ACCELERATED SULFURIC ACID AND BORIC SULFURIC ACID ANODIZE PROCESS

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ABSTRACT

The process of anodizing aluminum or an aluminum alloy in an aqueous solution of about 60 g/L to about 100 g/L sulfuric acid and optionally about 0.1 g/L to about 10.7 g/L boric acid, maintained between a temperature of about 70° F to about 90° F. An aluminum object is immersed in the acid bath, where it acts as an anode. A voltage of 6 V to 16 V is applied to the object at a current density, which varies with the alloy. The object is maintained in the anodizing conditions until an aluminum oxide coating is achieved with a weight of about 30 to about 800 mg/ft².
ACCELERATED SULFURIC ACID AND BORIC SULFURIC ACID ANODIZE PROCESS

FIELD OF THE INVENTION
[0001] The invention relates to a method of rapidly anodizing aluminum and aluminum alloys using sulfuric acid or combinations of boric and sulfuric acids.

BACKGROUND OF THE INVENTION
[0002] Aluminum alloys are susceptible to corrosion. In addition, decorative and/or protective organic coatings, such as paints, do not adhere to aluminum without an adequate surface treatment. Currently, a preferred method of surface treatment of aluminum is to form a surface layer of porous aluminum oxide by anodizing the aluminum in an acid solution. Then organic coatings may be applied. In some cases, the top of the anodic oxide coating is sealed for added corrosion resistance.

[0003] A particularly useful method of anodizing aircraft grade aluminum is recited in Wong et al., U.S. Pat. No. 4,894,127. In Wong, an aluminum alloy is provided with a protective aluminum oxide coating in the preferred thickness range of about 1 to 3 microns by anodizing in a bath containing low concentrations of sulfuric and boric acids. The method comprises providing an aqueous anodizing solution of about 3 to 5 weight percent sulfuric acid and from about 0.5 to 1 percent boric acid. The bath is maintained at room temperature. An aluminum alloy object is immersed in the bath where it acts as the anode. The voltage applied across the object is ramped from about 5 V to about 15 V to maintain a substantially uniform current density that on the average does not exceed about ten amperes per square foot. The object is maintained in the bath to achieve an aluminum oxide coating weight between about 200 and 600 milligrams per square foot. The anodized object is thereafter sealed and coated.

[0004] The Wong process is exemplary of anodizing processes based upon sulfuric acid or combinations of sulfuric and boric acids. Such processes were developed to replace chromic acid anodizing processes because of extreme environmental hazards related to the use of chromic acid. The voltage, amperage, sulfuric and boric acid concentration ranges in the sulfuric and boric acid based processes have been chosen to produce an anodic oxide coating that performed similarly in painted adhesion and corrosion tests to the chromic acid anodize process that they were meant to replace.

[0005] Sulfuric acid based anodizing systems usually provide anodized aluminum with acceptable quality for use in aircraft manufacture. However, the anodizing process is relatively slow, lasting anywhere from 18 minutes to several hours. These processing times are becoming of greater concern as advances in manufacturing techniques have shortened the processing time in other stages of the aluminum finishing and assembly process. Thus, in many cases the anodizing step has become the bottleneck in the production of aluminum parts.

[0006] It is therefore desired to provide a method of anodizing aluminum in a shorter amount of time than previously required while maintaining the surface quality and material properties required of aluminum and aluminum alloys for aircraft manufacture. In particular, it is desired to provide a method of anodizing aluminum in a shorter amount of time than previously required wherein the final performance of the resulting oxide has satisfactory adhesion performance, fatigue life, and corrosion resistance.

SUMMARY OF THE INVENTION
[0007] The invented process enables the use of sulfuric acid and sulfuric acid-boric acid anodizing baths for the anodizing of aluminum and aluminum alloys to produce uniform coatings of 30 to 800 mg/ft². The process provides aluminum oxide coatings with paint adhesion, fatigue life, and corrosion resistance properties similar to or better than previous anodizing methods for this coating weight range, but provides the coatings in a much more rapid manner, thus decreasing the overall time to produce an anodized aluminum part.

[0008] The process provides an aqueous solution of about 60 g/L to about 100 g/L sulfuric acid and optionally about 0.1 g/L to about 10.7 g/L boric acid, maintained between a temperature of about 70°F to about 90°F.

[0009] To anodize the aluminum, an aluminum or aluminum alloy object is immersed in the acid bath, where it acts as an anode. A voltage of about 6 V to about 16 V is applied to the object. As a result, the current density varies between about 1 and about 20 A/ft². The object is maintained in the anodizing conditions until an aluminum oxide coating is achieved with a weight of about 30 to about 800 mg/ft².

BRIEF DESCRIPTION OF THE DRAWINGS
[0010] Having thus described the invention in general terms, reference will now be made to the accompanying figures, which are not necessarily drawn to scale, and wherein:

[0011] FIG. 1 is an illustration of the anodizing process according to an embodiment of the invention, and

[0012] FIG. 2 is a line graph showing the change in coating mass with anodize time for an embodiment of the instant invention.

DETAILED DESCRIPTION OF THE INVENTION
[0013] Aluminum or aluminum alloy components are anodized in a bath of 60 g/L to about 100 g/L sulfuric acid and optionally about 0.1 g/L to about 10.7 g/L boric acid which is maintained at a temperature of about 70°F to about 90°F. The process is run with a voltage differential between the anode and the cathode of 6 to 16 V. In a more particular embodiment, the process provides for use of about 75 g/L to about 100 g/L sulfuric acid. It is generally preferred that boric acid not be used with the process, though concentrations of about 0.1 g/L to about 10.7 g/L boric acid may provide favorable results for the sealed and unpainted corrosion resistance of particular alloys of aluminum.

[0014] The sulfuric and boric acids for use in the process are commercial or technical grades. Though the invention, as described, is broadly applicable to aluminum alloys in general, the invented method has particular usefulness for those alloys typically used in the manufacture of aircraft,
specifically the 2000, 3000, 5000, 6000, and 7000 series, bare or clad, aluminum alloys.

[0015] Prior to anodizing, the aluminum object 10 is typically degreased and subjected to alkaline cleaning followed by a deoxidizing or desmutting step. Rinsing must occur after the alkaline cleaning and deoxidizing steps.

[0016] Referring to FIG. 1, to anodize an aluminum object, the object 10 is then suspended on a conductive metallic rack 12 within the anodizing bath 14. Once the object is in the bath 14, current is applied from a power supply 18 which provides voltage across the body of the aluminum object 10, acting as the anode, to another metallic object 16, which acts as a cathode. The voltage is ramped up to a predetermined voltage at the rate of about 1 to 10 volts/min, and preferably between about 5 volts/min and 10 volts/min. In this case, the predetermined anodizing voltage is between about 6 V and about 16 V, with higher values being preferred.

[0017] It is to be understood that the resulting current density will vary considerably with the particular aluminum alloy used. Increasing voltage potential causes an increase in current density. An applied voltage of 20 V causes significant end grain pitting. A voltage below about 6 V does not provide the desired accelerated anodizing. Therefore, the anodizing process is operable from 6 V to 12 V and a preferred voltage range is 12 V to 16 V, preferably 15 +/- 1 V. Resulting current densities are between 1 and 20 A/ft².

[0018] While anodizing, the bath is maintained at a temperature of from about 70°F to about 90°F. Lower temperatures result in an anodic coating, which does not have sufficient porosity for paint adhesion. Higher temperatures will result in excessive dissolution of the oxide. The preferred temperature is from about 75°F to about 85°F, and more preferably about 80°F. Tank heaters or tank coolers may be provided as needed, in order to maintain the bath at the described temperature.

[0019] An aluminum object having an anodized surface often suffers from a reduction in fatigue strength. The effect of loss in strength can be mitigated or eliminated by careful choice of the aggressiveness of the anodizing solution. Too high of a sulfuric acid concentration can cause surface pitting. Surface pitting can reduce the fatigue life of a surface. At the same time, the anodized layer must be of a thickness and porosity suitable for corrosion protection and as a substrate for paints and other coatings. Too low of a sulfuric acid concentration can result in thin, less porous films. Therefore, as mentioned previously, the process provides an aqueous solution of about 60 g/L to 100 g/L sulfuric acid, which does not promote unacceptable pitting while providing a thickness and porosity suitable for corrosion protection.

[0020] It has been found that anodized films having a thickness of 30 mg/ft² to 800 mg/ft² exhibit acceptable paint adhesion and painted corrosion protection while showing no appreciable signs of reduction in fatigue strength. For these reasons, anodizing of the aluminum is continued until an oxide film having a weight of 30 mg/ft² to 800 mg/ft² is formed upon the surface of the aluminum object.

[0021] Aluminum for use as a painted part may be anodized to an oxide coating thickness of as little as 30 mg/ft² up to about 800 mg/ft². For sealed aluminum parts, a coating of at least 200 mg/ft² is preferred, and coatings between about 200 mg/ft² and 700 mg/ft² are particularly preferred. Anodizing to a thickness of 30 mg/ft² to 800 mg/ft² takes between 5 and 8 minutes, depending upon the alloy being anodized. For any given thickness of oxide coating, the invented method provides an increased rate of anodizing aluminum when compared to prior sulfuric and boric acid based processes, such as Wong '127.

[0022] Subsequent to anodizing, the anodized coatings of this invention can be sealed and coated in the same manner as anodized coatings formed in the sulfuric acid, boric acid, and chromate acid baths of the past. For example, sealing may be accomplished in a dilute chromium solution or deionized water. The anodized aluminum may also be painted as formed or after sealing.

[0023] Most corporate and industrial research into acid anodizing processes has focused upon either the environmental aspects of the chemicals or the desired properties of the oxide film provided upon the aluminum surface. Most improvements to the anodizing process have focused on the removal of chromic acid from the aluminum anodizing process due to environmental hazards associated therewith, and the replacement of chromic acid with sulfuric and/or boric acid. The goal of past innovation in sulfuric acid anodizing has been to replicate the favorable anodizing characteristics of chromic acid.

[0024] Unlike previous innovations in anodizing, this invention provides a method of speeding up the anodizing process without detriment to any other attributes of the anodized object. This faster anodizing method releases the bottleneck previously caused by the extended period of time which was heretofore needed to anodize aluminum objects using sulfuric and/or boric acids.

[0025] The end grain pitting severity in the anodized objects does not appear to be worsened, in comparison to objects prepared in accordance with traditional methods of anodizing aircraft grade aluminum, when tested for samples prepared at a 90 g/L sulfuric acid concentration according to the present invention. Also, corrosion resistance of sealed samples, prepared in accordance with the present invention, were equivalent to those samples prepared in accordance with traditional methods of anodizing. Moreover, aluminum objects anodized with the accelerated process do not exhibit decreased fatigue resistance. Also, the paint adhesion performance of aluminum specimens anodized with the accelerated process was equivalent to the performance of specimens anodized by traditional methods. See Examples 1 through 4.

[0026] Thus, the invented process may be used to produce anodized aluminum objects, which have similar corrosion resistance and fatigue resistance as those objects produced using prior techniques. However, the invented method provides anodized objects in less than half the time previously required in the art.

EXAMPLES

Example 1

Growth Rate

[0027] FIG. 2 shows the oxide growth rate of oxide coatings using an accelerated anodizing processes of one
embodiment of the invention using sulfuric acid (Fast-SAA), one embodiment of the invention using sulfuric and boric acids (Fast-BSAA), and a boric-sulfuric acid anodizing (Traditional) process of the prior art. The anodizing process was carried out on bare coupons of 2024-T3 aluminum alloy. The 2024-T3 alloy was chosen for testing because it has a slower oxide growth rate than alloys of the 5000, 6000, or 7000 series alloys.

[0028] A number of coupons were degreased for 15 minutes at 118°F with a Brulin™ 815GD degreasing agent, cleaned for 10 minutes at 140°F with an Isoprep™ 44 alkaline cleaning solution, and decocidized for 10 minutes at ambient temperature with an Amchem™ 6-16 decocidizing agent. The coupons were then used for three series of anodization experiments.

[0029] A first series of samples were anodized for 5, 8, 10, 12, 15, and 18 minutes under prior art anodization conditions (Traditional) at 43 g/L sulfuric acid, 9 g/L boric acid and 15 V of applied voltage, ramped up 0 V to 15 V at 5 V/min, at 80°F+/−5°F. These are the same parameters that are commonly used in the art and which are generally described in U.S. Pat. No. 4,894,127.

[0030] A second series of samples were anodized for 5, 8, 10, 12, 15, and 18 minutes in a rapid anodize sulfuric acid process (Fast SAA) under conditions of 90 g/L sulfuric acid and 15 V of applied voltage, ramped up 0 V to 15V at 5 V/min, at 80°F+/−5°F.

[0031] A third series of samples were anodized for 5, 8, 10, 12, 15, and 18 minutes in a rapid anodize sulfuric-boric acid process (Fast BSAA) under conditions of 90 g/L sulfuric acid and 9 g/L boric acid at 15 V of applied voltage, ramped up from 0 V to 15 V at 5 V/min, at 80°F+/−5°F.

[0032] The prior art process (Traditional) produced a minimum desired coating weight of 200 mg/ft² within 10 minutes after increasing voltage to 15 V. Both of the invented accelerated processes (Fast-SAA and Fast-BSAA) produced an acceptable 200 mg/ft² coating weight within 5 minutes after increasing voltage to 15 V. The rate of oxide growth above 200 mg/ft² for the accelerated process was nearly twice that for the prior art process. The rates of oxide growth at 90 g/L sulfuric acid with or without boric acid were comparable and showed no statistically relevant difference between anodizing with or without boric acid for this type of alloy.

Example 2
Corrosion Resistance

[0033] The anodized samples of Example 1 were sealed in a dilute chrome seal solution of 26 g/100 gal chromic acid and 18 g/100 gal sodium chromate at 105°F. The three sets of samples were then exposed to salt spray for 14 days in accordance with ASTM B117 at an angle of 6 degrees from vertical. Multiple sets of samples were subjected to the salt spray test and pit counts were obtained. Pit counts in sealed aluminum components subjected to this test are known to correspond to overall corrosion resistance of the tested component. Two series of tests were run, and the results of both are shown below. The pits of Series 1 were counted extremely conservatively, with any initiation site included (even those without visible tails). The Pits of Series 2 were counted normally. Table 1 lists the average number of pit counts for each set of samples.

<table>
<thead>
<tr>
<th>Surface Finish</th>
<th>43 g/L sulfuric acid</th>
<th>9 g/L boric</th>
<th>90 g/L sulfuric acid</th>
<th>9 g/L boric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td>18 min. anod. - 10, 5, 12, 9, 10</td>
<td>5 min. anod. - 0, 1, 0</td>
<td>5 min. anod. - 3, 3</td>
<td>5 min. anod. - 1, 0, 0</td>
</tr>
<tr>
<td>Series 2</td>
<td>5 min. anod. - 1, 0, 0</td>
<td>10 min. anod. - 1, 0, 0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

[0034] There was no significant difference in the number of pits produced after environmental exposure with the prior art samples and with the accelerated anodize samples. Analysis of pits in the first series of samples indicate that corrosion resistance of the rapidly anodized components was the same as or better than the corrosion resistance of the samples anodized with conventional processes. Note, 18 minute anodizing using the prior art process was compared with 5 minute anodizing using the invented process, because those times corresponded to creation of a roughly 200 mg/ft² oxide coating on the respective aluminum alloy components, as shown in FIG. 2.

[0035] Samples of Series 2 demonstrate a comparison between the prior art process and an embodiment of the invented process, using similar anodizing times. The accelerated anodizing process results in the same or lower pit count as traditional anodizing techniques.

[0036] Thus, evaluation of pit counts indicates that the invented method provides corrosion resistance equivalent to or better than the slower anodizing processes of the prior art.

Example 3
Adhesion Test

[0037] The coating adhesion tests were conducted by applying a thin coat, on the order of 1-2 mils, of a two-part epoxy fuel tank primer to multiple samples of each of three sets of samples. The first set of samples were prepared by anodizing for 18 minutes under the conditions of the first series of samples from Example 1. The second set of samples were prepared by anodizing for 5 minutes in 93 g/L H₂SO₄ and 9.6 g/L H₃BO₃, otherwise in accordance with the third series of samples from Example 1. The third set of samples were prepared by anodizing for 5 minutes in 94 g/L H₂SO₄ and 9.6 g/L H₃BO₃, otherwise in accordance with the third series of samples from Example 1.

[0038] In the "rod" test, after the primer was cured, an aluminum rod with ends rounded to 0.12 inches was scraped across the primed surface at an angle of 45° to score it. If the primer removed had a width greater than ½ in., the adhesion of the primer to the test panel was termed a failure. If the width of the removal path was narrower, the panel passed, indicated with a "P." In the scribe test, a cross-hatch pattern is made through the paint to the metal substrate. Tape is applied firmly across the crosshatch pattern and then pulled off. If any paint is removed by the tape, then a score of less than 10 is noted. This test was performed on dry panels and
on panels that had been soaked in water for 42 days prior to the test. The results of both tests are shown in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Test</th>
<th>1st set</th>
<th>20th set</th>
<th>39th set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry scribe adhesion</td>
<td>10, 10, 10</td>
<td>10, 10, 10</td>
<td>10, 10, 10</td>
</tr>
<tr>
<td>Scribe adhesion after</td>
<td>10, 10, 10</td>
<td>10, 10, 10</td>
<td>10, 10, 10</td>
</tr>
</tbody>
</table>

The samples anodized in accordance with the invention passed these adhesion tests, indicating that the process provides samples, which have adhesion strength equivalent to aluminum anodized with prior art methods.

### Example 4

**Fatigue Analysis**

Fatigue testing was performed to compare the fatigue performance of an accelerated sulfuric acid anodize process of the invention with the traditional boric sulfuric acid anodize of the prior art. The testing involved flexure coupons. The flexure samples included 2024-T3 bare aluminum sheet (machined vs. shot peening), 2024-T3 clad aluminum sheet, and 7075-T76 bare aluminum plate (machined vs. shot peening). Following fatigue testing, the fracture surface of the coupons were examined. Optical evaluation of the fractured flexure and lap splice fatigue samples indicated that in all cases fracture initiated and propagated due to fatigue.

A first grouping of each type of sample was anodized according to a method of the prior art. The first samples were anodized for 18 minutes under prior art anodization conditions at 43 g/L sulfuric acid, approximately 1% boric acid, and 15V of applied voltage, ramped up 0 V to 15 V at 5 V/min, at 80°-85°F. These are the same parameters that are commonly used in the art and which are generally described in U.S. Pat. No. 4,894,127.

A second grouping of each type of sample was anodized for 10 minutes in a rapid anodize sulfuric acid process under conditions of 100 g/L sulfuric acid and 15V of applied voltage, ramped up 0 V to 15 V at 5 V/min, at 80°-84°F.

The specimens were optically examined at 12× to identify the location of the fatigue origins. The fatigue origins are described in Table 3, below.

### Table 3

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Surface</th>
<th>Processed</th>
<th>Avg. Cycles to Failure</th>
<th>Avg. # of origins</th>
<th>Location of origins</th>
</tr>
</thead>
<tbody>
<tr>
<td>2024</td>
<td>machined</td>
<td>Prior art</td>
<td>X1</td>
<td>1</td>
<td>all on edge</td>
</tr>
<tr>
<td>2024</td>
<td>machined</td>
<td>Inverted</td>
<td>5.4X1</td>
<td>1</td>
<td>all on edge</td>
</tr>
<tr>
<td>2024</td>
<td>peened</td>
<td>Prior art</td>
<td>X2</td>
<td>1</td>
<td>on edge, some samples did not fracture</td>
</tr>
<tr>
<td>2024</td>
<td>peened</td>
<td>Inverted</td>
<td>1.1X2</td>
<td>1</td>
<td>mostly on</td>
</tr>
</tbody>
</table>

### Table 3-continued

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Surface</th>
<th>Processed</th>
<th>Avg. Cycles to Failure</th>
<th>Avg. # of origins</th>
<th>Location of origins</th>
</tr>
</thead>
<tbody>
<tr>
<td>2024</td>
<td>machined</td>
<td>Prior art</td>
<td>X1</td>
<td>multiple</td>
<td>edge, 1 on corner, and 2 no fracture</td>
</tr>
<tr>
<td>2024</td>
<td>machined</td>
<td>Inverted</td>
<td>1.1X1</td>
<td>multiple</td>
<td>all edge, some both edges</td>
</tr>
<tr>
<td>7050</td>
<td>machined</td>
<td>Prior art</td>
<td>X1</td>
<td>multiple</td>
<td>all edge, some both edges</td>
</tr>
<tr>
<td>7050</td>
<td>machined</td>
<td>Inverted</td>
<td>2.2X1</td>
<td>1</td>
<td>edge, edge-base</td>
</tr>
<tr>
<td>7050</td>
<td>peened</td>
<td>Prior art</td>
<td>X1</td>
<td>1</td>
<td>corner, edge, and some no fracture</td>
</tr>
<tr>
<td>7050</td>
<td>peened</td>
<td>Inverted</td>
<td>2.1X1</td>
<td>1</td>
<td>no fracture</td>
</tr>
</tbody>
</table>

In general, for a given sample material and machining type, the average number of cycles to failure for sample anodized with the invented process were the same or higher than the anodizing process of the prior art. This indicates that the accelerated anodize process does not result in a decreased fatigue resistance of the material.

Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

What is claimed is:

1. A method of anodizing an aluminum or aluminum alloy object comprising maintaining an acid bath around the object of between about 60 g/L and about 100 g/L sulfuric acid and a temperature of between about 70°F and about 90°F; applying a voltage of about 6 V to about 16 V across the object thereby providing a coating of aluminum oxide to the object; and maintaining that voltage until the aluminum oxide has a coating weight of between about 30 mg/ft² and about 800 mg/ft².

2. The method of claim 1, wherein the acid bath further comprises between about 0.1 g/L and about 16.5 g/L boric acid.

3. The method of claim 1, wherein the voltage is applied by ramping the voltage upward at a rate of between about 1 V/min and about 10 V/min.

4. The method of claim 1, wherein the bath temperature is maintained between about 75°F and about 85°F.

5. The method of claim 4, wherein the bath temperature is maintained at about 80°F.

6. The method of claim 1, wherein the sulfuric acid concentration of the bath is maintained between 75 g/L and 100 g/L.
7. The method of claim 6, wherein the sulfuric acid concentration of the bath is maintained between 90 g/L and 100 g/L.

8. The method of claim 1, further comprising the steps of degreasing, cleaning, and deoxidizing the aluminum object prior to the step of maintaining the acid bath around the object.

9. The method of claim 1, further comprising the step of sealing the aluminum object after anodizing.

10. A process for anodizing aluminum at an accelerated rate while maintaining fatigue resistance of the metal comprising

   providing an anodizing bath of between about 60 g/L and about 100 g/L sulfuric acid and a temperature of between about 70° F. and about 90° F.;

   immersing the object into the anodizing bath;

   applying a voltage of about 6V to about 16V across the object thereby providing a coating of aluminum oxide to the object; and

   maintaining said voltage for a period of about 5 to about 8 minutes.

11. The process of claim 10, wherein the anodizing bath further comprises between about 0.1 g/L and about 10.7 g/L boric acid.

12. The process of claim 10, wherein the voltage is applied by ramping the voltage upward at a rate of between about 1 V/min and about 10 V/min.

13. An aluminum alloy article, anodized according to the process of claim 1.