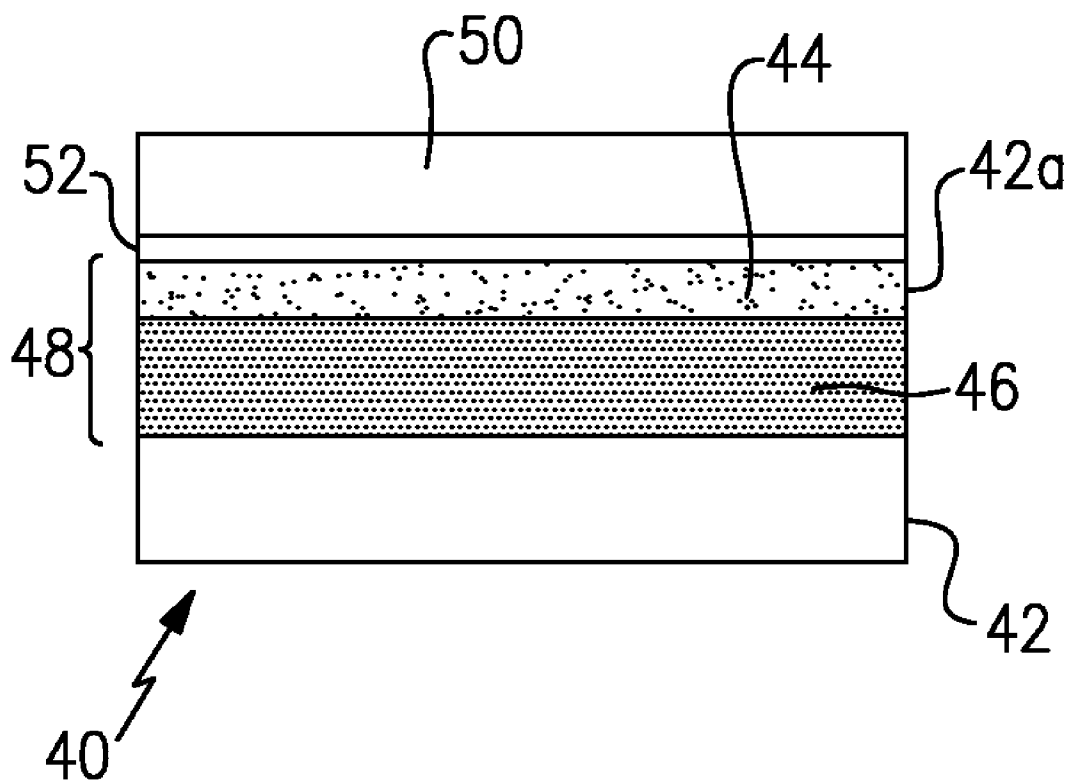




US 20160017510A1

(19) **United States**(12) **Patent Application Publication**
Jaworowski et al.(10) **Pub. No.: US 2016/0017510 A1**(43) **Pub. Date: Jan. 21, 2016**(54) **MULTIFUNCTIONAL ANODIZED LAYER**(71) Applicant: **United Technologies Corporation**,
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CT (US)(21) Appl. No.: **14/792,913**(22) Filed: **Jul. 7, 2015****Related U.S. Application Data**(60) Provisional application No. 62/026,823, filed on Jul.
21, 2014.**Publication Classification**(51) **Int. Cl.**
C25D 11/12 (2006.01)
C25D 11/24 (2006.01)(52) **U.S. Cl.**CPC **C25D 11/12** (2013.01); **C25D 11/24**
(2013.01)(57) **ABSTRACT**

A method of anodizing includes immersing an aluminum alloy workpiece in a phosphoric acid anodizing solution and applying a voltage to form a porous oxide layer on the workpiece. The workpiece is then removed from the phosphoric acid anodizing solution and immersed in a controlled anodizing solution. A voltage is applied to form a dense oxide layer under the porous oxide layer. Dissolution of the porous oxide layer is controlled during the formation of the dense oxide layer by using tartaric acid in the controlled acid solution such that the thickness of the porous oxide layer is substantially equivalent before and after the formation of the dense oxide layer. The duplex anodized layer can be further sealed by soaking in a sealing solution to protect the porous oxide layer from hydrolytic decomposition, to improve corrosion protection, and to enhance the bonding with other structural components through adhesives.



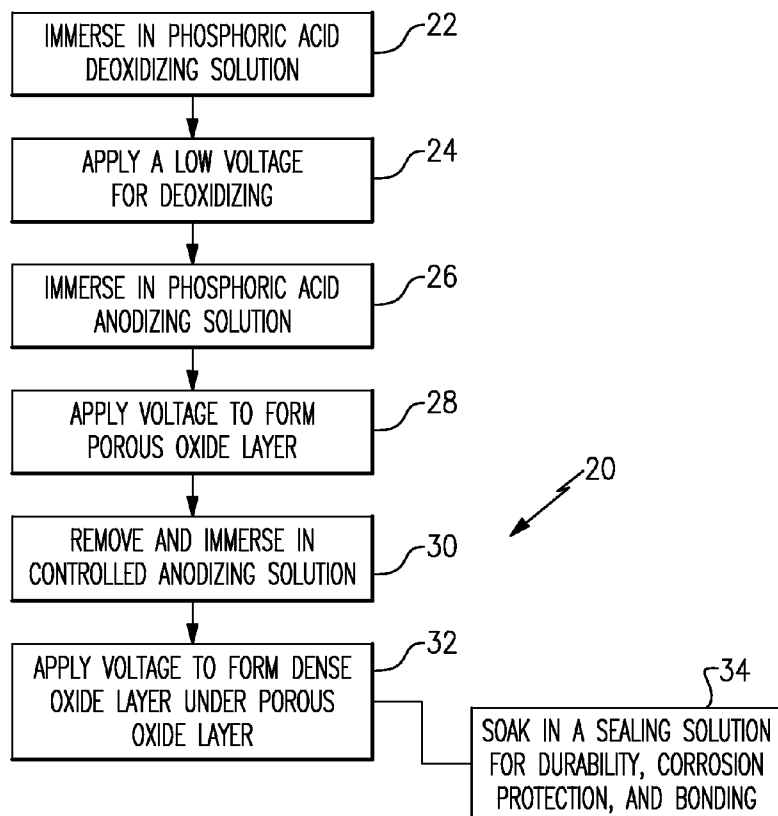


FIG.1

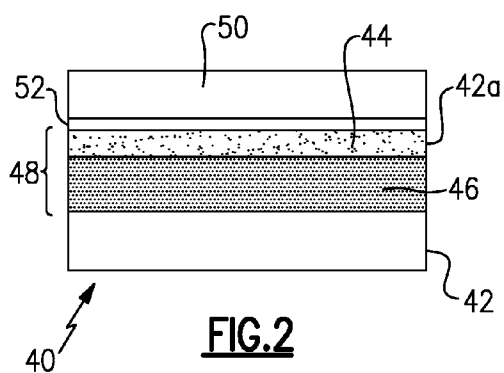


FIG.2

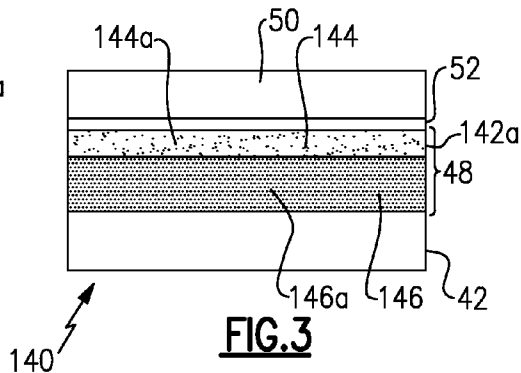


FIG.3

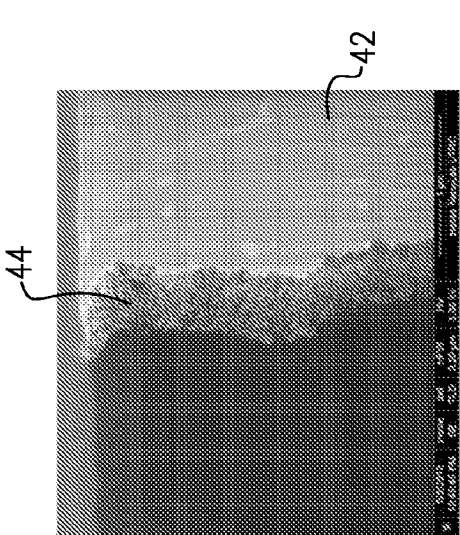


FIG.4

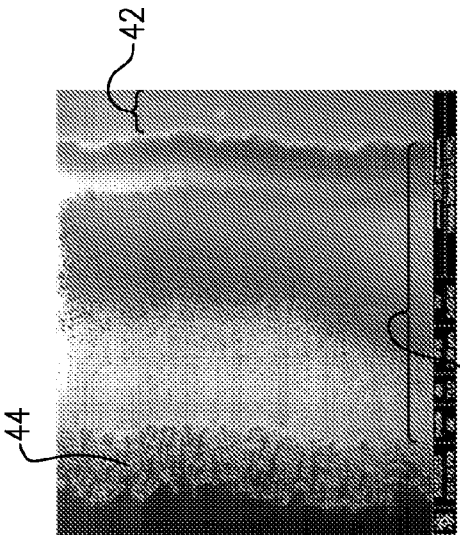


FIG.5

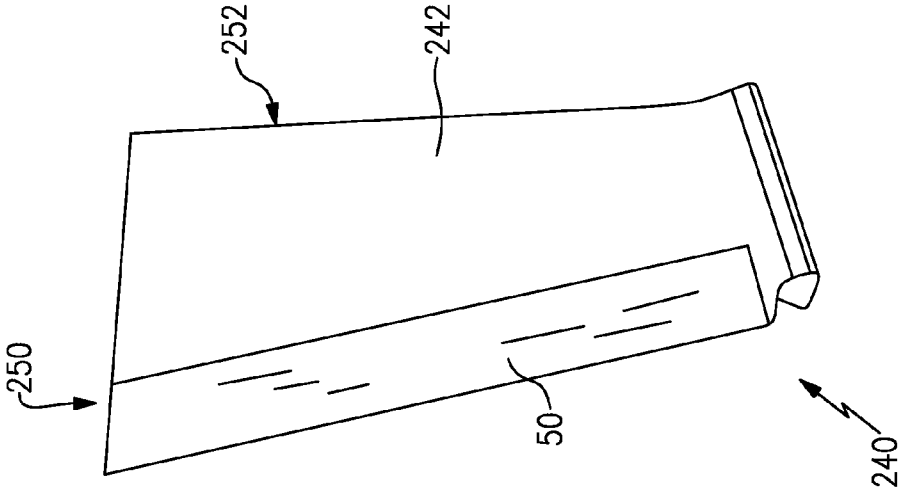


FIG.6

MULTIFUNCTIONAL ANODIZED LAYER

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present disclosure claims priority to U.S. Provisional Patent Application No. 62/026,823, filed Jul. 21, 2014.

BACKGROUND

[0002] This disclosure relates to anodizing aluminum alloys.

[0003] Anodized coatings are used to protect aluminum alloys from corrosion and to provide good adhesive bond strength. Some anodized coatings provide relatively good corrosion protection, but also have a relatively smooth surface that does not promote good bonding strength. Alternatively, other anodized coatings are textured and thus have good bonding strength but are porous and do not provide good corrosion resistance.

SUMMARY

[0004] A method of anodizing according to an example of the present disclosure includes immersing an aluminum alloy workpiece in a phosphoric acid anodizing solution, and applying a voltage to the aluminum alloy workpiece in the phosphoric acid anodizing solution. The phosphoric acid anodizing solution and the voltage act to form a porous oxide layer on the aluminum alloy workpiece. The method includes the steps of removing the aluminum alloy workpiece from the phosphoric acid anodizing solution and then immersing the aluminum alloy workpiece in a controlled anodizing solution, and applying a voltage to the aluminum alloy workpiece in the controlled anodizing solution. The controlled anodizing solution and the voltage act to form a dense oxide layer on the aluminum alloy workpiece under the porous oxide layer. The method includes the step of controlling dissolution of the porous oxide layer during the formation of the dense oxide layer by using tartaric acid in the controlled acid solution such that the thickness of the porous oxide layer is substantially equivalent before and after the formation of the dense oxide layer.

[0005] In a further embodiment of any of the foregoing embodiments, the controlled anodizing solution includes the tartaric acid and sulfuric acid.

[0006] In a further embodiment of any of the foregoing embodiments, the step of applying the voltage to the aluminum alloy workpiece in the controlled anodizing solution includes ramping the voltage to a predetermined hold voltage within three minutes, and then holding at the predetermined hold voltage for no more than 30 minutes.

[0007] In a further embodiment of any of the foregoing embodiments, the controlled anodizing solution has a temperature of 20-35° C. during the step of applying the voltage.

[0008] In a further embodiment of any of the foregoing embodiments, the tartaric acid has a concentration in the controlled acid solution of 60-100 gram/L.

[0009] In a further embodiment of any of the foregoing embodiments, the controlled anodizing solution consists essentially of the tartaric acid and sulfuric acid.

[0010] In a further embodiment of any of the foregoing embodiments, the controlled anodizing solution has a ratio of the tartaric acid to the sulfuric acid from 1:1 to 4:1.

[0011] In a further embodiment of any of the foregoing embodiments, the controlled anodizing solution has a ratio of the tartaric acid to the sulfuric acid of approximately 2:1.

[0012] In a further embodiment of any of the foregoing embodiments, the phosphoric acid anodizing solution is a 7.5 volume % phosphoric acid aqueous solution, and the phosphoric acid anodizing solution is at room temperature of 20-25° C. during the step of applying the voltage to the aluminum alloy workpiece in the phosphoric acid anodizing solution.

[0013] In a further embodiment of any of the foregoing embodiments, the phosphoric acid anodizing solution consists essentially of an aqueous phosphoric acid solution, and the controlled anodizing solution consists essentially of the tartaric acid and sulfuric acid.

[0014] A further embodiment of any of the foregoing embodiments includes immersing the aluminum alloy workpiece that has the porous oxide layer and the dense oxide layer in a nitrilotrismethylene solution.

[0015] A further embodiment of any of the foregoing embodiments includes immersing the aluminum alloy workpiece that has the porous oxide layer and the dense oxide layer in an aqueous trivalent chromium-containing sealing solution to deposit a chromium compound in the dense oxide layer.

[0016] An anodized article according to an example of the present disclosure includes an aluminum alloy substrate with a surface portion that is converted to a porous oxide layer of aluminum oxides/phosphates, a dense oxide layer under the surface portion, wherein the porous oxide layer of aluminum oxides/phosphates and the dense oxide layer together are a duplex coating that has an electric resistance of at least 10⁹ Ohms, and an electrically conductive material adjacent the duplex coating. The electrically conductive material is different in composition from the aluminum alloy, and the electric resistance of the duplex coating provides a galvanic corrosion barrier between the aluminum alloy substrate and the electrically conductive material.

[0017] In a further embodiment of any of the foregoing embodiments, the dense oxide layer includes residual tartaric acid and sulfate ions.

[0018] In a further embodiment of any of the foregoing embodiments, the dense oxide layer is sealed with a chromium compound.

[0019] In a further embodiment of any of the foregoing embodiments, the dense oxide layer is thicker than the porous oxide layer.

[0020] An anodized airfoil according to an example of the present disclosure includes an aluminum alloy airfoil extending between a leading end and a trailing end, with at least a surface portion of the leading end being converted to a porous oxide layer of aluminum oxides/phosphates, a dense oxide layer under the surface portion, wherein the porous oxide layer of aluminum oxides/phosphates and the dense oxide layer together are a duplex coating that has an electric resistance of at least 10⁹ Ohms, and a sheath formed of an electrically conductive material and mounted adjacent the duplex coating at the leading end of the aluminum alloy airfoil. The electrically conductive material is different in composition from the aluminum alloy, and the electric resistance of the duplex coating provides a galvanic corrosion barrier between the aluminum alloy airfoil and the electrically conductive material of the sheath.

[0021] In a further embodiment of any of the foregoing embodiments, the dense oxide layer includes residual tartaric acid and sulfate ions.

[0022] In a further embodiment of any of the foregoing embodiments, the dense oxide layer is sealed with a chromium compound.

[0023] In a further embodiment of any of the foregoing embodiments, the dense oxide layer is thicker than the porous oxide layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The various features and advantages of the present disclosure will become apparent to those skilled in the art from the following detailed description. The drawings that accompany the detailed description can be briefly described as follows.

[0025] FIG. 1 illustrates an example method of anodizing.

[0026] FIG. 2 illustrates an example anodized article.

[0027] FIG. 3 illustrates another example anodized article.

[0028] FIG. 4 illustrates a micrograph of an in-process workpiece during the method of FIG. 1.

[0029] FIG. 5 illustrates a workpiece after the method of FIG. 1.

[0030] FIG. 6 illustrates an anodized airfoil.

DETAILED DESCRIPTION

[0031] FIG. 1 schematically illustrates an example method 20 of anodizing an aluminum alloy workpiece. As will be described, the method 20 can be employed to anodize the aluminum alloy workpiece to provide good corrosion resistance, good bonding strength, and good electrical barrier properties.

[0032] As will be appreciated, the steps or actions described with respect to the method 20 can be employed with additional steps or other processes as desired. In this example, the method 20 includes a first immersion step 22, a first voltage application step 24, a second immersion step 26, a second voltage application step 28, a third immersion step 30, and a third voltage application step 32.

[0033] The first immersion step 22 includes immersing the aluminum alloy workpiece in a phosphoric acid deoxidizing solution. At the first voltage application step 24, a voltage is applied to the aluminum alloy workpiece in the phosphoric acid deoxidizing solution. The phosphoric acid deoxidizing solution and the voltage act to remove surface contaminants and native oxide on the aluminum alloy workpiece. In addition, the phosphoric acid deoxidizing solution and the voltage act to form a thin porous oxide layer with very fine filaments on the aluminum alloy workpiece.

[0034] The second immersion step 26 includes immersing the aluminum alloy workpiece from step 24 in a phosphoric acid anodizing solution. At the second voltage application step 28, a voltage is applied to the aluminum alloy workpiece in the phosphoric acid anodizing solution. The phosphoric acid anodizing solution and the voltage act to form a porous oxide layer on the aluminum alloy workpiece. For example, the porous oxide layer has aluminum oxides and phosphates.

[0035] The aluminum alloy workpiece is then removed from the phosphoric acid anodizing solution and in the third immersion step 30 is immersed in a controlled anodizing solution. At the third voltage application step 32, a voltage is applied to the aluminum alloy workpiece in the controlled

anodizing solution. The controlled anodizing solution and the voltage act to form a dense oxide layer under the porous oxide layer.

[0036] The resulting coating is a duplex coating with the porous oxide layer exposed at the surface and the dense oxide layer formed underneath. The porous oxide layer is relatively fragile and can be susceptible to dissolution in during the anodization. In this regard, dissolution of the porous oxide layer during the formation of the dense oxide layer is controlled by using tartaric acid in the controlled acid solution. The tartaric acid facilitates the formation of the dense oxide layer, but its action is not so severe such to dissolve the porous oxide layer. Therefore, the thickness of the porous oxide layer is substantially equivalent before and after the formation of the dense oxide layer.

[0037] As an example, the porous oxide layer has a filament structure of an amorphous oxide. The filament structure is also substantially preserved by use of the controlled acid solution. By preserving these features and thickness of the porous oxide layer, the properties of the porous oxide layer can also be preserved in the resulting duplex coating. In this regard, the duplex coating that is formed has an electric resistance of at least 10^9 ohms. Particularly where the duplex layer is used both as a corrosion resistant layer and for adhesive bonding with another, dissimilar and electrically conductive material, the high electrical resistance of the duplex layer serves as a galvanic barrier between the underlying aluminum alloy and the overlying electrically conductive material. Thus, the duplex layer in some examples can serve the multiple functions of corrosion resistance, adhesion promotion, and galvanic protection.

[0038] In a further example, the controlled anodizing solution includes the tartaric acid and also sulfuric acid in a mixed acid solution. For example, the concentration of the tartaric acid in the mixed acid solution can be 60-100 gram/L. In further examples, the controlled anodizing solution includes only the tartaric acid and the sulfuric acid, and possibly impurities. The ratio of tartaric acid to the sulfuric acid is from 1:1 to 4:1, and can be 2:1 for best control over preserving the porous oxide layer. In further examples, the tank temperature of the controlled anodizing solution during the formation of the dense oxide layer is 20-35° C.

[0039] The resulting duplex layer can be further treated to improve the properties as desired. In one example, the duplex coating is further treated by immersion in a nitrilotri(methylene) (NTMP) solution, as in step 34. The NTMP solution acts to stabilize the porous oxide layer, to enhance bonding with a later-applied adhesive, such as epoxy, and to improve the corrosion barrier properties of the duplex oxide layer. Without being bound, the NTMP adsorbs onto the porous oxide layer to form a monolayer that renders the porous oxide layer hydrophobic and promotes bonding with epoxy or other later-applied adhesives.

[0040] Alternatively, or in addition to the NTMP solution, the duplex coating can also be treated to further enhance corrosion resistance by immersion in an aqueous trivalent chromium-containing sealing solution. In this regard, the aqueous chromium solution seals the dense oxide layer through formation of a chromium compound in the dense oxide layer. Therefore, the NTMP solution and the aqueous chromium solution can be used singly or in cooperation, with the NTMP solution enhancing bonding and the aqueous chromium solution enhancing corrosion resistance.

[0041] FIGS. 4 and 5 are micrographs of a workpiece at various points through the example method 20. FIG. 4 shows a workpiece having an aluminum alloy substrate 42 and a porous oxide layer 44 formed during the voltage application step 28 but prior to the formation of a dense oxide layer 46. FIG. 5 shows the workpiece after the formation of the dense oxide layer 46. The thickness of the porous oxide layer 44, along a direction substantially perpendicular to the surface of the aluminum alloy substrate 42, is substantially equivalent before and after the formation of the dense oxide layer 46.

[0042] The following examples illustrate further embodiments of the method 20.

[0043] An Al alloy sheet (Al2024) was washed with organic solvent to remove surface paints or stains. The sheet was then etched with sodium hydroxide aqueous solution and rinsed with water. The etched Al alloy sheet was then deoxidized in nitric acid solution and rinsed with water. The Al alloy sheet was then electrochemically deoxidized in phosphoric acid under the following conditions:

[0044] 15 v % phosphoric acid aqueous solution;

[0045] 29° C. solution temperature;

[0046] voltage ramp from 0V to 7.5V within a minute;

[0047] maintain voltage at 7.5V for 15 minutes.

[0048] The Al alloy sheet was removed from the deoxidizing bath and rinsed with water.

[0049] The Al alloy sheet was then anodized in phosphoric acid anodizing solution under the following condition, to form the porous oxide layer:

[0050] 7.5 v % phosphoric acid aqueous solution;

[0051] room temperature (approximately 23° C.);

[0052] voltage ramp at approximately 5V/min to 15V within 3 minutes;

[0053] maintain the voltage at 15V for 20 minutes.

[0054] The Al alloy sheet was removed from the phosphoric acid anodizing bath and rinsed with water. The Al alloy sheet was then immersed in the controlled anodizing solution of a mixture of sulfuric acid and tartaric acid, under the following conditions:

[0055] tartaric acid 80 g/L+Sulfuric acid 40 g/L;

[0056] 35° C. electrolyte bath temperature;

[0057] voltage ramp at approximately 5V/min to 13V within 3 minutes;

[0058] maintain the voltage at 13V for 20 minutes.

[0059] The Al alloy sheet was removed from the controlled anodizing solution and rinsed with water.

[0060] The Al alloy sheet was then immersed in a 300 ppm nitrilotris(methylene phosphoric acid (NTMP) at room temperature for 15 minutes for sealing.

[0061] FIG. 2 illustrates an example anodized article 40 produced by the method 20. In this example, the anodized article 40 includes the aluminum alloy substrate 42 with a surface portion 42a that is converted to the porous oxide layer 44, corresponding to the steps 22 to 28 above. The porous oxide layer 44 includes aluminum oxides/phosphates that are formed during the voltage application step 28 of the method 20. The porous oxide layer 44 can be 0.2-0.8 micrometers in thickness and more specifically may be 0.3-0.5 micrometers in thickness.

[0062] The anodized article 40 also includes the dense oxide layer 46 that is under the surface portion 42a. The dense oxide layer 46 can be 1-4 micrometers in thickness, but is usually 2-3 micrometers for enhanced fatigue resistance. The dense oxide layer 46 can include residual tartaric acid and sulfate ions from the method 20 described above. The porous

oxide layer 44 and the dense oxide layer 46 together are a duplex coating 48 that has an electric resistance of at least 10⁹ ohms

[0063] The article 40 also includes an electrically conductive material 50 adjacent the duplex coating 48. For example, the electrically conductive material 50 is bonded to the duplex coating 48 with an intermediate adhesive layer 52. The intermediate adhesive layer 52 can be a polymeric-based adhesive. One example polymeric-based adhesive is epoxy-based adhesive, but this disclosure is not limited to epoxy-based adhesives.

[0064] The electrically conductive material 50 is different in composition from the aluminum alloy of the substrate 42. Due to the electrical conductivity of the electrically conductive material 50 and of the aluminum alloy substrate 42, along with the close proximity of these materials to each other, a galvanic couple could form and accelerate corrosion. However, the relatively high electric resistance of the duplex coating 48 provides a galvanic corrosion barrier between the aluminum alloy of substrate 42 and the electrically conductive material 50 to prevent galvanic corrosion.

[0065] FIG. 3 illustrates a modified example of an anodized article 140. In this disclosure, like reference numerals designate like elements where appropriate and reference numerals with the addition of one-hundred or multiples thereof designate modified elements that are understood to incorporate the same features and benefits of the corresponding elements. In this example, the article 140 also includes a surface portion 142a that has a porous oxide layer 144, but the porous oxide layer 144 has been treated with the NTMP solution as described above, as represented at areas 144a. The article 140 also includes a dense oxide layer 146. Alternatively to the NTMP treatment, or in addition thereto, the dense oxide layer 146 can be treated with an aqueous chromium solution to locally form chromium compounds, represented at 146a. The chromium compounds seal the dense oxide layer 146 and further enhance the corrosion resistance of the duplex coating 48.

[0066] FIG. 6 illustrates another example of an anodized article, namely an anodized airfoil 240. The anodized airfoil include an aluminum alloy airfoil (substrate) 242 that extends between a leading end 250 and a trailing end 252, with at least a surface portion of the leading end 250 being converted to a porous oxide layer of aluminum oxides/phosphates, as described herein above. In this example, the anodized airfoil 240 is substantially as described with reference to the article 40 of FIG. 2, and the electrically conductive material 50 is a sheath that is mounted adjacent the duplex coating at the leading end 250 of the anodized airfoil 240. For example, the electrically conductive material 50 of the sheath is titanium or a titanium-based alloy. The duplex coating (FIG. 2) provides a galvanic corrosion barrier between the aluminum alloy airfoil 242 and the electrically conductive material 50 of the sheath.

[0067] Although a combination of features is shown in the illustrated examples, not all of them need to be combined to realize the benefits of various embodiments of this disclosure. In other words, a system designed according to an embodiment of this disclosure will not necessarily include all of the features shown in any one of the Figures or all of the portions schematically shown in the Figures. Moreover, selected features of one example embodiment may be combined with selected features of other example embodiments.

[0068] The preceding description is exemplary rather than limiting in nature. Variations and modifications to the disclosed examples may become apparent to those skilled in the art that do not necessarily depart from the essence of this disclosure. The scope of legal protection given to this disclosure can only be determined by studying the following claims.

What is claimed is:

1. A method of anodizing comprising:
 - immersing an aluminum alloy workpiece in a phosphoric acid anodizing solution;
 - applying a voltage to the aluminum alloy workpiece in the phosphoric acid anodizing solution, the phosphoric acid anodizing solution and the voltage acting to form a porous oxide layer on the aluminum alloy workpiece;
 - removing the aluminum alloy workpiece from the phosphoric acid anodizing solution and then immersing the aluminum alloy workpiece in a controlled anodizing solution;
 - applying a voltage to the aluminum alloy workpiece in the controlled anodizing solution, the controlled anodizing solution and the voltage acting to form a dense oxide layer on the aluminum alloy workpiece under the porous oxide layer; and
 - controlling dissolution of the porous oxide layer during the formation of the dense oxide layer by using tartaric acid in the controlled acid solution such that the thickness of the porous oxide layer is substantially equivalent before and after the formation of the dense oxide layer.
2. The method as recited in claim 1, wherein the controlled anodizing solution includes the tartaric acid and sulfuric acid.
3. The method as recited in claim 1, wherein the applying of the voltage to the aluminum alloy workpiece in the controlled anodizing solution includes ramping the voltage to a predetermined hold voltage within three minutes, and then holding at the predetermined hold voltage for no more than 30 minutes.
4. The method as recited in claim 1, wherein the controlled anodizing solution has a temperature of 20-35° C. during the applying of the voltage.
5. The method as recited as claim 1, wherein the tartaric acid has a concentration in the controlled acid solution of 60-100 gram/L.
6. The method as recited in claim 1, wherein the controlled anodizing solution consists essentially of the tartaric acid and sulfuric acid.
7. The method as recited in claim 6, wherein the controlled anodizing solution has a ratio of the tartaric acid to the sulfuric acid from 1:1 to 4:1.
8. The method as recited in claim 6, wherein the controlled anodizing solution has a ratio of the tartaric acid to the sulfuric acid of approximately 2:1.
9. The method as recited in claim 1, wherein the phosphoric acid anodizing solution is a 7.5 volume % phosphoric acid aqueous solution, and the phosphoric acid anodizing solution is at room temperature of 20-25° C. during the applying of the voltage to the aluminum alloy workpiece in the phosphoric acid anodizing solution.
10. The method as recited in claim 1, wherein the phosphoric acid anodizing solution consists essentially of an aque-

ous phosphoric acid solution, and the controlled anodizing solution consists essentially of the tartaric acid and sulfuric acid.

11. The method as recited in claim 1, further comprising immersing the aluminum alloy workpiece that has the porous oxide layer and the dense oxide layer in a nitrilotrismethylene solution.

12. The method as recited in claim 1, further comprising immersing the aluminum alloy workpiece that has the porous oxide layer and the dense oxide layer in an aqueous trivalent chromium-containing sealing solution to deposit a chromium compound in the dense oxide layer.

13. An anodized article comprising:

- an aluminum alloy substrate with a surface portion that is converted to a porous oxide layer of aluminum oxides/phosphates;
- a dense oxide layer under the surface portion, wherein the porous oxide layer of aluminum oxides/phosphates and the dense oxide layer together are a duplex coating that has an electric resistance of at least 10^9 Ohms; and
- an electrically conductive material adjacent the duplex coating, the electrically conductive material being different in composition from the aluminum alloy, and the electric resistance of the duplex coating providing a galvanic corrosion barrier between the aluminum alloy substrate and the electrically conductive material.

14. The anodized article as recited in claim 13, wherein the dense oxide layer includes residual tartaric acid and sulfate ions.

15. The anodized article as recited in claim 13, wherein the dense oxide layer is sealed with a chromium compound.

16. The anodized article as recited in claim 13, wherein the dense oxide layer is thicker than the porous oxide layer.

17. An anodized airfoil comprising:

- an aluminum alloy airfoil extending between a leading end and a trailing end, with at least a surface portion of the leading end being converted to a porous oxide layer of aluminum oxides/phosphates;
- a dense oxide layer under the surface portion, wherein the porous oxide layer of aluminum oxides/phosphates and the dense oxide layer together are a duplex coating that has an electric resistance of at least 10^9 Ohms; and
- a sheath formed of an electrically conductive material and mounted adjacent the duplex coating at the leading end of the aluminum alloy airfoil, the electrically conductive material being different in composition from the aluminum alloy, and the electric resistance of the duplex coating providing a galvanic corrosion barrier between the aluminum alloy airfoil and the electrically conductive material of the sheath.

18. The anodized airfoil as recited in claim 17, wherein the dense oxide layer includes residual tartaric acid and sulfate ions.

19. The anodized airfoil as recited in claim 17, wherein the dense oxide layer is sealed with a chromium compound.

20. The anodized airfoil as recited in claim 17, wherein the dense oxide layer is thicker than the porous oxide layer.

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