hexahydroxyplatinate in concentration ranging from 5-30 gpl platinum, in the presence of an addition agent such as CTAB, 1-10 gpl followed by rinsing. The electroplating is carried out at a current density of 5-100 mA per sq. cm. and at a temperature of 30-90°C, the duration being varied from 2 seconds to 3 hours depending on the thickness required.

The wide range of conditions and concentrations possible as well as the good stability and reproducible characteristics of the cleaning bath and the plating bath make this process readily adoptable for obtaining adherent, bright and porefree deposit of platinum of desired thickness on titanium. The deposit does not require any further heat treatment.

The process developed and described hareir does not call for close control of operating conditions in order to obtain reproducibility adherent deposits of platinum on titanium. The novel features of the invention are the electrolytic cleaning which removes the oxide film on titanium and renders it ready to receive the platinum plating and the electrodeposition bath which helps to plate platinum on titanium to a thickness as high as 10 microns without need for subsequent heat treatment.

Description of the process.—The surface of titanium or titanium-based alloy required to be plated is first degreased in a suitable organic solvent like trichloroethylene to remove grease spots etc., which will hinder the plating and full coverage of the metal. Then the specimen is placed or dipped in a solution containing sodium and/or potassium fluoride (20 gpl) and nitric or hydrochloric acid (50 gpl) for one minute. Anodic and/or cathodic cleaning is next carried out at a current density of 0.2 amp per sq. cm. for two minutes at room temperature in a bath containing sodium/potassium fluoride (50 gpl), hydrochloric acid (40 gpl) and CTAB (4 gpl.). The clean specimen is transferred to the plating bath and made the cathode, the anode being platinum. The bath consists of platinum as hexahydroxyplatinate 5-20 gpl, potassium acetate 20-50 gpl, potassium hydroxide 20-100 gpl, CTAB 1-10 gpl, pH 10-14. The range of current densities that can be employed is 5-100 mA per sq. cm. and the operating temperature can be 30-90°C. Depending on the thickness of platinum required to be plated out, the duration of plating can be from 2 seconds upto 3 hours. After carrying out the plating the specimen is rinsed and dried.

The following typical examples are given to illustrate the invention:

	Example 1	Example 2
Pretreatment – Degreasing :		
Solvent used	Trichloroethylene	Benzene
Temprature	30°C	30°C
Duration	2 minutes	1 minute
Chemical cleaning :		
Composition of solution	Sodium fluoride 20 gpl hydrochloric acid 50 gpl	10 gpl
Temperature	30–70°C	50°C
Duradion	2 minutes	1 minute
Electrolytic cleaning :		
Anodic or cathodic or both		
Composition of solution		
Sodium fluoride	50 gpl	40 gpl
Hydrochloric acid	50 gpl	5o gpl
Inhibitor & concentration	2 gpl	4 gpl
Temperature	50°C	60°C
Current density	0.2A/cm²	0.1A/cm²
Duration	2 minutes	5 minutes

Electroplating of platinum :

Composition of the bath :	1	2	3
Potassium hexahydroxy platinate	20 gpl	12 gpl	20 gpl
Potassium hydroxide	50 gpl	30 gpl	60 gpl
Addition agent & concentration	2 gpl	1 gpl	2 gp
pH of the bath	12-13	11-12	13-12
Temperature	80°C	70°C	30°C
Current density	30 mA/cm²	10 mA/cm²	40 mA/cm²
Duration	2 hours	3 hours	2 hours

In both the examples cited above, the plating of platinum was smooth, bright, uniform, porefree and adherent. In example 1, the plating was 10 microns thick and in example 2, the thickness was 5 microns.

The following are among the main advantages of the invention:

(i) The pretreatment bath is stable and helps to clean the titanium surface free of oxide film with little metal loss, which is a prerequisite for obtaining an adherent electroplate.

(ii) The inhibitor incorporated in the pretreatment bath is not decomposed during use or during storage.

(iii) The wide limits of composition and operating conditions possible with the bath developed for platinum plating make for good flexibility.

(iv) The cathode efficiency of the bath is high (nearly 80-90%) and the deposits are smooth and crack free, ductile or hard.

(v) The plating bath is stable, easily controlled and readily regenerable.

(vi) The titanium or titanium-based alloy specimens directly plated with platinum by the process described hereinbefore are robust and stand mechanical operations without the platinum being chipped off or peeled from the substrate. (Tested by bend tests & drilling tests).

(vii) The platinum plating is very adherent and can be built up to a thickness of 10 microns.

The process developed for the plating of platinum directly on titanium or titanium-based alloys makes use of an electrolytic cleaning step in which the type of inhibitor used helps to remove the tenacious titanium dioxide film present on the surface and to keep the substrate in the active state during the subsequent plating operation. The stable platinum plating bath in which a new addition agent is incorporated leads to an electroplate which is smooth. porefiee and adherent and can be built to thicknesses not possible with baths reported earlier. This process does not require the post-deposition heat treatment considered essential to make good adhesion possible by allowing diffusion of platinum on to titanium.

WE CLAIM :

1. A process for the electroplating of platinum directly on titanium or titanium-based alloy comprising the pre-cleaning of the surface free of oxide film followed by the electro-deposition of platinum wherein the substrate surface is first degreased with an organic solvent like acetone, benzene or trichloroethylene and is next subjected to a chemical cleaning step for one minute in a mixture containing alkali metal halides such as sodium and potassium fluorides in the presence of mineral acids followed by anodic and/or cathodic cleaning at a current density of 0.2 amp per sq. cm. at room temperature for two minutes in an acid solution containing alkali metal fluorides, hydrochloric acid and an inhibitor of the tetraalkyl ammonium halide type such as cetyl trimethyl ammonium bromide (CTAB) in concentrations ranging from 25-100 gpl, 10-70 gpl and 2-10 gpl respectively and finally plating platinum on the surface thus cleaned making use of an alkaline bath (at pH 10-14) containing alkali hexahydroxy-platinate in concentration ranging from 5 to 30 gpl platinum in the presence of an addition agent of the tetra alkyl ammonium halide type such as CTAB (1-10 gpl) at a current density of 5-100 mA per sq. cm. at a temperature of 30 to 90°C the duration being varied from 2 seconds to 3 hours depending on the thickness of the plating required and rinsing the plated specimen free of electrolyte and drying.

2. A process as described in claim 1 wherein the specimen made of titanium or titanium based alloy is electrolytically precleaned by making it an anode or cathode.

3. A process as given in claims 1 and 2 wherein the electrolytic cleaning bath contains 25-100 gpl of alkali metal fluorides, 10-70 gpl of hydrochloric acid and 2-10 gpl of an inhibitor of the tetraalkyl ammonium halide type such as CTAB.

4. A process as described in the preceding claims wherein the electrolytic cleaning is carried out for two minutes at room temperature at a current density of 0.2 amp. per sq. cm.

5. A process as described by the aforesaid claims wherein the electrolytically cleaned specimen is directly electroplated with platinum, the plating bath containing 5-30 gpl platinum in the form of alkali hexahydroxyplatinate at a pH of 10-14 and 1-10 gpl of an addition agent of the tetraalkyl ammonium halide type such as CTAB.

6. A process as described in the previous claims wherein the cathodic current density for the electrodeposition can be varied in the range 5 to 100 mA per sq. cm. and the temperature of electrodeposition from 30 to 90°C.

7. A process as set out in the preceding claims wherein the electrodeposition of platinum can be carried out for a period of 2 seconds to 3 hours depending on the thickness required.

8. A process as described hereinbefore leading to a smooth, porefree and adherent electrodeposit of platinum directly on titanium or titanium-based alloys.

Dated this 21st day of November, 1968.

Sd./-
(R. BHASKAR PAI)
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GIPN—8(51)CP&D Cal./73—22-5-75—100