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PLATINIZING PROCESS

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ABSTRACT OF THE DISCLOSURE

A method for the adhesive deposition of a platinum metal group on a material consisting of titanium or its alloy or a material coated with titanium or its alloy by activating the surface of the material with a mixture of nitric acid, and hydrochloric acid, washing and drying the activated surface, depositing the platinum group metal thereon, and then heating said material with the deposit to a temperature of 300° C.

This invention relates to a process for platinizing titanium and titanium alloys, and more particularly to a process for producing an adhesive deposit of a metal of the platinum group upon a piece of titanium, of a titanium alloy, and a piece of material coated with titanium or with a titanium alloy.

The use of titanium or titanium alloy pieces are electrodes or current lead-ins for operations of aqueous or molten bath electrolysis is known. Such pieces may have a more conductive core than titanium. For example, cores of copper, iron, or aluminum coated with a sheath of titanium or of a titanium alloy have been used.

It is also known that titanium cannot be used as anode because a titanium oxide layer is formed which is a great resistance to current flow. This disadvantage is decreased by depositing on the titanium surface a noble metal of the platinum group.

Numerous processes have been proposed to impart to this deposit such qualities of corrosion resistance and of adhesion to the supporting metal as render its utilization possible in aqueous or molten bath electrolysis. Accordingly, it has been proposed to activate the titanium or titanium alloy surface by treatment with certain reagents before depositing the noble metal thereon. Examples of these reagents are as follows:

Hot or cold concentrated hydrochloric acid,
Hydrofluoric acid,
Mixtures of hydrofluoric acid and chromic acid or salts of the latter,
Mixtures of hydrofluoric acid, phosphoric acid and ammonia,
Nitric acid,
Mixtures of sodium fluoride and nitric acid.

After the activating treatment of the titanium surface, platinum is deposited thereon, either chemically or electrolytically, or by vacuum metallizing. Then the platinized piece is generally submitted to a thermal treatment under a vacuum or in the presence of an inert gas such as argon, neon, helium, or in the presence of hydrocarbons. The temperatures employed in the thermal treatment range between 400° C. and 1400° C.

These treatments have various disadvantages and in many of them there is a very important emission of hydrogen which diffuses into the titanium and causes a poor adhesion of the subsequent platinum deposit. This hydrogen diffusion also produces an embrittlement of the titanium during the mechanical stresses to which the piece is subjected when in service.

The thermal treatment of the platinized titanium is designed to eliminate the major part of the occluded hydrogen and/or to diffuse oxygen towards the interior of the piece by heating to a temperature at or above 400° C. Additionally, this thermal treatment improves the adhesion of the metal to the titanium. However, at the high temperatures generally used, an unwanted deformation of the pieces occurs and must be prevented for pieces partly coated with plastic materials and/or comprising a titanium sheath and a core made of another metal.

Hydrofluoric acid, or its salts used with an acid, corrode titanium strongly and irregularly; so they require a precise control over the conditions of the activating treatment to avoid perforation of the titanium, chiefly when the latter is a thin sheet. This is the case, in particular, for the pieces with a core formed of a conductive metal coated with a thin drawn or extruded titanium film. In all cases, a strong corrosion of the piece is observed and on micro-examination, comprises a substantial surface roughness which increases the porosity of the deposited metal for a given weight deposited per surface unit. For amounts less than about 20 mg. of metal per dm.^{2} of surface to be treated, platinum is deposited on certain points and a substantial portion of the titanium surface is left uncoated with the noble metal. For greater amounts of metal, the deposit looks continuous, but, in fact, does not adhere over the whole surface and thereby it is easily removable.

It has been suggested to oxidize titanium by electrolytic, chemical and/or thermal means before or after platinizing, but the formation of this titanium oxide layer requires particular precautions. Thus, if the oxide layer is formed thermally before platinizing, it is necessary during subsequent electrolytic platinizing that the reducing conditions be such as not to destroy this oxide layer. This requires a low voltage to limit the emission of the cathode hydrogen, or the addition to the electrolyte of a depolarizer such as hydrogen peroxide or any other oxidizing compound. If the oxide layer is formed thermally after platinizing on the zones uncoated with the noble metal, it is necessary to gradually cool down the piece under treatment.

The prior known treatments do not allow simultaneous obtention of desired activating conditions, such as a low production of a hydrogenizing agent during the activating, and the desired qualities for the activated or platinized piece. More specifically, these include smoothness of the activated piece; activating without noticeable dissolution of metal, irregular corrosion, modification in the sizes of the piece and embrittlement; good distribution of a thin deposit; good adhesion of a thin or a thick deposit; strength of the deposit regarding the mechanical stresses and during use of the piece in an electrolytic cell; possibility of using a heat treatment temperature which allows the application of such a treatment to bi-metallic assemblies or to pieces made partly of materials easily destroyed by heat.

My invention obviates these various disadvantages and complies with the requirements of a suitable previous pickling or activating treatment which is likely to produce the most favorable surface conditions, and of a post-platinizing heat treatment of the titanium to obtain the greatest adhesion of the platinum and a degassing of the titanium at relatively low temperatures. This invention relates to a process for obtention of an adhesive deposit of a metal of the platinum group on pieces of titanium or of titanium alloys and on pieces coated with titanium or one of its alloys. It comprises, after degreasing, activating the surface of the pieces to be platinized with a mixture of hydrochloric and nitric acids, washing and drying the activated surfaces, depositing the metal of the platinum group, rinsing and drying if need be, and lastly heating the pieces in air to a temperature not above 300° C.

Studies undertaken of the surface conditions of the base metal after various picklings have proven that, contrary to the common opinion, adhesion of the metallic deposit does not obligatorily depend upon surface rugosity prior to the deposit. I have observed that a low but regular rugosity leads to strongly adhesive deposits.

For this purpose, I measured, on the one hand, the rugosity with different kinds of rugometers on titanium previously submitted to various activating treatments and, on the other hand, the adhesion of the deposits produced on the same surfaces. As regards the rugosity, Swedish standards were used and these use a distance perpendicular to the surface between a level where a section plane cuts a length of crests equal to 5% of the base length, and a level where another section plane cuts a length of depressions equal to 10% of the base length. As regards the adhesion, classic methods of bending at 90° or 180° could not be used because the methods did not allow a differentiation between the deposits obtained on surfaces activated according to different means. A method which includes applying an adhesive tape under a pressure on the surface to be tested, taking off the tape under a charge and evaluating the amount of platinum taken off with the tape was used. The following Table gives some examples of the results obtained.

Activation of a Titanium Surface	Rugosity in Microns According to the Swedish Standards	Adhesion of a 200 mg. Platinum Deposit per dm.²
By HF at 10% for 15 seconds at 20° C..	1–1.5	Bad.
By HF at 10% for 15 seconds, then by HCl for 2 minutes at 60° C.	1.5	Good.
By HCl at 35% for 2 minutes at 60° C..	0.5–1	Do.
By a HCl-HNO_3 mixture for 30 minutes at 90° C.	0.3	Excellent.

Investigations with an electron microscope show that when the activation is carried out according to the invention with HCl-HNO_3 mixtures, platinum deposits corresponding to about 50 mg./dm.² cover practically the whole surface of the titanium; while, for an equal amount of platinum deposited, pickling with hydrofluoric acid leads to deposits which leave about 40% of the base metal surface uncoated.

It has been found that the titanium activation of the invention results from the action of the hydrochloric acid-nitric acid mixture. Hydrochloric acid used alone leads to a strong, irregular corrosion of the titanium; and nitric acid used alone tends to form on the titanium surface an oxidized layer with a structure which is unfavorable to the adhesion of the platinum deposit. The treatment of the titanium surface by a hot mixture, around the boiling point, of hydrochloric and nitric acids effects an excellent adhesion of the platinum. In this mixture the quantity of water can vary from 50 to 60% by weight; the quantity of HCl from 20 to 30% and the quantity of HNO_3 from 12 to 30%. It is possible, for instance, to obtain mixtures utilizable in the process of the invention by adding from 2 to 5 parts (by volume) of concentrated nitric acid of 1.42 density, to 10 parts (by volume) of concentrated hydrochloric acid at about 35%. After a 30-minute attack, a regularly distributed and perfectly adhesive deposit is obtained for platinum in amounts equal to or higher than 20 mg./dm.² of surface to be coated.

The metal of the platinum group is deposited by any known means, e.g., chemically, electrolytically, by vacuum metallizing, or by successively using two or several of these processes.

If the deposit is made electrolytically, it is necessary when platinizing to take the usual precautions such as tensioning the piece before the electrolysis, maintaining the tension while the piece is being extracted, agitating the bath and keeping its concentration within narrow limits, and watching the temperature and the pH.

After an eventual drying, the platinized piece is submitted to a thermal treatment which comprises heating in the presence of air, for instance in a ventilated oven, at a temperature between 200° C. and 300° C., and preferably near 250° C., for 1 to 3 hours, preferably 2 hours. The quality of the deposit is excellent, even if its thickness reaches several microns. To obtain very thick adhesive deposits, new deposits on the surface already platinized and thermally treated can be made. Thus, thicknesses of several tens of microns are obtained without any diminution of the adhesion.

The following non-limitative example illustrates the process of the invention, as well as three of its applications which aid in pointing out its advantages.

Example 1

Cells for the electrolytic production of sodium chlorate were equipped with graphite anodes. Current was supplied to these anodes through copper rods fitted in the graphite and having the end in contact with the graphite coated with titanium. The titanium sheath of 10.5 mm. in diameter and 150 mm. in length, had been platinized under the following conditions:

(1) Degreasing with trichloroethylene;
(2) Treating with a HCl-HNO_3 mixture formed of 2 parts of HCl at 35% and 1 part of concentrated HNO_3 at the boiling point of the mixture for 30 minutes;
(3) Washing, drying;
(4) Electrolytic platinizing in a Pfanhauser-type bath at a rate of 20 mg./dm.²;
(5) Washing, then drying at 110° C.;
(6) Annealing for 2 hours at 250° C. in an oven with an air circulation.

The pieces obtained were introduced into their housing without any deterioration of the platinum layer and due to the perfect adhesion of the layer; the copper-graphite potential drop was 3 mv. for an intensity of 50 amperes.

It would have been impossible to obtain such a value if the platinized piece had had to be annealed above 300° C. Effectively, it has been proven that the contact between copper and titanium is substantially deteriorated when the whole is treated at temperatures at least equal to 500° C., such as is recognized and generally used in the heat treatment of a platinized piece.

After one year's working, the copper-graphite potential drop was only 8 mv. With a similar piece, pickled under conventional conditions and unannealed, the potential drop reached 100 mv.

Example 2

A plant for the production of cobalt by electrolysis of a cobalt chloride solution was equipped with cells comprising 25 mm. thick graphite anodes, surrounded with a diaphragm. Each anode assembly had a total thickness of 60 mm. The average service life of these anodes was near 6 months. After this period, the graphite thickness was irregularly reduced, which rendered the cathode deposit heterogeneous because of a bad distribution of the current lines. Moreover, substantial corrosion of the graphite caused a formation of sludges which tended to clog the anode diaphragms. On the whole, the terminal voltage passed from 3.316 volts to 3.55 volts for a cathode current density of 3.5 a./dm.².

On one of the electrolytic cells, the graphite anodes were replaced by titanium parts coated with a platinum layer of 200 mg. per dm.² of surface to be coated and obtained according to the process of Example 1. These anodes were formed of 3 mm. thick, 360 mm. long and 800 mm. high perforated titanium sheets. One of these anodes and its surrounding diaphragm were 15 mm. thick, which allowed 16 anode-cathode assemblies to be placed in this cell instead of 10.

After 6 months with the same cathode current intensity

as above, the terminal potential remained 3.1 volts. Then, the anodes were dismounted to be examined and, after this examination, again placed into service without any further platinizing.

Example 3

Platinized titanium anodes prepared as in Example 1 were used instead of graphite anodes in an electrolytic cell for the production of sodium chlorate.

The apparatus equipped with graphite anodes operated at 30° C. with an anode current density of 3 a./dm.^{2} under a voltage of 3.2 v. The graphite anodes were used for about 4 years.

The base metal of the platinized titanium anodes had been activated and platinized according to the process described in Example 1, with an amount of platinum deposited of 600 mg./dm.^{2}. It was possible to work under electrolytic conditions unbearable for the graphite, that is, with an electrolyte temperature of 70° C. and an anode current density of 25 a./dm.^{2}. The Faraday yield reached 90% instead of 84% for the graphite, and the terminal voltage was 3.7 volts.

Despite such stricter conditions, the anode dismounted after 4 years presented a regular wear of the platinum layer which had become thinner without any showing of the base metal, and, accordingly, is a proof of the adhesive qualities of the platinum deposit on titanium.

While I have described preferred embodiments of my

invention, it may be otherwise embodied within the scope of the appended claims.

I claim:

1. A process for producing an adhesive deposit of a metal of the platinum group on a piece of titanium, of a titanium alloy, of a material coated with titanium, and of a material coated with titanium alloy, said process comprising activating the surface of said piece which is to receive said deposit by treating same with a mixture containing 20–30% by weight hydrochloric acid, 12–30% by weight nitric acid and 50–60% by weight water, washing and drying said activated piece, depositing said metal on said activated surface and heating said piece with said metal deposited thereon in air to a temperature between 200° C. and 300° C. for 1 to 3 hours.

2. The process of claim **1** characterized by carrying out said treating with said mixture of acids being substantially at the boiling point of said mixture.

3. The process of claim **1** characterized by said deposit being effected chemically.

4. The process of claim **1** characterized by said deposit being effected electrolytically.

5. The process of claim **1** characterized by said deposit being effected by vacuum metallizing.

No references cited.

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