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(54) **MULTILAYER STACK INCLUDING GOLD- AND PLATINUM-BASED LAYERS AND RELATED METHODS**

(57) Described is a multilayer stack comprising: a Cu-based layer; a Ni-based layer provided over the Cu-based layer; an Au-based layer provided over the Ni-based layer; and a Pt-based layer provided over the Au-based layer. The multilayer stack exhibits excellent corrosion resistance, especially in chlorinated environments and under oxidizing conditions, and improves the catalytic performance, mechanical properties and/or lifetime of the multilayer stack. A method of manufacturing the aforementioned multilayer stack, the use of the aforementioned multilayer stack as an electrode or an electrical conductor in electrical connectors and/or electric circuits, and a method of improving the corrosion resistance of Ni-plated Cu by making use of the stack configuration are likewise described. In addition, a biosensor comprising the aforementioned multilayer stack is described.

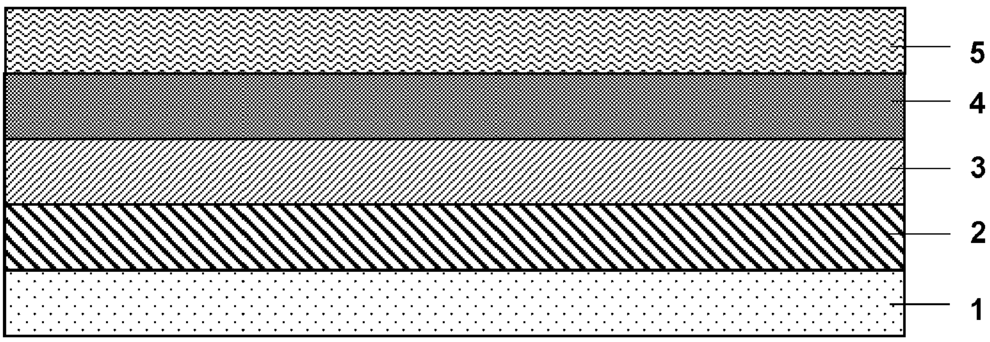

Fig. 1

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Description

FIELD OF INVENTION

[0001] This invention relates to a multilayer stack comprising layers based on copper, nickel, gold and platinum, in the given order, which may be used for the preparation of electrodes or electrical conductors with enhanced corrosion resistance.

[0002] In certain embodiments, this invention relates to a method of manufacturing said multilayer stack and its use, as well as to a method of improving the corrosion resistance of nickel-plated copper.

BACKGROUND OF THE INVENTION

[0003] Platinum (Pt) is a commonly used material for electrical contacts, particularly in wet chemical processing, and serves as a catalyst for many commercial applications, including fuel cells, petroleum industry and autocatalytic converters. Platinum electrodes with catalytic activity find widespread use throughout all fields of electrochemistry. Especially for medical applications (e.g. in neural stimulators or biochemical sensors, working or counter electrodes), electrodes comprising Pt have gained increased interest due to its biocompatibility and resistance to oxidation (e.g., by blood, sweat or saline solution).

[0004] Since Pt is of low abundance and expensive, a cost reduction is typically achieved by forming a stack of multiple metal layers including a Pt layer as outermost layer.

[0005] For this purpose, it is known to use a copper (Cu) layer, plate the same with a nickel (Ni) layer for improved mechanical strength and corrosion stability and forming a Pt layer on the Ni layer. By using Ni in the intermediate layer, problems with poor adhesion between the Cu and Pt layer due to the relatively large potential difference between the metals may be avoided. For instance, CN 113394417 B discloses the aforementioned three-layer structure in a core-shell configuration and reports a higher stability of the catalyst compared with pure Pt.

[0006] CN 105154931 A discloses a method of electroplating a base layer made of nickel, titanium, tantalum, copper or silver with platinum by electrodeposition from an electroplating solution.

[0007] However, the corrosion resistance of the described multilayer stacks tends to be insufficient for many applications. Moreover, it has been found that copper and/or nickel may diffuse into the platinum layer in corrosive environments (especially in chlorinated media and under oxidizing conditions, e.g. in presence of H_2O_2) and thus negatively affect the catalytic performance, mechanical properties and/or lifetime of the multilayer stack.

[0008] Therefore, it remains desirable to provide a Pt-containing multilayer stack which exhibits an improved corrosion resistance and enables prolonged functionality (e.g. as electrode catalyst or electrical conductor), thus widening the options for potential applications while still maintaining lower manufacturing costs compared to pure Pt.

[0009] Moreover, it would be desirable to provide a method of effectively improving the corrosion resistance of nickel-plated copper.

SUMMARY OF THE INVENTION

[0010] The present invention solves this object with the subject matter of the claims as defined herein. The advantages of the present invention will be further explained in detail in the section below and further advantages will become apparent to the skilled artisan upon consideration of the invention disclosure.

[0011] Generally speaking, in one aspect the present invention provides a multilayer stack comprising: a Cu-based layer; a Ni-based layer provided over the Cu-based layer; an Au-based layer provided over the Ni-based layer; and a Pt-based layer provided over the Au-based layer.

[0012] In another aspect, the present invention provides a method of manufacturing the aforementioned multilayer stack, comprising: providing a Ni/Cu-multilayer film comprising a Ni-based layer and a Cu-based layer; depositing a layer of Au on the Ni-based layer to form an Au-based layer, and depositing a layer of Pt on the Au-based layer to form a Pt-based layer.

[0013] In a further aspect, the present invention relates to the use of the aforementioned multilayer stack as an electrode or an electrical conductor in electrical connectors and/or electric circuits.

[0014] In yet another aspect, the present invention provides a method of improving the corrosion resistance of Ni-plated Cu, the method comprising the steps of: depositing a layer of Au on the surface of the Ni-plated Cu to form an Au-based layer, and depositing a layer of Pt on the Au-based layer to form a Pt-based layer.

[0015] In a further aspect, the present invention porvides a biosensor or a medical device comprising aforementioned multilayer stack.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

FIG. 1 is a schematic representation of an exemplary embodiment of the multilayer stack of the present invention.
FIG. 2A is a schematic representation of an exemplary embodiment of the multilayer stack of the present invention including a substrate.
FIG. 2B is a schematic representation of an exemplary embodiment of the multilayer stack of the present invention including a substrate with a channel/cavity.
FIG. 3 is a schematic representation of an exemplary embodiment of the multilayer stack of the present invention with covered edges and substrate.
FIG. 4A illustrates an exemplary embodiment of the multilayer stack of the present invention with a core-shell structure.
FIG. 4B is a schematic representation of an exemplary embodiment of the multilayer stack of the present invention including a substrate with a channel/cavity.

DETAILED DESCRIPTION OF THE INVENTION

[0017] For a more complete understanding of the present invention, reference is now made to the following description of the illustrative embodiments thereof:

Multilayer Stack

[0018] In a first embodiment, the present invention generally relates to a multilayer stack comprising: a Cu-based layer; a Ni-based layer provided over the Cu-based layer; an Au-based layer provided over the Ni-based layer; and a Pt-based layer provided over the Au-based layer.

[0019] Specifically, it has been found that a surprisingly high improvement of the corrosion resistance may be achieved by utilizing the specific order of layers within the stack. Although Cu, Ni and Au are substantially more prone to corrosion than Pt (especially in chlorinated media such as salt spray solution or phosphate-buffered saline) and oxidizing electrochemical environment (e.g. upon exposure to hydrogen peroxide), providing said three-layer stack underneath the Pt-based layer enhances the properties attributed to the Pt-based layer to an unexpected degree (i.e. synergistically).

[0020] Although other layers may be interposed between each layer of the stack, it is preferred that the Pt-based layer is in contact with the Au-based layer. Independently or in combination, it is preferred that the Cu-based layer is provided in contact with the Ni-based layer. Independently or in combination, the Ni-based layer is provided in contact with the Au-based layer. In an especially preferred embodiment, no layers are interposed between the Cu-, Ni-, Au- and Pt-based layers. An exemplary configuration of said embodiment is illustrated in Fig. 1, with the Cu-based layer (1), Ni-based layer (2), Au-based layer (3) and Pt-based layer (4) being provided in contact with each other. In Fig. 1, an optional additional functional layer (5), which will be described in further detail below, is provided over and in contact with the Pt-based layer (4).

[0021] The multilayer stack may further comprise a substrate on which the stack is placed, deposited or adhered to via chemical adhesives, preferably via the Cu-based layer.

[0022] Figures 2A and 2B show preferred configurations of a multilayer stack on a substrate (17/27).

[0023] The substrate (17/27) is not particularly limited and may include polymer, silicon, ceramic substrates, glass, fabric, paper and combinations thereof. As examples of polymers, polyetheretherketone (PEEK), polyphenylsulfone (PPSU), polyethylene terephthalate (PET), polyimide (PI), polyetherimide (PEI), liquid crystal polymer (LCP) or epoxy glass may be mentioned, for example), ceramics or paper. Preferred substrate materials from the perspective of biocompatibility include epoxy glass, polyethylene terephthalate (PET), polyetherimide (PEI), among which polyetherimide (PEI) is especially preferred. Typically, the substrate thickness ranges from 20 to 200 μm, more preferably between 50 and 150 μm.

[0024] The substrate may further comprise one or more channels or cavities (28), as illustrated in Fig. 2B, which may be punched into the substrate, for example. In such a configuration, the Cu-based layer (21) may be provided with deposits of further metal layers (preferably a Ni layer (29a) and an Au layer (29b) in this order, with the Ni layer (29a) being in contact with the Cu-based layer (21)) extending into the channel or cavity (28) and covering the Cu-based layer (21) from the side opposed to the Ni-based layer (22). In general, the Cu-based layer essentially consists of Cu or an alloy having Cu as its principal component. Accordingly, the Cu-based layer comprises at least 50 wt.-% of Cu, and preferably comprises at least 85 wt.-%, more preferably at least 90 wt.-% Cu based on the total weight of the Cu-based layer. In a further preferred embodiment, the Cu-based layer essentially consists of Cu.

[0025] Notably, the expression "essentially consists of" used herein is understood to define that the respective layer consists of the material except from unavoidable impurities, which may be present in an amount of up to 0.5 wt.-% of the respective layer.

[0026] In analogy, Ni-based layer essentially consists of Ni or an alloy having Ni as its principal component. Accordingly, the Ni-based layer comprises at least 50 wt.-% of Ni and preferably comprises at least 85 wt.-%, more preferably at least 90 wt.-% Ni based on the total weight of the Ni-based layer. The presence of the Ni-based layer provides an improved adhesion to subsequent coating layers (e.g. the Au-based layer).

[0027] Ni plating is generally also thought of as a barrier which prevents the diffusion of copper into the outer layers. However, it has been found that the Ni-based layer cannot prevent Cu from diffusing into the Pt-layer and degrading the corrosion resistance and ultimately the electrical properties of the Pt layer. For this purpose, the present invention comprises the Au-based layer as an effective barrier preventing diffusion of both Cu and Ni into the Pt-based layer.

[0028] In a preferred embodiment, a layer of Ni-P alloy (see 16 and 26 in Figs. 2A and 2B, respectively) may be deposited between the Ni-based layer and the Au-based layer to improve the mechanical, tribological and electrochemical features.

[0029] The Au-based layer essentially consists of Au or an alloy having Au as its principal component. Accordingly, the Au-based layer comprises at least 50 wt.-% of Au and preferably comprises at least 85 wt.-%, more preferably at least 90 wt.-% Au based on the total weight of the Au-based layer. In a further preferred embodiment, the Au-based layer essentially consists of Au.

[0030] In another preferred embodiment, the Au-based layer comprises a sub-layer of flash-deposited Au having a higher porosity than the rest of the Au-based layer, with a preferred thickness in the range of 5 to 30 nm, more preferably between 8 to 20 nm. In this configuration, the flash-deposited sub-layer is preferably in contact with the Ni-based layer or the layer of NiP alloy, if present.

[0031] It is preferred that the Pt-based layer comprises at least 95 wt.-%, more preferably at least 97 wt.-% and further preferably at least 99 wt.-% Pt based on the total weight of the Pt-based layer. In an especially preferred embodiment, the Pt-based layer essentially consists of Pt.

[0032] Alternatively, the Pt-based layer essentially consists of a Pt alloy comprising Pt as its principal component. Accordingly, the Pt-based layer comprises at least 50 wt.-% Pt based on the total weight of the Pt-based layer, more preferably at least 60 wt.-% of Pt.

[0033] A layer containing one or more platinum group metals other than Pt (i.e. ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os) and/or iridium (Ir)) may be interposed between the Au-based layer and the Pt-based layer. Among these metals, Pd is preferred. Such layer may essentially consist of one or more of Ru, Rh, Pd, Os and Ir, or essentially consist of an alloy having one of the aforemention metals as its principal component.

[0034] If Cu, Ni, Au and/or Pt are present as principal components of alloys in any of the aforementioned layers, such alloys preferably comprise one or more metals selected from transition metals. Among preferred transition metals, Au, Co, Cu, Ni, and/or Fe may be mentioned.

[0035] In addition, metal oxides (including, but not limited to CeO_2, WO_3, $TazO_5$, Nb_2O_5, and ZrO_2) may be present in the Pt-based layer to alter the catalytic activity for the desired purpose.

[0036] The thickness of each layer is not particularly limited and may be suitably selected by the skilled artisan depending on the desired properties and purpose of the multilayer stack.

[0037] While not being limited thereto, the Cu-based layer typically has a thickness of from 1 to 50 μm, in embodiments from 10 to 40 μm, more preferably from 15 to 30 μm.

[0038] Independently or in combination, the Ni-based layer typically has a thickness of from 0.4 to 50 μm, in embodiments from 0.5 to 20 μm, more preferably from 1 to 5 μm.

[0039] It may be preferred that the Au-based layer has a minimum thickness of 15 nm and preferably a thickness of from 20 nm to 500 nm.

[0040] Moreover, in order to make full use of the advantages of the present invention, the Pt-based layer has a thickness of 15 nm or larger, preferably from 20 nm to 600 nm and further preferably from 25 to 500 nm.

[0041] An additional functional layer (5) may be optionally provided over and preferably in contact with the Pt-based layer (4).

[0042] Normally, a Pt-based layer obtained by electroplating through an electroplating solution will be smooth, shiny and low in porosity. One approach to increase the surface area of the Pt-based layer without increasing the surface is to electroplate Pt rapidly, which results in a Pt surface which commonly known as "platinum black". Pt black has a porous and rough surface which is less dense and less reflective than shiny Pt.

[0043] In embodiments, it may be therefore preferable that the multilayer stack additionally comprises a layer of platinum black over the Pt-based layer as an additional functional layer (5), which is further preferably in contact with the Pt-based layer (4). In further preferred embodiments, the layer of platinum black preferably has a specific surface area in the range of from 2 to 50 m^2/g, more preferably of from 20 to 50 m^2/g. The thickness of the platinum black layer is not particularly limited and may be suitably adjusted to balance the structural integrity with the desired catalytic activity.

[0044] In an alternative embodiment, as illustrated in Figs. 2A and 2B, the multilayer stack of the present invention may further comprise a second Au-based layer (15/25) over the Pt-based layer (14/24) as an additional functional layer, which is further preferably in contact with the Pt-based layer (14/24). The second Au-based layer (15/25) may cover the Pt-based layer (14/24) partly or entirely and may provide the multilayer stack with an enhanced metallic appearance. The second Au-based layer (15/25) may consist of Au or an alloy having Au as its principal component. Accordingly, the Au-based layer (15/25) comprises at least 50 wt.-% of Au. A non-limiting example of an Au-Cu alloy deposited on a metal surface to provide electric contact pads with a rose gold appearance is disclosed in EP 3 892 759 A1.

[0045] In a preferred embodiment also shown in Fig. 2A and 2B, the second Au-based layer (15/25) may also comprise a sub-layer (15a/25a) of flash-deposited Au having a higher porosity than the rest of the second Au-based layer (15/25), with a preferred thickness in the range of 5 to 30 nm, more preferably between 8 to 20 nm. In this configuration, the flash-deposited sub-layer (15a/25a) is preferably in contact with the Pt-based layer (14/24).

[0046] In order to exert the corrosion protection function more effectively, it may be preferred that each cover layer of the stack extends over the sides of the underlying layer. An example thereof is illustrated in Fig. 3, wherein the Ni-based layer (32) extends over and covers the sides of the Cu-based layer (31), the Au-based layer (33) extends over and covers the sides of the Ni-based layer (32), the Pt-based layer (34) extends over and covers the sides of the Au-based layer (33). In such a configuration, the optional functional layer (35) may or may not extend over and cover the sides of the Pt-based layer (34), The shape in which the multilayer stack is provided is not particularly limited and may include cylindrical, rod-shaped and flat (e.g. rectangular, circular, etc.) geometries.

[0047] In a preferred embodiment illustrated in Fig. 4A, the multilayer stack exhibits a core-shell configuration, wherein the Cu-based layer (41) represents the core and is enclosed by a shell formed by - in the given order - the Ni-based layer (42), the Au-based layer (43), the Pt-based layer (44) and the optional functional layer (45). Such a configuration is especially preferred for substrateless stacks.

[0048] However, the configuration may also be used in combination with a continous substrate (not shown) or a substrate comprising a channel or cavity, as illustrated in Fig. 4B.

Method of Manufacturing a Multilayer Stack

[0049] In a second embodiment, the present invention relates to a method of manufacturing a multilayer stack according to the first embodiment described above, comprising: providing a Ni/Cu-multilayer film comprising a Ni-based layer and a Cu-based layer; depositing a layer of Au on the Ni-based layer to form an Au-based layer, and depositing a layer of Pt on the Au-based layer to form a Pt-based layer.

[0050] The method of providing a Ni/Cu-multilayer film comprising a Ni-based layer and a Cu-based layer is not particularly limited any may be brought about by any method known to the skilled artisan. For instance, the Ni-layer may be deposited on a Cu foil or wire (e.g. by electrodeposition from a Ni-salt solution).

[0051] Notably, the Ni/Cu-multilayer film comprising a Ni-based layer and a Cu-based layer may be provided in the form of a conductive layer of an electrical circuit (e.g. a printed circuit board or printed wiring board).

[0052] The layer of Ni-P alloy, if present, may be deposited by methods known in the art. A. Lelevic et al., Surface and Coatings Technology 2019, 369, 198-220 discloses exemplary electrodeposition methods for this purpose.

[0053] The method depositing a layer of Au on the Ni-based layer to form an Au-based layer is not particularly limited either and may include electrolytic plating methods and electroless plating methods (e.g., by using electroless nickel immersion gold (ENIG)) known in the art.

[0054] A flash-deposited Au sublayer may be provided according to methods known in the art, including, but not limited to electroless methods, such as immersion and chemical reduction.

[0055] While electroless deposition is also possible, the Pt-based layer is preferably deposited via electrodeposition from a solution containing a Pt precursor. Generally, such a precursor will be selected from Pt(II) and Pt(IV) salts. Examples of Pt (II) precursors include, but are not limited to $PtCl_4 \cdot 5\ H_2O$, $H_2PtCl_6 \cdot 6\ HzO$, $(NH_4)PtCl_6$, $Pt(NH_3)_2(NO_2)_2$ and dinitrosulphatoplatinites (e.g. based on the complex dihydrogen bis(nitrito-N)[sulphato(2-)-O,O']platinate(2-), $H_2Pt(NO_2)_2SO_4$), whereas suitable Pt (IV) precursors include, but are not limited to alkali hexahydroxyplatinates (e.g. $Na_2Pt(OH)_6$ or $K_2Pt(OH)_6$), phosphate salts (e.g. $(NH_4)_2HPO_4$, Na_2HPO_4).

[0056] Preferably, the Pt-based layer is deposited via electrodeposition from a solution comprising dihydrogen bis(nitrito-N)[sulphato(2-)-O,O']platinate(2-) ($H_2Pt(NO_2)_2SO_4$), which favors the deposition of a high-quality Pt-based layer with excellent coverage and low porosity. The electrodeposition solution may further comprise water-soluble phosphate, sodium dodecyl sulfate or dodecyl sulfate as an additive. In addition, the pH conditions may be suitably adjusted according to the selected precursor by addition of acid or base.

[0057] The reduction of Pt precursor by electroless deposition proceeds in almost the same manner as in electrochemical deposition, with the difference that electrons are not provided by an external source but a reducing agent.

[0058] The electrodeposition step as such can be performed by galvanostatic, potentiostatic or by potentiocyclic methods, which may be suitably selected by the skilled artisan depending on the desired surface roughness and layer stability, for example. Pulsed electrodeposition can be employed to alternate different potentials and thus different processes.

[0059] A Pt-based layer comprising a Pt alloy can be fabricated by co-deposition of two or more metals from their salts.

[0060] Notably, the steps of manufacturing the multilayer stack of the present invention may be carried out efficiently and economically through a reel-to-reel process.

Uses of the Multilayer Stack

[0061] In general, the multilayer stack according to the present invention may be of use in any application which requires superior electrical characteristics, catalytic activity, biocompatibility, stability and corrosion resistance.

[0062] In a third embodiment, the present invention therefore relates to the use of the multilayer stack according to the first embodiment described above as an electrode or an electrical conductor in electrical connectors and/or electric circuits, particularly in medical devices and biosensors.

[0063] The type of electrodes is not particularly limited. Non-limiting examples include biosensor electrodes or medical electrodes (e.g., reusable disc type electrodes). For instance, biosensor applications may involve the use of the multilayer stack of the present invention as an electrochemical catalyst (e.g. to accelerate the reaction of enzymes), as a sensor electrode to enhance electron transfer, and for enzymatic reactions.

[0064] Non-limiting examples of electrical connectors and electric circuits include connector pads and integrated circuits in smart cards (SC) (i.e. chip cards, or integrated circuit cards (ICC or IC cards)), respectively. Herein, the multilayer stack of the present invention may be used to provide improved resistance against corrosion by sweat, salt water or oxidizing agents.

Method of improving Corrosion Resistance

[0065] As discussed in the description above, the specific multilayer stack arrangement according to the present invention provides improved resistance towards corrosion when compared to configurations without an Au-based layer and/or without a Pt-based layer.

[0066] A fourth embodiment of the present invention therefore relates to a method of improving the corrosion resistance of Ni-plated Cu, the method comprising the steps of: depositing a layer of Au on the surface of the Ni-plated Cu to form an Au-based layer, and depositing a layer of Pt on the Au-based layer to form a Pt-based layer.

[0067] The steps of depositing the Au-based layer and the Pt-based layer are described in conjunction with the second embodiment.

[0068] The method according to the fourth embodiment is in principle applicable to all types of electric components and/or circuits comprising conductors based on Ni-plated Cu.

[0069] While not being limited thereto, an improvement in corrosion resistance may be evaluated with a neutral salt spray method (5% NaCl) according to ISO 9227 standard tests, for example. Another test includes the immersion of the specimen in H_2O_2 at ambient temperature (23 $\pm$ 2 °C) according to ASTM G31 - 21 (Standard Guide for Laboratory Immersion Corrosion Testing of Metals) removal of the specimen from the solution, rinsing with DI water, and measuring corrosion metal loss according to ASTM G1 - 03 (Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens) and/or analyzing the surface morphology of the tested specimen after a predetermined immersion duration by scanning electron microscopy (SEM) and/or X-ray photoelectron spectroscopy (XPS).

Biosensors and Medical Devices

[0070] In a fifth embodiment, the present invention relates to a biosensor or a medical device comprising the multilayer stack in accordance with the first embodiment.

[0071] A biosensor is understood as an analytical device that combines a biological component with a physicochemical detector and is used for the detection of a chemical substance. Herein, components comprising the multilayer stack according to the first embodiment may be used as electrochemical catalysts (to accelerate the reaction of enzymes, for example), as sensor electrodes to enhance electron transfer, and as a precursor material for enzyme modified electrodes, wherein the surface of the multilayer stack is modified into an enzyme to fix the substrate and maintain enzyme activity. While not being limited thereto, the biosensor may employed for the detection of bioactive substances such as glucose, glutamic acid, neurotransmitters or hormones.

[0072] A medical device may also comprise a medical sensor (e.g. sensors in medical pumps minimally invasive equipment, respiratory care or vital signs monitoring), but is not limited thereto. For instance, examples of the medical device may also comprise surgical instrumentation (e.g. marker bands and guidewires for catheters, electrodes for catheters), electro-medical implants (e.g. pacemakers, hearing aids, heart pumps, defibrillators, neuromodulation devices), interventional devices (e.g., stents), othopaedic devices (e.g. knee or hip implants, spinal fixation devices) or the like.

[0073] These embodiments are advantageous in that they fully exploit the excellent biocompatibility, durability, conductivity and radiopacity of Pt.

[0074] It will be appreciated that the present invention may employ any of the preferred features specified above with respect to the description of the first to fifth embodiments, and that the preferred features may be combined in any combination, except for combinations, where at least some of the features are mutually exclusive.

[0075] Once given the above disclosure, many other features, modifications, and improvements will become apparent to the skilled artisan.

Reference Numerals

[0076]

1 / 11 / 21 / 31 / 41 / 51	copper (Cu)-based layer
2 / 12 / 22 / 32 / 42 / 52	nickel (Ni)-based layer
3 / 13 / 23 / 33 / 43 / 53	gold (Au)-based layer
13a / 23a	flash gold (Au) layer (optional)
4 / 14 / 24 / 34 / 44 / 54	platinum (Pt)-based layer
5	additional functional layer (optional)
15/25	second gold (Au)-based layer (optional)
15a / 25 b	flash gold (Au) layer (optional)
16/26	Ni-P layer (optional)
17 / 27 / 37 / 57	substrate (optional)
28 / 58	channel (optional)
29a	Ni layer (optional)
29b	Au layer (optional)

Claims

1. Multilayer stack comprising:

   a Cu-based layer;
   a Ni-based layer provided over the Cu-based layer;
   an Au-based layer provided over the Ni-based layer; and
   a Pt-based layer provided over the Au-based layer.

2. Multilayer stack according to claim 1, wherein the Pt-based layer is in contact with the Au-based layer.

3. Multilayer stack according to claim 1 or claim 2, wherein the Cu-based layer is provided in contact with the Ni-based layer.

4. Multilayer stack according to any one of claims 1 to 3, wherein the Ni-based layer is provided in contact with the Au-based layer.

5. Multilayer stack according to any one of claims 1 to 4, wherein the Cu-based layer comprises at least 85 wt.-% and preferably at least 90 wt.-% Cu based on the total weight of the Cu-based layer; and/or wherein the Ni-based layer comprises at least 85 wt.-% and preferably at least 90 wt.-% Ni based on the total weight of the Ni-based layer; and/or wherein the Au-based layer comprises at least 85 wt.-% and preferably at least 90 wt.-% Au based on the total weight of the Au-based layer.

6. Multilayer stack according to any one of claims 1 to 5, wherein the Au-based layer has a minimum thickness of 15 nm and preferably a thickness of from 20 nm to 500 nm.

7. Multilayer stack according to any one of claims 1 to 6, wherein the Pt-based layer comprises at least 95 wt.-%, preferably at least 97 wt.-% and more preferably at least 99 wt.-% Pt based on the total weight of the Pt-based layer.

8. Multilayer stack according to any one of claims 1 to 6, wherein the Pt-based layer consists of a Pt alloy comprising at least 60 wt.-% of Pt based on the total weight of the Pt-based layer, and the Pt alloy preferably further comprises a metal selected from one or more transition metals.

9. Multilayer stack according to any one of claims 1 to 8, wherein the Pt-based layer has a thickness of 15 nm or larger, preferably from 20 nm to 600 nm and further preferably from 25 to 500 nm.

10. Multilayer stack according to any one of claims 1 to 9, further comprising a layer of platinum black over and in contact with the Pt-based layer, the layer of platinum black preferably having a specific surface area in the range of from 2 to 50 m^2/g.

11. Multilayer stack according to any one of claims 1 to 9, further comprising a second Au-based layer over and in contact with the Pt-based layer.

12. Multilayer stack according to any one of claims 1 to 11, further comprising a substrate selected from a polymer, silicon, a ceramic substrate, glass, fabric, paper and combinations thereof.

13. Method of manufacturing a multilayer stack according to any one of claims 1 to 12, comprising:

providing a Ni/Cu-multilayer film comprising a Ni-based layer and a Cu-based layer;
depositing a layer of Au on the Ni-based layer to form an Au-based layer, and
depositing a layer of Pt on the Au-based layer to form a Pt-based layer.

14. Method of manufacturing a multilayer stack according to claim 13, wherein the Pt-based layer is deposited via electrodeposition from a solution comprising dihydrogen bis(nitrito-N)[sulphato(2-)-O,O']platinate(2-) ($H_2Pt(NO_2)_2SO_4$).

15. Use of the multilayer stack according to any one of claims 1 to 12 as an electrode or an electrical conductor in electrical connectors and/or electric circuits.

16. Method of improving the corrosion resistance of Ni-plated Cu, the method comprising the steps of:

depositing a layer of Au on the surface of the Ni-plated Cu to form an Au-based layer, and
depositing a layer of Pt on the Au-based layer to form a Pt-based layer.

17. Biosensor or medical device, comprising the multilayer stack according to any one of claims 1 to 12.

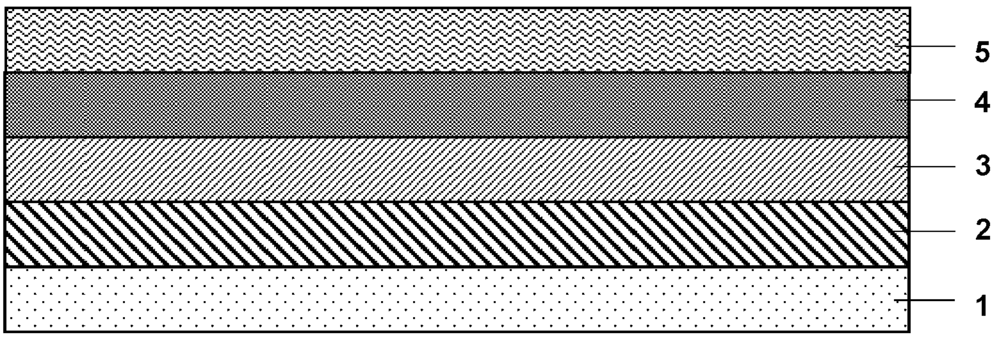

Fig. 1

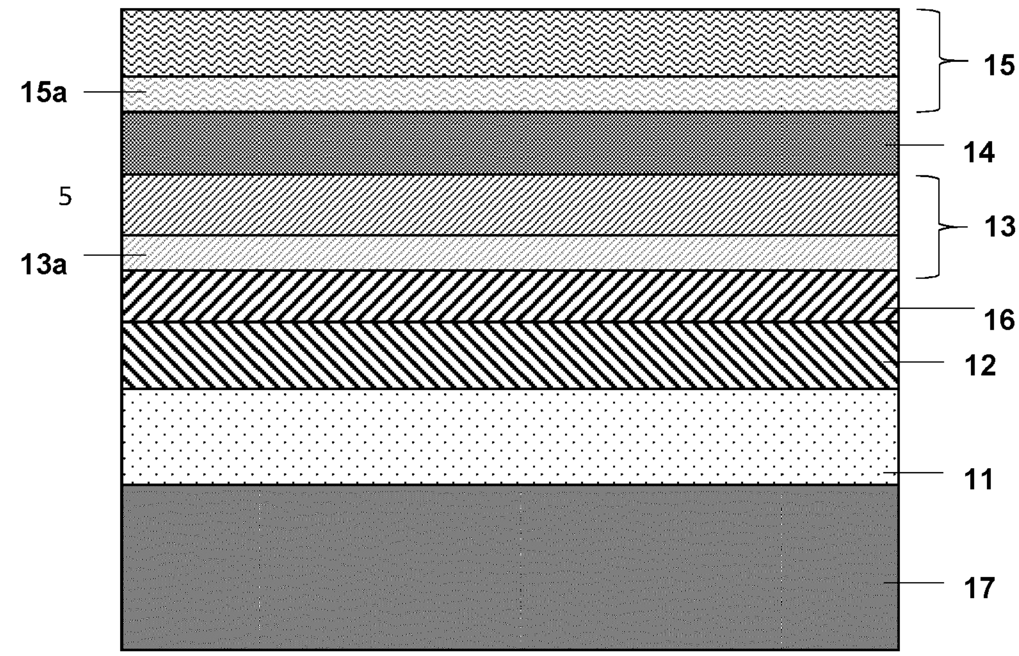
15
15a
14
13
13a
16
12
11
17

Fig. 2A

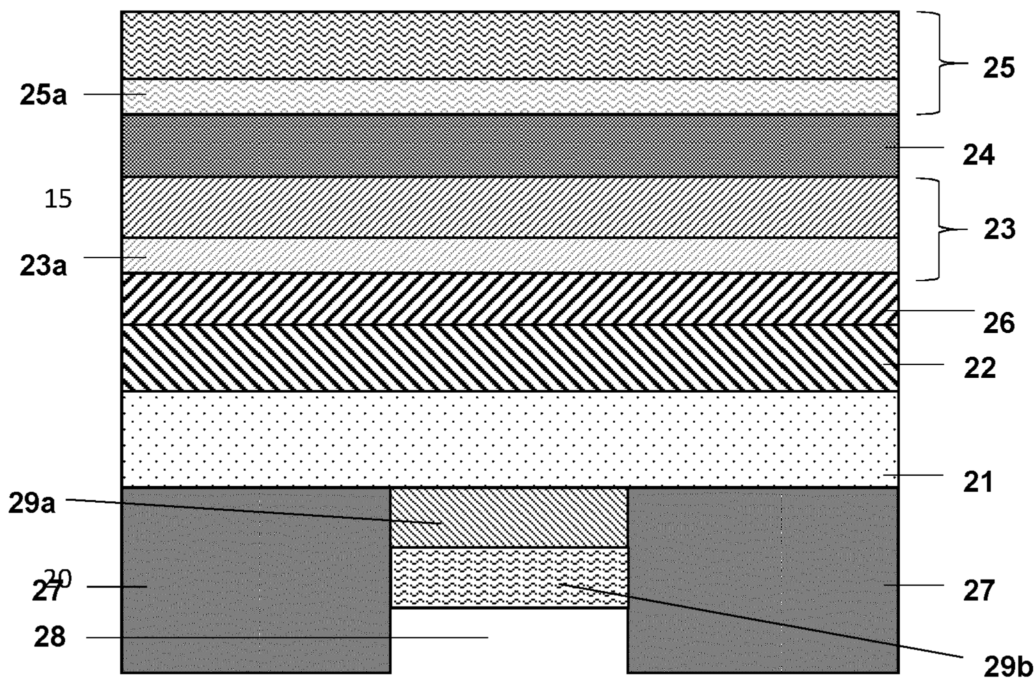
25
25a
24
23
23a
26
22
21
29a
27
27
28
29b

Fig. 2B

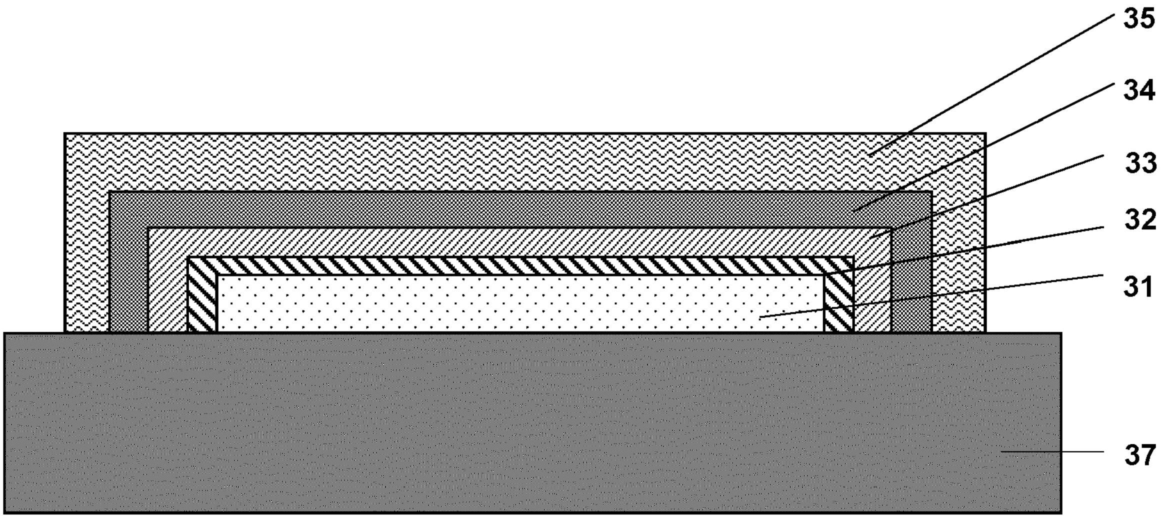

Fig. 3

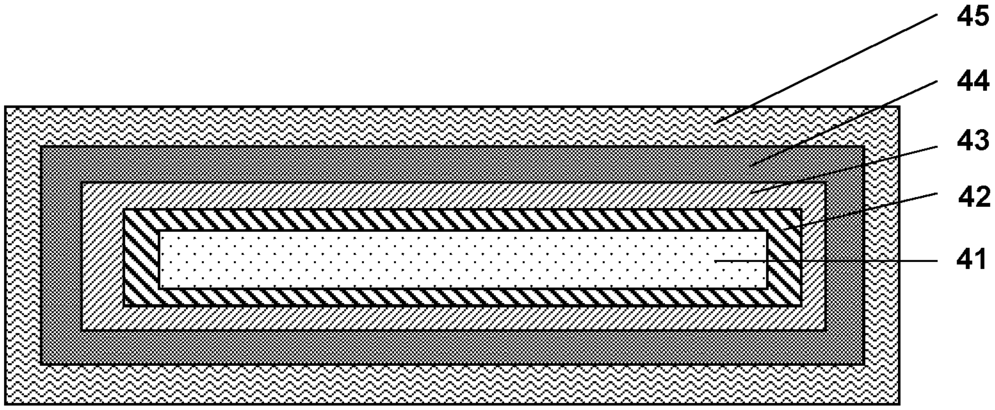

Fig. 4A

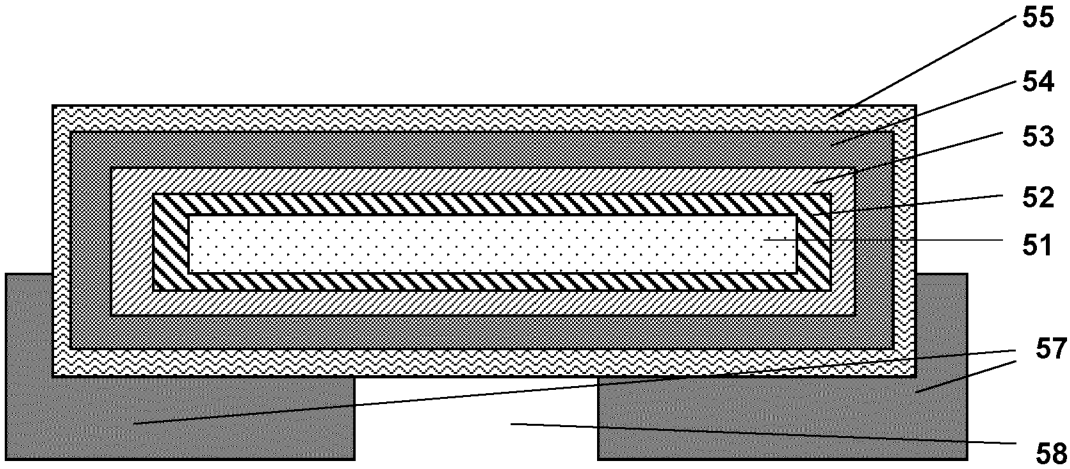

Fig. 4B

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EUROPEAN SEARCH REPORT

Application Number
EP 23 30 7309

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	CN 217 387 609 U (SHENZHEN MINGXINHUA TITANIUM TECH CO LTD) 6 September 2022 (2022-09-06) * paragraph [0006] * * paragraph [0048] - paragraph [0049] * * paragraph [0066] * * paragraph [0070] *	1-9, 11-13, 15,16 14	INV. C25D3/50 C25D5/12 C25D7/00
Y	JP 2022 107487 A (EEJA CO LTD) 21 July 2022 (2022-07-21) * paragraph [0019]; example 1 * * paragraph [0059] * * paragraph [0063] *	14	
X Y	CN 116 165 259 A (GUANGZHOU YUXIN SENSING TECHNOLOGY CO) 26 May 2023 (2023-05-26) * claims 1-3, 10 *	17 10	
Y	THOMAS C A ET AL: "A miniature microelectrode array to monitor the bioelectric activity of cultured cells", EXPERIMENTAL CELL RESEARCH, ELSEVIER, AMSTERDAM, NL, vol. 74, no. 1, 1 September 1972 (1972-09-01), pages 61-66, XP024852088, ISSN: 0014-4827, DOI: 10.1016/0014-4827(72)90481-8 [retrieved on 1972-09-01] * Summary Material and methods; figure 1 *	10	TECHNICAL FIELDS SEARCHED (IPC) C25D G01N C12Q

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	6 August 2024	Telias, Gabriela

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Application Number
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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

- [ ] Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

- [ ] No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- [X] All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

- [ ] As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

- [ ] Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

- [ ] None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

- [ ] The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 23 30 7309

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 13-16(completely); 1-9, 11, 12(partially)

   Electrical conductor for electrical connectors and/or electric circuits

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2. claims: 10, 17(completely); 1-9, 11, 12(partially)

   Biosensor or medical device

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 23 30 7309

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-08-2024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 217387609 U	06-09-2022	NONE	
JP 2022107487 A	21-07-2022	NONE	
CN 116165259 A	26-05-2023	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 113394417 B **[0005]**
- CN 105154931 A **[0006]**
- EP 3892759 A1 **[0044]**

Non-patent literature cited in the description

- **A. LELEVIC et al.** *Surface and Coatings Technology*, 2019, vol. 369, 198-220 **[0052]**