United States Patent Office 3,729,392 Patented Apr. 24, 1973

3,729,392

PLATING OF TITANIUM WITH CHROMIUM

John Edwin Bride, Mentor, Ohio, assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.

No Drawing. Filed Feb. 19, 1971, Ser. No. 117,101
Int. Cl. C23b 5/06
U.S. Cl. 204—51 3 Claims

ABSTRACT OF THE DISCLOSURE

Titanium or titanium-base alloys can be plated with a semi-bright chromium plate of good appearance and durability. The titanium is plated by electrodeposition from a plating medium containing a solution of a particular chromic-compound. More especially the bath contains a solution of a complex, water-soluble trivalent chromic compound containing particular carboxylic acid constituents and halogen. Plated titanium articles can be used alone and exhibit a decorative surface, or they may be used as a base for subsequent coating operation.

BACKGROUND OF THE INVENTION

Plating of titanium or titanium-base alloys with chromium can provide a decorative effect or such effect with wear resistance. The coating is thus combined with a substrate offering desirable thermal stability coupled for example with high mechanical strength. However, electrodeposition onto a titanium-base metal of chromium plate has not always provided satisfactory results, as discussed, for example, in U.S. Patent 2,856,333. In view of this, novel methods have been employed with titanium, as for example the method disclosed in U.S. Patent 2,946,728, whereby there is formed a unique plated surface, by chemical displacement, from a solution where trivalent chromium ions are present with the etching substance. Further, U.S. Patent 3,065,154 discloses the formation of an ostensibly complex oxide film on the metal surface, with such film dissolving in the plating bath and thereby enhancing chromium plating conditions.

Various pretreatment techniques of the titanium substrate, prior to plating, have been reviewed in "Metal Finishing," vol. 67, pages 50–55. As is disclosed therein, close control is generally needed between etching conditions and plating criteria for satisfactory plate, and results are not always reproducible. Alternatives that ostensibly provide for adequate and reproducible surface preparation, may call for a multi-step pretreatment process, including a pretreatment bath of complex make-up, or for such treatment than can also involve additional expense as disclosed, for example, in U.S. Patent 3,207,679 and 3,412,000.

SUMMARY OF THE INVENTION

It has now been found that a semi-bright, or matte, chromium plate of good adhesion and endurance can be readily deposited onto a titanium or titanium-base alloy surface. Such surface can be prepared for plating by routine, straightforward techniques which need not involve complex preparation methods. The plate achieved on the titanium surface displays desirable resistance to flaking and cracking and can be used alone for decorative effect. Also, such plate provides an excellent basis coating on the titanium surface for subsequent coating operation, such as electrodeposited chromium plates from hexavalent chromium plating compositions.

Broadly the method of the present invention involves electrodepositing bright chromium plate onto a metal surface of titanium or titanium-base alloy, by establishing such surface as a cathode in contact with a chromium plating medium, providing contact between the medium and an anode, and passing current between the anode

and such cathode. The chromium plating medium comprises a complex, water-soluble, chromic compound containing carboxylic acid constituents and halogen constituents selected from the group consisting of chlorine, fluorine, bromine, iodine, and mixtures thereof. Further, the plating medium contains a molar concentration of chromium within the range from about 0.5 to about 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For plating the titanium or titanium-base alloy metal surface there is used a chromium plating medium containing a complex, water-soluble chromic compound. This compound contains carboxylic acid constituents plus halogen constituents that can be chlorine fluorine, bromine, iodine or mixtures thereof. However, in typical plating operation the bromine and iodine may lead to evolution of noxious fumes at the anode which may require special venting techniques for the plating bath. Therefore, chlorine, fluorine and their mixtures are preferred for the complex.

Although the water-soluble trivalent chromic compound need not have acid constituents representative of only an especial group of carboxylic acids, such acids which can or have been used for the chromic compounds are typically exemplified by monocarboxylic and dicarboxylic acids, with or without hydroxyl groups. For plating efficiency and water-solubility, advantageously the acids are non-aromatic acids containing less than about 10 carbon atoms, and for best efficiency contain less than about 6 carbon atoms and are saturated acids free from carbon-to-carbon unsaturation. Representative acids include glycolic acid, formic acid, oxalic acid and their mixtures. The compound of any of these acids such as a salt or ester thereof, which acts in any of the reactions such as those disclosed in more detail hereinbelow whereby the complex is formed, in the same manner as the free acid, can be used.

The complex virtually always contains a molar ratio of chromium atoms to carboxyl constituent within the range of 1:0.7 to 1:3, and further contains a molar ratio of chromium atoms to halogen atoms within the range of 1:0.1 to 1:3.5. Especially preferred ratios, based upon desirable plating performance and economy, can depend upon the acid as well as the halogen constituents of the complex. Thus, for example, for a complex containing a substantial amount of the carboxyl constituents supplied by glycolic acid, which complex is thus the preferred complex, and wherein such complex further contains chloride as the major amount, to all, of the halogen, the molar ratio of chromium atoms to halogen is preferably within the range of about 1:0.4 to 1:1. However, when the halogen in such a complex is preponderantly to all fluoride, the molar ratio of chromium atoms to halogen atoms is preferably within the range of about 1:2.6 to 1:3.2.

The complex can be prepared by any of several methods, and a representative of such methods will be discussed herein, which methods should not be construed as being exhaustive. One method is the straightforward combination of chromium metal with carboxylic acid plus hydrochloric acid. When such combination includes particulate chromium metal to reduce reaction time, the reaction can be highly exothermic, and therefore, caution needs to be taken in carrying out same. Typically for enhanced reaction efficiency, as the reaction proceeds and the evolved heat starts to diminish, external heating is applied; and, where the reaction proceeds in a liquid medium such as an aqueous medium, such external heating can involve refluxing of the reaction mixture to augment completion of the reaction.

The complex may also be prepared from the carboxylic acid and hydrochloric acid in admixture with chromic acid, typically charged to the reaction medium as a solution of chromic acid in water. The chromic acid can be supplied by any of the suitable substances for forming chromic acid in water, e.g., chromium trioxide. The reaction resulating from this method is also exothermic and caution in the use of such method is thus advisable. The complex may further by prepared by reaction of chromic halide, with such halide corresponding to the halide that is to be present in the complex, which chromic halide is reacted with the carboxylic acid, this reaction further involving the addition of strong base, e.g., an alkali metal hydroxide. For example, $CrF_3 \cdot 9H_2O$ may be used in this method and will readily prepare a chromium/carboxylic acid/fluoride complex involving exothermic reaction conditions.

The resulting complex is employed in a liquid medium typically, for efficiency and economy, supplied simply by water. However, the plating medium can contain other liquids, for example, polar aprotic liquids, with the preponderant amount of such liquid being water. Thus, the plating medium is typically referred to herein as an aqueous medium. Such polar aprotic liquids, referred to more particularly hereinafter, can provide certain plating benefits such as enhanced rate of deposition.

The complex is present in the bath in an amount to provide from about 25 to about 150 grams of chromium per liter, that is, the molar concentration of chromium in the plating medium is within the range from about 0.5 to about 3. The more highly concentrated baths having augmented viscosity are not well suited for deposition of chromium onto a titanium substrate which is immersed therein. Thus, such baths having a molar concentration of chromium above about 1.5 may be employed for brush plating of the titanium surface, but for bath operation wherein the article is immersed in the bath, such baths most always contain an amount of complex providing from about 25 to about 75 grams of chromium per liter. Within this concentration range the bath will be supplied with sufficient complex to avoid frequent bath replenishment during working, while retarding drag-out losses and avoiding any foam production during deposition operation.

Before deposition of chromium onto a titanium substrate, the bath is adjusted to a pH within the range from about 1.8 to 4.9. Such adjustment of pH can be readily carried out with a base, particularly alkali metal carbonates or hydroxides, with sodium or potassium hydroxide or their mixtures being preferred. Before addition to the bath, such material for adjusting the bath pH can be initially dissolved in water and the water solution then added to the bath.

The temperature of the bath during plating may range from about 20° C. up to advantageously, not substantially above about 50° C. for enhanced plating performance. For plating, the cathode current density will range between about 10 to about 700 amperes per square foot (a.s.f.). This range, preferably for enhanced plating performance, will be between about 70–300 a.s.f. When the titanium substrate to be plated is to be immersed in the plating bath, care should be taken that the surface to be plated is fully wetted by the plating bath prior to current flow. It is also advantageous for augmenting plating performance to start the current flow at the low current requirement and slowly increase the amperage during plating, i.e., during operation wherein the titanium article is immersed in the bath, and during typically not substantially longer than about seven minutes, which will provide a chromium deposit on the titanium surface having a thickness not substantially above about 0.0002 inch.

The bath can also contain a salt of a strong acid, preferably for economy, an alkali metal salt. Such salts enhance the conductivity achieved in the electroplating operation. Most preferably, for economy, the cation of the salt is sodium, potassium or their mixtures, and the strong acid anions should be those of an acid having a dissociation constant of at least $K=10^{-2}$, for example, chloride. The plating bath usually contains between about 50–200 grams per liter of such salts. The bath can also contain boric acid, or an equivalent to boric acid in aqueous solution, such as borax, boron oxide, or sodium oxyfluoborate. Such compounds operate in the bath to augment the rate of deposition of the chromium and are typically used in an amount between about 10–70 grams per liter of bath.

Typically for enhancing the chromium rate of deposition from the bath in the high current density area, minor amounts of organic additives can be added, as mentioned hereinabove. Such additives include polar aprotic substances which can be cyclic or acyclic organic materials or their mixtures. Representative of these additives are dimethyl formamide, tetrahydrofuran, dimethylsulfoxide, and mixtures thereof. These organic additives for enhancing the chromium rate of deposition in the high current density area may also be various ethers, thioethers, glycol hydroxy ethers, such compounds that also contain carboxyl groups, and their mixtures. These ethers and other substances should have more than 4 carbon atoms per molecule and have an atomic ratio of oxygen to carbon atoms within the range of 0.25:1 to 0.9:1.

The bath may also contain a sulfite component, for enhancing the chromium rate of deposition in the low current density area typically after considerable working of the bath, which component can be contributed by at least one compound, where such exists, of a metal sulfite, or metal bisulfite or metal meta-bisulfite, or trialkylammonium bisulfite as well as with mixtures of these. The substances may be added to the bath or formed in situ and those that are particularly preferred are the alkali metal and alkaline earth metal sulfites and bisulfites, e.g., sodium bisulfite.

Prior to carrying out the plating of the titanium or titanium alloy, the surface is first cleaned, typically by any suitable method employed in the electroplating art. For example, grease and oil can first be removed by vapor degreasing or by immersion of the article to be plated in emulsion or alkaline cleaner. The more difficult oxide coating can be removed by brushing or grinding or such operation in combination with pickling, e.g., dilute hydrofluoric acid pickling. Generally after such cleaning treatment the surface is further conditioned, suitably for initial or further removal of oxide films, by contacting with an etching composition. In general, such etch compositions include sulfuric acid, hydrochloric acid, acetic acid-hydrofluoric acid, ethylene glycol-hydrofluoric acid and this treatment may be combined with an activation plating treatment. The surface can be suitably rinsed with water and is then ready for plating.

Such plating is typically carried out in any vessel useful for chromium electroplating such as tanks lined with corrosion resistant material, including glass, ceramic material, polyvinyl chloride, and the like. The finished plated articles prepared in accordance with this invention show evidence of a tenaciously adherent bond between the chromium plate and the titanium base metal. Such bond may then be subsequently enhanced by any method suitable for augmenting interdiffusion in the bond between a metal coating and base metal, e.g., annealing.

In addition to employing the method of the present invention in coating, for example, the surface of titanium plate in conventional plating technique, the method of the present invention is also applicable to the plating of titanium and titanium alloy articles, that are made the cathode in a rotating receptacle coating apparatus immersed in the plating bath. Further, such method is applicable to the plating of a titanium surface by the use of a brush or stylus means for applying the plating composition to the titanium surface.

Regardless of plating technique, the resulting article may be used as is, i.e., the decorative effect of the chromium plate can be employed for its own desirable ap-

pearance. Also, such plated article may be subjected to subsequent coating operation. Such subsequent coating operation may be any of the coating applications that are applied over a chromium electrodeposit, e.g., application of a plastic film, but such coating is often a subsequent metal coating operation, that, in addition to including electroless plating, cladding, hot-dip plating, and vapor deposition, can be additional electroplating. Thus, the electroplating method of the present invention is further extended to include the further deposition on the chromium plated titanium basis metal of a hexavalent chromium plate. Such articles are found to offer excellent adhesion for the subsequent hexavalent chromium plate.

The following examples show ways in which the invention has been practiced, but should not be construed as limiting the invention.

Example 1

Three 1" x 4" titanium panels are prepared for coating by first cleaning in acetone and then placing the panels, as cathodes, in an alkaline electrocleaning solution, and thereafter passing a current in the bath for 3 minutes at 8 amps. Following this cathode cleaning, the panels are rinsed and are immersed for 5 minutes in a titanium etch solution containing 440 parts by volume of hydrochloric acid in 320 parts by volume of water, which solution is held near boiling during immersion. Thereafter, the panels are rinsed in distilled water and are ready for plating.

The plating bath is prepared by adding 42 weight parts of 50 percent chromium hydroxydichloride containing 50 weight percent of such compound dissolved in a balance of water, and 37 weight parts of 70 percent strength glycolic acid, i.e., glycolic acid containing 30 percent by weight water, into a reaction vessel followed by stirring of these substances in the vessel for 20 minutes. Thereafter, 32.5 weight parts of liquid potassium hydroxide containing 45 percent KOH in a balance of water, are slowly added to the reactor as agitation is continued. The reaction is exothermic and the temperature thereof rises to about 165° F. as the addition is continued for 2 hours. Thereafter, 7.5 weight parts of water are added to the reactor and the mixture is permited to cool.

A 667 milliliter (ml.) portion of the resulting chromic-containing plating complex having an approximate molar ratio of chromium atoms to carboxyl constituent of 1:2.25 and of chromium atoms to halogen atoms of 1:0.75 is diluted with water to 1100 mls. and heated to 140° F. To this, during heating, there is added 173 grams of potassium chloride and 84 grams of pulverulent, dry boric acid, and the resulting mixture is held at the 140° F. temperature for one-half hour. Subsequently, there is added to this mixture 15 mls. bis(2-methoxyethyl) ether and 5 grams of sodium meta-bisulfite to prepare a plating bath.

The bath is electrolyzed at a rate of about 30 amperes/gal., the pH readjusted to 2.8–3.2, and then the panels, one at a time, are made a cathode and immersed in the plating composition opposite a graphite anode. Each panel is plated for a time of five minutes at a plating bath temperature of 76° F. and the panels are each located with 3 inches anode to cathode spacing. The first two panels are plated at a current of 5 amps and 5.4 volts and the third panel is plated at a current of 4 amps and 5.2 volts. After plating, panels are removed from the bath and placed in distilled water.

Panels are then removed from the distilled water and are dipped for 15–30 seconds in an activator solution which comprises a water soluble dry acid powder dissolved in water at a concentration of 4 ounces of powder per gallon. This solution is used typically for activating electroplated nickel and for rinsing nickel brighteners from plated material. Following this dipping, the panels are water rinsed. After rinsing, panels are plated by immersing, as cathodes, in a proprietary hexavalent chromium plating bath prepared by adding plating salts to water at a rate of 180 grams per liter of the bath. Thereafter, sulfuric acid is added to the bath in a concentration of 5.2 fluid ounces of 66° Baumé sulfuric acid per 100 gallons of plating solution to provide 0.9 gram per liter of sulfate. Prior to plating the bath is electrolyzed for about 1–2 hours at a rate of about 300 amps per 100 gallons of bath with about 3 square feet of dummy cathode per 100 gallons of bath.

The first panel is plated in this proprietary bath for 30 minutes at a current of 7.5 amps and 4.7 volts and a bath temperature of 115° F. The second panel is plated therein for a time of 30 minutes with a current of 8.5 amps and 4.7 volts followed by plating for 20 minutes with a current of 12 amps and 5 volts, the bath being maintained during such plating at 115° F. The last panel is plated for 30 minutes with a current of 10 amps and 4.8 volts and the bath is maintained at a temperature during plating of 116° F.

By visual observation, the initial plating, on the prepared titanium surface, from the chromic-compound containing Cr(III) bath is observed to be a smooth, uniform plate with no visible evidence of chipping, cracking, flaking or other surface discontinuities. Visual observation following plating of such test panels with the proprietary hexavalent bath also shows the presence of a smooth, uniform bright chromium plate of good coverage and free from surface discontinuities and ostensible checking.

The first panel is then held in a Bunsen burner flame until the panel attains a cherry-red coloration, whereupon the panel is maintained in the flame for an additional three minutes, then removed and immediately quenched in unheated tap water. Upon removal from the tap water the panel is observed to have a typical light blue chromium coloration ostensibly arising from the chromium plate and still providing a plate of good adhesion on the base titanium metal, protecting same from oxidation.

The second panel is retained without heating, for comparative purposes, and the third panel is placed in a Bunsen burner flame and heated, so that about the bottom 1" x 1" portion attains a cherry-red coloration. The panel is then maintained in the burner flame for three minutes followed by quenching as described above. Like the first panel, this 1" x 1" area of the third panel upon removal from the tap water quench is observed to have the same blue coloration exhibiting desirable adhesion for the chromium plating on the base titanium metal, and hence affording desirable oxidation protection for such metal. Such visual inspection thus confirms the good adhesion of the Cr(III) chromium plate to the basic titanium metal. Also, such inspection shows that the Cr(VI) chromium deposit is still adherent to the Cr(III) deposit, even after the severe heat treatment.

A comparative Cr(III) plating bath, not contemplated for use in the present invention, but of interest for comparative purposes, is prepared as above described, e.g., containing, in water, potassium chloride and boric acid, and having a pH of about 3 as adjusted by sodium hydroxide. However, the bath contains a simple trivalent chromium glycolate plating complex not contemplated for use in the present invention, and more particularly described in U.S. Patent 3,006,823, and which is not the above prepared chromium/glycolate/chloride complex. After the bath is electrolyzed, and titanium panels are prepared for plating as above described, the titanium panels are immersed therein and are plated in a manner similar, but with even greater current intensity and for a longer period, to that described hereinabove for the Cr(III) bath, i.e., at a current intensity of 12 amps and 5 volts, and for a plating time of 15 minutes, while the bath is maintained at 80° F. It is noteworthy that such process, even with the greater intensity and longer time, fails to deposit a chromium plate on the titanium substrate, in contrast to the above-discussed results.

Example 2

Into a reaction vessel is added 1250 mls. of the 70 percent strength glycolic acid of Example 1 and 290 mls. of 37.3 percent strength hydrochloric acid which is 37.3 percent by weight HCl in water. Separately, into 1200 mls. of water, there is added sufficient chromic acid to provide 577 grams of chromium, expressed as CrO_3, in the resulting solution. As the glycolic acid and the hydrochloric acid are agitated, the chromic acid solution is gradually added with caution thereto and, without external heating, the reaction temperature is permitted to reach 95° C. After the chromic acid solution is added, the reaction medium is permitted to cool to room temperature and sufficient water is added to provide a volume of 2000 mls. of complex.

To a bath preparation vessel there is added 400 mls. of this freshly prepared complex and 500 mls. of water. These materials are then heated to 140° F., with stirring, and as agitation is continued there is added 83 grams of boric acid, 225 grams of potassium chloride, 100 mls. of a solution containing 10 milliliters of bis(2-methoxyethyl)ether in a balance of water. Following this, the pH of the bath is adjusted to about 3 with the addition of NaOH solution in water, the bath is then permitted to cool and is then electrolyzed at approximately 20 to 30 amp. hrs./gal.

A 3" x 5" expanded metal titanium coupon is given a scratch brush surface to prepare the coupon for plating. Thereafter the coupon is rinsed in tap water. The outside edge of the coupon is then taped to give a center 2" x 3" area for plating. This area is then brush plated by repeatedly dipping the stylus of a brush into plating solution from the above-described bath and after each dipping, manually brushing the freshly dipped stylus across the surface of the panel in short circular strokes.

The commercially available stylus is composed of a graphite block which is padded with a felt pad made from fibrous polyethylene terephthalate, which pad is then covered with an acid resisting cloth. With this type of plating, the stylus is made the anode and the titanium the cathode. For enhanced adhesion of the deposited chromium to the titanium substrate, the titanium surface is first completely wetted by the padded stylus when no current is flowing. Following this, the brush plating application is initiated while using low current at the start. The temperature of the plating bath is maintained at 80° F. and the current eventually reaches about 150 amps per square foot. Plating of both sides of the panel in this manner is completed in about 5 minutes. After this plating, the panel is rinsed in tap water and the plate visually inspected. Such plate is seen to be a smooth and uniform plate, free from visible checking and cracking and is deemed to be of desirable appearance and adhesion.

I claim:

1. The method of electrodepositing chromium plate onto a metal surface of titanium or titanium-base alloy, which method comprises establishing said surface as a cathode in contact with a chromium plating medium, providing contact between said medium and an anode, and passing current between said anode and said cathode, wherein said chromium plating medium comprises a complex, water-soluble, trivalent chromium compound containing carboxylic acid constituents of less than about 10 carbon atoms and halogen constituents, said carboxylic acid constituents being selected from the group consisting of non-aromatic dicarboxylic acids, monocarboxylic acids, dicarboxylic and monocarboxylic acids containing hydroxyl groups, and mixtures thereof, and said halogen constituents being selected from the group consisting of chlorine, fluorine, bromine, iodine and mixtures thereof, said plating medium containing a molar concentration of chromium within the range from about 0.5 to about 3 and said medium being maintained within a pH of between about 1.8–4.9 and at a temperature not substantially above about 50° C.

2. The method of claim 1 wherein said medium is supplied with chromic compound having a molar ratio of chromium atoms to carboxyl constituent within the range of 1:0.7 to 1:3, and a molar ratio of chromium atoms to halogen atoms within the range of 1:0.1 to 1:3.5.

3. The method of claim 1 wherein said halogen constituents are selected from the group consisting of chlorine, fluorine, and their mixtures and said anode comprises brush means.

References Cited

UNITED STATES PATENTS

2,829,091	4/1958	Missel	204—32 R
2,856,333	10/1958	Topelian	204—29
3,065,154	11/1962	Wiesner	204—32 R
3,069,333	12/1962	Deyrup	204—51
3,475,294	10/1969	Seyb et al.	204—51
3,560,274	2/1971	Ogden	148—31.5

FREDERICK C. EDMUNDSON, Primary Examiner