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[54] **SURFACE TREATMENT OF TITANIUM**

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[63] Continuation of Ser. No. 558,243, June 17, 1966, abandoned.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **156/18,** 117/49, 117/50, 204/32, 252/79.1

[51] **Int. Cl.** **C23f 1/00**

[58] **Field of Search** 156/3, 18; 117/49–51, 106, 107, 119; 252/79.1, 79.4; 204/32, 143

[56] **References Cited**

UNITED STATES PATENTS

2,060,365	11/1936	Curtin	148/6.14
2,935,431	5/1960	Shaw et al	148/6.14

OTHER PUBLICATIONS

Timet, Titanium Metals Handbook for the Chemical Processor, printed by Titanium Metals Corp. of America, 1961

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[57] **ABSTRACT**

A matt etched surface is provided of titanium metal or titanium alloy, suitable for the deposition of an adhesive coating thereon by treating the surface of the metal or alloy with an aqueous solution of oxalic acid at a temperature greater than ambient temperature. Preferably the concentration of the oxalic acid solution should be greater than five percent.

9 Claims, No Drawings

SURFACE TREATMENT OF TITANIUM

This application is a continuation of application Ser. No. 558,243, filed June 17, 1966, now abandoned.

This invention relates to the surface treatment of titanium or titanium-base alloy articles prior to the deposition of a metallic or nonmetallic coating thereon.

Titanium or titanium-base alloys which are hereinafter referred to as "titanium alloys" for brevity, may be employed successfully in the manufacture of electrodes for electrochemical applications, provided that at least part of the surface of the titanium is coated with an adherent layer of a noble metal. However, in order to obtain satisfactory adhesion between the noble metal and titanium, it is necessary to pretreat the surface of the titanium prior to coating.

Hitherto, this has been accomplished by etching the surface of the titanium by immersion in concentrated hydrochloric acid. Satisfactory adhesion between deposit and substrate may be obtained in this way, but the etching process has several attendant difficulties.

As examples, at ambient temperatures the action of hydrochloric acid is slow and variable, treatment times of three days or more being required; alternatively, the acid may be used at its boiling point, thus shortening the treatment time to 30 minutes, but considerable difficulty is then encountered in dealing with the copious acidic fumes evolved and in containing the extremely corrosive acid. Furthermore, when titanium is etched in hydrochloric acid it becomes fouled with a black smutty deposit composed mainly of titanium hydride, which interferes with the subsequent coating process. It is, therefore, necessary to remove the deposit before attempting to electroplate the etched titanium, the only practicable method being to scour the etched surface with a mild abrasive. This is time-consuming and demands considerable skill on the part of the operator to remove the deposit without damaging the delicate structure of the etched titanium surface.

According to the invention, a process for treating at least part of a "titanium alloy" article to provide a surface suitable for the deposition of an adherent coating thereon, comprises treating said part with an aqueous solution of oxalic acid at a temperature greater than ambient temperatures.

Preferably the concentration of the solution should be greater than 5 percent weight/volume and its temperature should be maintained at at least 70° C, in order to produce the desired surface condition in a conveniently short time, but the optimum concentration and temperature will depend on the material to be etched and the surface required. For example, treatment with a solution containing 10 percent of oxalic acid at 80° C. (± 5° C.) will produce a satisfactory surface on commercial purity titanium sheet in 16 hours, whereas a similar surface may be produced in 8 hours by treating the metal in a 15 percent solution at 95–100° C. Thus it will be appreciated that etching conditions are not critical provided that they are kept fairly constant during the treatment.

The process of the invention provides a matt etched surface on titanium which acts as a suitable key for a variety of metallic or nonmetallic coatings. For example, metals may be deposited by means of electrolysis or thermal or chemical decomposition of metal salts; and nonmetallic coatings may be deposited by gas phase polymerization, vacuum decomposition or vacuum evaporation. An example of nonmetallic coating material is polytetrafluoroethylene which may be used to provide a low friction film on the titanium surface.

It is desirable to degrease the surface of the titanium before etching, but it is not necessary to remove oxide films which have been formed at low temperatures. Indeed, titanium articles which had been oxidized for 60 hours at 460° F. for one hour at 700° C. were successfully etched in an oxalic acid solution.

On removal from the oxalic acid etching solution, the titanium articles normally require only a simple water rinse before being subjected to the coating operation. However, on occasions, articles emerge from the solution with a light grey bloom on their surface, but unlike the smutty deposit previously referred to in connection with the hydrochloric acid treatment, this grey bloom can be removed by light brushing during the rinsing operation. In fact its removal is not essential for satisfactory electroplating.

Oxalic acid etching is less sensitive to variations in both metallurgical condition of the titanium and purity of the etching solution, compared with etching in cold hydrochloric acid. For example, commercially pure titanium articles having grain sizes from 0.01 (i.e., fine) to 0.08 mm. were etched satisfactorily in oxalic acid solution, whereas the fine grained commercially pure titanium is only etched with difficulty in hydrochloric acid. Furthermore, titanium containing up to 0.2 percent by weight of iron may be successfully etched, whereas even lower amounts of iron in titanium render it quite unsuitable for etching by hydrochloric acid. This latter difference is of economic importance, since it allows the use of technical quality rather than "Analytical Reagent" quality oxalic acid.

Under the preferred conditions, the metal loss of the titanium sheet etched is approximately 0.023g. per square centimeter of surface. Since the limit of solubility of titanium in 10 percent oxalic acid is 7–8g. per liter and, when this is exceeded, a very tenacious insoluble layer of crystals forms on the surface of the titanium being treated, it is advisable to limit the concentration of titanium salts in the solution. A practical limit of six g. per liter is recommended, equivalent to a throughput of about 260 square centimeters of titanium surface per liter solution.

The reaction between oxalic acid and titanium produces titanous oxalate which is, up to the limit mentioned above, freely soluble forming a brown solution. Upon exposure of this solution to air, the titanous titanium is readily oxidized to the colorless titanic form, and this inhibits further attack on metallic titanium. No difficulty arises from this effect in the 16 hour treatment, but because of this oxidation partly used solutions rapidly lose their potency on subsequent contact with air. This may be largely prevented by covering the surface of the etching solution with plastic chips or balls to exclude air. Alternatively, the titanium oxalate may be kept in the titanous form by continuous electrolytic reduction using a porous diaphragm, or by chemical reduction by means of pure aluminum sheet.

Assessment of the suitability of an etching pretreatment can, with experience, be made by visual and microscopic examination, but is made more often by determining how successful the coating proves to be in its subsequent application. Quantitive laboratory methods of assessment include measurement of surface roughness, adhesion of coatings subsequently deposited by electrodeposition, thermal decompositon and the like. Yet another method is to assess the durability of coatings in electrochemical applications.

Three comparative tests were used in assessing the surface quality of etched titanium produced by the present process.

1. Surface Roughness Test

This was applied to etched samples of titanium by means of a standard Talysurf examination, the degree of roughness being expressed as a centerline average (CLA), which may be defined as:

$$CLA = \frac{\Sigma \text{ areas of Talysurf trace above and below a mean line}}{\text{length over which areas measured}}$$

and is expressed in micro inches.

2. Adhesion Test

This was applied to etched and coated samples of titanium, by bonding the head of a mild steel bolt to the coated surface with an epoxy resin, and subsequently pulling the bolt from the sample with a standard tensile testing machine, the adhesion being proportional to the force required to remove the bolt from the sample. This force is expressed in pounds per square inch (p.s.i.) and is hereinafter referred to as the "Adhesion Value."

3. Stripping Test

This was applied to electroplated, etched titanium samples by pressing a strip of pressure-sensitive adhesive tape on the coating so as to expel all air bubbles between the tape and the coating and then removing the tape in a single sharp movement. The comparative results of the test were assessed by visual examination of the test were assessed by visual examination of the tested coating.

The invention will be further illustrated by the following examples, in which all solution concentrations are expressed as percentage weight/volume:

Example 1

A sheet of commercially pure titanium was etched in a 10 percent aqueous solution of technical grade oxalic acid maintained at 80° C. ± 5° C. for 16 hours. The sheet was then removed from the solution, rinsed in water and dried.

The surface roughness (CLA) of the sheet was then measured and found to be 150 micro inches. The CLA value before etching was 55 micro inches.

Example 2

Sheets of the same titanium stock material were heat-treated so that half had a grain size of 0.013 mm. and the remainder had a grain size of 0.080 mm. Sheets from each group were then etched in 10 percent oxalic acid solution using varying temperatures and times of immersion, and equivalent sheets etched in concentrated hydrochloric acid at room temperature for 72 hours.

The etched sheets were electroplated with platinum to a thickness of 100 micro inches and the plated sheets subjected to the aforementioned adhesion test. The results are tabulated below:

Grain size of sheet	Adhesion value (p.s.i.)							
	Etched in cold hydrochloric acid for 72 hrs.	Etched in 10% oxalic acid						
		1 hr., 80° C.	4 hr., 80° C.	16 hr., 80° C.	4 hr., 90° C.	8 hr., 90° C.	16 hr., 90° C.	8 hr., 95° C.
0.013 mm	301	273	820	800	780	700	820	708
0.081 mm	805	320	840	860	750	870	896	1,026

In each case the adhesion value is the mean of three tests.

Example 3

Two stocks of commercial purity titanium were selected, one having higher impurities than the other. Sheets were then cut from each stock and heat-treated so that half had a grain size of 0.020 mm. and the remainder 0.080 mm. The sheets were then etched in 10 percent oxalic acid at 80° C. for 16 hours or in concentrated hydrochloric acid at room temperature for 72 hours.

The etched sheets were coated with platinum to a thickness of 40 micro inches by thermal decomposition of a platinum-organic base paint composition which was applied to the surface of the sheets. The coated sheets were subjected to the adhesion test, the results being tabulated below:

Grain Size of Sheet	Adhesion levels in p.s.i.			
	Purer grade of titanium		Less pure grade of titanium	
	Etched in Hydrochloric Acid	Etched in Oxalic Acid	Etched in Hydrochloric Acid	Etched in Oxalic Acid
0.020 mm.	~4	480	~4	445
0.080 mm.	379	526	~8	546

Example 4

Sheets of commercial purity titanium were etched in 10 percent oxalic acid for varying times and at varying temperatures and similar sheets were etched in cold concentrated hydrochloric acid for 72 hours.

The etched sheets were then electroplated with platinum to a thickness of 100 micro inches and each sheet was inserted as anode in an electrolytic cell containing five liters of saturated sodium chloride solution as electrolyte and having a titanium cathode. The cells were operated continuously at an anode current density of 1,000 amperes per square foot for one week, at the end of which time the electrolyte was drained and the adhesion of the platinum coating on the anode assessed by means of the aforementioned "Stripping Test." The electrolyte in the cell was then renewed and the electrolysis continued for another week, this procedure was repeated to the end of the respective test. The results of the tests are tabulated below:

Grain size in mm.	Etchant	Etching time and temperature	Initial platinum adhesion in p.s.i.	Results of stripping test
0.013	Hydrochloric acid	Cold 3 days	301	Almost all platinum removed after 4 weeks.
0.013	10% oxalic acid	80° C., 1 hr.	500	Considerable platinum removed after 8 weeks.
0.013	do	80° C., 16 hr.	800	No platinum removed after 12 weeks.
0.013	do	90° C., 4 hr.	780	Do.
0.080	Hydrochloric acid	Cold 3 days	807	Do.
0.080	10% oxalic acid	80° C., 4 hr.	840	Do.
0.080	do	80° C., 16 hr.	860	Do.
0.080	do	90° C., 8 hr.	870	Do.

It will be seen from the above examples that etching titanium in oxalic acid solutions provides a convenient method of producing an etched surface on the titanium which provides a satisfactory key for coatings subsequently deposited thereon. Since no mechanical abrasion of the etched surface is necessary, the process is ideally suited to large scale production, particularly when applied to articles of large nonplanar or discontinuous surface area, such as wire, expanded mesh and the like.

What is claimed is:

1. In a process for depositing an adherent coating onto at least a part of a "titanium alloy" article wherein said part is contacted with acid to provide a matt etched surface and the coating is thereafter applied to said matt etched surface, the improvement which comprises using, as the acid, an aqueous solution of oxalic acid wherein the concentration of oxalic acid is greater than five percent weight/volume, and at a temperature of at least 70° C. and for a period of at least four hours, said temperature and time being sufficient to give said matt etched surface for application of said adherent coating thereon.

2. A process according to claim 1 wherein the acid concentration is greater than five percent but not in excess of 15 percent weight/volume and the acid solution is used for said etching treatment for only as long as titanium removed from said surface is soluble therein.

3. A process according to claim 1 wherein the temperature for contacting said part with the solution is at least 70° C. and up to 100° C.

4. A process according to claim 1 wherein said part is contacted with a 10 percent weight/volume aqueous solution of oxalic acid at between 75° C. and 85° C. for approximately 16 hours.

5. A process according to claim 1 wherein said part is contacted with a 15 percent weight/volume aqueous solution of oxalic acid at between 95° C. and 100° C. for approximately eight hours.

6. A process according to claim 1 comprising degreasing said part before contacting the same with the aqueous solution of oxalic acid.

7. A process according to claim 1 comprising rinsing said part with water after contact with the aqueous solution of oxalic acid.

8. A process according to claim 1 wherein the article is immersed in said acid solution and an adherent metal coating is applied to the matt etched surface.

9. In a process for providing a matt etched surface on at least a part of a "titanium alloy" article by contacting said part with an acid, the improvement which comprises using, as the acid, an aqueous solution of oxalic acid wherein the concentration of oxalic acid is greater than five percent weight/volume, and contacting the article with said oxalic acid solution at a temperature of at least 70° C. and for a period of at least four hours, said temperature and time being sufficient to give said matt etched surface.

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