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ADHERENT ELECTROPLATING ON TITANIUM

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The present invention is generally concerned with the plating art and more particularly relates to a novel method of providing an adherent coating of chromium on a titanium or titanium alloy surface and with a unique plated titanium or titanium alloy body which combines strength and weight characteristics of titanium with the desirable surface characteristics of other metals.

Titanium offers important special advantages as a material of construction, but heretofore its use has been restricted because of one serious shortcoming of this metal and the alloys which contain it in major or preponderant portions. Titanium has a high strength-weight ratio and, accordingly, is of special interest in the aircraft industry. However, titanium cannot be used for any purpose where there is rubbing contact between two bodies of this metal. There is a marked tendency for titanium surfaces to seize when they are rubbed together so that ordinary bolts and nuts and landing gear parts cannot be made of titanium and its alloys with the expectation of satisfactory service even for the shortest periods of time.

It has been suggested previously by others that this difficulty could be eliminated or substantially minimized by providing coatings of harder metals such as nickel or chromium on titanium or titanium alloy bodies. However, to the best of our knowledge, no one has heretofore been able to provide coatings of this type which would bear up under the ordinary conditions of use. The problem is to establish a sufficient degree of adhesion between the coatings and the titanium base article; and, recognizing this, others skilled in the art have made many serious efforts along a number of different lines to improve adhesion of these coatings to titanium articles.

One of the apparently promising efforts to solve this problem was directed along the mechanical line, in that, it was attempted to establish a keyed-type of bond between the coating and the base article. Thus, the titanium body was deeply etched prior to electroplating to provide the pits and grooves necessary to the establishment of this type of attachment. It has been found, however, that in practice, this procedure cannot be relied upon to produce consistently adherent coatings; and it is, therefore, generally regarded as inadequate and unsuccessful.

The conventional electroplating procedures of the art developed in connection with the plating of other metals have been attempted with titanium and its alloys without success. Any films, coatings or plates which are thus established on the surface of the titanium body are not sufficiently adherent to the base metal for any practical use of the resulting article.

By making the present invention, we have provided the art, for the first time, with a completely satisfactory solution to this problem. Thus, not only can films, coatings or plates be provided on titanium articles to produce an object of practical utility under a wide variety of conditions where titanium was previously unsuitable, but also this result can be obtained without incurring any offsetting disadvantages economic or otherwise. The re-

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agents and plating baths employed in accordance with our invention may be inexpensive and easily compounded. Furthermore, the use of these reagents and baths in accordance with our discoveries is relatively simple, easy and straight forward, no complicated or difficult controls being necessary, and no special operator's skills being required for consistently satisfactory results.

There are several important and surprising discoveries we have made which provide the basis for the present invention in both its method and article aspects. In particular, we found that films having unique and valuable properties can be deposited on titanium and titanium alloy surfaces when these surfaces are contacted with certain solutions containing chromic and hydrofluoric acids. We also found that nickel can be electroplated directly on these films to produce a composite plate which adheres to the titanium base metal far more strongly than any other plate heretofore known. Still further, we have found that, by heat treating the resulting composite plate under certain time and temperature conditions, the adherence of the plate to the base article was improved, apparently through the establishment of an alloy bond so that the resulting article is capable of withstanding severe mechanical stress. We consider these discoveries surprising and unpredictable because the prior art did not suggest that such results could be obtained and because there is no precedent for pursuing the courses which resulted in these discoveries and in the integration of them into the present invention.

Described in a broad general way, the method of our present invention comprises the steps of immersing a surface of an article of titanium or titanium alloy in an aqueous acid solution of a chromium compound which contains trivalent chromium and fluoride ions and removing the article from contact with the said solution when a coating has been formed on the said article. As indicated above, in the production of an adherent composite coating, this method includes the additional steps of electroplating nickel on the said coating and then heating the resulting article and thereby forming a strong alloy bond between the composite coating and the article. Plates or deposits of chromium or other suitable metals may readily be established upon the resulting composite coating in subsequent operations to produce articles of a wide variety of surface characteristics.

Those skilled in the plating art will recognize that our present process embodies certain entirely new features and phenomena in the chemistry and electrochemistry of plating operations and novel reactions of chromium compounds. Thus, to the best of our knowledge, it has never before been known that films of this type could be deposited on a surface of another metal from an acidified aqueous solution of a chromium compound by the technique of immersion plating. In the course of the reactions leading to this result, hydrogen is evolved; and, at the same time, hexavalent chromium is reduced through the trivalent and possibly through the divalent form and is deposited on the titanium base metal as a film or in a film. We are inclined to believe that this film consists of metallic chromium, but because of the extreme thinness of it, we have not been able to prove this conclusively. Nevertheless, this reduction of chromium compounds by titanium is entirely unique to the best of our knowledge. Also, the deposition of such films on titanium was never heretofore known, so far as we know. Furthermore, the utilization of a film of this type on a titanium or titanium alloy article as a base for subsequent adherent plates of nickel is entirely new and, in addition, represents, as indicated above, a most unexpected characteristic of chromium.

We have found in pursuing the aforesaid discoveries and in the development of the process of the present

invention and of its preferred form that there are certain conditions which are critical to consistently satisfactory results. No films, coatings or plates of this type can be established on a titanium or titanium alloy surface by immersion deposition from freshly prepared solutions of chromic and hydrofluoric acids without some activating means through which some trivalent chromium is provided in solution. This means may take a variety of forms but, in every instance, will act as a chemical reducing agent in respect to the hexavalent chromium solution. Thus, for example, oxalic acid or titanium shavings may be added to and dissolved in the solution or a titanium or titanium alloy body may be immersed in the solution for a substantial period of time sufficient to result in the reduction of enough chromium ions to the trivalent form to start the coating operation at the desired rate. Alternatively, the initial solution may be composed of a trivalent chromium salt and a suitable acid. Best results may be obtained in accordance with our researches to date through the use of chromium trifluoride and oxalic acid, but we contemplate the use of other trivalent chromium compounds as well as other acids such as hydrofluoric, sulfuric, hydrochloric, fluoboric and trichloroacetic. It is, however, essential that both trivalent chromium and fluoride ions be present in these coating solutions.

We believe that the thickness of the films or coatings formed on the titanium articles treated in accordance with this invention is self-limiting and that only the thinnest type of deposit can be formed, regardless of time or temperature circumstances or reagent concentrations or ratios. Apparently, there can be no deposition on an article once the titanium surface portion thereof has been covered as a result of chromium compound reduction; and, while the addition of more titanium metal or alloy to the chromium compound immersion solution will result in more chromium reduction, any resulting deposition of chromium reduction product will be confined to the exposed titanium containing surfaces of such added material. A deposit of only a few molecules in thickness is sufficient to arrest deposition on a surface, and we have found that the articles of this invention invariably bear deposits of this magnitude, when sufficient time has been allowed for the system to arrive at an equilibrium condition with respect to the coating reactions.

In its article aspect, the present invention uniquely combines the strength and weight characteristics of titanium and its alloys with the surface characteristics of chromium or other metals. Such an article is produced by immersing in an aqueous acid solution of a chromium compound containing trivalent chromium and fluoride ions, a work piece of titanium or titanium alloy and removing the work piece from the solution when a coating has been formed on the said article. However, this invention also includes an article which has a composite coating made by electrodepositing nickel on the aforesaid article and then heating the article and thereby forming a strong alloy bond between the composite coating and the article. Still further, this invention includes those articles made by plating or depositing other metals on these composite coatings.

In practice, as we prefer to carry out our invention, the surface of the titanium or titanium alloy to be plated is first cleaned by suitable conventional means in use in the electroplating art. Thus, grease and oil are removed by vapor degreasing or by immersion in emulsion or alkaline cleaners, as necessary. Relatively heavy scale or oxide surface formations are removed by grinding or brushing or by dilute hydrofluoric acid pickle. After the cleaned article has been rinsed with water, it is immersed in a chromium immersion plating bath selected from among the several composition examples listed below; and, under the conditions therein specified, oxide films are thereby removed from the article, and the way is open for the deposition of a coating of this invention on

the resulting exposed titanium surface. After such coating has been established, the article is removed from the immersion plating bath and thoroughly rinsed with water and then preferably immediately plated with nickel from a suitable bath, such as a Watts type nickel bath, under standard conditions. We have employed a bath containing 240 gms. per liter of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 45 gms. per liter $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 30 gms. per liter of H_3BO_3 . The article is kept in the bath for twenty minutes, while the temperature of the bath is maintained at about 43°C . with the pH between about 4.5 and 5.0 and the cathode density between about 20 and about 65 amps. per square foot. The length of time devoted to this phase of the process of this invention will be determined by the thickness of the plate desired since time bears a direct relationship to plate thickness.

Best results can be obtained in this electroplating operation through the use of relatively low current densities of 10 to 20 amps. per square foot during the first few minutes of plating at which time the current can be increased to conventional plating levels. We contemplate the provision of a chromium plate on top of the resulting nickel plate; and, for this purpose, we prefer to use the electroplating bath disclosed in U.S. Patent Nos. 1,581,188 and 1,802,463 to Fink. A bath composition of about 250 gms. per liter of chromic anhydride and about 2.5 gms. per liter of sulfuric acid will produce consistently good results where the bath temperature is about 50°C . and the cathode current density is approximately 150 amps. per square foot.

Where it is desired to improve the degree of adhesion of the resulting composite coating and the base metal body for special uses under severe conditions, the resulting article can be heated to a temperature between about 300°C . and about 600°C ., suitably about 400°C ., and maintained at that temperature for between about 10 minutes and about 90 minutes, a period of about 30 minutes being preferred when the temperature approximates 400°C . The articles prepared in accordance with this procedure show evidence of interdiffusion and the formation of an alloy bond between the coating or plate and the titanium base article. It will be understood, however, that variations on this procedure may be employed with the expectation of consistently obtaining equally satisfactory results through the inter-relation of the time and temperature of the heat treating step. Generally, the higher the temperature, the shorter the time, and the lower the temperature, the longer time to produce a given bonding effect.

The following examples of solution compositions for producing uniformly satisfactory immersion chromium films on titanium surfaces are offered not by way of limitation of this disclosure or the appended claims, but merely for the purpose of illustration of this particular aspect of our invention:

Example I

	Preferred	Range
Chromic Acid, CrO_3	250 gms./l.	10 gms./l. to saturation
Hydrofluoric Acid, HF (50%).....	60 ml./l.	10 ml./l. to 240 ml./l.
Temperature.....	25°	20° to 80°C .
Time of immersion.....	7 min.	1 to 10 min.

This solution is treated at the outset with a reducing agent in the form of titanium turnings or oxalic acid for the production of trivalent chromium from the chromic acid constituent, the latter acting as a reservoir for chromium and being apparently reduced at a rate stoichiometrically equivalent to the removal of chromium from the solution in the form of metallic chrome.

Those skilled in the art will understand that the time-temperature-concentration relationships are such that the

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higher the temperature or concentration, the shorter the time required to produce a film.

Example II

	Preferred	Range
Chromium Trifluoride, CrF_3	20 gms./l.	10 gms./l. to 100 gms./l.
Oxalic Acid, $\text{H}_2\text{C}_2\text{O}_4$	40 gms./l.	20 gms./l. to 200 gms./l.
Temperature, 80-100° C.....	Time of immersion, 1 to 10 min.	

This solution has the special advantage of enabling the elimination of chemical controls and the additional advantage of being inexpensive. At the outset, this solution is deep violet in color and is effective as a coating solution as long as this color remains substantially unchanged. When its color becomes brownish-green, the bath is essentially exhausted. This bath may be made in quantity and stored without deterioration and used as required and is easy to use and offers the advantages of flexibility of the bath of Example I since the same general time-temperature-concentration relationships prevail here as well.

Example III

	Preferred	Range
Chromic Trifluoride, CrF_3	40 gms./l.	5 gms./l. to 50 gms./l.
Hydrochloric Acid, HCl (36%).....	40 ml./l.	10 ml./l. to 100 ml./l.
Temperature, 70° C.....	Time of immersion, about 3 min.	

Example IV

	Preferred	Range
Chromium Trifluoride, CrF_3	20 gms./l.	10 gms./l. to 100 gms./l.
Hydrofluoric Acid, HF (50%).....	12 ml./l.	5 ml./l. to 20 ml./l.
Oxalic Acid, $\text{H}_2\text{C}_2\text{O}_4$	20 gms./l.	10 gms./l. to 100 gms./l.
Temperature, Room.....	Time of immersion, about 20 min.	

Example V

	Preferred	Range
Chromic Acid, CrO_3	200 gms./l.	10 gms./l. to 1,000 gms./l.
Fluoboric Acid, HBF_4	14 ml./l.	6 ml./l. to 20 ml./l.
Oxalic Acid.....	20 gms./l.	5 gms./l. to 100 gms./l.
Temperature, 60° C.....	Time of immersion, about 15 min.	

Example VI

	Preferred	Range
Chromic Chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	5 gms./l.	0.1 gm./l. to 20 gms./l.
Hydrofluoric Acid, HF (50%).....	100 ml./l.	10 ml./l. to 200 ml./l.
Temperature, Room.....	Time of immersion, about 15 min.	

Example VII

	Preferred	Range
Chromic Chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	10 gms./l.	2 gms./l. to 25 gms./l.
Fluoboric Acid, HBF_4 (50%).....	25 ml./l.	10 ml./l. to 50 ml./l.
Temperature, Room.....	Time of immersion, about 20 min.	

There must be at least 2.8 grams per liter of fluoride ions, as shown in Example 4, where a minimum amount of 5 ml. per liter of a 50% hydrofluoric acid is added. This acid has a density of 1.198. Therefore, the weight of the hydrofluoric acid is $5 \times 1.198 = 2$. The amount of fluoride ions would be $\frac{1}{20}$ of this amount. This is equal to 2.8 grams per liter of fluoride ions. There must be a

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minimum amount of 0.02 gram of trivalent chromium ions per liter, as shown in Example 6, where there is 0.1 gram per liter of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ added (mol. wt. 266.38). 0.1 gram therefore is the equivalent of 0.02 gram of trivalent chromium.

Having thus described the present invention so that others skilled in the art may be able to understand and practice the same, we state that what we desire to secure by Letters Patent is defined in what is claimed.

What is claimed is:

1. A method of providing a chemical displacement coating on an article of a metal selected from the group consisting of titanium and titanium-base alloys which comprises the steps of contacting the surface of said article with an electrolyte consisting essentially of an aqueous acid solution containing at least 0.02 gram per liter of trivalent chromium ions and at least 2.8 grams per liter of fluoride ions at a temperature between about 20° C. and about 80° C. for between about one minute and about 30 minutes, and depositing chromium by chemical displacement from said solution onto said surface.

2. A method of providing a composite coating on an article of a metal selected from the group consisting of titanium and titanium-base alloys which comprises the steps of contacting a cleaned surface of said article with an electrolyte consisting essentially of an aqueous solution containing at least 0.02 gram per liter of trivalent chromium ions and at least 2.8 grams per liter of fluoride ions at a temperature between about 20° C. and about 80° C. and depositing chromium by chemical displacement from said solution onto said surface, removing said article from contact with said acid solution when said chemical displacement deposit has been established on the article and contacting the article as a cathode with a Watts-type nickel plating solution at a cathode density between about 10 to about 65 amperes per square foot and forming a nickel plate on said deposit.

3. The method according to claim 2 comprising the step of thereafter heating said article and maintaining the temperature of said article at about 400° C. for about thirty minutes.

4. The method of providing a composite coating on an article of a metal selected from the group consisting of titanium and titanium-base alloys which comprises the steps of contacting a surface of said article with an electrolyte consisting essentially of an aqueous acid solution containing at least 0.02 gram per liter of trivalent chromium ions, and at least 2.8 gram per liter of fluoride ions, depositing the chromium from said bath by chemical displacement onto said surface, removing the article from contact with said bath when said chromium has been formed on said article, and thereafter depositing a coating of nickel on said chromium coating.

5. The method of providing a coating on an article of metal selected from the group consisting of titanium and titanium-base alloys which comprises the steps of immersing a de-greased and de-scaled surface of said article in an electrolyte consisting essentially of an aqueous acid solution containing at least 0.02 gram per liter of trivalent chromium ions, and at least 2.8 grams per liter of fluoride ions, depositing chromium from said solution by chemical displacement onto said surface and removing the article from contact with said solution when the chromium coating has been formed on said surface.

6. The method according to claim 5 including the steps of electroplating nickel on said chromium coating and thereafter heating the article and forming a strong alloy bond between the composite coating and the article.

7. The method according to claim 5 including the steps of electroplating nickel on said chromium coating and then electroplating chromium on the nickel plate.

8. The method of providing a coating on an article of a metal selected from the group consisting of titanium and titanium-base alloys which comprises the steps of

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immersing a de-greased and de-scaled surface of said article in an electrolyte consisting essentially of an aqueous solution containing at least 0.02 gram per liter of trivalent chromium ions and about 25% by weight of chromic anhydride and about 6% by volume of 50% hydrofluoric acid for approximately seven minutes at a temperature of about 250° C. and depositing a coating of chromium by chemical displacement from said solution onto said surface.

9. A method of providing a coating on an article of a metal selected from the group consisting of titanium and titanium-base alloys which comprises the steps of immersing a surface of said article in an electrolyte consisting essentially of an aqueous acid solution containing at least 0.02 gram per liter of trivalent chromium ions, 10 to 1000 grams per liter of chromic acid, 6 ml. to 20 ml. per liter of 50% fluoboric acid solution, and 5 to 100 grams per liter of oxalic acid for between about 10 to 20 minutes at a temperature between about 20° C. and about 60° C. and depositing chromium by chemical displacement from said solution onto said surface.

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