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TITANIUM ANODIZING PROCESS

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ABSTRACT OF THE DISCLOSURE

An electrolyte composition for anodizing titanium or titanium base alloys comprising a mixture of chromic trioxide, sulfuric acid and phosphoric acid.

BACKGROUND OF THE INVENTION

This invention relates to a novel electrolyte composition for producing an anodic coating on articles composed of titanium or titanium base alloys, and more particularly to improvements in a method of providing an anodized coating with many desirable and useful properties.

The application of anodizing techniques for producing a protective anodic film on magnesium and aluminum alloys has greatly extended their usefulness. The lack of such a process for titanium has prevented the utilization of this material in applications demanding good wear resistance and in applications where titanium would be exposed to halogens, nitrogen and/or oxygen at elevated temperatures and to certain stress corrosion inducing chemical species at ambient temperatures. The use of titanium in these applications is desirable because of its high strength to weight ratio.

In general terms as heretofore practiced the anodizing process involves suspending the article to be anodized in an electrolyte which normally consists of an aqueous solution of acids, salts or bases.

A cathode of any suitable conductive material is also suspended in the solution so that when an external electric current source is used an oxidizing reaction is promoted between the anode, the article to be anodized, and the electrolyte to form an oxide type coating. The characteristics of the coating and its usefulness depends on the composition of the electrolyte used in the process.

The novel electrolyte described in this invention is particularly useful in preventing embrittlement during the prolonged exposure of titanium to sodium chloride at temperatures in the 900° F. range and to air at temperatures in the range of 1,000° F. to 1,500° F. Protection is also provided at still higher temperatures for shorter time durations depending on the exposure temperature. A further object of the invention is to provide a coating which prevents the catastrophic failure of titanium and its alloys as a result of combination of high tensile stresses and high temperature exposures during contact with halide containing materials.

Further objectives of the invention are to produce an anodized coating which serves as a bonding surface for the application of dry film lubricant, adhesives and organic or inorganic coatings, to produce a high emissivity coating for temperature control of space vehicles or vacuum equipment and to produce an inert decorative coating.

SUMMARY OF THE INVENTION

This invention comprises an electrolyte for anodizing titanium or titanium base alloys comprising anodic aqueous mixture of chromate, sulfate, and phosphate ions. Each individual ion may be used in the form of an acid or a salt which contains the chromate, sulfate or phosphate species in the ionic form. This invention also comprises a method of anodizing titanium and titanium base alloys utilizing the foregoing composition.

DETAILED DESCRIPTION

This invention in its broadest aspects contemplates anodizing the surface of an article fabricated from titanium or its alloys in an electrolyte consisting of an acidic aqueous solution compirsing three cations; chromate, sulfate and phosphate. In the anodizing process itself the tanks should be fabricated from acid resistant materials such as a nickel base alloy or austinitic stainless steel or from an acid resistant plastic. Although the anodizing temperature is not critical, it should be high enough to promote good electrolyte conductivity and low enough to prevent boiling of the electrolyte or degradation of the maskant material. A typical range is 25 to 190° F.

Cooling coils will be necessary when high density loads are anodized because of the heat developed by the electrical resistance of the electrolyte and the anodized coating. A current source is required which will provide a minimum potential of 140 volts and a minimum current density of 4 amperes per square foot of anode surface. Normal anodizing practice is followed in that the voltage must be gradually increased as the coating thickness increases to maintain a constant current density. The process may be stopped at any desired voltage depending on the coating thickness required. In order to achieve a coating thickness of 0.0003" (0.3 mil), which has been found to be the optimum for high temperature protection, the anodizing process is continued until a voltage range of 140 to 170 volts has been reached. This normally requires 20 to 40 minutes depending on the current density used for anodizing.

The final anodic coating on the titanium may be from about 0.3 mil to about 0.7 mil, preferably 0.5 mil thick. The temperature of the solution may vary from about 25° F. to about 190° F., preferably about 40° F. The cathode may be made of titanium or other material such as a 300 series stainless steel. The anode is the titanium or titanium alloy to be anodically coated and is spaced 3 to 36 inches from the anode, preferably about 6 inches. The voltage is from 140 to 195 volts, preferably about 180 volts. The current density is from 1 to 16 amps/sq. ft., preferably about 4 amps/sq. ft. The time is from 10 to 50 minutes, depending on the desired coating thickness.

The composition of the electrolyte is from about 0.01% to about 63%, by weight of a water soluble chromium compound calculated as CrO_3, preferably about 1%. This is usually and preferably in the form of chromic trioxide. A phosphate, calculated as about 0.15% to about 36%, by weight P_2O_5, preferably about 3.6%, is in the electrolyte. This is preferred to be in the form of phosphoric acid, 75% by weight. Sulfate ions calculated as SO_4 comprise about 0.7 to 80%, by weight, preferably about 5% of the composition. Again, this is preferred to be in the form of 66° Bé. sulfuric acid. The pH of the electrolyte is below 7, preferably about pH 0.1.

The following examples illustrate preferred embodiments of the practice of this invention:

Example 1

A stainless steel container is used to contain the electrolyte. A cooling coil is used to maintain the temperature and the solution is stirred to promote heat transfer between the anode, the electrolyte and the cooling coils.

An electrolyte of the following composition is used.

Chromic trioxide flake	percent by weight	1
Sulfuric acid—66° Bé.	percent by volume	18
Phosphoric acid—75%	do	30

A 1" x 4" x .050 gauge AMS 4910 titanium specimen is solvent cleaned using trichloroethylene solvent, masked to prevent arcing at the liquid-air interface, attached to the

anode contacts and lowered into the solution. For the purpose of this example, the temperature is controlled at 100° F. A titanium cathode equal to the anode is spaced approximately 6" from the anode. The current is turned on and within one minute the voltage has risen from 10 volts to 104 volts at a current density of 5 amp/sq. ft. The voltage rises more slowly to 145 volts during the next twenty minutes before the test run is terminated. The anode is removed, rinsed and dried. The coating is continuous, dense, smooth, adherent and dark grey in color. The coating is 0.0003 inch in thickness.

Example 2

The following electrolyte was made up—

Chromic trioxide flake	percent by weight	1
Sulfuric acid—66° Bé.	percent by volume	5
Phosphoric acid—75%	do	10

The same process is repeated as described in Example 1 except that the anodizing time is 17 minutes, the temperature is controlled at 40° F. and the final voltage is 160. The coating produced has an olive green color but the other physical properties appear to be identical to the coating produced in Example 1.

These coatings are tested along with 18 other anodic coatings which have been anodized according to instructions contained in the literature.

The scratch resistance of the coatings is determined by a Bell scratch tester. A load of 100 grams is applied to a needle point having a 0.010" radius and the needle is pulled across the specimen at a constant rate. Several coatings, including the Example 1 and 2 coatings, passed the test in that the needle did not penetrate the coating. Several soft coatings passed the test because of a greater coating thickness than that produced in Example 1 or 2.

The high temperature resistance of the coating is tested by anodizing 1" x 4" specimens and exposing them in an air furnace at 1500° F. for 60 hours. The specimens are then bent slightly in a mandrel and then placed in a Baldwin testing machine and bent to failure by bringing the platents together. Specimens anodized as described in Examples 1 and 2 were the only specimens showing the same ductility as the as-received material. The remainder suffered brittle failure at various degrees of bend.

In addition, the coatings produced in Examples 1 and 2 were the only ones which did not spall off the specimen surface at the concave surface of the bend.

Stress corrosion tests are performed by bending the specimen after anodizing over a 0.313 mandrel to produce a 90° bend. The inside of the bend, which was under tensile stress because of spring-back, is coated with salt. The specimens withstood 900° F. for 16 hours without evidence of corrosion or stress corrosion cracking. Other coatings tested failed to pass this test.

A more accurate test involves the use of sodium chloride to coat tensile specimens of AMS 4910 titanium which are loaded in a creep frame at a stress level of 25 Ks.i. and heated to 900° F. A specimen anodized as described in Example 2 was exposed at these conditions for 350 hours. The test was discontinued since it appeared that the specimen would run for an indefinite period without failure as the coating did not discolor or show any other signs of deterioration. The non-anodized specimens broke by brittle failure after an average exposure period of 40 hours. Another set of sodium chloride coated specimens were exposed at a temperature of 900° F. and at an increased stress level of 40,000 p.s.i. One anodized specimen did not fail after 434.2 hours. Two others failed at an average time of 200 hours as a result of "necking" without any loss in ductility. Non-anodized specimens subjected to the same conditions failed in an average time of 2 hours.

Physical tests to determine tensile properties; tensile strength, yield strength, percent elongation and uniform elongation properties proved that the anodizing process as described in Examples 1 and 2 does not affect the mechanical properties of AMS 4910 titanium.

It has been established that the anodixed coatings described in this disclosure greatly increase the wear resistance of titanium parts coated with oils, greases or solid film lubricants. Anodized specimens coated with MIL–G–23827 grease had a wear life of 20 hrs. under a 5 lb. load in the MacMillin wear tester. Non-anodized specimens coated with MIL–G–23827 grease failed immediately under the same load. Furthermore titanium specimens which were grit blasted and coated with Molykote X106 failed under a 20 lb. load in 27.5 hours. Under the same test conditions specimens which were grit blasted and anodized as described in Example 2 before applying Molykote X106 had a wear life of 90 hours, an increase of 300%. Furthermore, as a result of this invention a coating can be produced on titanium alloys which has many applications because of its decorative appearance, high emissivity, scratch resistance and stability.

Thus, it is seen that the present invention achieves all of the objects and advantages sought therefor.

This invention is intended to cover all changes and modifications of the examples of the invention herein chosen for purposes of the disclosure which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A process of anodizing titanium or titanium base alloy comprising the steps of placing a titanium or titanium alloy member to be anodized in an aqueous electrolyte consisting essentially of about 0.01% to about 63% by weight CrO_3 equivalent, about 0.7% to about 80% SO_4 equivalent and about 0.15% to about 36% P_2O_5 equivalent, placing a cathode in the electrolyte, attaching the anode contacts to the object to be anodized, and applying an anodizing voltage between the cathode and the object to be anodized.

2. The process of claim **1** wherein the anodizing voltage is between about 140 to about 195 volts at a current density of about 1 to about 16 amps/sq. ft. for about 10 to about 50 minutes.

3. The process of claim **1** wherein the temperature of the electrolyte is from about 25° F. to about 190° F.

4. The process of claim **1** wherein the electrolyte is about 1% by weight CrO_3 equivalent, about 3.6% by weight P_2O_5 equivalent and about 5% by weight SO_4 equivalent.

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