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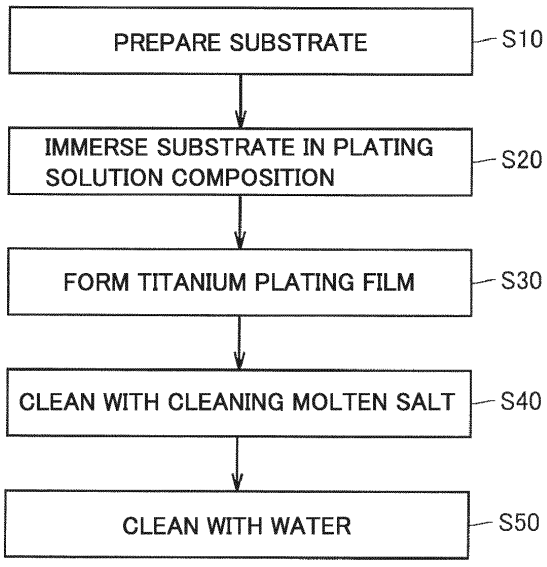
(54) METHOD FOR PRODUCING TITANIUM-PLATED MEMBER

(57) A method for manufacturing a titanium-plated member includes: preparing a substrate having an electrically conductive surface; immersing the substrate in a molten-salt titanium plating solution composition containing ions of at least one Group I metal selected from the group of Li^+ and Na^+, F^-, and Ti^{n+}; forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium; cleaning the titanium plating film by bringing the titanium plating film into contact with a cleaning molten salt, to remove a first adhering matter caused to adhere to a surface of the titanium plating film during the forming of the titanium plating film, the cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride; and cleaning the titanium plating film with water to remove a second adhering matter caused to adhere to the surface of the titanium plating film during the cleaning with the cleaning molten salt.

FIG.2



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a method for manufacturing a titanium-plated member. The present disclosure claims priority to Japanese Patent Application No. 2017-100758 filed on May 22, 2017, the disclosure of which is hereby incorporated by reference in its entirety.

BACKGROUND ART

[0002] As a titanium plating method, a method of plating in molten salt has been studied. For example, Japanese Patent Laying-Open No. 2015-193899 (PTL 1) discloses that a plating bath containing KF-KCl to which K_2TiF_6 and TiO_2 are added is used to form an alloy film of Fe and Ti on the surface of an Fe wire. NPL 1 discloses that a plating bath containing LiF-NaF-KF to which K_2TiF_6 is added is used to form a titanium film on the surface of a substrate of Ni and Fe.

CITATION LIST

PATENT LITERATURE

[0003] PTL 1: Japanese Patent Laying-Open No. 2015-193899

NON PATENT LITERATURE

[0004] NPL 1: A. ROBIN et.al., "ELECTOLYTIC COATING OF TITANIUM ONTO IRON AND NICKEL ELECTRODES IN THE MOLTEN LiF+NaF+KF EUTECTIC", Journal of Electroanal. Chem., 230 (1987), pp. 125-141

SUMMARY OF INVENTION

[0005] According to an aspect of the present disclosure, a method for manufacturing a titanium-plated member includes: preparing a substrate having an electrically conductive surface; immersing the substrate in a molten-salt titanium plating solution composition containing ions of at least one Group I metal selected from the group of lithium and sodium, fluoride ions, and titanium ions; forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium; cleaning the titanium plating film by bringing the titanium plating film into contact with a cleaning molten salt, to remove a first adhering matter caused to adhere to a surface of the titanium plating film during the forming of the titanium plating film, the cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride; and cleaning the titanium plating film with water to remove a second adhering matter caused to adhere to the surface of the titanium plating film during the cleaning with the cleaning molten salt.

BRIEF DESCRIPTION OF DRAWINGS

[0006]

Fig. 1 is a schematic cross-sectional view showing an example of a part of a titanium-plated member.
Fig. 2 is a flowchart showing a procedure for manufacturing a titanium-plated member.
Fig. 3 is a schematic cross-sectional view showing an example of a state in which a substrate is immersed in a molten-salt titanium plating solution composition.
Fig. 4 is a graph showing the corrosion current density of each electrode in a physiological saline solution.
Fig. 5 is a graph showing a correlation between the potential and the current density of each electrode in a simulated seawater.
Fig. 6 is a graph showing a correlation between the potential and the current density of each electrode in a simulated electrolyte for a polymer electrolyte fuel cell (PEFC).
Fig. 7 is another graph showing a correlation between the potential and the current density of each electrode in a simulated electrolyte for a polymer electrolyte fuel cell (PEFC).

DETAILED DESCRIPTION

[Problem to be Solved by the Present Disclosure]

[0007] In order to obtain a titanium plating film having a smooth surface in titanium plating, it is important that fluoride ions be present in a plating bath. Fluoride ions, however, may bond with metal ions present in the plating bath to form a poorly water-soluble metal fluoride. The poorly water-soluble metal fluoride remaining on the surface of the titanium plating film of the plated member is difficult to remove sufficiently by cleaning with water. There has thus been a demand for a method for manufacturing a titanium-plated member that enables reduction of the amount of a poorly water-soluble fluoride remaining on the surface of a plated member.

[0008] It is one of objects to provide a method for manufacturing a titanium-plated member that enables reduction of the amount of a poorly water-soluble fluoride remaining on the surface of a titanium plating film.

[Advantageous Effect of the Present Disclosure]

[0009] According to the method for manufacturing a titanium-plated member, the amount of a poorly water-soluble fluoride remaining on the surface of a titanium plating film can be reduced.

[Description of Embodiments of the Present Disclosure]

[0010] Initially, embodiments of the present disclosure are described one by one.

[1] According to an aspect of the present disclosure, a method for manufacturing a titanium-plated member includes: preparing a substrate having an electrically conductive surface; immersing the substrate in a molten-salt titanium plating solution composition containing ions of at least one Group I metal selected from the group of lithium and sodium, fluoride ions, and titanium ions; forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium; cleaning the titanium plating film by bringing the titanium plating film into contact with a cleaning molten salt, to remove a first adhering matter caused to adhere to a surface of the titanium plating film during the forming of the titanium plating film, the cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride; and cleaning the titanium plating film with water to remove a second adhering matter caused to adhere to the surface of the titanium plating film during the cleaning with the cleaning molten salt.

Because of a strong bonding strength of titanium with oxygen, titanium is likely to react with water to form oxide and hydroxide, and is therefore not suitable for plating from an aqueous solution. In order to form a titanium plating film on a substrate, a plating bath of a molten-salt titanium plating solution composition made up of a molten salt containing titanium ions is therefore used.

It is known that, in order to obtain a titanium plating film having a smooth surface from a molten-salt titanium plating solution composition, the presence of fluoride ions in the molten-salt titanium plating solution composition is important. Therefore, as a molten-salt titanium plating solution composition, a composition containing a predetermined amount of a metal fluoride serving as a source of fluoride ions is selected. Potassium fluoride is used as a metal fluoride serving as a source of fluoride ions.

Further, as typical metal fluorides serving as a source of fluoride ions, there are alkaline metal fluorides such as lithium fluoride (LiF) and sodium fluoride (NaF). Lithium fluoride (LiF)/sodium fluoride (NaF) is ionized, in a molten salt, into lithium ions (Li^+)/sodium ions (Na^+) and fluoride ions (F^-). While Li^+, Na^+, and F^- act effectively in a molten salt for plating, there is a problem that LiF and NaF formed again after plating are poorly water-soluble and therefore difficult to remove sufficiently by cleaning with water. In particular, if a substrate to be plated is a structure having a complicated shape such as porous shape, it is difficult to remove a poorly water-soluble metal fluoride sufficiently by only cleaning with water. Thus, reduction of the amount of poorly water-soluble fluoride remaining on the surface of a titanium plating film is required.

The method for manufacturing a titanium-plated member in the present disclosure includes, after forming a titanium plating film, the step of cleaning the titanium plating film by bringing the titanium plating film into contact with a cleaning molten salt which contains at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride, to remove a first adhering matter caused to adhere to a surface of the titanium plating film during the step of forming the titanium plating film. The first adhering matter includes any one or both of poorly water-soluble LiF and NaF. Because the aforementioned compounds contained in the cleaning molten salt have a higher compatibility with LiF and NaF, as compared with water. Therefore, through the step of cleaning with the cleaning molten salt to remove the first adhering matter, the amount of LiF and NaF

remaining on the surface of the titanium plating film can be reduced.

The method for manufacturing a titanium-plated member in the present disclosure further includes the step of cleaning the titanium plating film with water to remove a second adhering matter caused to adhere to the surface of the titanium plating film during the step of cleaning with the cleaning molten salt. The alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride contained in the cleaning molten salt have a higher solubility in water as compared with LiF and NaF. Therefore, after the step of cleaning with the cleaning molten salt, the surface of the titanium plating film can be cleaned with water to remove the second adhering matter and thereby reduce the amount of residues on the surface of the titanium plating film.

[2] In the step of removing the first adhering matter, the titanium plating film may be brought into contact with the cleaning molten salt by immersing, in the cleaning molten salt, the substrate on which the titanium plating film is formed. As a method for bringing the titanium plating film into contact with the cleaning molten salt, the method for immersing, in the cleaning molten salt, the substrate on which the titanium plating film is formed can be employed to bring the entire surface of the titanium plating film sufficiently into contact with the cleaning molten salt. As a result, the amount of poorly water-soluble substances such as LiF and NaF remaining on the surface of the titanium plating film can be reduced more appropriately.

[3] The molten-salt titanium plating solution composition may further contain chloride ions. The molten-salt titanium plating solution composition containing fluoride ions as well as chloride ions can be reduced in melting point by depression of melting point. As a result, titanium plating can be done at a lower temperature.

[4] The molten-salt titanium plating solution composition may contain more than or equal to 30 mol% and less than or equal to 50 mol% of the fluoride ions, with respect to 100 mol% of a total of the chloride ions and the fluoride ions. The content falling in this range enables further reduction of the melting point of the molten-salt titanium plating solution composition. As a result, titanium plating can be done at a still lower temperature.

[5] The molten-salt titanium plating solution composition may contain more than or equal to 0.1 mol% and less than or equal to 12 mol% of the titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition. Accordingly, a titanium-plated member having a titanium plating film as a protective film that is high in hardness and surface smoothness and excellent in corrosion resistance and wear resistance can be manufactured with a high yield.

[6] The titanium-plated member is preferably an insoluble electrode. Accordingly, an insoluble electrode having a titanium plating film with a reduced amount of residues on the surface of the film can be provided.

[7] The titanium-plated member is preferably a current collector. Accordingly, a current collector having a titanium plating film with a reduced amount of residues on the surface of the film can be provided.

[8] The titanium-plated member is preferably a biomaterial. Accordingly, a biomaterial having a titanium plating film with a reduced amount of residues on the surface of the film can be provided. Such a biomaterial can also have an excellent corrosion resistance.

[Details of Embodiments of the Present Disclosure]

[0011] Next, with reference to the drawings, an embodiment of the method for manufacturing a titanium-plated member in the present disclosure is described in detail. The expression "A to B" herein specifies an upper limit and a lower limit of a range (i.e., more than or equal to A and less than or equal to B). In the case where A is not accompanied by a unit but only B is accompanied by a unit, the unit for B is identical to the unit for A.

[Method for Manufacturing Titanium-Plated Member]

[0012] Referring to Figs. 1 to 3, a method for manufacturing a titanium-plated member in the present embodiment is described. Fig. 1 is a schematic cross-sectional view showing an example of a part of a titanium-plated member. Fig. 2 is a flowchart showing a procedure for manufacturing a titanium-plated member. Fig. 3 is a schematic cross-sectional view showing an example of a state in which a substrate is immersed in a molten-salt titanium plating solution composition.

[0013] Referring to Fig. 1, a titanium-plated member 1 is made up of a substrate 10 and a titanium plating film 20 (hereinafter also referred to simply as "plating film 20") formed on a surface of substrate 10. Plating film 20 is a film made of titanium. Titanium-plated member 1 is manufactured through steps S10 to S50 shown in Fig. 2.

[0014] The method for manufacturing titanium-plated member 1 according to the present embodiment includes: the step of preparing substrate 10 having an electrically conductive surface (S10); the step of immersing substrate 10 in a molten-salt titanium plating solution composition (hereinafter also referred to as "plating solution composition") 50 containing ions of at least one Group I metal selected from the group of lithium and sodium, fluoride ions, and titanium ions (S20); the step of forming titanium plating film 20 on the surface of substrate 10 by applying electric current to cause substrate 10 immersed in molten-salt titanium plating solution composition 50 to serve as a cathode and cause the surface of substrate 10 to be coated with titanium (S30); the step of cleaning a surface of titanium plating film 20 with a

cleaning molten salt (S40); and cleaning the surface of titanium plating film 20 with water (S50).

[0015] The step of cleaning the surface of titanium plating film 20 with the cleaning molten salt (S40) is the step of cleaning titanium plating film 20 by bringing titanium plating film 20 into contact with a cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride, to remove a first adhering matter caused to adhere to a surface of titanium plating film 20 during the step of forming titanium plating film 20. The step of cleaning titanium plating film 20 with water (S50) is the step of cleaning titanium plating film 20 with water to remove a second adhering matter caused to adhere to the surface of titanium plating film 20 during the step of cleaning with the cleaning molten salt. The method for manufacturing titanium-plated member 1 of the present embodiment may include any step besides S10, S20, S30, S40, and S50. In the following, these steps are described.

[0016] First, substrate 10 having an electrically conductive surface is prepared (S10). The material forming substrate 10 is not particularly limited as long as the material has an electrically conductive surface. Examples of substrate 10 include, for example, a substrate made of iron or nickel, a substrate made of an alloy of them, or a multilayer substrate having a surface made of a layer of iron or nickel or an alloy thereof.

[0017] The shape of substrate 10 is not particularly limited. For example, substrate 10 in the shape of any of various shapes such as plate, column, pipe, mesh, or the like may be employed as substrate 10.

[0018] Next, substrate 10 is immersed in plating solution composition 50 (S20). Referring to Fig. 3, plating solution composition 50 contains ions of at least one Group I metal selected from the group of lithium (Li^+) and sodium (Na^+), fluoride ions (F^-), and titanium ions (Ti^{n+} (n is an integer of 2 or more and 4 or less, the same applies as well to the following)). In this case, plating solution composition 50 may contain ions of multiple types of titanium that are different in valence. Preferably, plating solution composition 50 further contains chloride ions (Cl^-).

[0019] Plating solution composition 50 can be prepared as a molten salt by dissolving a titanium compound serving as a source of Ti^{n+} in a mixture of at least one of lithium fluoride (LiF) and sodium fluoride (NaF) and at least one of lithium chloride (LiCl) and sodium chloride (NaCl), for example.

[0020] Examples of the titanium compound serving as a source of Ti^{n+} may include hexafluorotitanic acid (H_2TiF_6), potassium hexafluorotitanate (K_2TiF_6), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$), sodium hexafluorotitanate (Na_2TiF_6), potassium titanium oxalate dihydrate ($K_2TiO(C_2O_4)_2{\cdot}2H_2O$), titanium chloride (III)($TiCl_3$), titanium chloride (IV)($TiCl_4$), and the like.

[0021] Plating solution composition 50 may contain cations other than Li^+ and Na^+. For example, plating solution composition 50 may contain potassium ions (K^+). If, however, plating solution composition 50 contains a large amount of K^+, metal fog of potassium may be generated during plating. Therefore, the content of potassium ions with respect to 100 mol% of all ion components in the plating solution composition is preferably less than or equal to 5 mol%. Potassium hexafluorotitanate (K_2TiF_6) and potassium titanium oxalate dihydrate ($K_2TiO(C_2O_4)_2{\cdot}2H_2O$) contain potassium ions. When these titanium compounds are used as a source of Ti^{n+}, it is preferable to use these titanium compounds at respective contents so that the K^+ content with respect to 100 mol% of all ion components contained in plating solution composition 50 is less than or equal to 5 mol%, or to use these titanium compounds together with another titanium compound (such as titanium chloride (IV) or the like, for example) that generates no K^+.

[0022] In the plating solution composition that is a molten salt, LiF, NaF, LiCl, and NaCl are ionized to be present in the form of Li^+, Na^+, F^-, and Cl^-. The titanium compound is also ionized to be present in the form of Ti^{n+}. It is preferable to prepare, as a molten salt, a plating solution composition containing: ions of at least one Group I metal selected from the group of Li^+ and Na^+; F^-; Cl^-; and Ti^{n+} in this way.

[0023] The fact that Li^+, Na^+, F^-, Cl^-, and Ti^{n+} are present in plating solution composition 50 of the present embodiment can be confirmed, for example, by dissolving plating solution composition 50 in a solution of a mixture of nitric acid and hydrofluoric acid, and analyzing the solution by ICP (Inductively Coupled Plasma Spectrometry). As an ICP apparatus, iCAP6200 or the like manufactured by Thermo Fisher Scientific Inc. may be used, for example.

[0024] Preferably, plating solution composition 50 contains more than or equal to 30 mol% and less than or equal to 50 mol% of F^-, with respect to 100 mol% of a total of Cl^- and F^-. When the ratio of Cl^- relative to F^- is increased, the melting point of the molten salt is once reduced by depression of melting point, and thereafter increased again. The melting point depression effect is large when the ratio of the F^- content relative to 100 mol% of the total content of Cl^- and F^- falls in a predetermined range. Specifically, reduction of the melting point is large when the content of F^- with respect to 100 mol% of the total of Cl^- and F^- is more than or equal to 30 mol% and less than or equal to 50 mol%, which facilitates plating at a lower temperature. More preferably, the content of F^- with respect to 100 mol% of the total of Cl^- and F^- is more than or equal to 30 mol% and less than or equal to 45 mol%, because reduction of the melting point is larger.

[0025] The fraction of anions F^- in plating solution composition 50 in the present embodiment (the ratio of F^- to the total amount of anions (molar ratio)) is preferably more than or equal to 0.1 and less than or equal to 0.9, and more preferably more than or equal to 0.25 and less than or equal to 0.75. If the fraction of anions F^- is more than or equal to 0.1, particularly more than or equal to 0.25, titanium-plated member 1 having plating film 20 with high surface smoothness can more reliably be obtained. In contrast, if the fraction of anions F^- is less than or equal to 0.9, particularly less than

or equal to 0.75, removal of substances remaining after formation of plating film 20 tends to be facilitated. It is therefore preferable that the fraction of anions F^- falls in the above-specified range.

[0026] The content of Ti^{n+} in the plating solution composition is not particularly limited, but set appropriately depending on plating conditions. However, an excessively high content of Ti^{n+} may cause unnecessary precipitates to be formed, which deteriorates reduction of current efficiency. In contrast, an excessively low content of Ti^{n+} does not allow a titanium plating film to be formed sufficiently. The content of Ti^{n+} is therefore preferably less than or equal to 20 mol% and more preferably less than or equal to 12 mol%, with respect to 100 mol% of all cations in the plating solution composition. The content of Ti^{n+} is preferably more than or equal to 0.1 mol%, and more preferably more than or equal to 0.5 mol%, with respect to 100 mol% of all cations in the plating solution composition. In other words, the content of titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition is preferably more than or equal to 0.1 mol% and less than or equal to 12 mol%.

[0027] Next, electric current is applied to cause substrate 10 immersed in plating solution composition 50 to serve as a cathode, and cause the surface of substrate 10 to be coated with titanium, to thereby form titanium plating film 20 on this surface (S30). The step of forming plating film 20 is performed in the following way. With substrate 10 immersed in plating solution composition 50, electric current is applied by applying a voltage between an anode 30 and substrate 10 serving as a cathode that are immersed in plating solution composition 50 to cause electrolysis of plating solution composition 50. Accordingly, on the surface of substrate 10 serving as a cathode, titanium ions are reduced to titanium and the surface of substrate 10 is coated with titanium. Thus, plating film 20 is formed on the surface of substrate 10.

[0028] Electrolysis of plating solution composition 50 is preferably performed so that the absolute value of the current density, on substrate 10, of current flowing between anode 30 and substrate 10 is more than or equal to 1 mA/cm^2 and less than or equal to 500 mA/cm^2, and more preferably performed so that the absolute value of the current density is more than or equal to 1 mA/cm^2 and less than or equal to 300 mA/cm^2. When electrolysis of plating solution composition 50 is performed so that the absolute value of the current density of current flowing between anode 30 and substrate 10 is more than or equal to 1 mA/cm^2, plating film 20 can be formed on the surface of substrate 10 in a shorter time. In contrast, when electrolysis of plating solution composition 50 is performed so that the absolute value of the current density of current flowing between anode 30 and substrate 10 is less than or equal to 500 mA/cm^2, particularly less than or equal to 300 mA/cm^2, plating film 20 having higher surface smoothness can be formed.

[0029] Next, the surface of plating film 20 is cleaned with a cleaning molten salt (S40). Specifically, titanium plating film 20 is cleaned by being brought into contact with a cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride. Accordingly, a first adhering matter caused to adhere to the surface of titanium plating film 20 during the step of forming titanium plating film 20 is cleaned away by means of the cleaning molten salt.

[0030] The first adhering matter includes any one or both of poorly water-soluble LiF and NaF. The aforementioned compounds contained in the cleaning molten salt have a higher compatibility with LiF and NaF, as compared with water. Therefore, through the step of cleaning with the cleaning molten salt, the amount of LiF and NaF remaining on the surface of plating film 20 can be reduced.

[0031] Examples of the alkaline metal chloride include lithium chloride (LiCl), sodium chloride (NaCl), and potassium chloride (KCl), for example. Examples of the alkaline earth metal chloride include magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$), for example. The molten salt may contain a single one of the alkaline metal chloride, the alkaline earth metal chloride, and the potassium fluoride, or contain two or more of them. The molten salt may contain a salt other than the alkaline metal chloride, the alkaline earth metal chloride, and the potassium fluoride.

[0032] Alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride (KF) have a higher compatibility with LiF and NaF, as compared with water. Therefore, plating film 20 can be brought into contact with the cleaning molten salt to thereby reduce the amount of LiF and NaF on the surface of plating film 20.

[0033] The method for bringing plating film 20 into contact with the cleaning molten salt is not particularly limited. For example, this method may be a method of immersing, in the cleaning molten salt, substrate 10 on which plating film 20 is formed, a method of feeding or spraying the molten salt on the surface of plating film 20 to clean the surface of plating film 20, or the like. The method for bringing plating film 20 into contact with a cleaning molten salt is preferably performed by immersing, in the cleaning molten salt, substrate 10 on which plating film 20 is formed. As the method for bringing it into contact with the molten salt, the method of immersing, in the cleaning molten salt, substrate 10 on which plating film 20 is formed may be performed, to thereby enable the cleaning molten salt to be in contact sufficiently with the entire surface of plating film 20. As a result, the poorly water-soluble substances such as LiF and NaF on the surface of plating film 20 can be cleaned more effectively.

[0034] Finally, the surface of plating film 20 is cleaned with water (S50). In this step, titanium plating film 20 is cleaned with water to remove a second adhering matter caused to adhere to the surface of plating film 20 during the step of cleaning with the cleaning molten salt (S40).

[0035] Through the step of cleaning the surface of plating film 20 with the cleaning molten salt (S40), the amount of poorly water-soluble LiF and NaF remaining on the surface of plating film 20 is reduced. After the step of cleaning with

the cleaning molten salt, the second adhering matter adhering to the surface of plating film 20 is mainly made up of components contained in the cleaning molten salt, i.e., made up of alkaline metal chloride, alkaline earth metal chloride, and KF. The alkaline metal chloride, the alkaline earth metal chloride, and KF have not only compatibility with LiF and NaF but also high water solubility. Therefore, the second adhering matter can be removed more easily than LiF and NaF by means of cleaning with water. Through the double cleaning step (S40 and S50), the substances remaining on the surface of plating film 20 can be reduced. As a result, high-quality titanium-plated member 1 having a reduced amount of remaining impurities can be manufactured.

[0036] For cleaning with water, other cleaning agents such as water-soluble solvent like alcohol and surfactant may be used together with water. In this way, titanium-plated member 1 having plating film 20 formed on the surface of substrate 10 is manufactured.

[Titanium-Plated Member]

[0037] Titanium-plated member 1 manufactured in this way is a member having a protective film with a high hardness and a high surface smoothness as well as excellent corrosion resistance and excellent wear resistance. Further, titanium-plated member 1 has a small amount of impurities remaining on plating film 20. This titanium-plated member can therefore be used in a variety of fields.

[0038] The ratio of average surface roughness Ra to average thickness R of plating film 20 ((Ra/R) $\times$ 100 (%)) of titanium-plated member 1 manufactured by the above-described method is preferably less than or equal to 10%, and more preferably less than or equal to 5%. With the ratio falling in this range, titanium-plated member 1 having plating film 20 with a sufficiently high surface smoothness can be provided.

[0039] Average surface roughness Ra of plating film 20 can be measured through observation of a cross section with an SEM (Scanning Electron Microscope) or by means of a surface roughness meter. Further, average thickness R of plating film 20 can be determined through observation of a cross section with an SEM. Average surface roughness Ra of plating film 20 refers to an arithmetic mean roughness Ra specified under JIS B 0601 (2001). Average thickness R of plating film 20 refers to an arithmetic mean thickness of plating film 20 determined from thicknesses at any 10 points on an SEM image, for example.

[0040] As seen from the above, the method for manufacturing titanium-plated member 1 according to the present embodiment can reduce the amount of poorly water-soluble fluoride remaining on the surface of the titanium plating film.

[0041] Regarding the above-described embodiment, molten-salt titanium plating solution composition 50 containing chloride ions (Cl^-) is described. Instead, molten-salt titanium plating solution composition 50 without containing Cl^- may be prepared. Molten-salt titanium plating solution composition 50 without Cl^- may be prepared to contain other anions instead of Cl^-. In this case, as the aforementioned other anions, preferably anions that are stable at the plating temperature and form no residue such as salt which is difficult to remove after plating are selected.

[0042] Preferably, the titanium-plated member is an insoluble electrode. Accordingly, an insoluble electrode having a titanium plating film with a reduced amount of residues on the surface of the film can be provided.

[0043] Such an insoluble electrode is preferably used for manufacturing hydrogen. An insoluble electrode for manufacturing hydrogen can be provided as a hydrogen-manufacturing insoluble electrode with a low resistance. Accordingly, hydrogen with a higher purity can be manufactured.

[0044] Preferably, the titanium-plated member is a current collector. Accordingly, a current collector having a titanium plating film with a reduced amount of residues on the surface of the film can be provided.

[0045] Such a current collector is preferably used for a fuel cell. A current collector for a fuel cell can be provided as a fuel-cell current collector having a good electrical conductivity. Particularly when the current collector is used for a fuel cell, the current collector is more preferably used for a polymer electrolyte fuel cell.

[0046] Preferably, the titanium-plated member is a biomaterial. Accordingly, a biomaterial having a titanium plating film with a reduced amount of residues on the surface of the film can be provided. Such a biomaterial can also be excellent in corrosion resistance.

[0047] The use of the biomaterial is preferably selected from the group consisting of spinal fixation device, fracture fixation device, artificial joint, artificial heart valve, intravascular stent, denture base, artificial dental root, and orthodontic wire.

EXAMPLES

[0048] The above-described embodiments are hereinafter described more specifically with reference to Examples. The present disclosure is not limited to these Examples.

«Example 1»

[Preparation of molten-salt titanium plating solution composition and manufacture of titanium-plated member]

[0049] In order to manufacture titanium-plated members to serve as specimens, molten-salt titanium plating solution compositions of Sample Nos. 1 to 4 were prepared first by dissolving, in 100 mol of a main agent for each molten-salt titanium plating solution composition shown in Table 1 below, 2 mol of K_2TiF_6 powder or 13 mol of $TiCl_4$ as a titanium source.

[0050] As shown in Table 1, in each of the molten-salt titanium plating solution compositions of Sample Nos. 1 to 4, the content of potassium ions with respect to 100 mol% of all ion components contained in the composition is less than or equal to 5 mol%. Further, in the molten-salt titanium plating solution composition of Sample No. 1, the content of fluoride ions with respect to 100 mol% of the total of chloride ions and fluoride ions is more than 50 mol% (51 mol%). In the molten-salt titanium plating solution composition of Sample No. 2, chloride ions are not contained. In each of the molten-salt titanium plating solution compositions of Sample Nos. 3 and 4, the content of fluoride ions with respect to 100 mol% of the total of chloride ions and fluoride ions is more than or equal to 30 mol% and less than or equal to 50 mol%. In each of the molten-salt titanium plating solution compositions of Sample Nos. 1 to 4, the content of titanium ions with respect to 100 mol% of all cations contained in the composition is more than or equal to 0.1 mol% and less than or equal to 12 mol% (1.9 mol% or 11.5 mol%).

[Table 1]

Sample No.		1	2	3	4
main agent		LiF-LiCl	LiF-NaF	LiF-LiCl	LiF-NaCl
makeup of plating solution composition (molar ratio)	LiF	45	30	50	40
	LiCl	55	0	50	0
	NaF	0	70	0	0
	KF	0	0	0	0
	KCl	0	0	0	0
	K_2TiF_6	2	2	0	2
	$TiCl_4$	0	0	13	0
	NaCl	0	0	0	60
ratio of K^+ (mol%) to 100 mol% of all ion components		1.8	1.8	0	1.8
$F^-/(Cl^-+F^-)$ (mol%)		51	100	33	46
ratio of Ti^{n+} (mol%) to 100 mol% of all cations		1.9	1.9	11.5	1.9

[0051] Next, through the steps S10 to S30 of the method for manufacturing a titanium-plated member described above (see Fig. 2), each of the molten-salt titanium plating solution compositions of Sample Nos. 1 to 4 was used to plate a surface of a respective substrate (made of nickel, 0.1 mm in thickness, 5 mm × 25 mm in size) with titanium. In this way, titanium-plated member precursors of Specimens Nos. 1 to 4 were produced.

[0052] The titanium-plated member precursor produced using the molten-salt titanium plating solution composition of Sample No. 1 corresponds to the titanium-plated member precursor of Specimen No. 1. The titanium-plated member precursor produced using the molten-salt titanium plating solution composition of Sample No. 2 corresponds to the titanium-plated member precursor of Specimen No. 2. The titanium-plated member precursor produced using the molten-salt titanium plating solution composition of Sample No. 3 corresponds to the titanium-plated member precursor of Specimen No. 3. The titanium-plated member precursor produced using the molten-salt titanium plating solution composition of Sample No. 4 corresponds to the titanium-plated member precursor of Specimen No. 4.

[0053] Further, through the steps S40 to S50 of the method for manufacturing a titanium-plated member as described above (see Fig. 2), cleaning molten salts A to D and pure water shown in Table 2 were used to clean the titanium-plated member precursor of Specimen No. 1 to remove a first adhering matter and a second adhering matter on the surface thereof. Specifically, five titanium-plated member precursors of Specimen No. 1 were prepared, and immersed in respective containers holding cleaning molten salts A to D and pure water shown in Table 2 for 10 minutes (S40). After this, the titanium-plated member precursors of Specimen No. 1 were removed from respective containers and subjected

to ultrasonic cleaning with pure water for 10 minutes (S50). In this way, the titanium-plated members of Specimen No. 1 were manufactured. Cleaning molten salt D and the pure water are cleaning agents provided for the sake of comparison.

[0054] Subsequently, for the five titanium-plated members of Specimen No. 1, EDX (product name: "X-act" manufactured by Oxford Instruments plc) installed in a scanning electron microscope (product name: "VE-8800" manufactured by Keyence Corporation) was used under a condition of an accelerated voltage of 15 kV to analyze whether there were residual components of the metal fluoride and cleaning molten salts A to D. The results are shown in the row EDX in Table 2. In Table 2, "salt component" refers to the residual components of the metal fluoride and cleaning molten salts A to D.

[Table 2]

Specimen No.1	cleaning molten salt A	cleaning molten salt B	cleaning molten salt C	cleaning molten salt D	comparative cleaning agent
makeup of cleaning molten salt (molar ratio)	LiCl-KCl (59:41)	KCl-KF (45:55)	$MgCl_2$-LiCl (30:70)	LiF-NaF (71:39)	pure water
temperature	400	650	600	700	room tempera ture
EDX	no salt component was detected	no salt component was detected	no salt component was detected	salt component was detected	salt component was detected
*"no salt component was detected" means that the detected value of the total salt component was less than or equal to 1 mass% (background).					

[0055] It is seen from the results in Table 2 that no residual component of the metal fluoride and the molten salt remained on the surface of the titanium-plated member cleaned with the cleaning molten salt (cleaning molten salts A to C) containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride.

<<Example 2>>

[0056] Five titanium-plated member precursors of Specimen No. 2 produced in Example 1 were prepared. On the titanium-plated member precursors of Specimen No. 2, the steps S40 to S50 of the method for manufacturing a titanium-plated member (see Fig. 2) were performed under the same condition as Example 1 to remove a first adhering matter and a second adhering matter on the surface of the titanium-plated member precursor. In this way, the titanium-plated members of Specimen No. 2 were manufactured. Further, for the titanium-plated members of Specimen No. 2, it was analyzed whether there were residual components of the metal fluoride and cleaning molten salts A to D under the same condition as Example 1. The results are shown in the row EDX in Table 3. In Table 3, "salt component" also refers to the residual components of the metal fluoride and cleaning molten salts A to D.

[Table 3]

Specimen No.2	cleaning molten salt A	cleaning molten salt B	cleaning molten salt C	cleaning molten salt D	comparative cleaning agent
makeup of cleaning molten salt (molar ratio)	LiCl-KCl (59:41)	KCl-KF (45:55)	$MgCl_2$-LiCl (30:70)	LiF-NaF (71:39)	pure water
temperature	400	650	600	700	room temperature

(continued)

Specimen No.2	cleaning molten salt A	cleaning molten salt B	cleaning molten salt C	cleaning molten salt D	comparative cleaning agent
EDX	no salt component was detected	no salt component was detected	no salt component was detected	salt component was detected	salt component was detected
*"no salt component was detected" means that the detected value of the total salt component was less than or equal to 1 mass% (background).					

[0057] It is seen from the results in Table 3 that no residual component of the metal fluoride and the molten salt remained on the surface of the titanium-plated member cleaned with the cleaning molten salt (cleaning molten salts A to C) containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride.

«Example 3»

[0058] Five titanium-plated member precursors of Specimen No. 3 produced in Example 1 were prepared. On the titanium-plated member precursors of Specimen No. 3, the steps S40 to S50 of the method for manufacturing a titanium-plated member (see Fig. 2) were performed under the same condition as Example 1 to remove a first adhering matter and a second adhering matter on the surface of the titanium-plated member precursor. In this way, the titanium-plated members of Specimen No. 3 were manufactured. Further, for the titanium-plated members of Specimen No. 3, it was analyzed whether there were residual components of the metal fluoride and cleaning molten salts A to D under the same condition as Example 1. The results are shown in the row EDX in Table 4. In Table 4, "salt component" also refers to the residual components of the metal fluoride and cleaning molten salts A to D.

[Table 4]

Specimen No.3	cleaning molten salt A	cleaning molten salt B	cleaning molten salt C	cleaning molten salt D	comparative cleaning agent
makeup of cleaning molten salt (molar ratio)	LiCl-KCl (59:41)	KCl-KF (45:55)	$MgCl_2$-LiCl (30:70)	LiF-NaF (71:39)	pure water
temperature	400	650	600	700	room temperature
EDX	no salt component was detected	no salt component was detected	no salt component was detected	salt component was detected	salt component was detected
*"no salt component was detected" means that the detected value of the total salt component was less than or equal to 1 mass% (background).					

[0059] It is seen from the results in Table 4 that no residual component of the metal fluoride and the molten salt remained on the surface of the titanium-plated member cleaned with the cleaning molten salt (cleaning molten salts A to C) containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride.

«Example 4»

[0060] Five titanium-plated member precursors of Specimen No. 4 produced in Example 1 were prepared. On the titanium-plated member precursors of Specimen No. 4, the steps S40 to S50 of the method for manufacturing a titanium-plated member (see Fig. 2) were performed under the same condition as Example 1 to remove a first adhering matter and a second adhering matter on the surface of the titanium-plated member precursor. In this way, the titanium-plated

members of Specimen No. 4 were manufactured. Further, for the titanium-plated members of Specimen No. 4, it was analyzed whether there were residual components of the metal fluoride and cleaning molten salts A to D under the same condition as Example 1. The results are shown in the row EDX in Table 5. In Table 5, "salt component" also refers to the residual components of the metal fluoride and cleaning molten salts A to D.

[Table 5]

Specimen No.4	cleaning molten salt A	cleaning molten salt B	cleaning molten salt C	cleaning molten salt D	comparative cleaning agent
makeup of cleaning molten salt (molar ratio)	LiCl-KCl (59:41)	KCl-KF (45:55)	$MgCl_2$-LiCl (30:70)	LiF-NaF (71:39)	pure water
temperature	400	650	600	700	room t empera ture
EDX	no salt component was detected	no salt component was detected	no salt component was detected	salt component was detected	salt component was detected
*"no salt component was detected" means that the detected value of the total salt component was less than or equal to 1 mass% (background).					

[0061] It is seen from the results in Table 5 that no residual component of the metal fluoride and the molten salt remained on the surface of the titanium-plated member cleaned with the cleaning molten salt (cleaning molten salts A to C) containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride.

[0062] As seen from the foregoing, the amount of residual components (LiF and NaF, for example) of the metal fluoride and the cleaning molten salt remaining on the surface of the titanium plating film can be reduced by bringing the titanium plating film into contact with the cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride, to thereby clean the titanium plating film, and also cleaning the titanium plating film with water.

«Example 5»

[Corrosion resistance to physiological saline solution]

[0063] The corrosion resistance of the following Ti-plated product to physiological saline solution was evaluated through the following procedure.

Production of Specimens

[0064] Through the steps S10 to S50 of the method for manufacturing a titanium-plated member described above, the surface of a nickel porous substrate (3 cm × 5 cm × 1 mmt, porosity: 96%, average pore size: 300 μm, hereinafter referred to as "nickel porous material") was plated with titanium to produce a Ti-plated product.

[0065] In contrast, as specimens of a comparative example, a Ni porous material (product name: "Celmet®" manufactured by Sumitomo Electric Industries, Ltd.) and a Ti metal sheet (manufactured by Nilaco Corporation) were prepared.

Corrosion Resistance Test

[0066] Cyclic voltammetry was conducted under the following conditions. The results are shown in Fig. 4. In Fig. 4, the specimen of the Example and the specimens of the Comparative Example (Ni porous material and Ti metal sheet) are expressed as "Ti-plated product," "Ni" and "Ti" respectively.

<Conditions for Cyclic Voltammetry>

[0067] electrolyte: 0.9 mass% sodium chloride aqueous solution (physiological saline solution)

working electrode: specimen of Example or specimen of Comparative Example (Ti-plated product, Ni, or Ti)
reference electrode: Ag/AgCl electrode
counter electrode: Ni metal sheet
scan rate: 10 mV/sec
solution temperature: 25°C

[0068] It has been proved from the results in Fig. 4 that the Ti-plated product of the Example is lower in corrosion current density than the Ni porous material of the Comparative Example, and is thus stable in an environment of physiological saline solution. It is seen from this result that the Ti-plated product of the Example is suitable as a biomaterial. Further, the Ti-plated product of the Example is lower in corrosion current density than the Ti metal sheet of the Comparative Example. It is seen from this result that the structure of a metal porous material instead of a metal sheet is used to further improve the stability in an environment of physiological saline solution.

«Example 6»

[Corrosion resistance to saline solution simulating seawater]

[0069] The corrosion resistance of the following Ti-plated product to saline solution simulating seawater was evaluated through the following procedure.

Production of Specimens

[0070] As a specimen of the Example, a Ti-plated product manufactured by the same method as the Ti-plated product used for Example 5 was prepared. As a specimen of the Comparative Example, a Ti metal sheet (manufactured by Nilaco Corporation) was prepared.

Corrosion Resistance Test

[0071] Cyclic voltammetry was conducted under the same conditions as those indicated above in the section [Corrosion resistance to physiological saline solution], except that 3.3 mass% saline solution simulating seawater was used as electrolyte. The results are shown in Fig. 5. In Fig. 5, the specimen of the Example and the specimen of the Comparative Example are expressed as "Ti-plated product" and "Ti commercial product" respectively.

[0072] It has been proved from the results in Fig. 5 that the Ti-plated product of the Example is lower in current density than the Ti commercial product of the Comparative Example, and thus exhibits high corrosion resistance to seawater. It is seen from the above that the Ti-plated product of the Example is promising as an insoluble electrode (anode) for electrolysis of salt.

<<Example 7>>

[Evaluation of suitability for polymer electrolyte fuel cell]

[0073] The suitability of the following Ti-plated product for polymer electrolyte fuel cell was evaluated through the following procedure.

Production of Specimen

[0074] As a specimen of the Example, a Ti-plated product manufactured by the same method as the Ti-plated product used in Example 5 was prepared. As specimens of the Comparative Example, an Ni porous material (product name: "Celmet®" manufactured by Sumitomo Electric Industries, Ltd.) and a Ti metal sheet (manufactured by Nilaco Corporation) were prepared.

Evaluation of Suitability

[0075] Cyclic voltammetry was conducted under the same conditions as those indicated above in the section [Corrosion resistance to physiological saline solution], except that 10 mass% sodium nitrate aqueous solution (adjusted to pH = 3 by adding nitric acid) (simulated PEFC electrolyte) was used as electrolyte. The results are shown in Figs. 6 and 7. In Figs. 6 and 7, the specimen of the Example and the specimens (Ni porous material and Ti metal sheet) of the Comparative Example are expressed as "Ti-plated product," "comparative Ni" and "comparative Ti" respectively. In Fig. 6, respective plots for "Ti-plated product" and "comparative Ti" depicting a correlation between the potential and the current density

of the electrode overlap each other, and therefore, Fig. 7 shows these plots by expanding the scale of the vertical axis (current density) so that the plot depicting the correlation for "Ti-plated product" can be distinguished from the plot depicting the correlation for "comparative Ti."

[0076] It has been proved from the results in Figs. 6 and 7 that the Ti-plated product for the Example is lower in current density than the comparative Ni of the Comparative Example, and therefore promising as a current collector material to be used for a polymer electrolyte fuel cell.

[0077] It should be construed that the embodiments and examples disclosed herein are given by way of illustration in all respects, not by way of limitation. It is intended that the scope of the present invention is defined by claims, not by the description above, and encompasses all modifications and variations equivalent in meaning and scope to the claims.

REFERENCE SIGNS LIST

[0078] 1 titanium-plated member; 10 substrate; 20 plating film; 30 anode; 40 container; 50 plating solution composition

Claims

1. A method for manufacturing a titanium-plated member, the method comprising:

   preparing a substrate having an electrically conductive surface;
   immersing the substrate in a molten-salt titanium plating solution composition containing

      ions of at least one Group I metal selected from the group of lithium and sodium,
      fluoride ions, and
      titanium ions;

   forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium;
   cleaning the titanium plating film by bringing the titanium plating film into contact with a cleaning molten salt, to remove a first adhering matter caused to adhere to a surface of the titanium plating film during the forming of the titanium plating film, the cleaning molten salt containing at least one compound selected from the group consisting of alkaline metal chloride, alkaline earth metal chloride, and potassium fluoride; and
   cleaning the titanium plating film with water to remove a second adhering matter caused to adhere to the surface of the titanium plating film during the cleaning with the cleaning molten salt.

2. The method for manufacturing a titanium-plated member according to claim 1, wherein in removing the first adhering matter, the titanium plating film is brought into contact with the cleaning molten salt by immersing, in the cleaning molten salt, the substrate on which the titanium plating film is formed.

3. The method for manufacturing a titanium-plated member according to claim 1 or 2, wherein the molten-salt titanium plating solution composition further contains chloride ions.

4. The method for manufacturing a titanium-plated member according to claim 3, wherein the molten-salt titanium plating solution composition contains more than or equal to 30 mol% and less than or equal to 50 mol% of the fluoride ions, with respect to 100 mol% of a total of the chloride ions and the fluoride ions.

5. The method for manufacturing a titanium-plated member according to any one of claims 1 to 4, wherein the molten-salt titanium plating solution composition contains more than or equal to 0.1 mol% and less than or equal to 12 mol% of the titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition.

6. The method for manufacturing a titanium-plated member according to any one of claims 1 to 5, wherein the titanium-plated member is an insoluble electrode.

7. The method for manufacturing a titanium-plated member according to any one of claims 1 to 5, wherein the titanium-plated member is a current collector.

8. The method for manufacturing a titanium-plated member according to any one of claims 1 to 5, wherein the titanium-plated member is a biomaterial.

FIG.1

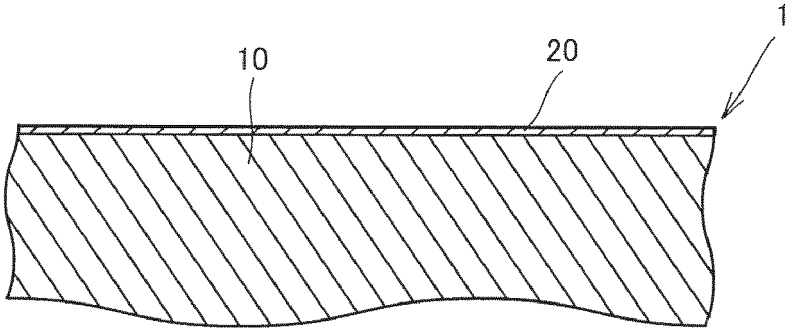

1
10
20

FIG.2

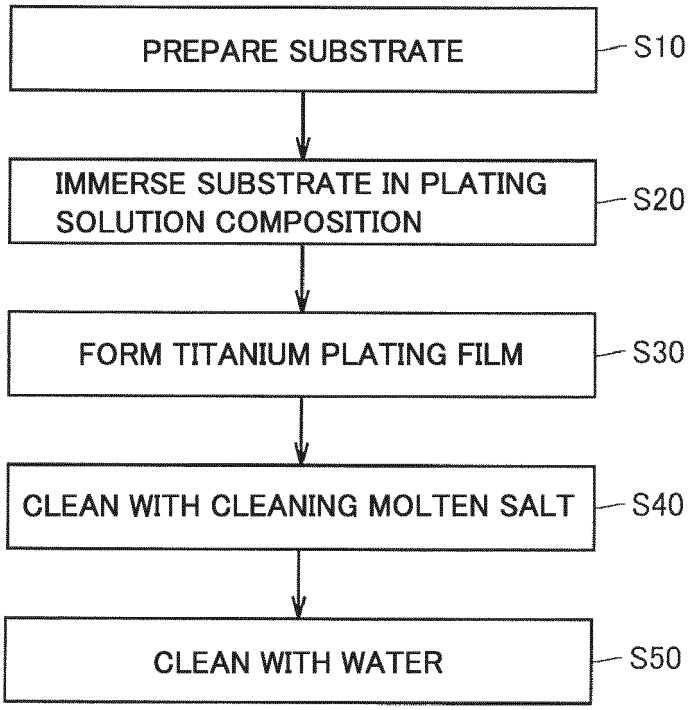

PREPARE SUBSTRATE
S10
IMMERSE SUBSTRATE IN PLATING SOLUTION COMPOSITION
S20
FORM TITANIUM PLATING FILM
S30
CLEAN WITH CLEANING MOLTEN SALT
S40
CLEAN WITH WATER
S50

FIG.3

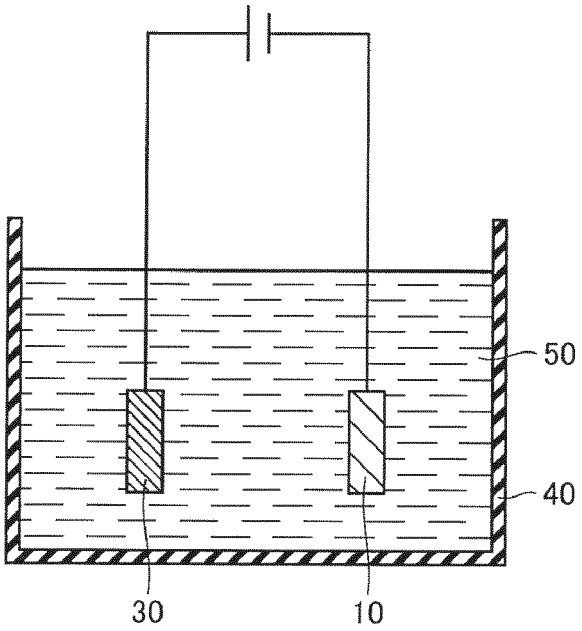


FIG.4

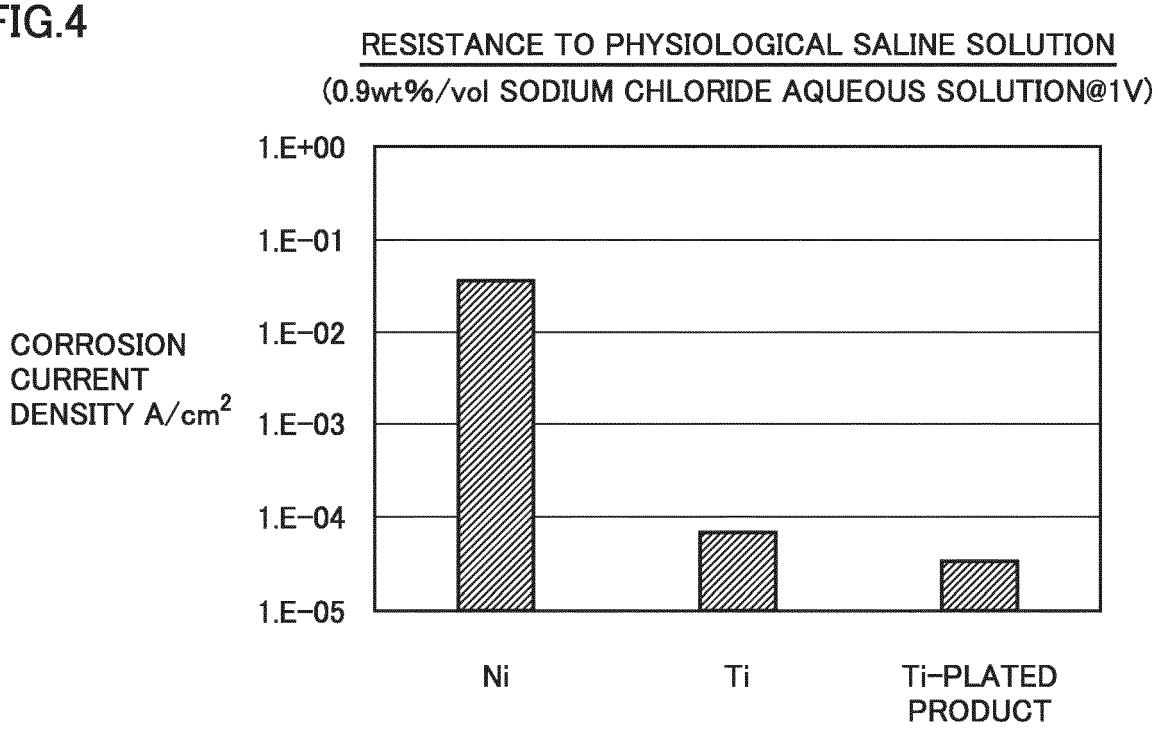

RESISTANCE TO PHYSIOLOGICAL SALINE SOLUTION
(0.9wt%/vol SODIUM CHLORIDE AQUEOUS SOLUTION@1V)
CORROSION CURRENT DENSITY A/cm2
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
Ni
Ti
Ti-PLATED PRODUCT

FIG.5

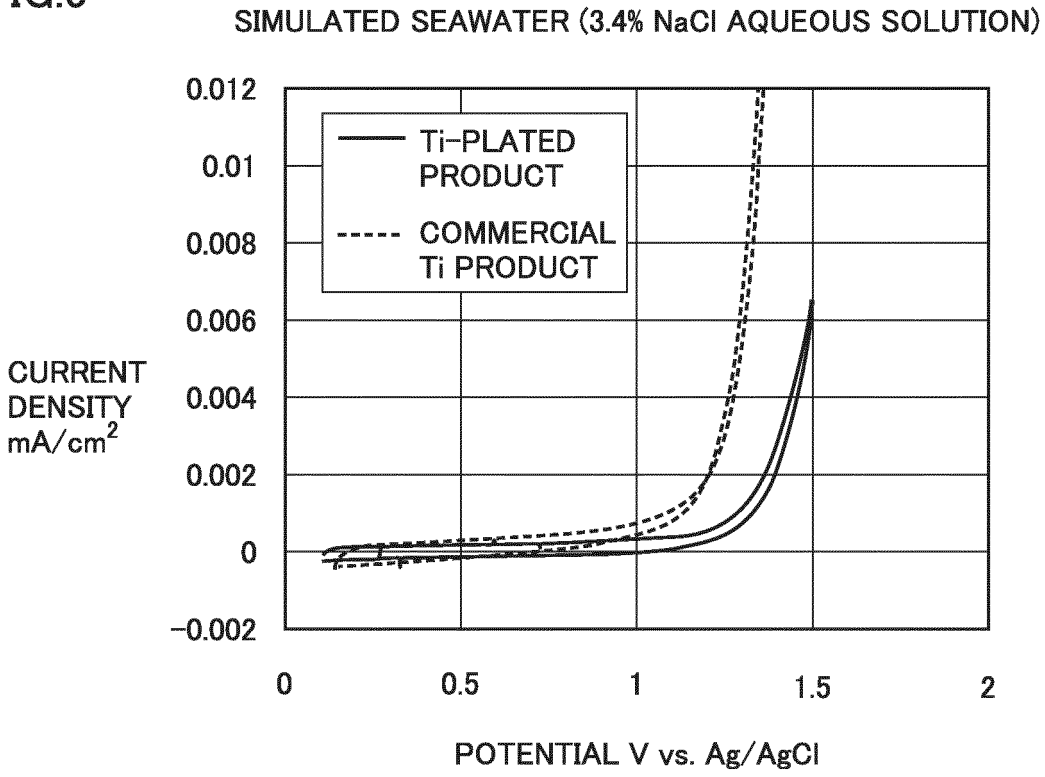

SIMULATED SEAWATER (3.4% NaCl AQUEOUS SOLUTION)
CURRENT DENSITY mA/cm2
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
Ti-PLATED PRODUCT
COMMERCIAL Ti PRODUCT
0
0.5
1
1.5
2
POTENTIAL V vs. Ag/AgCl

FIG.6

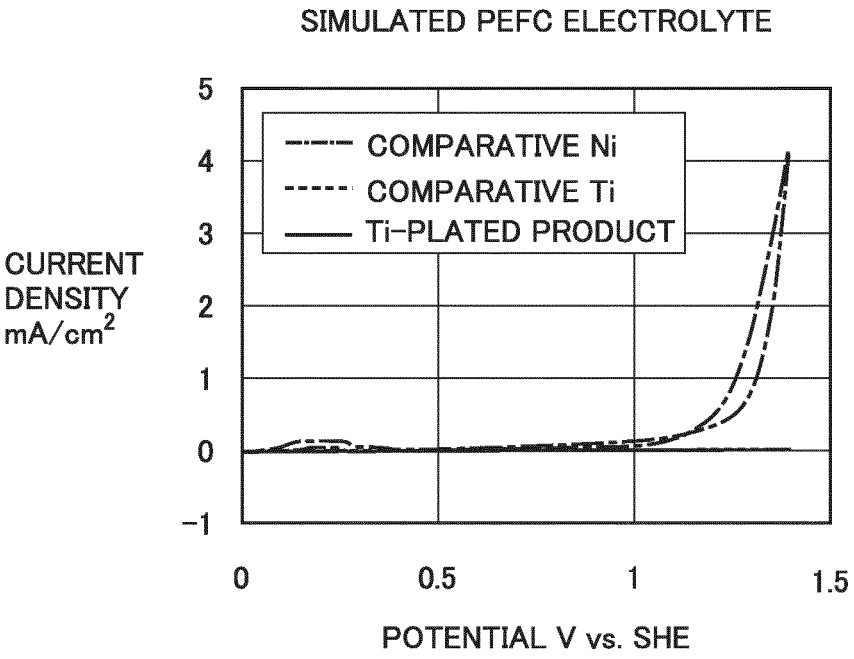
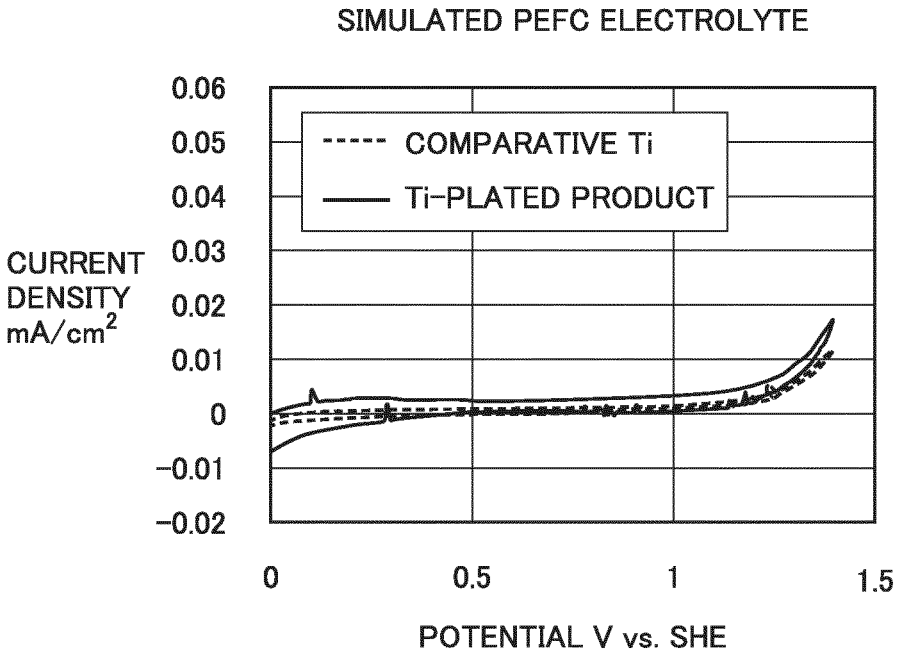

SIMULATED PEFC ELECTROLYTE
COMPARATIVE Ni
COMPARATIVE Ti
Ti-PLATED PRODUCT
CURRENT DENSITY mA/cm2
5
4
3
2
1
0
−1
0
0.5
1
1.5
POTENTIAL V vs. SHE

FIG.7


SIMULATED PEFC ELECTROLYTE
COMPARATIVE Ti
Ti-PLATED PRODUCT
CURRENT DENSITY mA/cm2
0.06
0.05
0.04
0.03
0.02
0.01
0
−0.01
−0.02
0
0.5
1
1.5
POTENTIAL V vs. SHE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/009738

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C25D5/48(2006.01)i, C23G1/32(2006.01)i, C25D3/66(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C25D5/48, C23G1/32, C25D3/66

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 51-138511 A (SONY CORP.) 30 November 1976, examples 2-3 & US 4082628 A, examples 1-2 & GB 1542074 A & DE 2623740 A & FR 2312575 A & SE 7606022 A & CA 1107229 A & AU 1424576 A	1-3, 5-8 4
Y A	JP 5-009763 A (MITSUBISHI MATERIALS CORP.) 19 January 1993, claim 2, paragraphs [0001]-[0009] (Family: none)	1-3, 5-8 4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 April 2018 (26.04.2018)	15 May 2018 (15.05.2018)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/009738

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	CLAYTON, F. R. et al., "Electrochemical Studies of Titanium in Molten Fluorides", J. Electrochem. Soc. ELECTROCHEMICAL SCIENCE AND TECHNOLOGY, 1973, vol. 120, no. 9, pp. 1193-1199	1-2, 5-8 3-4
Y A	JP 2000-256898 A (PERMELEC ELECTRODE LTD.) 19 September 2000, claim 2 & US 6432293 B1, claim 2	6 1-5, 7-8
Y A	JP 2008-192758 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 21 August 2008, paragraphs [0019], [0024] (Family: none)	7 1-6, 8
Y A	JP 9-215743 A (JAPAN ENERGY CORP.) 19 August 1997, claim 1, paragraph [0029] (Family: none)	8 1-7
A	JP 6-173065 A (JAPAN ENERGY CORP.) 21 June 1994, claims, example 1 (Family: none)	1-8
A	JP 2015-193899 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 05 November 2015, claims, paragraph [0011] (Family: none)	1-8
A	SONG, Jianxun et al., "The Influence of Fluoride Anion on the Equilibrium between Titanium Ions and Electrodeposition of Titanium in Molten Fluoride-Chloride Salt", Materials Transactions, 2014, vol. 55, no. 8, pp. 1299-1303	1-8

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2017100758 A **[0001]**
- JP 2015193899 A **[0002] [0003]**

Non-patent literature cited in the description

- **A. ROBIN.** ELECTOLYTIC COATING OF TITANIUM ONTO IRON AND NICKEL ELECTRODES IN THE MOLTEN LiF+NaF+KF EUTECTIC. *Journal of Electroanal. Chem.,* 1987, vol. 230, 125-141 **[0004]**