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(54) **METHODS FOR THE PRODUCTION OF COATINGS CONTAINING NICKEL-TUNGSTEN PLATING LAYERS**

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PROCÉDÉS DE PRODUCTION DE REVÊTEMENTS CONTENANT DES COUCHES DE PLACAGE
DE NICKEL-TUNGSTÈNE

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Description

TECHNICAL FIELD

[0001] The following disclosure relates generally to methods for producing coatings formed over articles of manufacture and, more particularly, to methods for producing coatings, which contain or consist of nickel-tungsten plating layers, over metallic components.

ABBREVIATIONS

[0002] Abbreviations appearing relatively infrequently in this document are defined upon initial usage, while abbreviations appearing more frequently in this document are defined below.

Au-Gold;
Cu-Copper;
Ni-Nickel;
NiW-Nickel-tungsten; and
W-Tungsten.

BACKGROUND

[0003] In high performance applications, Au plating layers are often electrodeposited over surfaces of electrical connectors to minimize resistance between points of contact. For example, in the case pin-and-socket electrical connectors, Au plating layers may be formed over the terminals (pins) of the male connector and over the terminals (sockets) of the female connector to decrease contact resistance across the connectors when joined. In certain instances, a barrier layer composed of essentially pure, electroplated Ni may be provided between the outer Au plating layer and the connector terminal body. The provision of the pure Ni plating layer may serve as a barrier layer, which reduces diffusion of the Au plating layer into the terminal body, which may be composed of a less costly, electrically-conductive metal or alloy, such as Cu. The Ni plating layer may also increase the wear resistance of the coated connector terminal and protect the connector terminal from corrosion or other chemical degradation, which may otherwise occur over time.

[0004] While providing the above-noted benefits, pure Ni plating layers remain limited in multiple respects. Often, the enhancements to wear and corrosion resistance achieved by incorporating a pure Ni plating layer into a particular coating system are modest. Further, while relatively straightforward and well-established, the plating processes utilized to electrodeposit pure Ni plating layers are likewise associated with various drawbacks. For example, Ni electrodeposition processes are often prone to relatively pronounced pH swings and the accumulation of undesired chemical species, such as sulfates (SO₄) and sodium (Na), within the plating bath. The accumulation of such undesired chemical species

tends to limit bath performance and lifespan, which, in turn, increases material and processing costs. As a yet further limitation, conventional Ni electrodeposition processes often achieve relatively sluggish deposition rates (e.g., on the order of 0.23 milliinch (mil) per hour) and may thus require several hours to deposit Ni plating layers to even moderate

[0005] JP2001158998 discloses a plating method for NiW alloy, wherein a Ni soluble anode is used.

[0006] There thus exists a continued demand for methods for electrodepositing Ni-containing layers having enhanced wear and corrosion resistance properties, while also possessing nanocrystalline structures lacking microcracks and other structural defects. More generally, there exists an ongoing demand for methods by which coatings containing nanocrystalline Ni-containing barrier layers can be fabricated, whether the Ni-containing layer is provided as a standalone protection solution (e.g., to provide enhanced wear resistance on sliding surfaces) or is instead combined with other materials layers (e.g., one or more Au plating layers) to form a coating system over surfaces of metallic articles, such as the contact surfaces of electrical connectors. Other desirable features and characteristics of embodiments of the present invention will become apparent from the subsequent Detailed Description and the appended Claims, taken in conjunction with the accompanying drawings and the foregoing Background.

BRIEF SUMMARY

[0007] The invention is set out in accordance with the appended claims. Methods for forming coatings containing NiW plating layers over metallic components are provided. In various embodiments, the method includes the steps or processes of preparing a plating bath containing a W ion source; inserting at least one consumable Ni electrode and at least a portion of the metallic component into the plating bath; and, after insertion of the at least one Ni electrode and the component surface into the plating bath, electrodepositing a NiW plating layer over the component surface by energizing the at least one consumable Ni electrode as an anode and the metallic component as a cathode to attract Ni ions and W ions to the component surface. An amount of anode corrosion accelerant in the plating bath, selected from the group consisting of nickel chloride, ammonia chloride or sodium chloride, is controlled to balance Ni dissolution at the anode to Ni deposition at cathode, as considered in conjunction with any additional Ni ion sources within the plating bath, to achieve a desired composition of the electrodeposited NiW layer.

[0008] The coating formation method includes the step or process of preparing a plating bath solution to contain: (i) about 0.0002 to about 0.01 moles of an anode corrosion accelerant, such as chloride, per liter of the plating bath solution; and (ii) a W ion source. At least one consumable Ni electrode and at least a portion of the metallic

component is inserted into the plating bath. The at least one consumable Ni electrode is then energized as an anode, while the metallic component is concurrently energized as a cathode to electrodeposit a NiW plating layer over the component surface. In certain embodiments, the NiW plating layer may be formed to consist essentially of between 25% and 35% W by weight, with the remainder Ni. In other embodiments, the plating bath solution may be prepared to further contain ammonium hydroxide ions in a concentration range between about 1.0 to about 2.0 moles per liter of the plating bath solution.

[0009] Coatings or coating systems are further provided but not claimed, which are formed over selected surfaces of metallic components. The coating includes an electrodeposited NiW plating layer, which is formed over and in contact with the component surface. The electrodeposited NiW plating layer contains at least 50% Ni by weight, as well as between 25% and 35% W by weight. At least one Au layer is formed over and contacts the electrodeposited NiW plating layer, with the at least one Au layer having a thickness less than a thickness of the NiW plating layer. The electrodeposited NiW plating layer consists essentially of about 30% W by weight, with the remainder Ni.

[0010] Various additional examples, aspects, and other useful features of embodiments of the present disclosure will also become apparent to one of ordinary skill in the relevant industry given the additional description provided below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] At least one example of the present invention will hereinafter be described in conjunction with the following figures, wherein like numerals denote like elements, and:

FIG. 1 is a flowchart of a method for producing a coating including or consisting of a NiW plating layer formed over selected surfaces of a metallic component, such as the terminals of an electrical connector or the sliding surfaces of a high temperature (e.g., engine) component, as illustrated in accordance with an exemplary embodiment of the present disclosure;

FIG. 2 is a schematic of an exemplary NiW plating apparatus, which can be utilized to electrodeposit an NiW plating layer over selected surfaces of a metallic component, when carrying-out the method of FIG. 1;

FIG. 3 is a simplified cross-sectional view of a limited region of an exemplary coating containing an NiW plating layer and an Au topcoat, which are formed over an underlying metallic component and which can be produced pursuant to the method of FIG. 1 in an exemplary embodiment; and

FIG. 4 is an isometric view of a female electrical

connector and the pins of a mating male electrical connector (the remainder of which is not shown for clarity), both of which contain terminals over which the disclosed coatings are usefully formed.

[0012] For simplicity and clarity of illustration, descriptions and details of well-known features and techniques may be omitted to avoid unnecessarily obscuring the exemplary and non-limiting embodiments of the invention described in the subsequent Detailed Description. It should further be understood that features or elements appearing in the accompanying figures are not necessarily drawn to scale unless otherwise stated.

DETAILED DESCRIPTION

[0013] The following Detailed Description is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. The term "exemplary," as appearing throughout this document, is synonymous with the term "example" and is utilized repeatedly below to emphasize that the description appearing in the following section merely provides multiple non-limiting examples of the invention and should not be construed to restrict the scope of the invention, as set-out in the Claims, in any respect. As further appearing herein, statements indicating that a first layer is "formed over," "formed on," "deposited over," or "deposited on" a second layer, surface, or body do not require that the first layer is directly bonded to and intimately contacts the second layer, surface, or body unless otherwise expressly stated by, for example, stating the first layer is "formed directly on," "deposited directly on," "is formed in contact with," or "contacts" the second layer, surface, or body.

DEFINITIONS

[0014] The following definitions apply throughout this document. Those terms not expressly defined here or elsewhere in this document are assigned their ordinary meaning in the relevant technical field.

[0015] Coating—One or more layers of material formed over a component surface. This term encompasses the more specific term "coating system" defined below.

[0016] Coating System—A coating structure containing at least two material layers having varying compositions, such as one or more Au layers joined to a component body by an intervening NiW plating layer.

[0017] Component—Any article of manufacture over which a coating can be formed. This term is synonymous with or encompasses similar terms including "substrate," "part," and "workpiece."

[0018] Electrical Connector—Any component or structure utilized to provide an a current- or signal-carrying electrical connection between two points or nodes including wirebonds and mating connector devices, such as male (e.g., pin), female (e.g., socket), and hybrid (e.g.,

pin and socket) connectors.

[0019] Gold (Au) Topcoat—One or more layers predominately composed of Au by weight and formed over an NiW plating layer.

[0020] Nickel (Ni) Barrier Layer—A layer composed essentially of pure Ni by weight and deterring unfavorable chemical reactions with an underlying material layer, component, or body of material.

[0021] Nickel-tungsten (NiW) plating layer—A layer composed predominately of Ni and W by weight and deterring unfavorable chemical reactions with an underlying material layer, component, or body of material.

[0022] Ni Pellets—Discrete bodies or pieces of material, such as shot, predominately composed of Ni by weight, regardless of shape or size.

OVERVIEW

[0023] As discussed briefly in the foregoing BACKGROUND, pure Ni plating layers are beneficially electrodeposited on selected surfaces of metallic components to improve wear properties and to prevent undesired chemical degradation, such as corrosion, of the underlying component or substrate. As a more specific example, pure Ni plating layers are usefully formed on contact surfaces of high performance electrical connectors over which Au topcoats are further deposited to lower contact resistance. In other instances, pure Ni plating layers may be formed over sliding surfaces, particularly over the sliding surfaces of high temperature components, to provide enhanced wear resistance. However, as further discussed above, pure Ni plating layers remain limited in certain respects and, in many instances, provide only modest improvements in the wear and corrosion properties of the coating system. Additionally, the plating processes utilized to electrodeposit pure Ni plating layers are often hampered by various constraints, such as bath instabilities, poor bath life longevity, relatively sluggish deposition rates, and correspondingly high process and material costs.

[0024] Relative to pure Ni plating layers, NiW plating layers can potentially provide greater enhancement to the wear and corrosion resistance properties of a coating or coating system. The plating processes utilized to electrodeposit NiW plating layers are, however, considerably more complex than those utilized to electrodeposit pure Ni. This is due, at least in part, to difficulties encountered when attempting to deposit a (typically binary) alloy having a specific fractional composition of W to Ni. Further, NiW electrodeposition processes are also typically prone to the accumulation of plating bath impurities, which can result in rough deposits leading to microcrack formation and propagation. Once formed, microcracks can detract from the intended functionality of the NiW plating layer to serve a physical shield against undesired chemical reactions with the underlying component, in applications in which the NiW plating layer is utilized as a barrier layer. Specifically, such microcracks can lead

to greater diffusion of outer material layers (e.g., an Au topcoat), if present, into the parent material of the underlying component or substrate. Still other challenges are also encountered when electrodepositing NiW plating layers. For example, if Ni ions are supplied to the plating bath in the form of a Ni-containing sulfate chemical additive, the gradual build-up of sulfates can occur over time thereby greatly reducing bath life and raising the cost of the NiW electrodeposition process. Similarly, if not deposited onto the plated component at a sufficiently controlled rate, an abundance of Ni ions can develop within the plating bath. Eventually, the plating bath may saturate with Ni ions, which may necessitate partial dumping of the plating bath and refilling with plating bath solution lacking Ni. This again prolongs, complicates, and adds cost to the NiW electrodeposition process.

[0025] To overcome many, if not all of the aforementioned challenges, the following provides improved processes for forming coatings and coatings systems containing NiW plating layers. Embodiments of the below-described NiW electrodeposition process reduce or eliminate the accumulation of sulfates and other undesired chemical species within the plating bath to significantly extend bath life and lower material costs. This is accomplished, in part, through the incorporation of consumable or dissolvable Ni electrodes into the NiW electrodeposition process, rather than utilizing inert (e.g., platinum-coated titanium) anodes as conventionally practiced in the context of pure Ni plating processes. Embodiments of the plating bath solution further contain at least one chemical serving as an anode corrosion accelerant, selected from the group consisting of nickel chloride, ammonia chloride, or sodium chloride, which promotes the controlled dissolution of the consumable Ni electrodes into the plating bath. The anode corrosion accelerant is maintained in the plating bath in a carefully controlled amount or fraction, which is sufficient to prevent scale build-up over the surfaces of the Ni electrodes, while further limiting dissolution of the Ni electrodes to a rate substantially equivalent to the rate of Ni ion deposition onto the component surfaces subject to plating.

[0026] In various embodiments, the controlled amount of anode corrosion accelerant added to and generally maintained within the NiW plating bath may be determined utilizing different approaches. In one approach, the amount of anode corrosion accelerant is determined based upon a target W content of the NiW plating layer, as well as an estimated cumulative surface area of the Ni electrodes submerged in the plating bath and energized as anodes during the NiW electrodeposition process. As the electrodeposition process progresses and the Ni electrodes dwindle in size, new or fresh Ni electrodes may be repeatedly introduced into the plating bath to maintain the cumulative surface area of Ni electrodes and plated surface area of the metallic component surface within a predetermined range or desired relationship. This may be accomplished by, for example, providing the Ni electrodes as consumable Ni pellets or shot,

which are retained within an inert mesh basket or other container and which are replenished periodically during the NiW electrodeposition process.

[0027] Through the usage of consumable Ni electrodes and tailored amounts of at least one anode corrosion accelerant, the gradual accumulation of undesired chemical species, such as sulfates, within the plating bath can be reduced or eliminated. Bath life is prolonged as a result, potentially to near infinite lifespans. Further, as compared to inert anodes, the consumable Ni electrodes utilized in the NiW electroplating process can be energized at reduced voltages, utilizing either a Direct Current (DC) or Alternating Current (AC) power source, to minimize oxygen evolution and carbonate production during the electroplating process. This, again, extends useful bath life and reduces processing costs. Finally, as a yet further benefit, embodiments of the below-described plating process can boost mass transfer within the plating bath diffusion zone to achieve deposition rates well-exceeding those attained by conventional Ni plating processes. Process efficiency is thus improved, while costs are reduced. These and other benefits may be further enhanced by formulating the plating bath to contain tailored amounts of additional constituents serving as chelating or structuring agents, such as ammonium hydroxide (NH₄OH) and/or other organic acids; and controlling other plating process parameters during the plating process, as further discussed below. Exemplary embodiments of a coating formation method including the electrodeposition of NiW plating layers will now be described in conjunction with FIG. 1.

EXAMPLES OF METHODS FOR FORMING COATINGS AND COATING SYSTEMS INCLUDING NiW PLATING LAYERS

[0028] FIG. 1 is a flowchart of an exemplary coating formation method **10** for forming a coating or coating system including NiW plating layers over metallic components, such as the terminals of high performance electrical connectors or the sliding surfaces of a high temperature (e.g., engine) component, as illustrated in accordance with an exemplary embodiment of the present disclosure. As a point of emphasis, a given coating or coating system may contain and, perhaps, may consist of a single NiW plating layer, which may be deposited over a metallic component. In certain applications, the NiW plating layer is beneficially deposited over the sliding surface of a metallic component, typically (although non-essentially) a metallic component utilized in a high temperature operating environment, such as a valve part or other component contained in an internal combustion or gas turbine engine. In other applications, the NiW plating layer may be combined with additional material layers to yield a multi-layer coating system. For example, and as further discussed below in conjunction with FIG. 3, one or more Au topcoat layers may be formed over the NiW plating layer when the plated component is the terminal of

an electrical connector. Various other coatings and coating systems can be formed pursuant to method **10**, as appropriately modified to suit a particular application or usage, providing that the coating or coating system consists of or includes at least one NiW plating layer as described below.

[0029] In the example of FIG. 1, coating formation method **10** includes a number of process steps identified as STEPS **12, 14, 16, 18, 20, 22**, with STEPS **14, 16, 18** performed pursuant to an overarching NiW plating sub-process identified as "PROCESS BLOCK **24**." Depending upon the particular manner in which coating formation method **10** is implemented, each illustrated process step (STEPS **12, 14, 16, 18, 20, 22**) may entail a single process or multiple sub-processes. Further, the steps shown in FIG. 1 and described below are offered by way of non-limiting example only. In alternative embodiments of method **10**, additional process steps may be performed, certain steps may be omitted, and/or the illustrated steps may be performed in varying sequences. For example, in further implementations, STEP **20** of method **10** may be omitted or modified such that the NiW plating layer is left as a standalone protection solution (e.g., as wear protection for sliding surfaces) or, instead, overlaid by one or more additional material layers other than an Au topcoat in the completed coating system.

[0030] For ease of description, coating formation method **10** is principally described below as carried-out to form a coating or multi-layer coating system over selected surfaces of a single metallic component. This notwithstanding, it will be appreciated that any practical number of metallic components may be processed in parallel to form coatings or coating systems over selected surfaces of a plurality of components in accordance with the below-described process steps. For example, in the case of smaller (e.g., stamped) metallic components, such as the terminals of an electrical connector, a reel-to-reel plating process can be utilized to form coatings or coating systems a connected series of parts or components, such as stamped pins or sockets, which are passed through the below-described NiW plating bath and other processing stages for large scale production.

[0031] With continued reference to FIG. 1, coating formation method **10** commences at STEP **12** during which the metallic component or components to be coated are obtained; e.g., by purchase from a third party supplier or by independent fabrication. The surfaces of the metallic component or components targeted for electrodeposition of the NiW plating layer are further prepared during STEP **12**. In embodiments, surface preparation may involve degreasing or otherwise cleaning the targeted component surfaces. For example, if desired, surface oxides may be removed from the component surfaces utilizing a sulfuric acid dip or similar process. Grinding, polishing, lapping, and/or other such mechanical operations can further be performed, as appropriate, to improve surface finish prior to NiW plating

layer electrodeposition. Finally, any component surfaces not desirably coated with the NiW plating layer may be masked during STEP 12.

[0032] Coating formation method 10 next advances to PROCESS BLOCK 24. During PROCESS BLOCK 24, at least one NiW plating layer is electrodeposited over the targeted component surfaces. As indicated at STEP 14, the NiW electrodeposition process involves formulating or preparing the plating bath solution to possess a chemistry suitable for electrodeposition of the NiW plating layer having a desired composition and other characteristics, such as a desired morphology. Generally, the formulation of the NiW plating bath will depend, at least in part, on the target W content of the NiW plating layer. As the W content of the NiW plating layer will vary among embodiments, so too will the composition of the NiW plating bath. However, by way of example, the target W content of the NiW plating layer may range from about 15% and 45% by weight, preferably from about 25% to about 35% by weight, and more preferably may be substantially equivalent to 30% by weight. In other embodiments, the W content of the NiW plating layer may be greater than or lesser than the aforementioned ranges.

[0033] In accordance with embodiments of the present disclosure, the NiW plating bath is formulated such that an amount of anode corrosion accelerant in the plating bath is controlled to balance the amount of Ni dissolution at the anode (the energized consumable Ni electrodes) to the amount of Ni deposition at cathode (the plated part), combined with any additional Ni ion source within the plating bath, to achieve a desired composition of the NiW layer. In many embodiments, the plating bath will not contain any additional Ni ion source such that anode corrosion accelerant concentration is tailored to achieve Ni dissolution at the anode relative to the Ni deposition at cathode to arrive at the desired composition of the NiW layer. However, in other embodiments, the Ni dissolution at the anode may be purposefully undershot with additional Ni ions introduced in the form of a chemical additive, such as Ni sulfate, to allow greater flexibility in adjusting chemistry during the electrodeposition process. In such embodiments, bath life may still be extended as a relatively small or reduced amount of the Ni sulfate (or other Ni-containing chemical) may be added to the plating bath.

[0034] The anode corrosion accelerant is a chloride added as nickel chloride (NiCl_2), ammonia chloride (NH_4Cl), or sodium chloride (NaCl). The amount of anode corrosion accelerant is carefully tailored in relation to the other constituents of the NiW plating bath and to prevent scale build-up over the surfaces of the Ni electrodes, while further limiting dissolution of the Ni electrodes to a rate substantially equivalent to the rate of N ion deposition onto the component surfaces subject to plating. The amount of anode corrosion accelerant added to the plating bath may be determined based, at least in part, on the target W content of the NiW plating layer and a cumulative surface area of the consumable Ni electrodes. As a

result, the amount of anode corrosion accelerant added to and generally maintained within the NiW plating bath will vary amongst different implementations of method 10. This notwithstanding, and by way of non-limiting example only, the chloride range in the plating bath ranges between about 0.0002 and about 0.01 moles per liter (mol/liter); and, more preferably, between 0.0008 and 0.0025 mol/liter. The foregoing exemplary molarity ranges apply when chloride is selected as the anode corrosion accelerant or as at least one of the anode corrosion accelerants, if multiple accelerant types are utilized. In other implementations, the chloride may be employed in a concentration greater than or less than the aforementioned ranges.

[0035] The controlled amount of anode corrosion accelerant introduced into and maintained in the NiW plating above may thus be defined, in part, based upon the desired Ni ion concentration in the bath. Other process parameters (e.g., voltages, temperatures, agitation intensities, etc.) and whether a supplemental Ni ion source (e.g., a Ni-containing chemical additive) is present within the bath will also impact the Ni ion concentration within the bath. As with the various other constituents of the NiW plating bath, the Ni ion concentration will vary among different implementations of method 10. However, by way of example, the Ni ion concentration within the NiW plating bath may be maintained through the NiW electrodeposition process in a range between about 5 grams and about 18 grams Ni per liter of plating bath solution; or, stated differently, between about 0.085 to about 0.307 mol/liter. In a more specific example, the Ni ion concentration within the NiW plating bath may be maintained in a range between about 11 and about 13.5 grams per liter; or between about 0.187 to about 0.230 mol/liter.

[0036] In addition to the anode corrosion accelerant, the NiW plating bath also contains at least one W ion source. The W ion source is conveniently provided as a water-soluble additive containing W, such as sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$). Additionally, the plating bath will further contain a liquid carrier, such as an aqueous or alcohol-based solvent. The plating bath chemistry may also be formulated to include other ingredients or constituents including chelating agents and pH balancing agents; e.g., in one embodiment, a complex of an organic acid, such as citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and ammonia (NH_3) may be provided within the bath (e.g., added in solution as NH_4OH) to serve as a chelating or structuring agent. With respect to the NH_3 additive, in particular, this additive may contribute ammonium hydroxide (OH^-) ions when reacted in the plating bath, which are highly effectively in service as chelating agents. In one embodiment, adequate NH_3 (or another OH^- donor) is introduced into the plating bath to provide ammonium hydroxide (OH^-) ions in the range of about 1.0 to about 2.0 mol/liter; and, more preferably, in the range of 1.3 to 1.7 mol/liter. Finally, as noted above, the NiW plating bath will also contain a Ni ion source in the form of the consumable NiW

electrodes; although the possibility that the NiW plating bath can be formulated to contain another Ni ion source, such as a Ni sulfate or other chemical species, in addition to the Ni ion electrodes is not precluded. Various other bath formulations are also possible.

[0037] At STEP 16, the consumable Ni electrodes and metallic components are inserted into the NiW plating bath, whether by inserting the Ni electrodes and the metallic component into the plating bath or by first positioning the at least one electrode and the component in a vessel and subsequently filling the vessel with plating bath solution. The Ni electrodes are then energized as anodes and the metallic components are energized as cathodes to carry-out the NiW electrodeposition process and thereby deposit the NiW plating layer over the selected component surfaces. The consumable Ni electrodes can generally be energized at reduced voltages, whether utilizing a Direct Current (DC) or Alternating Current (A/C) power source, to minimize oxygen evolution and carbonate production within the plating bath. Advantageously, the usage of soluble Ni anodes generally enables reduced anode voltages to lower decomposition products and thereby prolong bath life. In one embodiment, the at least one consumable Ni electrode and the metallic component are energized at a current density (e.g., a direct current density) between 1 and 5 ampere per decimeter squared.

[0038] Various parameters are controlled during the NiW electrodeposition process. Bath agitation may be applied and, in embodiments, may range from about 100 to about 1000 revolutions per minute (RPM). The temperature and pH level of the plating bath may also be monitored and controlled. In one implementation, bath chemistry is formulated to maintain NiW plating bath at a pH between about 5 and about 9 and, more preferably, a pH of about 7 ± 1 through the electroplating process. In other instances, the pH level of the plating bath may be greater or less than the aforementioned range. As the plating process progress and the Ni electrodes dwindle in size, new or fresh Ni electrodes may be repeatedly introduced into the plating bath to maintain the cumulative surface area of Ni electrodes and plated surface area of the metallic component surface within a predetermined range or desired relationship. This may be accomplished by, for example, providing the Ni electrodes as consumable Ni pellets or shot, which are retained within an inert mesh basket or other container and which are replenished periodically during the NiW electrodeposition process, as further described below in conjunction with FIG. 2.

[0039] FIG. 2 is a schematic of an exemplary NiW plating apparatus 26, which can be utilized to electrodeposit an NiW plating layer 30 over surfaces of a metallic component 32 during PROCESS BLOCK 24 of coating formation method 10 (FIG. 1). As schematically depicted in FIG. 2, plating apparatus 26 includes a vessel 34 retaining a plating bath solution 36. Metallic component 32 is electrically connected, either directly or indirectly

(e.g., through an intervening bracket or fixture) to a negative terminal of power source 38 by a first electrical connection 40. The positive terminal of power source 38 is further connected, either directly or indirectly, to one or more consumable Ni electrodes by a second electrical connection 42. In the illustrated example, specifically, power source 38 is electrically coupled to a mesh basket 44 composed of an inert electrically-conductive material, such as titanium. Ni shot 46 is held within mesh basket 44 and is energized when with the application of a controlled voltage across mesh basket 44 and metallic component 32. As Ni shot 46 dissolves during the plating process, new or fresh Ni shot 46 may be added to mesh basket 44, as indicated in FIG. 2 by arrow 48. Certain variations in the cumulative surface area of consumable Ni shot 46 (the anodes) will occur, with the surface area-to-volume ratio increasing as the pieces of shot decrease in size. However, by repeatedly adding fresh consumable Ni pellets 46 to NiW plating bath 36 as the electroplating process progresses, a ratio between a cumulative surface area of the consumable Ni pellets and a surface area of the component surface can be maintained within a predetermined range. In embodiments, Ni pellets 46 may be added and process parameters controlled to maintain a Ni ion concentration within the above-described molarity ranges (between about 0.085 to about 0.307 mol/liter; and, perhaps, between about 0.187 to about 0.230 mol/liter) throughout a majority and, perhaps, the substantial entirety of the electroplating process.

[0040] Returning once again to FIG. 1, coating formation method 10 next progresses to STEP 20 (if performed) during which an Au topcoat is formed over the newly-deposited NiW plating layer. When formed, the Au topcoat will often have a thickness less than the thickness of the NiW plating layer; e.g., in embodiments, the Au topcoat may have a thickness ranging from 0.381 micron (μm) to 1.016 μm , while the NiW plating layer will often have a thickness ranging between 1.27 μm and 5.08 μm . In this regard, and as noted above, the provision of a microcrystalline, essentially microcrack-free NiW plating layer may allow the thickness the Au topcoat to be appreciably reduced for cost savings. In other high performance applications, the thickness of the Au topcoat may approach or potentially exceed that of the NiW plating layer. For example, when the coating is formed over the terminals of an electrical connector deployed onboard a spacecraft or aircraft, the Au topcoat may range between 2.54 μm and 5.08 μm , with the NiW plating layer having a thickness as specified above. In still further implementations, the NiW plating layer and/or the Au topcoat may be thicker or thinner than the aforementioned ranges; or STEP 20 of method 10 may be omitted. The provision of such an essentially microcrack-free NiW plating layer may also serve as an effective barrier layer for preventing undesired diffusion of Au topcoat (or other overlying material layer) into the substrate in at least some realizations of method 10.

[0041] Finally, at STEP 22 of coating formation method

10 (FIG. 1), zero or more additional processing steps are performed to complete fabrication of the coating or coating system. This may include machining (e.g., lapping, polishing, and/or grinding) of the newly-deposited Au topcoat to achieve a desired surface finish and/or dimensional tolerance. Heat treatment can also be performed for densification or other purposes. Coating formation method **10** then concludes and can be repeated, as needed, on an iterative basis to further form similar or identical coatings or coating systems over other metallic components. In other implementations of method **10**, and as previously indicated, STEPS **20**, **22** may not be performed such that the NiW plating layer electrodeposited during PROCESS BLOCK **24** serves as a standalone protection solution; e.g., as may be useful when the NiW plating layer is deposited onto a sliding surface or other contact surface for enhanced wear resistance. Alternatively, other coating layer or coating systems may be formed over the NiW plating layer in still further embodiments, such as an environmental barrier coating and/or thermal barrier coating.

[0042] FIG. 3 is a simplified cross-sectional view of a limited region of a coating system **52**, which is formed over an underlying metallic component **54** and which may be produced pursuant to coating formation method **10** in accordance with an exemplary embodiment of the present disclosure. In this example, coating system **52** includes an Au topcoat **56** and an electrodeposited NiW plating layer **58**, which is formed between Au topcoat **56** and metallic component **54**. Specifically, NiW plating layer **58** is formed over and in contact with component surface **60** of metallic component **54**. Au topcoat **56** is, in turn, formed over and in contact with outer surface **62** of NiW plating layer **58**. As indicated in FIG. 3 by dashed line **64**, Au topcoat **56** can be formed as two (or more) layers. In various implementations, Au topcoat **56** is formed to include a first or base Au layer **66**, which is plated directly onto NiW plating layer **58**; and a second or outer Au layer **68**, which is plated directly onto base Au layer **66**. Such an arrangement may be beneficial when Au topcoat **56** is desirably formed to have a relatively high thickness and is utilized within a high performance application, such as a spaceborne or an airborne connector. In such embodiments, base Au layer **66** may be formed as relatively thin strike plating layer (e.g., a layer having a thickness equal to or less than 1 μm) to enhance adhesion between NiW plating layer **58** and the thicker outer Au layer **68**. Wear testing has shown that coating systems similar or identical to coating system **52** perform comparably and, in certain cases, outperform conventional coating systems containing pure Ni plating layers in useful life cycle limits.

[0043] Turning lastly to FIG. 4, there is shown an isometric view of a female electrical connector **70** and a number of pins **72**, which may be included in a non-illustrated mating male electrical connector. Pins **72** engage into sockets **74** when the non-illustrated male electrical connector is plugged into female electrical connector **70**. To decrease contact resistance across the elec-

trical interface formed between each pin **72** and its mating socket **74**, the above-described coatings or coating systems (e.g., coating system **52** shown in FIG. 3) may be formed over the outer contact surfaces of pins **72** and/or over the inner contact surfaces of sockets **70**. In this particular example, female electrical connector **70** is of the type deployed onboard spacecraft and aircraft and, thus, a coating having a relatively thick Au topcoat may be formed over the interior of sockets **74** and over pins **72** of the mating male electrical connector. The provision of the NiW plating layer, as previously noted, may further enhance the wear and corrosion resistance properties of sockets **74** and pins **72**, as may be desired in such applications to satisfy stringent mission requirements in certain instances. The example of FIG. 4 notwithstanding, it is again emphasized that the coatings or coating systems described herein can be formed over any type of metallic article or component, without limitation.

CONCLUSION

[0044] There has thus been provided describes processes for depositing NiW plating layers in an essentially crack-free, nanocrystalline state. Additionally, embodiments of the plating process minimize, if not eliminate the accumulation of sulfates and undesired chemical species within the plating bath to greatly extend bath life. By virtue of its nanocrystalline microcrack-free morphology, the NiW plating layer provides excellent shielding of undesired chemical reactions between the Au topcoat (when present) and the underlying substrate material or component body, as is beneficial when the NiW plating layer is utilized as a barrier layer. This, in turn, may allow the thickness of the Au topcoat to be reduced for cost savings, while maintaining coating system performance at desired levels in embodiments in which the NiW plating layer is included in a coating system further containing such an Au topcoat. Alternatively, in such embodiments, the NiW plating layer may be utilized to enhance coating system performance, while leaving the thickness of the Au topcoat unchanged. This latter approach may be preferable in high performance application, as in the case of electrical connectors deployed onboard aircraft or spacecraft. Generally, the NiW plating layer may help improve oxidation, corrosion, and/or wear resistance of the plated part in certain instances. This material system is beneficially utilized to coat current-carrying electronic structures, such as electrical terminals or connectors. Examples of current-carrying electronic structures include wirebonds, as well as larger mating interconnect structures or devices, such as male (e.g., pin) and female (e.g., socket) connectors. In yet other embodiments, the NiW plating layer may be utilized in isolation or, perhaps, with other types of material layers to provide other performance enhancements, such as increasing sliding surface wear resistance.

[0045] Terms such as "comprise," "include," "have," and variations thereof are utilized herein to denote

non-exclusive inclusions. Such terms may thus be utilized in describing processes, articles, apparatuses, and the like that include one or more named steps or elements, but may further include additional unnamed steps or elements.

Claims

1. A method for forming a coating over a component surface of a metallic component, the method comprising:

preparing a plating bath containing a tungsten (W) ion source;

inserting at least one consumable nickel (Ni) electrode and at least a portion of the metallic component into the plating bath;

after insertion of the at least one Ni electrode and the component surface into the plating bath, electrodepositing a nickel-tungsten (NiW) plating layer over the component surface by energizing the at least one consumable Ni electrode as an anode and the metallic component as a cathode to attract Ni ions and W ions to the component surface; and

maintaining an amount of anode corrosion accelerant, selected from the group consisting of nickel chloride, ammonium chloride or sodium chloride, in the plating bath to balance Ni dissolution at the anode to Ni deposition at cathode, considered in conjunction with any additional Ni ion sources within the plating bath, to achieve a desired composition of the electrodeposited NiW layer, wherein the anode corrosion accelerant is maintained in the plating bath in a sufficient amount to prevent scale build-up over the surface of the at least one Ni electrode whilst limiting dissolution of the at least one Ni electrode to a rate substantially equivalent to the rate of Ni

ion deposition onto component surfaces subject to plating.

2. The method of claim 1, further comprising maintaining the anode corrosion accelerant in a range between about 0.0002 to about 0.01 moles chloride per liter of plating bath solution during the electrodeposition process.
3. The method of claim 1 wherein maintaining comprises maintaining the anode corrosion accelerant in a range between 0.0008 to about 0.0025 moles chloride per liter of plating bath solution during the electrodeposition process.
4. The method of claim 1 further comprising preparing the plating bath to further contain ammonium hydro-

xide ions in a concentration range of about 1.0 to about 2.0 moles per liter of plating bath solution.

5. The method of claim 4 wherein the plating bath is prepared to further contain ammonium hydroxide ions in a concentration range of 1.3 to 1.7 moles per liter of plating bath solution.
6. The method of claim 1 further comprising formulating the plating bath and controlling process parameters during electrodeposition of the NiW plating layer such that Ni ions are present within the plating bath in a concentration range of about 0.085 to about 0.307 moles per liter of plating bath solution.
7. The method of claim 6 wherein formulating comprises formulating the plating bath and controlling process parameters during electrodeposition of the NiW plating layer such that Ni ions are present within the plating bath in a concentration range of 0.187 to 0.230 moles per liter of plating bath solution.
8. The method of claim 1 further comprising selecting the at least one consumable Ni electrode to comprise consumable Ni pellets.
9. The method of claim 8 further comprising repeatedly adding fresh consumable Ni pellets to the plating bath as the electroplating process progresses to maintain a ratio between a cumulative surface area of the consumable Ni pellets and a surface area of the component surface within a predetermined range.
10. The method of claim 1 wherein energizing comprises energizing the at least one consumable Ni electrode and the metallic component at a current density between 1 and 5 ampere per square decimeter.
11. The method of claim 1 further comprising formulating the plating bath to further contain citric acid in a quantity ranging from 90 to 150 grams per liter of the plating bath.
12. The method of claim 1 wherein the metallic component comprises a connector terminal having a contact resistance, wherein electrodepositing comprises electrodepositing the NiW plating layer directly onto the component surface, and wherein the method further comprises depositing at least one gold layer directly onto the NiW plating layer to decrease the contact resistance of the connector terminal.
13. The method of claim 1 further comprising selecting a target W content of the NiW plating to range from about 25% to about 35% by weight.

Patentansprüche

1. Verfahren zum Ausbilden einer Beschichtung auf einer Komponentenfläche einer Metallkomponente, das Verfahren umfassend:

Herstellen eines Plattierungsbades, das eine Wolfram-(W-)Ionenquelle enthält;
Einführen von mindestens einer verbrauchbaren Nickel-(Ni-)Elektrode und mindestens eines Teils der Metallkomponente in das Plattierungsbad;
nach Einführung der mindestens einen Ni-Elektrode und der Komponentenfläche in das Plattierungsbad, galvanisches Abscheiden einer Nickel-Wolfram-(NiW-)Plattierungsschicht auf der Komponentenfläche durch Anregen der mindestens einen verbrauchbaren Ni-Elektrode als Anode und der Metallkomponente als Kathode, um Ni-Ionen und W-Ionen an die Komponentenfläche anzuziehen; und
Aufrechterhalten einer Menge von Anodenkorrosionsbeschleuniger, der ausgewählt ist aus der Gruppe bestehend aus Nickelchlorid, Ammoniumchlorid oder Natriumchlorid, in dem Plattierungsbad, um eine Ni-Auflösung an der Anode gegenüber einer Ni-Abscheidung an der Kathode auszugleichen, berücksichtigt in Verbindung mit allen zusätzlichen Ni-Ionenquellen innerhalb des Plattierungsbad, um eine gewünschte Zusammensetzung der galvanisch abgeschiedenen NiW-Schicht zu erreichen, wobei der Anodenkorrosionsbeschleuniger in dem Plattierungsbad in ausreichender Menge aufrechterhalten wird, um eine Belagbildung auf der Fläche der mindestens einen Ni-Elektrode zu verhindern, während eine Auflösung der mindestens einen Ni-Elektrode auf eine Rate begrenzt wird, die im Wesentlichen äquivalent zu der Rate der Ni-Ionenabscheidung auf Komponentenflächen ist, die Plattieren unterworfen sind.

2. Verfahren nach Anspruch 1, ferner umfassend Aufrechterhalten des Anodenkorrosionsbeschleunigers in einem Bereich zwischen etwa 0,0002 bis etwa 0,01 Mol Chlorid pro Liter Plattierungsbadlösung während des Prozesses der galvanischen Abscheidung.
3. Verfahren nach Anspruch 1, wobei das Aufrechterhalten des Aufrechterhalten des Anodenkorrosionsbeschleunigers in einem Bereich zwischen 0,0008 bis etwa 0,0025 Mol Chlorid pro Liter Plattierungsbadlösung während des Prozesses der galvanischen Abscheidung umfasst.
4. Verfahren nach Anspruch 1, ferner umfassend Her-

stellen des Plattierungsbades, sodass es ferner Ammoniumhydroxidionen in einem Konzentrationsbereich von etwa 1,0 bis etwa 2,0 Mol pro Liter Plattierungsbadlösung enthält.

5. Verfahren nach Anspruch 4, wobei das Plattierungsbad dazu hergestellt wird, dass es ferner Ammoniumhydroxidionen in einem Konzentrationsbereich von 1,3 bis 1,7 Mol pro Liter Plattierungsbadlösung enthält.
6. Verfahren nach Anspruch 1, ferner umfassend Formulieren des Plattierungsbades und Steuern von Prozessparametern während der galvanischen Abscheidung der NiW-Plattierungsschicht, sodass Ni-Ionen innerhalb des Plattierungsbades in einem Konzentrationsbereich von etwa 0,085 bis etwa 0,307 Mol pro Liter Plattierungsbadlösung vorhanden sind.
7. Verfahren nach Anspruch 6, wobei das Formulieren des Plattierungsbades und das Steuern von Prozessparametern während der galvanischen Abscheidung der NiW-Plattierungsschicht so umfasst, dass Ni-Ionen innerhalb des Plattierungsbades in einem Konzentrationsbereich von 0,187 bis 0,230 Mol pro Liter Plattierungsbadlösung vorhanden sind.
8. Verfahren nach Anspruch 1, ferner umfassend Auswählen der mindestens einen verbrauchbaren Ni-Elektrode, sodass sie verbrauchbare Ni-Pellets umfasst.
9. Verfahren nach Anspruch 8, ferner umfassend wiederholtes Hinzufügen von frischen verbrauchbaren Ni-Pellets zu dem Plattierungsbad, wenn der Elektroplattierungsprozess fortschreitet, um ein Verhältnis zwischen einem kumulativen Flächenbereich der verbrauchbaren Ni-Pellets und einem Flächenbereich der Komponentenfläche innerhalb eines vorbestimmten Bereichs aufrechtzuerhalten.
10. Verfahren nach Anspruch 1, wobei das Anregen das Anregen der mindestens einen verbrauchbaren Ni-Elektrode und der Metallkomponente mit einer Stromdichte zwischen 1 und 5 Ampere pro Quadratdezimeter umfasst.
11. Verfahren nach Anspruch 1, ferner umfassend Formulieren des Plattierungsbades, sodass es ferner Zitronensäure in einer Menge enthält, die im Bereich von 90 bis 150 Gramm pro Liter der Plattierungsbadlösung liegt.
12. Verfahren nach Anspruch 1, wobei die Metallkomponente einen Verbinderauschluss umfasst, der einen Kontaktwiderstand aufweist, wobei das galva-

nische Abscheiden das galvanische Abscheiden der NiW-Plattierungsschicht direkt auf die Komponentenfläche umfasst, und wobei das Verfahren ferner das Abscheiden von mindestens einer Goldschicht direkt auf die NiW-Plattierungsschicht umfasst, um den Kontaktwiderstand des Steckverbinders zu reduzieren.

13. Verfahren nach Anspruch 1, ferner umfassend Auswählen eines angestrebten W-Gehalts der NiW-Plattierung, sodass er in einem Bereich von etwa 25 Gew.-% bis etwa 35 Gew.-% liegt.

Revendications

1. Procédé de formation d'un revêtement sur une surface de composant d'un composant métallique, le procédé comprenant :

la préparation d'un bain de placage contenant une source d'ions tungstène (W) ;

l'introduction d'au moins une électrode consommable en nickel (Ni) et d'au moins une partie du composant métallique dans le bain de placage ; après introduction de ladite au moins une électrode en Ni et de la surface de composant dans le bain de placage, l'électrodéposition d'une couche de placage nickel-tungstène (NiW) sur la surface de composant en mettant sous tension ladite au moins une électrode consommable en Ni en tant qu'anode et le composant métallique en tant que cathode pour attirer des ions Ni et des ions W vers la surface de composant ; et

le maintien d'une quantité d'accélérateur de corrosion d'anode, sélectionné à partir du groupe constitué de chlorure de nickel, de chlorure d'ammonium ou de chlorure de sodium, dans le bain de placage afin d'équilibrer la dissolution du Ni à l'anode avec le dépôt de Ni à la cathode, considérée en conjonction avec toute source supplémentaire d'ions Ni dans le bain de placage, afin d'obtenir une composition souhaitée de la couche de NiW électrodéposée, dans lequel l'accélérateur de corrosion d'anode est maintenu dans le bain de placage en une quantité suffisante pour empêcher la formation d'incrustations sur la surface de ladite au moins une électrode en Ni tout en limitant la dissolution de ladite au moins une électrode en Ni à un taux sensiblement équivalent au taux de dépôt des ions Ni sur des surfaces de composant soumises au placage.

2. Procédé selon la revendication 1, comprenant en outre le maintien de l'accélérateur de corrosion d'anode dans une plage comprise entre environ 0,0002

et environ 0,01 mole de chlorure par litre de solution de bain de placage pendant le processus d'électrodéposition.

3. Procédé selon la revendication 1, dans lequel le maintien comprend le maintien de l'accélérateur de corrosion d'anode dans une plage comprise entre 0,0008 et environ 0,0025 mole de chlorure par litre de solution de bain de placage pendant le processus d'électrodéposition.

4. Procédé selon la revendication 1, comprenant en outre la préparation du bain de placage de manière à contenir en outre des ions hydroxyde d'ammonium dans une plage de concentration d'environ 1,0 à environ 2,0 moles par litre de solution de bain de placage.

5. Procédé selon la revendication 4, dans lequel le bain de placage est préparé de manière à contenir en outre des ions hydroxyde d'ammonium dans une plage de concentration de 1,3 à 1,7 moles par litre de solution de bain de placage.

6. Procédé selon la revendication 1, comprenant en outre la formulation du bain de placage et la commande des paramètres de processus pendant l'électrodéposition de la couche de placage NiW de sorte que des ions Ni soient présents dans le bain de placage dans une plage de concentration d'environ 0,085 à environ 0,307 mole par litre de solution de bain de placage.

7. Procédé selon la revendication 6, dans lequel la formulation comprend la formulation du bain de placage et la commande des paramètres de processus pendant l'électrodéposition de la couche de placage NiW de sorte que des ions Ni soient présents dans le bain de placage dans une plage de concentration de 0,187 à 0,230 mole par litre de solution de bain de placage.

8. Procédé selon la revendication 1, comprenant en outre la sélection de ladite au moins une électrode consommable en Ni pour comprendre des granulés de Ni consommables.

9. Procédé selon la revendication 8, comprenant en outre l'ajout répété de nouveaux granulés de Ni consommables au bain de placage à mesure que le processus de placage électrolytique progresse afin de maintenir un rapport entre une aire de surface cumulée des granulés de Ni consommables et une aire de surface de la surface de composant dans une plage prédéterminée.

10. Procédé selon la revendication 1, dans lequel la mise sous tension comprend la mise sous tension

de ladite au moins une électrode consommable en Ni et du composant métallique à une densité de courant comprise entre 1 et 5 ampères par décimètre carré.

11. Procédé selon la revendication 1, comprenant en outre la formulation du bain de placage de manière à contenir en outre de l'acide citrique en une quantité allant de 90 à 150 grammes par litre du bain de placage. 5
- 10
12. Procédé selon la revendication 1, dans lequel le composant métallique comprend une borne de connecteur présentant une résistance de contact, dans lequel l'électrodéposition comprend l'électrodéposition de la couche de placage NiW directement sur la surface de composant, et dans lequel le procédé comprend en outre le dépôt d'au moins une couche d'or directement sur la couche de placage NiW afin de diminuer la résistance de contact de la borne de connecteur. 15
- 20
13. Procédé selon la revendication 1, comprenant en outre la sélection d'une teneur cible en W du placage NiW comprise entre environ 25 % et environ 35 % en poids. 25

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35

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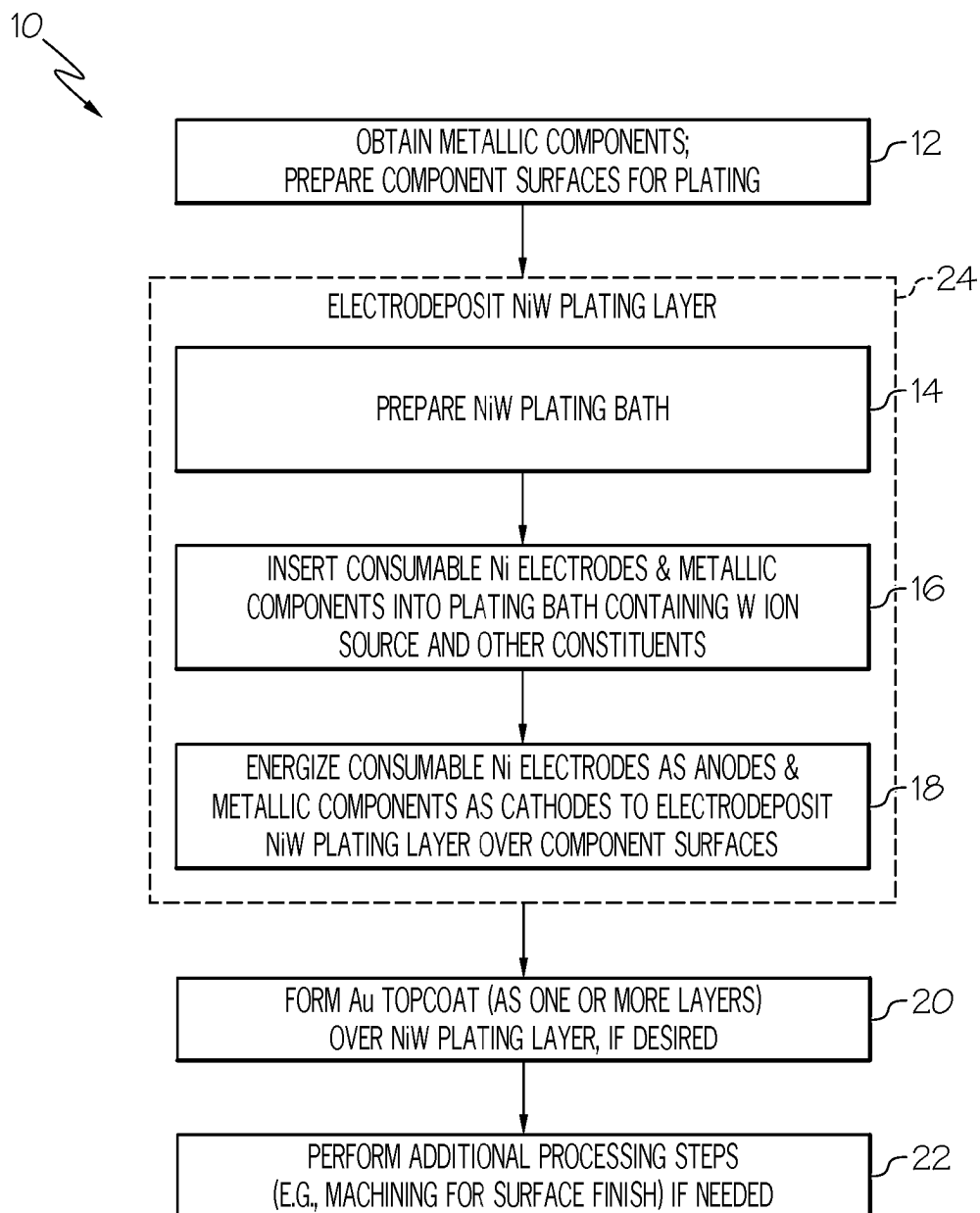


FIG. 1

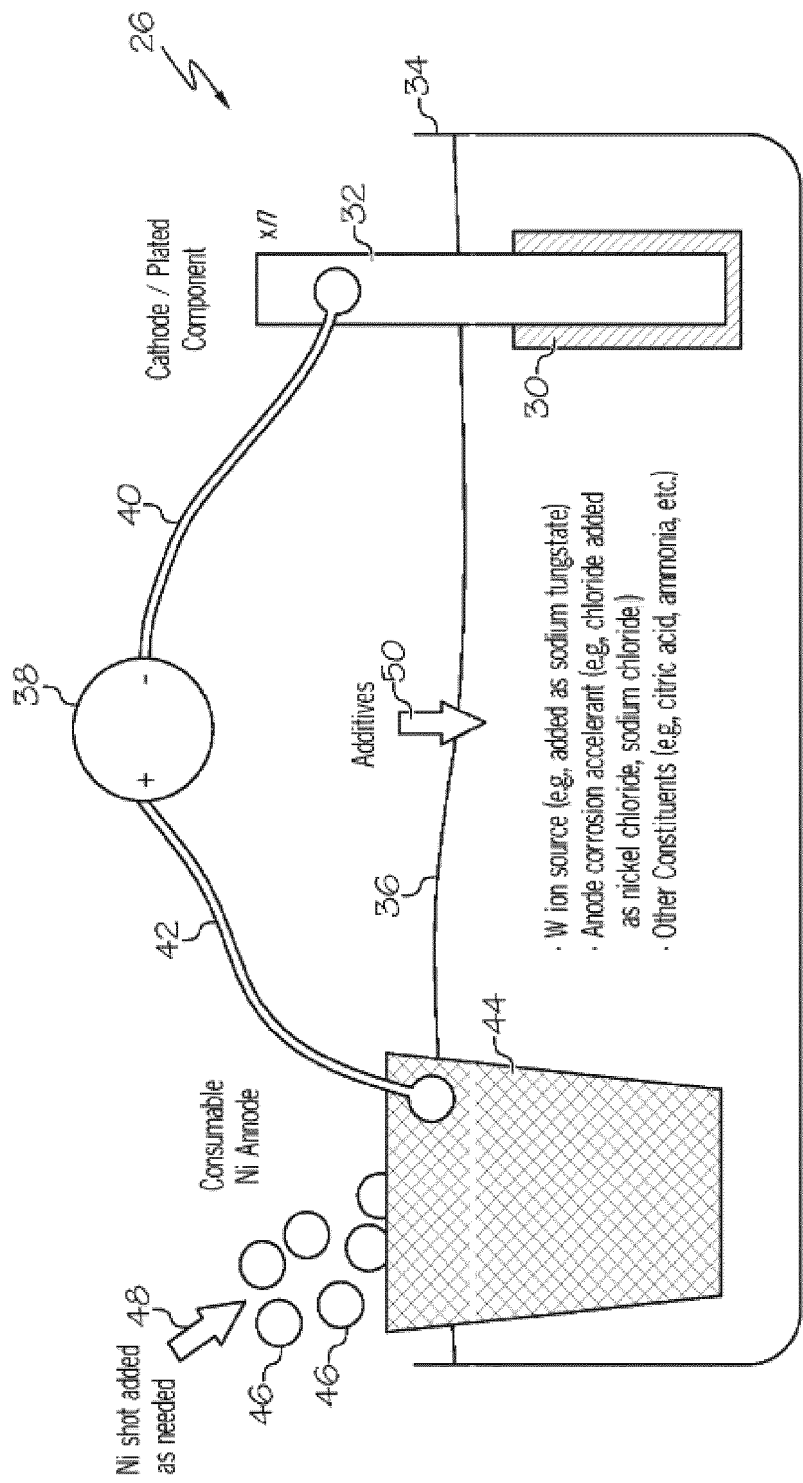


FIG. 2

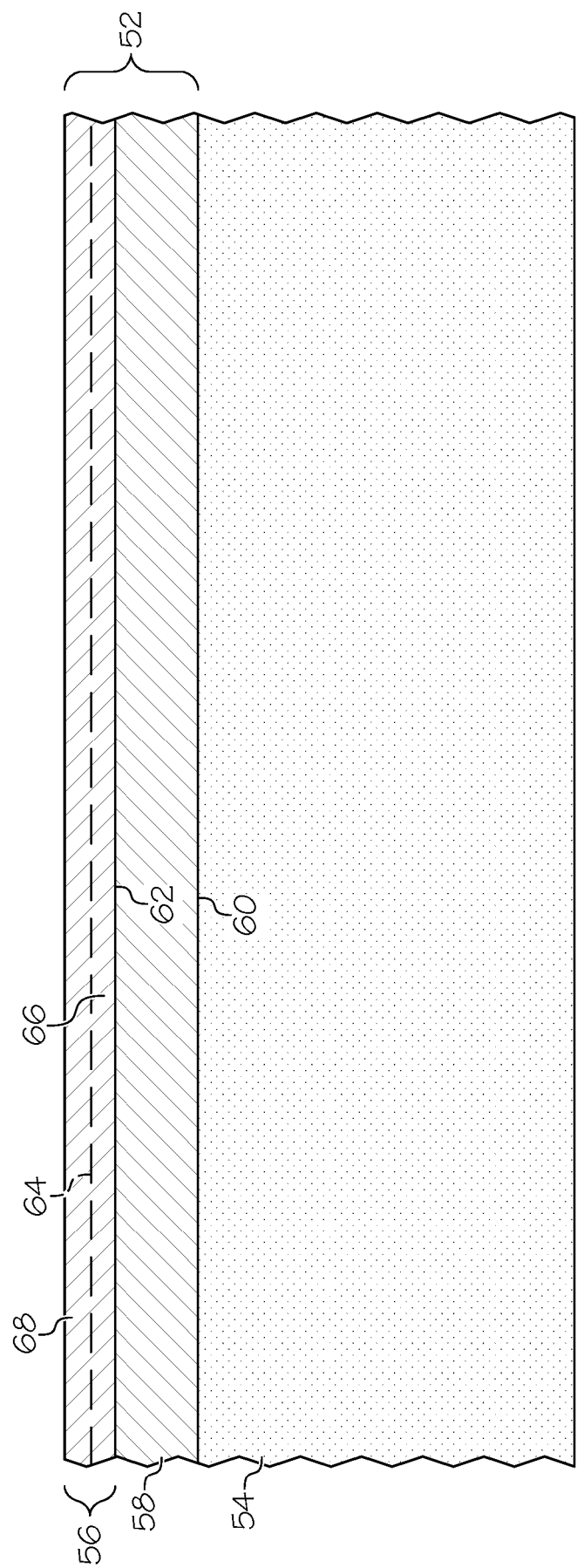


FIG. 3

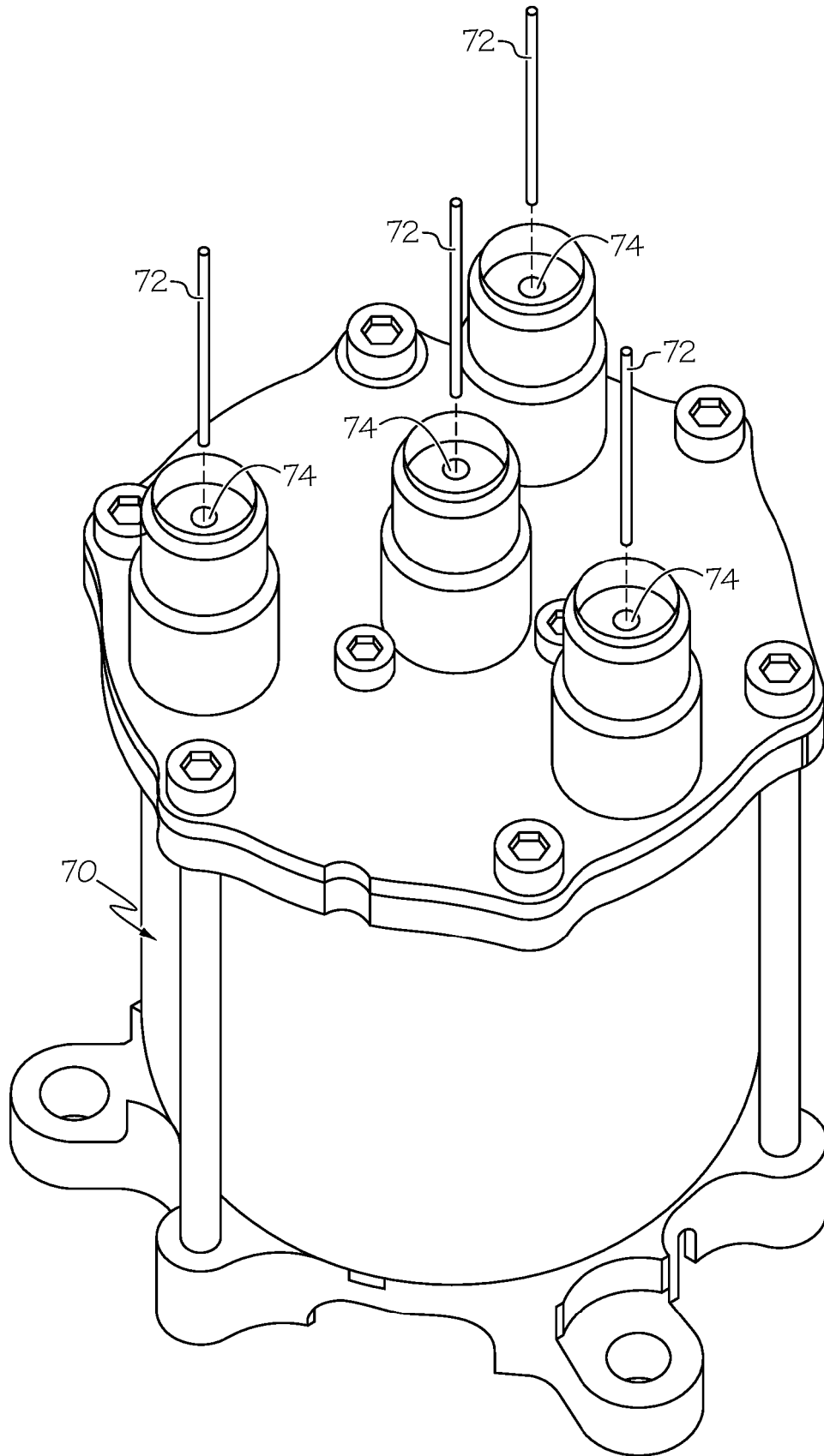


FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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