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PROCESS FOR ANODIZING TITANIUM SURFACES

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ABSTRACT OF THE DISCLOSURE

The tendency for mating titanium or titanium alloy surfaces to gall or seize under load can be virtually eliminated by the anodic treatment of such surfaces in an electrolyte composed of selected amounts of sodium hydroxide, sodium silicate, titanium dioxide and activated carbon under continuous agitation at a controlled ambient temperature. Under this treatment, the oxide coating normally present on the surface of the titanium and the adjacent portion of the basis metal therebeneath are converted to a hard glassy surface highly resistant to abrasion and sliding wear.

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment to us of any royalty thereon.

This invention relates to wear and corrosion-resistant surfaces on titanium and the alloys thereof and is more particularly directed to a method for producing such surfaces by means of anodic oxidation.

Although titanium and the alloys thereof possess a relatively high ratio of strength to weight as well as an outstanding degree of resistance to corrosion, the full utilization of this metal for the fabrication of movable machine parts of all types has heretofore been limited by the tendency for the mating surfaces thereof to gall and seize when subjected even to a moderate degree of loading. Previous attempts at overcoming this undesirable physical characteristic of titanium have met indifferent success primarily due to the extremely adherent oxide film found on all exposed titanium surfaces. While various types of refractory coatings can be deposited on exposed titanium surfaces from aqueous solutions or from the vapor state, the adherence of these coatings is generally unsatisfactory especially from the standpoint of resistance to wear.

Accordingly, it is a general object of this invention to provide a new and improved method for producing an antigalling surface on titanium and the alloys thereof in a simple and practical manner particularly well suited to current mass production techniques.

It is a further object of this invention to anodize a titanium surface in a manner which will provide an antigalling layer characterized by a greater degree of fatigue strength and resistance to wear than heretofore without, at the same time, incurring any appreciable reduction in the tensile and other physical properties of the base metal.

More specifically, it is an object of this invention to provide a method for nullifying the oxide coating normally found on the surface of titanium and the alloys thereof and simultaneously converting such coating as well as the metal therebeneath to a barrier layer which is not subject to galling and seizing upon contact with sliding surfaces of titanium or other metals and which will readily accept any organic or inorganic lubricating compound.

A final object of this invention is the provision of a new and novel electrolytic solution capable of an anodic

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reaction with the titanium surfaces in a manner which will provide the aforesaid antigalling layer.

The manner in which these and other objects and features of the invention are attained will appear more fully from the following description thereof, in which reference is made to typical and preferred procedures in order to indicate more fully the nature of the invention but without intending in any way to limit the scope of the invention thereby.

Although all metals possess a tendency to gall and seize to some extent when mating surfaces thereof are brought into slidable contact under applied load, this problem has been satisfactorily resolved in most instances by forming a barrier layer between the surfaces through the utilization of suitable organic and inorganic lubricating compounds or the formation of a wear-resistant coating on one or both of the mating surfaces. A suitable coating of this type may be provided by the deposition of any of a number of abrasion-resisting metals from aqueous solutions by electrolysis or immersion procedures. In some cases the required metal coating may be deposited directly from the vapor state.

However, these procedures do not provide the same degree of success insofar as titanium and the alloys thereof are concerned, primarily due to the extremely thin but remarkably tenacious oxide layer present on all exposed surfaces thereof. Experience has shown that, although little or no difficulty is encountered in depositing wear resistant metals on titanium, the resulting coating will not adhere to the oxide surface layer to the extent required to withstand even a moderate degree of loading.

Consequently, numerous attempts have been made to remove the oxide layer from the titanium prior to the deposition of the desired coating or at least to improve the adherence of the deposited coating. These attempts have included exposure of the titanium surfaces to elevated temperatures in a normal or vacuum atmosphere, and various treatments with nitrogen, oxygen or carbon in the several commercial forms thereof, as well as by immersion in aqueous solutions of many of the commonly known acids, bases, and peroxides. None of these attempts have been able to condition a titanium surface for the proper adherence of a coating capable of resisting the usual galling, seizure, and resultant scoring customarily encountered between mating titanium surfaces. In fact, experimental duplication of these prior art attempts revealed that the anti-galling ability of the various deposits and other forms of protective layers was invariably reduced in almost direct ratio to the cumulative effect of the stresses and strains imparted thereto under the loading conditions normally encountered by the moving parts of conventional machinery.

In view of the excellent abrasion-resisting coatings which have been applied to aluminum surfaces by anodic oxidation, consideration was given to the possibility of applying this process to titanium surfaces. However, it was discovered that the aqueous sulfuric acid bath employed in the treatment of aluminum did not produce the same desirable effect on titanium. This finding led to further experimentation which disclosed that anodic oxidation of titanium was feasible provided the electrolyte employed was not acid in nature. Specifically, it was discovered that successful results could be achieved if the bath was composed of selected amounts of sodium hydroxide, sodium silicate, titanium dioxide and activated carbon under continuous agitation at a controlled ambient temperature.

Although the complexity of the chemical composition of the protective surface provided by the treatment to be described hereinafter has up to now defied standard qualitative analysis, it has been ascertained that relatively uni-

form results are invariably produced whenever the same unique electrolyte is employed under the same conditions of current density and temperature. These results are substantially the same regardless of the purity of the titanium or the identity of the alloying constituents thereof. Unlike conventional electroplating processes, the resulting coating is not a deposit but an actual electrolytic conversion of the surface metal in contact with the solution. Thus, the converted metal covering the surface of the titanium is an integral part thereof and does not raise the problems of bonding and adhesion encountered in the deposition of an additional layer of metal on the surface of the titanium. Since the layer of converted metal occupies a slightly greater volume than the titanium replaced thereby, the formation thereof may be described as a "growth" which proceeds both inwardly and outwardly in the portion of the titanium metal subject to conversion.

The actual anodizing treatment may be carried out in any conventional plating tank in which the titanium part to be treated can be suspended to serve as the anode. The cathode is preferably fabricated of pure lead and may consist of any economical configuration adapted to be suspended in the same manner as the anode. In many cases, the cathode may even be in the form of a protective lining on the interior surfaces of the tank. However, if the tolerances of the titanium part being treated are extremely critical, the cathode is preferably formed as a separate member suspended in relatively close proximity to the titanium anode and shaped to approximate the exterior configuration of the latter.

In order to effect the desired transformation of the surface of a typical titanium part, it must be fully immersed in an aqueous bath in which each liter or gallon of water contains the following ingredients in quantities substantially as specified in Table I:

TABLE I

Ingredient	Grams/liter	Oz./gal.
Sodium Hydroxide (NaOH)-----	214.5	28.5
Sodium Silicate (Na ₂ SiO ₃)-----	18.75	2.5
Activated Carbon (C)-----	3.75	.5
Titanium Dioxide (TiO ₂)-----	15.0	2.0

While these concentrations provide optimum results, they may, of course, be varied in accordance with the degree of antigalling resistance required by the type and quantity of loading to which the titanium part is expected to be subjected in use. Thus, in some cases, the foregoing concentrations may vary as much as 10% and still provide acceptable results. However, the best approach to the required content of the aqueous solution is to establish the above specified amounts as a desired goal. This will, of course, necessitate periodic chemical analysis of the solution. In those cases wherein repeated analysis of the solution is not feasible, the necessity for additions to the ingredients listed in Table I will be signaled by the behavior of the bath or the appearance of the titanium part being treated. Such indications as an abnormal increase in processing time, failure of the current to rise or fall in the predicted manner, and slight etching of the titanium anode are examples of such signals.

Since the optimum concentrations listed in Table I will, of course, deteriorate during continuous use of the anodic solution, daily replenishment of some, or all of the ingredients thereof will be necessary. It has been found that insofar as the carbon and the titanium dioxide content of the anodic solution is concerned, additions of about 1% of the recommended concentrations of Table I are generally required for each eight hours of use. Experimentation has also shown that the pH of the processing solution must be maintained between 13.0 and 14.0 in order to insure maximum conductivity of the electrolyte and optimum hardness of the converted surface of the titanium being treated, as well as complete solubility of the sodium silicate. This control can be readily achieved by adding calcu-

lated amounts of sodium hydroxide to the bath. These additions also serve to control the Baumé of the solution which should be maintained as close to 19.4° as possible.

An important element of the anodic treatment of titanium surfaces is the maintenance of the temperature of the processing bath at a relatively constant 68° F. While the process is operable at lower temperatures, it has been found that 68° F. will provide maximum hardness to the converted titanium surface. Accordingly, the best results can be achieved in the most economical fashion by maintaining the temperature between 66°-68° F. In order to meet this requirement, the processing equipment should include some means for continuously sensing and controlling the temperature in the vicinity of the titanium part under treatment. Although the particular type of cooling apparatus which may be utilized will, of course, depend on the volume of the anodic solution and the quantity and size of the titanium parts to be processed in a given interval of time, cold water cooling coils or relatively simple heat exchangers will provide the required results in the most economical fashion.

In addition to this cooling apparatus, suitable means must also be provided for continuously circulating the solution through the tank in order to prevent the ingredients from settling out and thereby reducing the effectiveness of the reaction with the surfaces of the titanium part undergoing treatment. The required agitation can, in most cases, be obtained by a simple circulating pump. However, where the treated titanium part is provided with one or more deeply recessed areas or is in the form of a relatively long tube, adequate agitation of the solution may require that the part itself be suspended in a manner permitting rotation thereof about its own axis. In any event, circulation of the anodic solution will provide a relatively uniform concentration thereof throughout the processing tank and, in addition, assist in the cooling thereof by dissipating the heat generated in the immediate vicinity of the surface undergoing the anodic treatment.

The electrical system required to treat titanium surfaces in accordance with the present invention may be of the same type utilized in conventional electroplating but should possess sufficient flexibility to provide up to 50 volts. In addition, some means must be provided for regulating the current density to a maximum of 45 amperes per square foot. In carrying out the process, current is applied to the anode by means of a constantly increasing voltage. As soon as the starting voltage of 25 volts is reached, the amperage will rise until a predetermined current density within a range of 35-45 amperes per square foot is reached. At this value, the voltage reaches a maximum of 40 volts. The current density then remains stable for a short period of time, approximately 30 seconds, and then slowly decreases during the formation of the conversion coating to a minimum of 10 amperes per square foot. The stabilization of the current density at this minimum value signals the completion of the process and the titanium article being treated may then be removed from the solution. The entire processing cycle generally does not require more than fifteen minutes.

As the coating is formed, a relatively soft, powdery, white substance appears on the surface of the titanium article being treated. This powder may readily be removed simply by brushing. At the same time, the titanium beneath this outer layer of powder is converted to a depth of about .004 inch to a dark, glossy, hard layer which is highly resistant to abrasion and sliding wear. In the event the temperature should be permitted to rise above 68° F. during the processing, the color of the antigalling layer will vary from a deep blue to a near golden hue depending on the alloying constituents of the titanium. This departure from the anticipated normal dark gray to black finish indicates that the antigalling layer does not possess the required hardness and steps can then be taken to correct or eliminate the conditions which resulted in the undesirable rise in temperature.

However, when the antigalling layer is properly formed on the surface area of an article fabricated from titanium or an alloy thereof, the hardness and impact strength thereof will attain a maximum value. This superiority is clearly demonstrated by comparing the results of testing equivalent anodized and unanodized samples of a 6A¹-4V titanium alloy in a Moore type of rotating beam fatigue tester operated at 10,000 r.p.m.

TABLE II

Sample No.	Type	Calculated Stress (p.s.i.)	Wt. of Sample (oz.)	Cycles Completed Before Failure
1A-----	Unanodized-----	84,000	40.8	66,000
2A-----	do-----	84,000	40.8	108,500
3A-----	do-----	61,475	27.2	(1)
4A-----	do-----	98,900	48.3	38,000
1B-----	Anodized 5 min-----	84,000	40.8	89,000
2B-----	Anodized 4 min-----	84,000	40.8	1,266,000
3B-----	Anodized 3 min-----	84,000	40.8	(2)
4B-----	Anodized 2 min-----	84,000	40.8	127,000

¹ Over 1,075,000.

² Shut off at 3,765,000.

As shown in the above table, the fatigue strength displayed by the samples with the anodized surfaces is significantly superior to the corresponding samples with the unanodized surfaces.

In addition to this desirable increase in fatigue strength which can be imparted to titanium and the alloys thereof, anodization of the surface provides an unusual decrease in the galling and seizing normally encountered whenever titanium surfaces are brought into slidable mating contact under load. This superiority was clearly demonstrated by testing the ability of various surfaces to withstand the sliding contact produced in a Modified MacMillan Wear Tester at an applied load of 40,000 p.s.i. The results of such testing are shown in the following table.

TABLE III

Type of surfaces tested:	No. of operating cycles
Lubricated hardcoat vs. lubricated hardcoat ----- (no failure) --	179,634
Lubricated hardcoat vs. 4340 Steel -----	51,471
Hardcoat vs. hardcoat -----	43,200
Lubricated hardcoat vs. titanium -----	37,726
Diffused electroless nickel (type A) ¹ vs. diffused electroless nickel (type A) -----	31,104
Diffused electroless nickel (type A) ¹ vs. steel -----	25,560
Steel vs. steel -----	9,792
Diffused electroless nickel (type B) ² vs. diffused electroless nickel (type B) -----	9,360
Hardcoat (not lubricated) vs. steel -----	1,588
Hardcoat (not lubricated) vs. titanium -----	593
Electroless nickel (type C) ³ vs. electroless nickel (type C) -----	360
Titanium vs. titanium -----	216
Titanium vs. steel -----	216

¹ Diffused electroless nickel type A—Applied to untreated titanium surface.

² Type B—Applied to titanium with oxide removed.

³ Type C—Plated on untreated titanium surface.

As shown in Table III, mating titanium surfaces treated by the method of the present invention and thereafter lubricated were able to withstand at least 5.8 times as many cycles of sliding wear as comparable titanium surfaces treated in the next best manner currently known. These statistics are even more significant in view of the fact that most anodizing and plating processes heretofore applied to titanium surfaces were incapable of increasing the fatigue life thereof and in some cases actually failed

much sooner than an untreated surface under substantially the same conditions.

Thus, the foregoing method for treating the surfaces of titanium and the alloys thereof provides an extremely simple and practical solution to the problem of preventing the galling and seizing ordinarily encountered whenever the surface of titanium or the alloys thereof is brought into sliding contact with a mating surface of titanium or other metal. Anodization of titanium surfaces is a relatively inexpensive procedure which does not require apparatus of special design and consumes far less electrical power than the other types of coating methods heretofore utilized. Furthermore, the relatively strong throwing power of the electrolyte provides excellent coverage of the titanium surfaces even though the configuration thereof may include deeply recessed areas or blind holes.

In addition, due to the relatively low temperatures employed in the anodizing process of this invention, titanium parts of all sizes and shapes can be treated without distortion or other adverse effect on the strength and corrosion resisting ability thereof. Since the treatment is an actual conversion of the surface metal, threaded and tapped components can be processed with no change in thread pitch and only a slight change in dimension. These advantages are of extreme importance in relatively large caliber ordnance such as mortars and recoilless rifles wherein the components thereof are continually subjected to unusually high impact stresses at elevated temperatures.

The present invention has been described in detail above for the purpose of illustration only and is not intended to be limited by this description or otherwise except as defined by the scope of the appended claims.

We claim:

1. The process of anodically converting the surface of titanium to a wear-resistant, antigalling coating comprising the steps of utilizing the titanium to be treated as the anode in a caustic aqueous solution containing titanium dioxide, sodium silicate and activated carbon in effective amounts sufficient to form a white powdery residue on the titanium surface during the anodic treatment thereof, passing electric current through the anode to provide a current density of 35–45 amperes per square foot, and simultaneously maintaining the temperature of the solution between 66° and 68° F. and the pH of said solution between about 13 and 14.

2. The process of converting the surface of alloys in which titanium is the predominant metal to a hard, wear-resistant, antigalling coating comprising the steps of utilizing the alloy to be coated as the anode in an aqueous electrolytic solution in which each liter contains about 214.5 grams of sodium hydroxide, about 18.75 grams of sodium silicate, about 15.0 grams of titanium dioxide, and about 3.75 grams of activated carbon, passing electric current through the anode while controlling the amperage and voltage to provide a maximum current density in the range of 35–45 amperes per square foot, and maintaining the temperature of the solution during the entire processing of the titanium alloy within a range of 66°–68° F. while simultaneously agitating the solution to equalize the temperature throughout.

3. The process of anodically converting the surface of titanium or the alloys thereof to a wear-resistant, antigalling coating comprising the steps of immersing the part to be coated as the anode in a caustic aqueous solution, consisting of about 214.5 grams per liter of sodium hydroxide, about 18.75 grams per liter of sodium silicate, about 15.0 grams per liter of titanium dioxide, and about 3.75 grams per liter of activated carbon, controlling the solution at a pH of 13–14 while maintaining the density thereof at a Baumé reading of 19.4°, passing electrical current through the anode and solution to provide a current density of between 35–45 amperes per square foot, and cooling the solution to a temperature between 66°–

68° F. while continuously agitating the solution to maintain the required temperature throughout.

4. A solution for use in the anodizing of metallic surfaces wherein titanium is predominant consisting of:

	Grams per liter
Sodium hydroxide -----	214.5
Sodium silicate -----	18.7
Titanium dioxide -----	15.0
Activated carbon -----	3.75

and the balance water.

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