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# (54) METHOD FOR PLATING A METALLIC MATERIAL ONTO A TITANIUM SUBSTRATE

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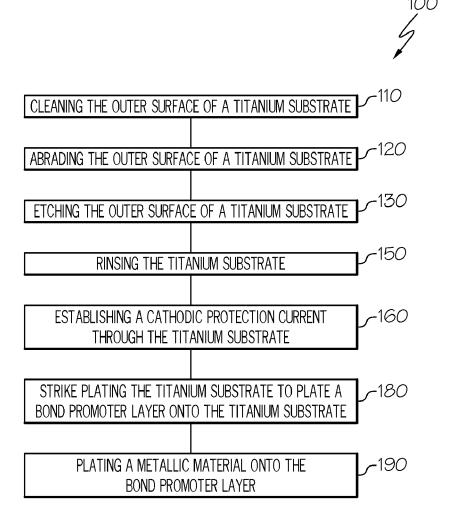
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#### (57)ABSTRACT

A method for plating a metallic material onto a titanium substrate, wherein the titanium substrate includes an outer surface and an oxide layer on the outer surface. The method includes chemically etching the outer surface of the titanium substrate to remove at least a portion of the oxide layer, thereby yielding an etched titanium substrate. The method also includes establishing a cathodic protection current through the etched titanium substrate while the etched titanium substrate is immersed in a cathodic electrolyte solution. The method further includes strike plating a bond promoter layer onto the outer surface of the etched titanium substrate after the establishing of the cathodic protection current. The method lastly includes plating the metallic material onto the bond promoter layer.



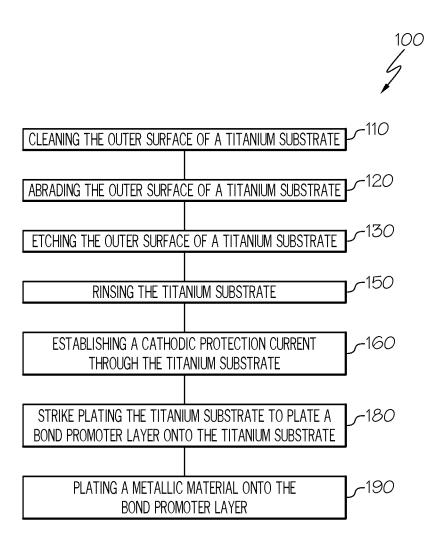


FIG. 1

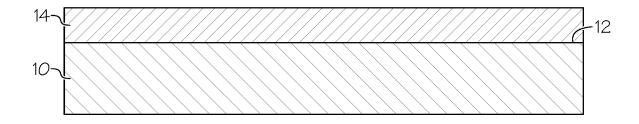


FIG. 2

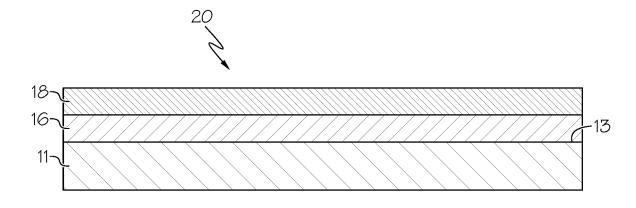


FIG. 3

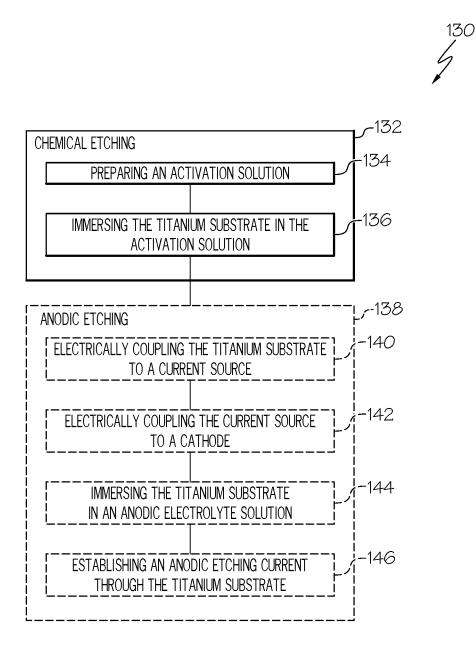


FIG. 4

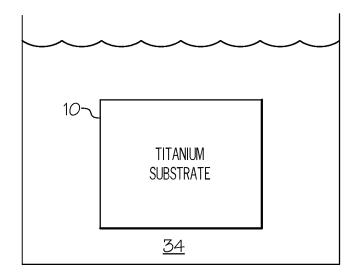


FIG. 5

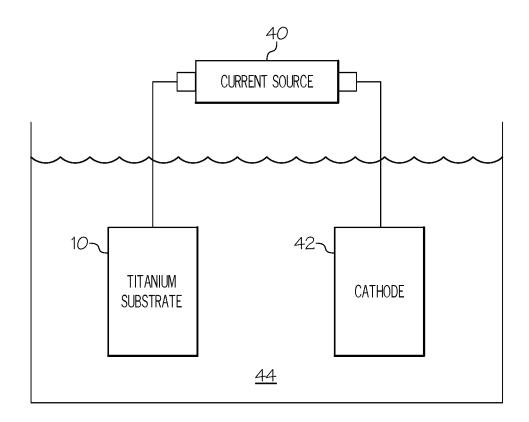


FIG. 6

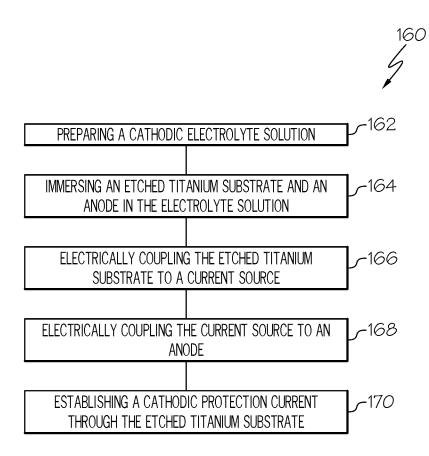


FIG. 7

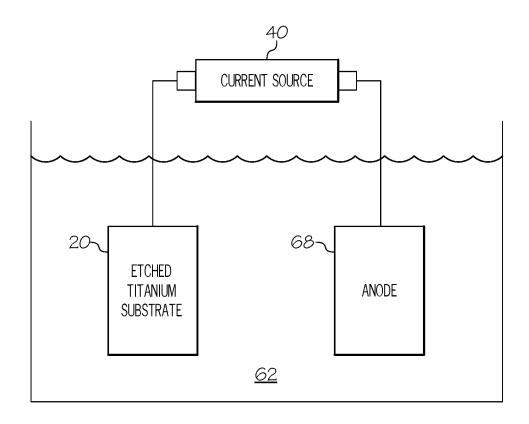


FIG. 8

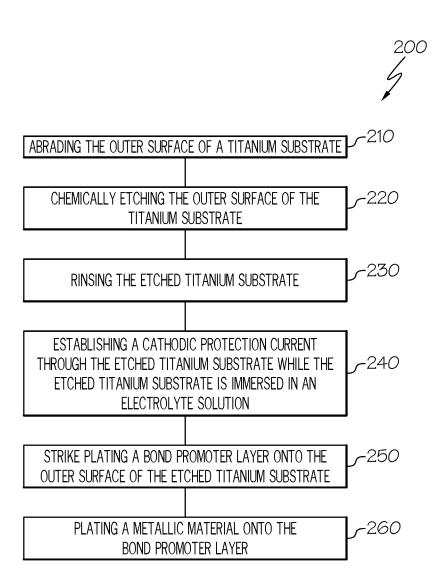


FIG. 9

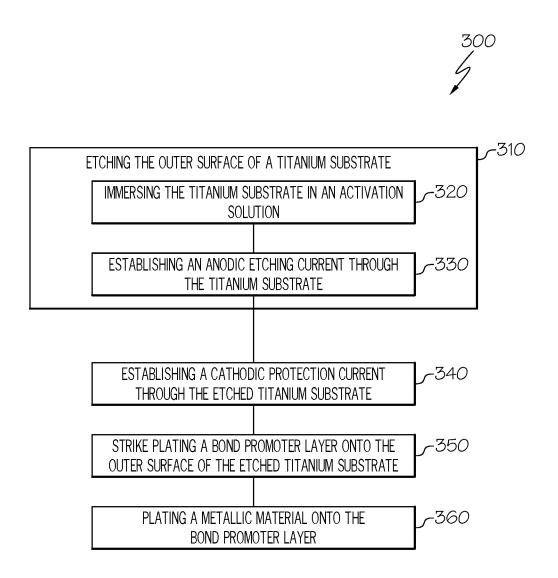


FIG. 10

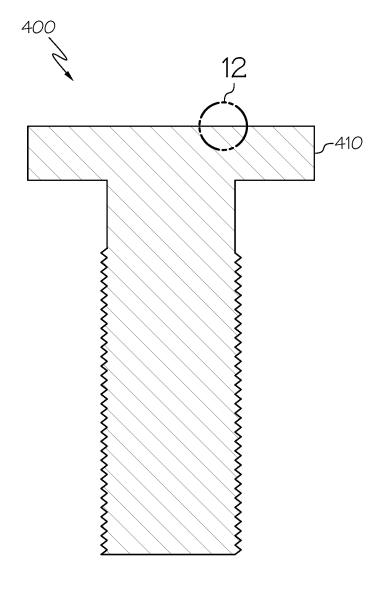


FIG. 11

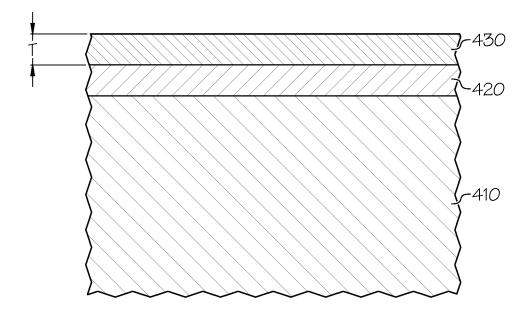


FIG. 12

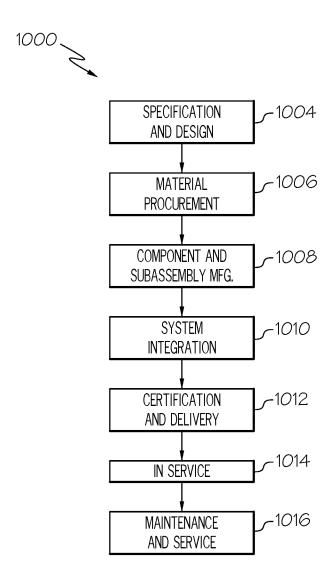


FIG. 13

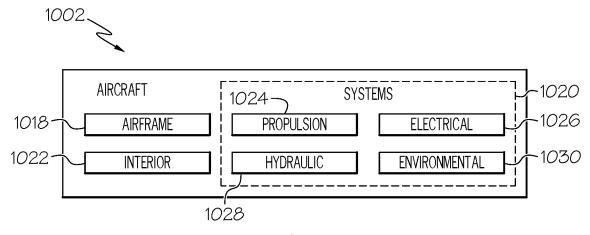


FIG. 14

# METHOD FOR PLATING A METALLIC MATERIAL ONTO A TITANIUM SUBSTRATE

#### **FIELD**

[0001] This application relates to plating a metallic material onto a titanium substrate and, more particularly, to methods for removing a protective oxide layer on the titanium substrate before electroplating the metallic material

#### BACKGROUND

[0002] Titanium substrates are plated with metallic materials for various reasons.

[0003] For example, mechanical fasteners are widely used for joining the structural components of the airframe of an aircraft. Such mechanical fasteners are often fabricated from titanium alloys due to the desirable light weight and corrosion resistant qualities of titanium. However, titanium alloys can suffer from poor wear resistance, can be galvanically incompatible with aluminum alloys that are used for major fuselage and wing structure applications, and can be embrittled by elevated temperature phosphate ester hydraulic fluid used in commercial aircraft.

[0004] Many of the drawbacks of titanium alloys can be addressed by plating. However, metallic plating on titanium substrates is often complicated by the extremely stable oxide formation on the surface of the titanium substrate, and also by the fact that very few chemical etchants are capable of attacking the oxide formation.

[0005] Accordingly, those skilled in the art continue with research and development efforts in the field of plating onto titanium substrates.

# SUMMARY

[0006] Disclosed are methods for plating metallic materials onto titanium substrates.

[0007] In one example, the disclosed method for plating a metallic material onto a titanium substrate (having an outer surface and an oxide layer on the outer surface) includes chemically etching the outer surface of the titanium substrate to remove at least a portion of the oxide layer, thereby yielding an etched titanium substrate. The method also includes establishing a cathodic protection current through the etched titanium substrate while the etched titanium substrate is immersed in a cathodic electrolyte solution, and then strike plating a bond promoter layer onto the outer surface of the etched titanium substrate after the establishing of the cathodic protection current. The method further includes plating the metallic material onto the bond promoter layer.

[0008] In another example, the disclosed method for plating a metallic material onto a titanium substrate (having an outer surface and an oxide layer on the outer surface) includes abrading the outer surface of the titanium substrate and chemically etching the outer surface of the titanium substrate to remove at least a portion of the oxide layer, thereby yielding an etched titanium substrate. The method also includes rinsing the etched titanium substrate and establishing a cathodic protection current through the etched titanium substrate while the etched titanium substrate is immersed in a cathodic electrolyte solution. The method further includes strike plating a bond promoter layer onto the outer surface of the etched titanium substrate after the

establishing of the cathodic protection current. The method lastly includes plating the metallic material onto the bond promoter layer.

[0009] In yet another example, the disclosed method for plating a metallic material onto a titanium substrate (having an outer surface and an oxide layer on the outer surface) includes etching the outer surface of the titanium substrate to yield an etched titanium substrate, wherein the etching includes immersing the titanium substrate in an activation solution and establishing an anodic etching current through the titanium substrate while the titanium substrate is immersed in the activation solution. The method also includes establishing a cathodic protection current through the etched titanium substrate while the etched titanium substrate is immersed in a cathodic electrolyte solution and then strike plating a bond promoter layer onto the outer surface of the etched titanium substrate after the establishing of the cathodic protection current. The method further includes plating the metallic material onto the bond promoter layer.

[0010] Also disclosed are articles manufactured using the disclosed methods for plating a metallic material onto a titanium substrate. Non-limiting examples of such articles include mechanical fasteners, ducts and struts.

[0011] Other examples of the disclosed methods and articles formed therefrom will become apparent from the following detailed description, the accompanying drawings and the appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a flow diagram depicting an example of the disclosed method for plating a metallic material onto a titanium substrate:

[0013] FIG. 2 is a schematic illustration of a titanium substrate having an outer surface and an oxide layer on the outer surface:

[0014] FIG. 3 is a schematic illustration of a plated structure manufactured in accordance with the method for plating depicted in FIG. 1;

[0015] FIG. 4 is a flow diagram depicting an example method for etching the outer surface of a titanium substrate in accordance with the method for plating depicted in FIG. 1:

[0016] FIG. 5 is a schematic illustration of a system for activating a titanium substrate in accordance with the method for plating depicted in FIG. 1;

[0017] FIG. 6 is a schematic illustration of an electrochemical cell for establishing an anodic etching current in accordance with the method for plating depicted in FIG. 1;

[0018] FIG. 7 is a flow diagram depicting an example method for establishing a cathodic protection current through a titanium substrate in accordance with the method for plating depicted in FIG. 1;

[0019] FIG. 8 is a schematic illustration of an electrochemical cell for establishing a cathodic protection current in accordance with the method for plating depicted in FIG. 1:

[0020] FIG. 9 is another flow diagram depicting an example of the disclosed method for plating a metallic material onto a titanium substrate;

[0021] FIG. 10 is yet another flow diagram depicting an example of the disclosed method for plating a metallic material onto a titanium substrate;

[0022] FIG. 11 is a cross-sectional view of an article, particularly a mechanical fastener (e.g., a bolt), manufactured in accordance with the method of FIG. 1;

[0023] FIG. 12 is a cross-sectional view of a portion of the article shown in FIG. 11;

[0024] FIG. 13 is a flow diagram of an aircraft manufacturing and service methodology; and

[0025] FIG. 14 is a block diagram of an aircraft.

#### DETAILED DESCRIPTION

[0026] The following detailed description refers to the accompanying drawings, which illustrate specific examples described by the disclosure. Other examples having different structures and operations do not depart from the scope of the present disclosure. Like reference numerals may refer to the same feature, element, or component in the different drawings.

[0027] Illustrative, non-exhaustive examples, which may be, but are not necessarily, claimed, of the subject matter according the present disclosure are provided below. Reference herein to "example" means that one or more feature, structure, element, component, characteristic and/or operational step described in connection with the example is included in at least one embodiment and/or implementation of the subject matter according to the present disclosure. Thus, the phrase "an example" and similar language throughout the present disclosure may, but do not necessarily, refer to the same example. Further, the subject matter characterizing any one example may, but does not necessarily, include the subject matter characterizing any other example.

[0028] Referring to FIGS. 1-3, the present disclosure provides examples of a method 100 for plating a metallic material 18 onto a titanium substrate 10 that includes an outer surface 12 and an oxide layer 14 on the outer surface 12. In performing the method 100, at least a portion of the oxide layer 14 may be removed so that the metallic material 18 may then be plated onto an etched titanium substrate 11 (FIG. 3). Further, an intermediate bond promoter layer 16 may be provided between the etched titanium substrate 11 and the metallic material 18 to promote plating adherence. As such, the resulting plated structure 20 may retain the desirable qualities of titanium (e.g., lightweight and corrosion-resistant) while also possessing the bonding and grounding attributes of the metallic material 18.

[0029] The method 100 includes etching (block 130) the outer surface 12 of the titanium substrate 10 and, at block 160, establishing a cathodic protection current through the titanium substrate 10 that has been etched. Blocks 130 and 160 may be performed to remove the oxide layer 14 on the outer surface 13 of the etched titanium substrate 11. Following oxide layer removal, the method 100 further includes, at block 180, strike plating the titanium substrate to plate a bond promoter layer 16 onto the titanium substrate 10 and, at block 190, plating a metallic material 18 onto the bond promoter layer 16.

[0030] The method 100 may be performed on any suitable titanium substrate 10 regardless of size, shape and function. In one example, the titanium substrate 10 may be a commercially available one-sided lockbolt mechanical fastener. By performing the method 100 on the mechanical fastener, the plated mechanical fastener may exhibit improved bonding and grounding capabilities. In another example, the titanium substrate 10 may be a custom-machined portion of

a fuselage, which may be plated on for similar reasons. Those skilled in the art will appreciate that various other types of titanium substrates 10 may be employed without departing from the scope of the present disclosure.

[0031] The material composition of the titanium substrate 10 may include pure titanium, any suitable titanium alloy and any combination thereof. One suitable titanium material may include, for example, Ti-6Al-4V. Further, the titanium substrate 10 may be homogenous in its composition or contain discrete regions of different titanium materials. For example, the titanium substrate 10 shown in FIGS. 2, 3, 5, 6 and 8 may be formed from a titanium alloy (e.g., Ti-6Al-4V). Those skilled in the art will appreciate that the suitability of any particular titanium alloy may be based, at least in part, on the compatibility of that titanium alloy with the bond promoter layer 16 to be strike plated.

[0032] Often, the outer surface 12 of a titanium substrate 10 may contain debris (e.g., foreign contaminants). This debris obstructs access to the oxide layer 14 and, if not removed, may hinder efforts to remove the oxide layer 14. Accordingly, the method 100 may begin at block 110 with cleaning the outer surface 12 of a titanium substrate 10 to remove debris (if any). In an example, the cleaning (block 110) may be performed by wiping the outer surface 12 of the titanium substrate 10 with a solvent wipe. In an example, the cleaning (block 110) may be performed by exposing the outer surface 12 to an organic solvent. In an example, the cleaning (block 110) may be performed by blasting the outer surface 12 with a dry abrasive. In an example, the cleaning (block 110) may be performed by vibratory finishing. In an example, the cleaning (block 110) may be performed by barrel tumbling. Those skilled in the art will appreciate that various other cleaning methods may be employed without departing from the scope of the present disclosure.

[0033] The method 100 may include, at block 120, abrading (e.g., roughening) the outer surface 12 of a titanium substrate 10. In doing so, the abrading (block 120) may mechanically remove at least a portion of the oxide layer 14, if not most of it. Those skilled in the art will appreciate that abrading (block 120) the outer surface 12 of the titanium substrate 10 may also increase the overall surface area of the outer surface 12, thereby increasing the dissolvability of the oxide layer 14.

[0034] A suitable abrasion method may be determined based on, among other things, the number of titanium substrates 10 to be abraded. In one example, batches of titanium substrates 10 may be abraded in a tumbler. Of course, this abrasion method may be preferred for applications involving large numbers of titanium substrates 10. For applications involving fewer titanium substrates 10, blasting the titanium substrates 10 with an abrasive medium may be adequate. In these examples, the blasting may be performed using either wet or dry abrasive mediums, and abrasive mediums of varying grit sizes. In one example, the abrading (block 120) may include blasting the titanium substrate 10 with an abrasive medium having a grit size of at least about 60 microns. In another example, the abrading (block 120) may include blasting the titanium substrate 10 with an abrasive medium having a grit size of at least about 100 microns. In yet another example, the abrading (block 120) may include blasting the titanium substrate 10 with an abrasive medium having a grit size of at least about 140 microns. Those skilled in the art will appreciate that various other abrasive mediums and abrasion methods may be employed without departing from the scope of the present disclosure.

[0035] Referring to FIG. 4, the method 100 includes, at block 130, etching the outer surface 12 of a titanium substrate 10 to remove at least a portion of the oxide layer 14, thereby yielding an etched titanium substrate 11. Like the abrading (block 120), the etching (block 130) may be performed to reduce the oxide layer 14 in preparation for subsequent plating (block 190).

[0036] Referring to FIG. 5, the etching (block 130) may be performed by chemical etching (block 132) the outer surface 12 of the titanium substrate 10. More specifically, a suitable activation solution 34 may be prepared (block 134 ("preparing an activation solution")) and the titanium substrate may be immersed (block 136 ("immersing the titanium substrate in the activation solution")) in it for a predetermined duration of time or until a desired amount of oxide layer 14 has been removed. The reason for the etching is to remove the top 0.5-5 micron layer on the surface that is disturbed material and slightly embedded grit (called the Bielby layer) that is detrimental to good plating adhesion. [0037] While any suitable oxide removal mechanism may

[0037] While any suitable oxide removal mechanism may be employed, it is generally contemplated that the activation solution 34 should include an oxide removal agent and a complexing agent. The oxide removal agent may remove oxygen ions from the oxide layer 14, thereby dissolving the oxide layer 14, and the complexing agent may complex with the oxygen ions in solution (e.g., oxygen scavenging) to prevent the oxide layer 14 from reforming.

[0038] The oxide removal agent may be fluoride-based (e.g., contains fluoride ions) and may be added to the activation solution 34 as a fluoride salt. For example, the activation solution 34 may include from about 2 grams to about 8 grams of sodium fluoride per liter of activation solution 34. In another example, the activation solution 34 may include from about 4 grams to about 6 grams of sodium fluoride per liter of activation solution 34. Those skilled in the art will appreciate that due to the relatively dilute concentration of fluoride in the activation solution 34, the activation solution 34 may be less toxic than most available chemical etchants.

[0039] Any suitable complexing agent (or complexing agents) may be employed to scavenge for oxygen ions in the activation solution 34. For example, reducing agents, such as ascorbic acid, oxalic acid, and bisulfite, can be used. It is generally contemplated, however, that the suitability of a complexing agent may be determined, at least in part, on the compatibility of the complexing agent with the oxide removal agent, and possibly other activation solution components as well (if included). The complexing agent should not interfere/hinder those associated mechanisms (e.g., oxide removal, etc.). One such type of a suitable complexing agent may include, for example, citric acid, or similar organic acids. In one example, the activation solution 34 may include at least about 30 grams of citric acid per liter of activation solution 34. In another example, the activation solution 34 may include at least about 50 grams of citric acid per liter of activation solution 34. In another example, the activation solution 34 may include at least about 70 grams of citric acid per liter of activation solution 34. In another example, the activation solution 34 may include about 30 to about 80 grams of citric acid per liter of activation solution 34. Those skilled in the art will appreciate that other complexing agents may be employed at various concentrations without departing from the scope of the present disclosure.

[0040] In addition to the oxide removal agent and the complexing agent, in one or more examples, the activation solution 34 may also include a non-oxidizing acid. Those skilled in the art will appreciate that non-oxidizing acids are less likely than oxidizing acids to oxidize the titanium substrate 10, and may be included to help keep the pH of the activation solution 34 relatively low (e.g., pH less than 5). Without being bound by any particular theory, it is believed that by keeping the pH of the activation solution 34 relatively low, the available concentration of hydroxide ions in solution may be suppressed and an optimal environment for oxide removal may be provided. However, it is also generally contemplated that the pH of the activation solution 34 need not be overly acidic (e.g., pH less than 3) or immersed for too long due to the potential of hydrogen ingress into the titanium substrate 10 (e.g., hydrogen embrittlement).

[0041] In one example, the non-oxidizing acid may include sulfuric acid. More specifically, the activation solution 34 may include sulfuric acid at concentrations dilute enough such that the reduction of sulfate to SO<sub>2</sub> (which is oxidizing) does not occur. For example, the activation solution 34 may include at least about 50 grams of sulfuric acid per liter of activation solution 34, such about 50 to 150 grams of sulfuric acid per liter of activation solution 34. In another example, the activation solution 34 may include at least about 90 grams of sulfuric acid per liter of activation solution 34. In yet another example, the activation solution 34 may include at least about 130 grams of sulfuric acid per liter of activation solution 34.

[0042] In other examples, the non-oxidizing acid may include phosphoric acid, phosphorous acid, fluoboric acid, or fluosilicic acid if the acid and fluoride sources are combined.

[0043] Referring back to FIG. 4, the etching (block 130) may also include anodic etching (block 138) the titanium substrate 10 to further remove the oxide layer 14. As shown in FIG. 6, the anodic etching (block 138) may be performed in a standard two-electrode bath, wherein the titanium substrate 10 (e.g., the anode) and a suitable cathode 42 is electrically coupled (blocks 140 ("electrically coupling the titanium substrate to a current source") and 142 ("electrically coupling the current source to a cathode")) to a current source 40, and immersed (block 144 ("immersing the titanium substrate in an anodic electrolyte solution")) in an anodic electrolyte solution 44. By establishing an anodic etching current through the titanium substrate 10, as shown in block 146, a reduction reaction may occur on the outer surface 12 of the titanium substrate 10, thereby causing the removal of surface-level titanium (e.g., etching). In doing so, at least a portion of the oxide layer 14 may be removed as well. The application of anodic current means hydrogen evolution occurs on the cathode and away from the part.

[0044] In one or more examples, the anodic etching (block 138) may be performed simultaneously with the chemical etching (block 132). More specifically, blocks 140-146 may be performed while the titanium substrate 10 is immersed in an activation solution 34. The activation solution 34 may be formulated to contain charge-carrying electrolytes, thereby completing the electrochemical cell (meaning that a separate anodic electrolyte solution is not needed). Without being bound by any particular theory, it is believed that by

performing blocks 132 and 138 simultaneously, the anodic etching (block 138) may enable the use of less toxic activation solutions 34 at lower temperatures because the anodic etching (block 138) compensates for the diminished capability of the activation solution 34 to remove the oxide layer. Thus, the activation solution 34 of the present disclosure may be safer to handle than typical chemical etchants.

[0045] A suitable activation solution 34 for performing blocks 132 and 138 simultaneously may include an oxide removal agent, a complexing agent and a non-oxidizing acid. The oxide removal agent may be, for example, sodium fluoride at about 2 grams to about 8 grams per liter of activation solution 34. The complexing agent may be, for example, citric acid at no less than about 30 grams per liter of activation solution 34 (e.g., about 30 to about 80 grams of citric acid per liter of activation solution 34. The nonoxidizing acid may be, for example, sulfuric acid at no less than about 50 grams per liter of activation solution 34, such as from about 50 to about 150 grams per liter of activation solution 34. Alternatively, some commercially available solutions may be suitable as well, such as Dipsol 602-AS Power Acid available from Dipsol of America, Inc. of Livonia, Mich. Those skilled in the art will appreciate however, that various other concentrations, reagents and solutions may be employed to perform blocks 132 and 138 simultaneously without departing from the scope of the present disclosure.

[0046] Depending on the size and shape of the titanium substrate 10, the current density of the anodic etching current may be adjusted as needed. For example, it may be appropriate to increase the current density of the anodic etching current to compensate for relatively large titanium substrates 10 due to their relatively large surface areas. Thus, increasing the current density of the anodic etching current may be required to ensure that an adequate degree of oxide removal is achieved across the outer surface 12 of the titanium substrate 10. In one example, the establishing (block 146) of the anodic etching current may include establishing an anodic etching current having a current density of at least about 2 amps per square foot. In another example, the establishing (block 146) of the anodic etching current may include establishing an anodic etching current having a current density of at least about 4 amps per square foot. In yet another example, the establishing (block 146) of the anodic etching current may include establishing an anodic etching current having a current density of at least about 6 amps per square foot.

[0047] The anodic etching current may be maintained for any suitable duration of time. Those skilled in the art will appreciate that it may take longer to remove the oxide layer 14 if, among other things, the oxide layer 14 is particularly thick and/or the titanium substrate 10 is particularly large. In one example, the establishing (block 146) of the anodic etching current includes establishing an anodic etching current through the titanium substrate 10 for at least about 150 seconds. In another example, the establishing (block 146) of the anodic etching current includes establishing an anodic etching current through the titanium substrate 10 for at least about 300 seconds. In yet another example, the establishing (block 146) of the anodic etching current includes establishing an anodic etching current through the titanium substrate 10 for at least about 450 seconds. The goal is to remove the Bielby layer and not affect part dimensions or modify (smooth out) the mechanically cleaned surface.

[0048] Following block 130 but before block 160, the method 100 may include, at block 150, rinsing the titanium substrate 10 that has been etched (i.e., the etched titanium substrate 11) to minimize cross-contamination and remove lingering oxygen ions surrounding the etched titanium substrate 11. Preferably, the rinsing (block 150) may be performed using a solution that contains a low oxygen concentration to minimize oxide layer 14 reformation. In an example, the etched titanium substrate 11 may be rinsed with the activation solution 34 used in block 132. In an example, the etched titanium substrate 11 may be rinsed with "dirty water" (e.g., water containing foreign contaminants). In an example, the etched titanium substrate 11 may be rinsed with the cathodic electrolyte solution 62 used in block 160 (described below). In an example, the etched titanium substrate 11 may be rinsed with an aqueous solution having a pH between about 3 and about 5. Those skilled in the art will appreciate that various other solutions maybe employed to rinse the etched titanium substrate 11, without departing from the scope of the present disclosure.

[0049] A cathodic protection current may be established through the etched titanium substrate 11 to convert the otherwise active outer surface 13 of the etched titanium substrate 11 into a passive site for the oxide formation reaction. By supplying free electrons to the etched titanium substrate 11 and distributing a negative charge across the outer surface 13, the cathodic protection current may thereby prevent negatively charged oxygen ions from bonding to the outer surface 13. The cathodic protection current may be maintained (e.g., cathodically held) for as long as needed in preparation for block 180, strike plating a bond promoter layer 16 onto the outer surface 13 of the etched titanium substrate 11. Thus, it is generally contemplated that block 160 may be performed before block 180, but that block 180 may be performed immediately thereafter.

[0050] Referring to FIGS. 7 and 8, blocks 160 and 180 may be performed using an electrochemical cell similar to the configuration used for the anodic etching (block 138) (e.g., a standard two-electrode bath). A cathodic electrolyte solution 62 may first be prepared (block 162 ("preparing a cathodic electrolyte solution")) so that a titanium substrate (e.g., the cathode) and a suitable anode 68 may be immersed (block 164 ("immersing an etched titanium substrate and an anode in the electrolyte solution")) in it and electrically coupled (blocks 166 ("electrically coupling the etched titanium substrate to a current source") and 168 ("electrically coupling the current source to an anode")) to a current source. A cathodic protection current may then be established (block 170 ("establishing a cathodic protection current through the etched titanium substrate")) for a duration of time before a strike current is applied (block 180) to deposit conductive metal ions in the cathodic electrolyte solution 62 onto the outer surface 13 of the etched titanium substrate 11, thereby forming the bond promoter layer 16. [0051] The cathodic electrolyte solution 62 may include, among other things, the conductive metal ions that will later be formed into the bond promoter layer 16 (following block 180). These conductive metal ions may include, for example, nickel ions, iron atoms, copper ions, and various other conductive metal ions that are suitable for strike plating. These conductive metal ions may be added to the activation solution 34 via any suitable source. For example, nickel sulfate hexahydrate (e.g., a nickel salt) may be added to the activation solution 34 to provide nickel ions. Further,

the cathodic electrolyte solution 62 may also include various additives such as non-oxidizing acids, reducing agents to prevent oxide formation, and complexing agents. Referring specifically to complexing agents, in one example, the cathodic electrolyte solution 62 may include at least one of citric acid and sodium citrate. Reducing agents like ascorbic acid are used, for example, to prevent the ferrous iron from being oxidized to the ferric ion that is not platable. Those skilled in the art will appreciate that various other conductive metal ions and additives may be added to the activation solution 34 without departing from the scope of the present disclosure.

[0052] The cathodic protection current may be applied at any voltage capable of preventing oxygen ions in the cathodic electrolyte solution 62 from binding to the outer surface 13 of the etched titanium substrate 11. The voltage may be predetermined prior to the performance of block 160, but may also be altered at any time if needed. In one example, the establishing (block 160) of the cathodic protection current includes applying a constant voltage of at least about 0 volts. In another example, the establishing (block 160) of the cathodic protection current includes applying a constant voltage of at least about 2 volts. In one example, the establishing (block 160) of the cathodic protection current includes applying a constant voltage of at least about 4 volts. The voltage is high enough to drive the oxide reaction but not so high that the hydrogen evolution reaction predominates.

[0053] The cathodic protection current may be maintained (e.g., "cathodically held") for a duration of time until the strike current is applied. This duration of time, however, is yet another processing consideration may be varied based on, among other things, the size and shape of the etched titanium substrate 11, and the time required to remove the oxygen ions surrounding the outer surface 13 of the etched titanium substrate 11. In one example, the establishing (block 160) of the cathodic protection current may include establishing a cathodic protection current for at least about 15 seconds. In one example, the establishing (block 160) of the cathodic protection current may include establishing a cathodic protection (oxide reduction) current for at least about 120 seconds. In another example, the establishing (block 160) of the cathodic protection current may include establishing a cathodic protection current for at least about 480 seconds. In yet another example, the establishing (block 160) of the cathodic protection current may include establishing a cathodic protection current for about 30 seconds to about 600 seconds.

[0054] Both the duration and current density of the strike current may be controlled to deposit varying quantities of conductive metal ions on the outer surface 13 of the etched titanium substrate 11. Those skilled in the art will appreciate that by increasing the current density, the density of conductive metal ions across the outer surface 13 may increase as well. Accordingly, increasing the current density may be employed as a way to form thicker bond promoter layers 16 that cover more of the outer surface 13. In one example, the strike plating (block 180) may include applying a strike current to the etched titanium substrate 11, the strike current having a current density of at least about 50 amps per square foot. In another example, the strike plating (block 180) may include applying a strike current to the etched titanium substrate 11, the strike current having a current density of at least about 70 amps per square foot.

[0055] Like the anodic etching current and the cathodic protection (oxide reduction) current, the duration of time that strike current is applied may be varied as needed. However, it is generally contemplated that consideration should be given to the desired physical dimensions of the bond promoter layer 16. The longer the strike current is applied, the greater the quantity of conductive metal ions is deposited. In one example, the strike plating (block 180) may include applying a strike current for at least about 120 seconds. In another example, the strike plating (block 180) may include applying a strike current for at least about 240 seconds.

[0056] The bond promoter layer 16 on the outer surface 13 of the etched titanium substrate 11 provides the etched titanium substrate 11 with a conductive surface upon which the metallic material 18 may be plated. The strike plating (block 180) may thus, in effect, render the outer surface 13 of the etched titanium substrate 11 active to the metallic metal, and thereby facilitate titanium-substrate-to-plating adherence. Further, the bond promoter layer 16 may also be impermeable to oxygen, thereby "locking in" the whatever remains of the oxide layer 14 (if any) and preventing any additional oxygen ions from binding to the outer surface 13 of the etched titanium substrate 11.

[0057] After having been formed, the method 100 includes plating (block 190) a metallic material 18 onto the bond promoter layer 16. The metallic material 18 may cover at least a portion (if not most) of the outer surface 13 of the etched titanium substrate 11, thereby yielding a plated structure 20.

[0058] Various metallic materials 18 may be plated on the etched titanium substrate 11. As one example (e.g., for mechanical fastener applications), the metallic material 18 can be an electrically conductive and lubricious material, such as an electrically conductive and lubricious material that includes indium and/or tin. As another example (e.g., for corrosion protection), the metallic material 18 can be a sacrificial material, such as a sacrificial material that includes cadmium, zinc, and/or nickel. As another example (e.g., for heat reflecting applications), the metallic material 18 can be a high reflectivity material, such as a high reflectivity material that includes aluminum and/or gold. As another example (e.g., for sliding applications, such as pistons and actuators), the metallic material 18 can be a wear-resistant material, such as a wear-resistant material that includes chromium and nickel (e.g., electroless nickel).

[0059] When selecting a metallic material 18, consideration may be given to the compatibility of the metallic material 18 with the bond promoter layer 16. For example, if the bond promoter layer 16 includes nickel, a metallic material 18 that may be suitable for plating (block 190) may include indium. Those skilled in the art will appreciate, however, that various other combinations of metallic materials and bond promoter layer compositions may be employed without departing from the scope of the present disclosure.

[0060] The plating (block 190) may be performed using any suitable method, many of which are well known in the art. For example, at least one of electrodeposition, thin-film deposition and sputter deposition may be employed to perform the plating (block 190), among other possible options. Further, the plating (block 190) may be performed such that the metallic material 18 is of a desired thickness and density. Accordingly, those skilled in the art will appre-

ciate that the physical dimensions of the metallic material 18 may vary without departing from the scope of the present disclosure.

[0061] Referring to FIG. 9, the present disclosure provides another example of a method 200 for plating a metallic material 18 onto a titanium substrate 10, wherein the titanium substrate includes an outer surface 12 and an oxide layer 14 on the outer surface 12. The method 200 includes, at block 210, abrading the outer surface 12 of a titanium substrate 10 and, at block 220, chemically etching the outer surface 12 of the titanium substrate 10 to remove at least a portion of the oxide layer 14, thereby yielding an etched titanium substrate 11. The method 200 also includes, at block 230, rinsing the etched titanium substrate 11 and, at block 240, establishing a cathodic protection (oxide reduction) current through the etched titanium substrate 11 while the etched titanium substrate 11 is immersed in an electrolyte solution 62. The method 200 further includes, at block 250, strike plating (block 250) a bond promoter layer 16 onto the outer surface 13 of the etched titanium substrate 11 after the establishing (block 240) of the cathodic protection current. The method 200 lastly includes, at block 260, plating a metallic material 18 onto the bond promoter layer

[0062] Referring to FIG. 10, the present disclosure provides yet another example of a method 300 for plating a metallic material 18 onto a titanium substrate 10, wherein the titanium substrate 10 includes an outer surface 12 and an oxide layer 14 on the outer surface 12. The method 300 includes, at block 310, etching the outer surface 12 of a titanium substrate 10 to yield an etched titanium substrate 11, the etching (block 310) includes, at block 320, immersing the titanium substrate 10 in an activation solution 34 and, at block 330, establishing an anodic etching current through the titanium substrate 10 while the titanium substrate 10 is immersed in the activation solution 34. The method 300 also includes, at block 340, establishing a cathodic protection current through the etched titanium substrate 11 while the etched titanium substrate 11 is immersed in a cathodic electrolyte solution 62. The method 300 further includes, at block 350, strike plating a bond promoter layer 16 onto the outer surface 13 of the etched titanium substrate 11 after the establishing (block 340) of the cathodic protection current, and, at block 360, plating a metallic material 18 onto the bond promoter layer 16.

[0063] Referring to FIGS. 11 and 12, the present disclosure provides examples of an article 400 that may be manufactured using any of the previously disclosed methods (e.g., 100, 200 and 300). The article 400 includes a titanium body 410, a bond promoter layer 420 that includes, for example, a nickel-chromium alloy, and plating 430 (e.g., indium) on at least a portion of the titanium body 410. For example, the plating 430 has a thickness (T) ranging from about 0.2 mils to about 0.5 mils. As shown, the titanium body 410 may be a mechanical fastener, such as a bolt. However, those skilled in the art will appreciate that the titanium body 410 may be fabricated into a variety of shapes including, but not limited to, a tapered pin, a straight pin, a threaded lockbolt, a tapered sleeve bolt, a bushing, a tapered lock, a nut, a screw, and the like.

[0064] Mechanical fasteners are just one application of the disclosed methods for plating a metallic material onto a titanium substrate. For example, aircraft experience electromagnetic effects (EME) from a variety of sources, such as

lightning strikes and precipitation static. Metallic aircraft structures are readily conductive and, therefore, are relatively less susceptible to electromagnetic effects. However, composite aircraft structures (e.g., carbon fiber reinforced thermoset and thermoplastic composite structures) do not readily conduct away the significant electrical currents and electromagnetic forces stemming from electromagnetic effects. Therefore, the disclosed methods can be used to direct the current into the mechanical fasteners, such as bolts, screws, rivets, blind fasteners and the like, that connect with metallic layers such as copper foil embedded within the wing.

[0065] Another application of the disclosed methods for plating a metallic material onto a titanium substrate is the use of sacrificial coatings like zinc-nickel to prevent dissimilar metal corrosion. Current practices to prevent corrosion when titanium is mated to aluminum is to prime the titanium surface and seal the joint against moisture intrusion. The problem is sealing is time-consuming and expensive for major subassemblies like a nacelle strut box. By plating the surface with a sacrificial coating, as is disclosed herein, the joint sealing process can be eliminated since the mating surfaces have a similar corrosion potential.

[0066] Yet another application of the disclosed methods for plating a metallic material onto a titanium substrate is plating titanium pneumatic ducts with a nickel coating that prevents damage due to phosphate ester fluid exposure. If the surface is bright (low emissivity) as well then it would prevent radiant heat from damaging aluminum and composite structure. The plating would replace an expensive gold coating that is a challenge to apply.

[0067] Examples of the disclosure may be described in the context of an aircraft manufacturing and service method 1000, as shown in FIG. 13, and an aircraft 1002, as shown in FIG. 14. During pre-production, the aircraft manufacturing and service method 1000 may include specification and design 1004 of the aircraft 1002 and material procurement 1006. During production, component/subassembly manufacturing 1008 and system integration 1010 of the aircraft 1002 takes place. Thereafter, the aircraft 1002 may go through certification and delivery 1012 in order to be placed in service 1014. While in service by a customer, the aircraft 1002 is scheduled for routine maintenance and service 1016, which may also include modification, reconfiguration, refurbishment and the like.

[0068] Each of the processes of method 1000 may be performed or carried out by a system integrator, a third party, and/or an operator (e.g., a customer). For the purposes of this description, a system integrator may include without limitation any number of aircraft manufacturers and major-system subcontractors; a third party may include without limitation any number of venders, subcontractors, and suppliers; and an operator may be an airline, leasing company, military entity, service organization, and so on.

[0069] As shown in FIG. 14, the aircraft 1002 produced by example method 1000 may include an airframe 1018 with a plurality of systems 1020 and an interior 1022. Examples of the plurality of systems 1020 may include one or more of a propulsion system 1024, an electrical system 1026, a hydraulic system 1028, and an environmental system 1030. Any number of other systems may be included.

[0070] The disclosed methods for plating a metallic material onto a titanium substrate may be employed during any one or more of the stages of the aircraft manufacturing and

service method 1000. As one example, the disclosed methods for plating a metallic material onto a titanium substrate may be employed during material procurement 1006. As another example, components or subassemblies corresponding to component/subassembly manufacturing 1008, system integration 1010, and or maintenance and service 1016 may be fabricated or manufactured using the disclosed methods for plating a metallic material onto a titanium substrate. As another example, the airframe 1018 and the interior 1022 may be constructed using the disclosed methods for plating a metallic material onto a titanium substrate. Also, one or more apparatus examples, method examples, or a combination thereof may be utilized during component/subassembly manufacturing 1008 and/or system integration 1010, for example, by substantially expediting assembly of or reducing the cost of an aircraft 1002, such as the airframe 1018 and/or the interior 1022. Similarly, one or more of system examples, method examples, or a combination thereof may be utilized while the aircraft 1002 is in service, for example and without limitation, to maintenance and service 1016.

[0071] The disclosed methods for plating a metallic material onto a titanium substrate are described in the context of an aircraft; however, one of ordinary skill in the art will readily recognize that the disclosed methods for plating a metallic material onto a titanium substrate may be utilized for a variety of applications. For example, the disclosed methods for plating a metallic material onto a titanium substrate may be implemented in various types of vehicles including, e.g., helicopters, passenger ships, automobiles and the like.

[0072] Although various examples of the disclosed methods for plating a metallic material onto a titanium substrate have been shown and described, modifications may occur to those skilled in the art upon reading the specification. The present application includes such modifications and is limited only by the scope of the claims.

1. A method for plating a metallic material onto a titanium substrate, said titanium substrate comprising an outer surface and an oxide layer on said outer surface, said method comprising:

chemically etching said outer surface of said titanium substrate to remove at least a portion of said oxide layer, thereby yielding an etched titanium substrate;

establishing a cathodic protection current through said etched titanium substrate while said etched titanium substrate is immersed in a cathodic electrolyte solution; strike plating a bond promoter layer onto said outer surface of said etched titanium substrate after said establishing said cathodic protection current; and

plating said metallic material onto said bond promoter layer.

- 2. The method of claim 1 wherein said metallic material is an electrically conductive and lubricious material comprising at least one of indium and tin.
- 3. The method of claim 1 wherein said metallic material is a sacrificial material comprising at least one of cadmium, zinc and nickel.
- **4**. The method of claim **1** wherein said metallic material is a high reflectivity material comprising at least one of aluminum and gold.
- 5. The method of claim 1 wherein said metallic material is a wear-resistant material comprising at least one of chromium and nickel.

- 6. The method of claim 1 further comprising cleaning said outer surface of said titanium substrate prior to said chemically etching.
  - 7-8. (canceled)
- 9. The method of claim 1 further comprising abrading said outer surface of said titanium substrate prior to said chemically etching.
- 10. The method of claim 9 wherein said abrading comprises blasting said titanium substrate with an abrasive medium having a grit size of at least about 60 microns.
  - 11-13. (canceled)
- 14. The method of claim 1 wherein said chemically etching comprises immersing said titanium substrate in an activation solution.
- 15. The method of claim 14 wherein said activation solution comprises at least one of fluoride ions and sodium fluoride.
- **16**. The method of claim **14** wherein said activation solution comprises from about 2 grams to about 8 grams of sodium fluoride per liter of activation solution.
- 17. The method of claim 14 wherein said activation solution comprises at least one of a complexing agent and citric acid.
- **18**. The method of claim **14** wherein said activation solution comprises at least about 30 grams of citric acid per liter of activation solution.
- 19. The method of claim 14 wherein said activation solution comprises sulfuric acid.
- 20. The method of claim 14 wherein said activation solution comprises at least about 50 grams of sulfuric acid per liter of activation solution.
- 21. The method of claim 14 further comprising establishing an anodic etching current through said titanium substrate while said titanium substrate is immersed in said activation solution.
- 22. The method of claim 21 wherein said establishing said anodic etching current comprises establishing an anodic etching current having a current density of at least about 2 amps per square foot.
- 23. The method of claim 21 wherein said establishing said anodic etching current comprises establishing said anodic etching current through said titanium substrate for at least about 150 seconds.
  - 24. (canceled)
- 25. The method of claim 1 further comprising rinsing said etched titanium substrate prior to said establishing said cathodic protection current.
  - **26-27**. (canceled)
- **28**. The method of claim **25** wherein said rinsing comprises rinsing said etched titanium substrate with an aqueous solution having a pH between about 3 to about 5.
- 29. The method of claim 1 wherein said cathodic electrolyte solution comprises at least one of nickel ions and copper ions.
- **30**. The method of claim **1** wherein said cathodic electrolyte solution comprises nickel sulfate hexahydrate.
- 31. The method of claim 1 wherein said cathodic electrolyte solution comprises a complexing agent.
- **32**. The method of claim **1** wherein said cathodic electrolyte solution comprises at least one of citric acid and sodium citrate.
- 33. The method of claim 1 wherein said establishing said cathodic protection current comprises applying a constant voltage of about 0 volts.

- **34**. The method of claim **1** wherein said establishing said cathodic protection current comprises establishing said cathodic protection current for at least about 15 seconds.
- **35**. The method of claim **1** wherein said strike plating comprises applying a strike current to said etched titanium substrate, said strike current having a current density of at least about 50 amps per square foot.
- **36**. The method of claim **1** wherein said strike plating comprises applying a strike current for at least about 120 seconds
- **37**. A method for plating a metallic material onto a titanium substrate, said titanium substrate comprising an outer surface and an oxide layer on said outer surface, said method comprising:

abrading said outer surface of said titanium substrate; chemically etching said outer surface of said titanium substrate to remove at least a portion of said oxide layer, thereby yielding an etched titanium substrate; rinsing said etched titanium substrate;

establishing a cathodic protection current through said etched titanium substrate while said etched titanium substrate is immersed in a cathodic electrolyte solution; strike plating a bond promoter layer onto said outer surface of said etched titanium substrate after said establishing said cathodic protection current; and plating said metallic material onto said bond promoter

**38**. A method for plating a metallic material onto a titanium substrate, said titanium substrate comprising an outer surface and an oxide layer on said outer surface, said method comprising:

etching said outer surface of said titanium substrate to yield an etched titanium substrate, said etching comprising immersing said titanium substrate in an activation solution and establishing an anodic etching current through said titanium substrate while said titanium substrate is immersed in said activation solution;

establishing a cathodic protection current through said etched titanium substrate while said etched titanium substrate is immersed in a cathodic electrolyte solution; strike plating a bond promoter layer onto said outer surface of said etched titanium substrate after said establishing said cathodic protection current; and plating said metallic material onto said bond promoter

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layer.