

PROCESS FOR COATING TITANIUM ARTICLES
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This invention relates to a process for finishing articles made of titanium.

Titanium is a relatively new metal of commerce. It is strong and light in weight. As a structural material it gives evidence of being a modern successor of aluminum for many purposes. It is difficult, however, to polish mechanically or by chemical or electrochemical techniques; and alloyed titanium structural members that are subjected to stress, in particular, are susceptible to corrosion, particularly salt corrosion. Moreover, titanium and its alloys have a tendency to gall and seize when in moving contact with other metals; and this restricts their utility.

One object of the invention is to provide a process for applying a durable, protective and decorative coating to titanium and its commercial alloys.

Another object of the invention is to provide a process for producing a coating for titanium and its alloys that is resistant to abrasion, and corrosion.

Another object of the invention is to provide a process for treating titanium and its alloys to produce on it a surface coating that has a lubricating quality.

Another object of the invention is to produce a coating for titanium and its alloys that is of uniform thickness and color.

A related object of the invention is to provide a process for producing a uniform, tough coating of substantial thickness on articles made of titanium or its alloys, where their fabrication or use demands freedom from seizure or galling.

Other objects of the invention will be apparent herein-after from the specification and from the recital of the appended claim.

We have found that a hard, opaque, non-porous, coating can be formed on unalloyed titanium, crystal-bar titanium, and titanium alloys by a high voltage anodizing process. In general, the process is performed by immersing the titanium article in an acidic or alkaline bath of a character that will not attack the titanium to an undesirable extent during anodizing, and making the article the anode in an electrical circuit. A voltage of about at least 1300 volts and up to about 2000 volts is then applied. The thickness of the coating can be regulated by controlling the voltage and the time during which the voltage is applied. The quality of appearance is somewhat affected, however, by the degree of chemical purity and of physical uniformity of the commercial titanium.

The process can be practiced at low voltage when thin anodic coatings are desired. Coating thickness does not exceed approximately 40 Angstrom units per volt of applied potential regardless of time.

In one embodiment of the invention, a sheet of commercially pure titanium is cleaned to remove all foreign substance from its surface; and the plate is immersed in an anodizing bath containing a solution of boric acid saturated at room temperature. Preferably a stainless steel tank is used as the container and cathode. The tank is immersed in a stoneware jar that contains circulating coolant to maintain the temperature of the bath near 32° F. Some acid precipitates from the solution at this operating temperature.

The stainless steel tank is grounded. The titanium

plate or sheet is connected in the circuit to the positive terminal, to function as the anode, and a high voltage is applied to it. Example: a sample of unalloyed titanium anodized in boric acid as described above at 1500 volts acquired a 0.25-mil thick coating as determined by metallographic examination of a tapered cross-section.

The voltage is usually raised gradually in increments of 200 volts up to 1500 to 2000 volts. It is also possible to raise the voltage rapidly to peak value. When the full voltage is built up in 200-volt increments, instead of being applied instantly, the resulting anodic coatings are more adherent.

The anode current density varies from 15 amp. per sq. ft. to 30 amp. per sq. ft. when peak voltage is attained. It decreases with time to about 1.5 amp. per sq. ft. as the anodic coating builds up to maximum thickness, about 0.1 mil to 0.2 mil. It has been found that the temperature of the bath and the shape of the plate or panel influence the current density corresponding to a given voltage. The current density increases with rising bath temperature, and is higher on panels with a larger edge length-to-surface area ratio than on other panels of the same area. Where the edge length-to-surface area is very large it is necessary to round off sharp edges to avoid corona discharge at the edges.

The coatings have proved to be very adherent to unalloyed titanium. They do not chip or powder off when a sheet is given a sharp 90° bend. Only a minute amount of the anodic film is loosened as a fine powder at the bend, but except for this negligible powdering, the coating remains on the metal and is not removed even by hard rubbing with a mild abrasive material. The tough, adherent coating is especially useful where seizure and galling are problems.

The following titanium alloys have been successfully anodized by the subject process: Ti-6Al-4V, Ti-4.5Al-12Zr, Ti-7Al-4Mo, Ti-4Al-3Mo-1V, and Ti-5Al-2.5Sn. Coatings on the vanadium-containing alloys sometimes have a yellow to yellow-golden color. None of alloys takes on coatings which are so adherent as the coating obtained on unalloyed titanium. The coatings are useful, however, against stress corrosion. Example: When round tensile bars of Ti-6Al-4V, Ti-4.5Al-12Zr, and Ti-7Al-4Mo were anodized in the boric acid bath up to near 1500 volts in 200 to 250-volt increments, the bars, without exceptions were not damaged by salt stress corrosion within 50 hours at 750° F. and 45 to 65 k.s.i. creep stress.

To control the thickness of the coating obtained, the peak voltage and the anodizing time are controlled. In general, a coating thickness on the order of at least 0.1 mil is required for practical resistance to abrasion. Titanium, that has been subjected to high voltage anodization to produce a hard non-porous coating having a substantially uniform thickness of about 0.1 mil, is eminently suitable in the manufacture of structural members and panels, as well as for other purposes.

In general, it is preferred to carry out the anodizing in a weakly acidic bath, at temperatures below about 100° F. in order to retard acid attack on the metal. Saturated solutions of boric acid, or dilute ammonium salt solutions of tartaric acid, and citric acid are eminently suitable.

Anodizing can also be effected at low voltages either with a strongly acid bath or a strongly alkaline bath. Sulphuric or chromic acids, or salts of these acids, such as potassium and lithium sulphates, have been employed, as have also baths containing potassium and lithium hydroxides. At low voltages, the films formed are thin and clear. The film thickness and color are controlled by cell voltage. Above a specific voltage (50 to 150 volts, or more, for strongly acid baths, and 25 to 50 volts for the alkaline baths tested) these thin films break down

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dielectrically with arcing. The breakdown voltages depend, of course, upon the bath composition. We have found, however, that if the baths contain lithium ions, they can be operated above the normal breakdown voltage. The presence of lithium ions in the bath promotes uniform anodic coatings on titanium. This is apparently due to the ability of the lithium ion to penetrate the coating and provide for conductivity in the TiO_2 film. In a fifty percent KOH bath, for instance, coating started at the edges of a panel or sheet and worked toward the center. Adding one percent LiOH to the bath allowed coating to start forming simultaneously all over the surface of the panel or sheet. A saturated (fifteen percent) solution of LiOH allowed a panel to be coated at high rate at very low current density (200-700 volts) without arcing. Even at high current densities no arcing occurred. Instead of lithium hydroxide minute amounts of lithium borate or lithium tartrate may be employed in the bath.

The hard, opaque, non-porous coatings formed by high-voltage anodizing according to the process of the invention provide a marked contrast to the coatings that are obtained through low voltage anodization when no lithium compound is used in the bath. At low voltages (but high enough to cause dielectric breakdown), the anodized coatings may be grey, light green, or light brown, and are absorbent, and porous. The coatings produced by the high voltage anodizing process of this invention are substantially uniform and tough.

High voltage coatings, being non-porous, cannot be dyed. Coated parts can be colored, however, by heating the coated parts in a tube furnace in an atmosphere of commercially available argon. The specimen is placed in a tube furnace and the furnace is brought to temperature and held at temperature for a suitable period. Then the specimen is furnace-cooled. Under these conditions, some of the coating oxide diffuses into the metal, and the rest of the oxide remains as a semi-transparent and very abrasion-resistant cover over the temper color. Commercial argon contains some nitrogen as an impurity, and it is believed, the nitrogen may be responsible for coloring the titanium. Two of the colors that can be obtained are yellow and blue. Other colors can be obtained by control over the temperature and holding time in the furnace.

The titanium base metal recrystallizes at temperatures above about 1625° F. Therefore, when a titanium part,

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that has a coating formed thereon by high voltage anodizing, is subjected to a temperature above 1625° F. in the process of coloring it, randomly oriented crystal faces are formed on the base metal, and the colored layer between the metal and its coating appears spangled because of its location on the randomly oriented crystal faces. This effect is very pleasing in appearance. At temperatures below 1625° F., the original reflectance and luster of the coated part is substantially retained.

While the invention has been described in connection with specific embodiments thereof, then, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth and as fall within the scope of the invention or the limits of the appended claim.

Having thus described our invention, what we claim is:

A process for producing a hard, substantially uniform, corrosion-resistant spangled coating on an article of titanium or titanium alloy, comprising anodizing said article in a boric acid bath at a voltage in excess of 1300 volts and at a temperature below 100° F., and then heating said anodized article in an atmosphere of commercial argon having a small, reactive amount of nitrogen, at a temperature of at least 1625° F. and then furnace-cooling said article to produce coloration.

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