This invention relates to the protection of surfaces of articles composed of titanium or titanium base alloys, and more particularly to improvements in a method for providing an anodized coating on such surfaces.

The general process by which an oxide coating is obtained by electrolytic action on the surface of a metal is well known. Anodizing has heretofore been most often employed in providing protective and decorative surfaces on aluminum and aluminum alloy articles. In general terms as heretofore practiced, the process involves suspending the article to be anodized in an electrolyte which may comprise an aqueous solution of an acid such as sulfuric, phosphoric or oxalic, or the electrolyte may comprise an alkali solution. A cathode, which may be composed of any convenient current carrying material, is also suspended in the electrolyte and current is passed between this cathode and the article to be anodized (the anode). Electrolytic action results in oxidation of the metal surface and a tightly adherent protective coating of oxide is readily formed. These oxide coatings vary considerably in their characteristics, some being more protective than others, while some are more readily adapted for certain specific purposes such as bases for dyeing or coloring operations or as primed surfaces upon which may be applied film forming compositions such as paints and lacquers.

Titanium metal and titanium base alloys are normally resistant to corrosion at ordinary temperatures. At elevated temperatures, however, and in the presence of halide salts such as sodium chloride, titanium base alloys particularly may be subject to rapid corrosion accentuated by service under stress. At temperatures of the order of 600 to 1000°F and higher, the corrosive effect of sodium chloride may be sufficient to seriously affect the structural strength of the article whose surface is attacked.

It is, therefore, the principal object of this invention to provide an improved method for providing a corrosion protective coating for titanium and titanium base alloy surfaces. A further object of this invention is to provide an anodized coating which will protect the surface of titanium and titanium base alloys against the corrosive effects of halide salts at elevated temperatures. Another object of this invention is to provide an improved method for anodizing titanium and titanium base alloy surfaces. These and other objects of this invention will be apparent from the following detailed description thereof.

This invention in its broadest aspects contemplates anodizing a titanium or titanium base alloy surface in an electrolyte which comprises an aqueous electrolytic solution of pH from pH 5 to pH 8 containing at least two cations selected from the group consisting of the alkali metals and ammonium, and a phosphate anion in amount at least 70 grams per liter. The anodized coating obtained employing this electrolyte will be found to be tightly adherent and dense providing excellent protection against the corrosive effects of halide salts at elevated temperatures.

The anodizing process itself is carried out according to known principles and follows generally the methods employed in anodizing aluminum surfaces. A suitable tank is provided to contain the electrolyte, and a cathode of a suitable metal, which may be titanium, is immersed in the electrolyte and connected to the negative pole of a source of direct electric current. The titanium or titanium base alloy article whose surface is to be anodized is also immersed in the electrolyte, preferably suspended therein, and connected electrically to the positive pole of the anodizing source. Electric current is supplied to provide a current density on the anode surface of between about 15 and 40 amperes per square foot. At the beginning of the anodizing operation, the voltage will range from just above zero to about 10 volts and as the resistance of the cell increases due to deposition of the oxide coating on the anode, the voltage must be raised to maintain the desired amperage. During the latter stages of the anodizing process, from 40 to 60 volts or higher may be required. The electrolyte may, if desired, be cooled during the anodizing process to remove heat formed as a result of electrolytic action. Formation of a dense brown coating on the metal surface is an indication of completion of the anodizing process. This may take from 15 minutes to one hour or longer, depending on the particular operating conditions employed and the nature of the titanium or titanium base alloy article being anodized. Completion of the anodizing process may be determined by visual inspection and when the desired dense brown coating is obtained the article is removed from the electrolyte, and rinsed and dried. It has been found that the coating may be sealed and made more dense and protective by a post treatment in boiling water or steam for a period of 15 minutes to one hour.

The electrolyte of this invention contains a relatively high concentration of salts with limited amounts of free acid or alkali and has a pH of from about pH 3 to pH 12. It contains at least two cations selected from the group consisting of the alkali metals and ammonium. Sodium and potassium are preferred alkali metals and combinations of either or both of these with ammonium are found to be especially effective. The phosphate anion may comprise the normal phosphate, PO_4^{3-}; the monohydrogen phosphate HPO_4^{2-}; the dihydrogen phosphate H_2PO_4^-; or combinations of these. The concentration of the phosphate anion is important and should be at least 70 grams per liter. Concentrations of various amounts of sodium and ammonium phosphates, according to this invention result in increased phosphate solubility over that obtainable when single or simple salts are employed. The solutions should be concentrated and preferably saturated; the presence of solid salt will not be harmful to the process and insured the presence of the greatest possible solubility of the phosphate anions.

Equimolar proportions of sodium and ammonium monohydrogen phosphate form an especially desirable combination. The salt NaNH_2PO_4.H_2O may be simply dissolved in water up to the limit of its solubility, or if more convenient, corresponding amounts of sodium and ammonium monohydrogen phosphate may be admixed in water solution.

The improved process of this invention employing the unique electrolyte described above will be found effective to produce anodized coatings on the surface of pure, or commercially pure metallic titanium and on pure titanium base alloys. The nature and amount of alloying ingredients do not appear to affect the character or usefulness of the anodized coating. Articles composed of, for example, titanium base alloys containing aluminum, tin, chromium, vanadium, molybdenum, iron, manganous and other elements, added singly or in combination to produce required mechanical properties, may be successfully anodized.
The following examples illustrate selected embodiments of the practice of this invention:

**Example 1**

A rectangular glass container was filled with an electrolyte formed by mixing the following salts in 1 liter of water:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_3PO_4·12H_2O</td>
<td>230</td>
</tr>
<tr>
<td>K_2PO_4</td>
<td>115</td>
</tr>
</tbody>
</table>

The electrolyte contained phosphate anion in amount about 96 grams per liter.

A bar of commercially pure titanium was suspended in the solution to serve as a cathode and connected to the negative pole of a direct current supply source. Specimen about 2 inches away from the cathode and also suspended and immersed in the electrolyte solution was a 2 inch by 4 inch section of 0.060 inch sheet of a titanium base alloy containing 6% aluminum and 4% vanadium. The sheet was connected to the positive pole of the current supply. The container was provided with a cooling jacket through which cold water was circulated to maintain the electrolyte at approximately room temperature.

The current was turned on and at the outset less than five volts was required to provide 2 amperes resulting in a current density of about 20 amperes per square foot on the sheet surface. As the oxide coating was formed on the sheet, it became necessary to continually raise the voltage to maintain the current density until 50 volts was required. After this point had been reached the required voltage remained constant.

After current had been passed for 30 minutes the titanium alloy sheet was observed to be covered by a dense, brown coating. Electrolysis was then discontinued and the coated sheet removed from the cell, rinsed with water and immersed in boiling water for 15 minutes. The sheet was then removed from the boiling water and dried. The sheet surface was found to be covered with a heavy, dense, brown, and firmly adherent anodized coating.

**Example 2**

An electrolyte was prepared by stirring into one liter of water, 180 grams of "microcosmic salt," NaNH_4HPO_4·4H_2O.

The salt was soluble to the extent of about 167 grams per liter to provide a phosphate anion content of about 73 grams per liter with excess salt remaining undissolved. The saturated solution and undissolved salt were placed in the same container employed in Example 1 and the same anodizing process carried out with the exception that a sheet of commercially pure titanium was employed at the anode. After anodizing, the titanium sheet was covered with a similar heavy dense, brown and firmly adherent anodized coating.

**Example 3**

The same container employed in Example 1 was filled with an electrolyte formed by mixing the following salts in one liter of water:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaH_2PO_4·12H_2O</td>
<td>70</td>
</tr>
<tr>
<td>KH_2PO_4</td>
<td>10</td>
</tr>
<tr>
<td>NH_4HPO_4</td>
<td>60</td>
</tr>
</tbody>
</table>

The solution contained phosphate anion in amount about 154 grams per liter. The same anodizing process as described in Example 1 was carried out except that a sheet of titanium base alloy containing 2% iron, 2% chromium, and 2% molybdenum was employed as the anode. After anodizing, the titanium alloy sheet was covered with a similar heavy, dense, brown and firmly adherent anodized coating.

The anodized sheet sections produced in Examples 1, 2 and 3 were tested for corrosion protection by covering a specimen with dry granular sodium chloride and heating to 600° C. for 24 hours. All three sheet sections showed no corrosion effects demonstrating excellent protection provided by the anodized coating. Similar sections of uncoated sheet of the same compositions showed serious corrosion attack with deeply pitted surfaces when tested under the same conditions.

In addition, specimens of the anodized alloy sheet sections produced in Examples 1 and 3 showed no corrosion effects when stressed at 50,000 p.s.i. and 400° C. in contact with NaCl for 300 hours. The commercially pure titanium sheet anodized in Example 2 did not have sufficient mechanical strength for such a test. Specimens of sheet of the same alloys but not anodized when tested under the same conditions showed evidence of severe attack by NaCl and failed in a comparatively short time due to stress corrosion.

The precise nature of the anodized coating formed by the practice of the process of this invention is not well understood, nor is the reason for its marked superiority as a protection against halide salt corrosion. Anodized coatings on titanium alloys formed employing other electrolytes have not shown the improved protection particularly at elevated temperatures under stress. For comparison titanium alloy sheet sections of the same alloy compositions used in Examples 1 and 3 were anodized in a number of different electrolytes including sulfuric acid, oxalic acid, ammonium oxalate, acetic acid, sodium acetate, ammonium acetate, boric acid, chromic acid, sodium chromate and sodium hydroxide. Of these only the specimen anodized in a sulfuric acid solution showed good protection when tested in contact with sodium chloride at 600° C. for 24 hours, but this specimen failed relatively quickly from corrosive attack by the salt when tested under stress of 50,000 p.s.i. at 400° C.

I claim:

1. A process for anodizing the surface of an article composed of metal selected from the group consisting of titanium and titanium base alloys, comprising, employing as an electrolyte in said anodizing process an aqueous solution of pH 3 to pH 12 consisting essentially of water and 1% to 5% of an acid to which has been added 0.1 to 1.0% of NaH_4HPO_4·4H_2O and containing 70 grams per liter of HPO_4_2-

2. The process of claim 1 in which the cations are sodium and ammonium.

3. The process of claim 1 in which the cations are sodium and potassium.

4. The process of claim 1 in which the cations are sodium, potassium and ammonium.

5. A process for anodizing the surface of an article composed of metal selected from the group consisting of titanium and titanium base alloys, comprising, employing as an electrolyte in said anodizing process an aqueous solution consisting essentially of water and NaNH_4HPO_4·4H_2O and containing at least 70 grams per liter of HPO_4_2-

6. In a process for anodizing the surface of an article composed of metal selected from the group consisting of titanium and titanium base alloys, the improvement which comprises, employing as an electrolyte in said anodizing process an aqueous solution consisting essentially of water and NaH_4HPO_4·4H_2O and containing at least 70 grams per liter of HPO_4_2-

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