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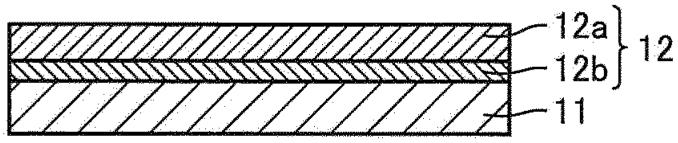
(54) CONDUCTIVE MATERIAL AND METHOD FOR PRODUCING SAME

(57) Provided is a conductive material including: a base material that is conductive at least at a surface thereof; and a titanium film on the surface of the base material, the titanium film having an average film thickness of not less than 1 μm and not more than 300 μm.

FIG.1



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a conductive material and a method for manufacturing the same. The present application claims a priority based on Japanese Patent Application No. 2016-055432 filed on March 18, 2016 and Japanese Patent Application No. 2016-128561 filed on June 29, 2016, the entire contents of which are incorporated herein by reference.

BACKGROUND ART

[0002] Titanium is a metal that is excellent in corrosion resistance, heat resistance, and specific strength. Titanium is, however, costly to manufacture and difficult to smelt and work, which hampers the widespread use of titanium. Dry deposition, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), is now industrially used in some cases, as one of the methods that take advantage of high corrosion resistance, high strength, and other properties of titanium and titanium compounds. Such deposition, however, cannot be applied to a complex-shaped substrate. As a method for depositing titanium that would solve this problem, electrodeposition of titanium in a molten salt may be used.

[0003] Various types of molten salt baths that can be used for the electrodeposition of titanium are known and under study. For example, NPD 1 describes a method for forming a titanium film on a Ni or Fe surface using a molten salt bath of LiF-NaF-KF with K_2TiF_6 added. NPD 2 describes a method for forming a titanium film on an Au or Ni surface using a molten salt bath of LiCl-KCl with $TiCl_3$ added. NPD 3 describes a method for forming a titanium film on a SUS304 surface using a molten salt bath of LiCl-NaCl-KCl with K_2TiF_6 added. Further, Japanese Patent Laying-Open No. 2015-193899 (PTD 1) describes forming an alloy film of Fe and Ti on a Fe wire surface using a molten salt bath of KF-KCl with K_2TiF_6 or TiO_2 added.

[0004] Besides, a smelting method for precipitating high-purity metallic titanium on a base material using a molten salt bath is also known. For example, Japanese Patent Laying-Open No. 08-225980 (PTD 2) describes a method for precipitating high-purity titanium on a Ni surface using a NaCl bath with $TiCl_4$ added, as a molten salt bath. Further, Japanese Patent Laying-Open No. 09-071890 (PTD 3) describes a method for precipitating high-purity titanium on the surface of a titanium bar using a NaCl bath or a Na-KCl bath.

CITATION LIST

PATENT DOCUMENT

[0005]

PTD 1: Japanese Patent Laying-Open No. 2015-193899
PTD 2: Japanese Patent Laying-Open No. 08-225980
PTD 3: Japanese Patent Laying-Open No. 09-071890

NON PATENT DOCUMENT

[0006]

NPD 1: A. Robin et.al., "Electrolytic Coating of Titanium onto Iron and Nickel Electrodes in the Molten LiF + NaF + KF Eutectic", Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1987, vol. 230, pp. 125-141
NPD 2: Hiroshi Takamura et al., "Smooth and Fine Electrodeposition of Titanium from LiCl-KCl-TiCl3 Melt", Journal of the Japan Institute of Metals and Materials, 1996, vol. 60, No. 4, pp. 388-397
NPD 3: Dawei Wei et al., "Characteristics of Ti Films Electrodeposited from Molten Salts by a Pulse Current Method", Journal of the Japan Institute of Metals and Materials, 1994, vol. 58, No. 6, pp. 660-667
NPD 4: Jianxun Song 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 NPD 5: Yang Song et.al., "The Cathodic Behavior of Ti(III) Ion in a NaCl-2CsCl Melt", Metallurgical and Materials Transactions B, 2016, vol.47B, February, pp.804-810

SUMMARY OF INVENTION

[0007] A conductive material of the present disclosure includes: a base material that is conductive at least at a surface thereof; and a titanium film on the surface of the base material, the titanium film having an average film thickness of not less than 1 μm and not more than 300 μm.

[0008] A method for manufacturing a conductive material of the present disclosure is a method for manufacturing the above conductive material, the method including: a molten salt bath formation step of preparing a molten salt bath that contains KF, KCl, and K_2TiF_6; a dissolving step of dissolving Ti in the molten salt bath; and an electrolyzing step of performing molten salt electrolysis using a cathode and an anode provided in the molten salt bath in which Ti is dissolved, to electrodeposit Ti on the surface of the cathode. In the dissolving step, Ti is supplied in at least a minimum amount necessary for Ti^{4+} in the molten salt bath to become Ti^{3+} by a comproportionation reaction expressed by Formula (1) below:

$$\text{Formula (1):} \qquad 3Ti^{4+} + \text{Ti metal} \rightarrow 4Ti^{3+}.$$

[0009] In the electrolyzing step, a base material that is conductive at least at a surface thereof is used as the cathode.

BRIEF DESCRIPTION OF DRAWINGS

[0010]

Fig. 1 is a schematic cross-sectional view showing an example conductive material in an embodiment.
Fig. 2 is a conceptual diagram for illustrating a method for measuring the average film thickness of a titanium film.
Fig. 3 is a photograph of the surface of the titanium film of conductive material No. 5 in an example observed with a scanning electron microscope (SEM).
Fig. 4 is a photograph, a secondary electron image, of a cross section of conductive material No. 5 in an example, observed with a scanning electron microscope (SEM).
Fig. 5 is a photograph, a reflected electron image, of a cross section of conductive material No. 5 in an example, observed with a scanning electron microscope (SEM).

DESCRIPTION OF EMBODIMENTS

[Problem to Be Solved by the Present Disclosure]

[0011] The method described in NPD 1 disadvantageously has poor water washability after the plating because LiF and NaF contained in the molten salt bath is hardly soluble in water. The molten salt baths described in NPD 2 and NPD 3, on the other hand, have good water washability and allow titanium to be electrodeposited at a lower temperature than the molten salt bath described in NPD 1. The molten salt baths of NPD 2 and NPD 3, however, cannot provide a smooth titanium film. A conceivable reason is that the molten salt bath of NPD 2 does not contain F ion and the molten salt bath of NPD 3 contains only insufficient F ion; the use of a bath containing F ion is effective for producing a smooth titanium film, as described in NPD 4 and NPD 5.

[0012] According to the results of studies conducted by the inventors of the present invention, although a Fe-Ti alloy film can be electrodeposited by the method described in PTD 1, a metallic titanium film cannot be electrodeposited by the method. Specifically, while a Fe-Ti alloy film is stable in the molten salt bath, metallic Ti is not suitable because it dissolves in the molten salt bath by a comproportionation reaction. The methods described in PTD 2 and PTD 3, on the other hand, are for smelting titanium. The titanium electrodeposited by the methods of PTD 2 and PTD 3 is in the form of a dendrite. That is, the methods described in PTD 2 and PTD 3 cannot provide a smooth titanium film.

[0013] In view of the above problems, an object of the present disclosure is to provide a conductive material that has a thin titanium film on its surface, the titanium film having little unevenness in film thickness.

[Advantageous Effects of the Present Disclosure]

[0014] According to the present disclosure, a conductive material is provided that has a thin titanium film on its surface, the titanium film having little unevenness in film thickness.

[Description of Embodiments]

[0015] First, embodiments of the present disclosure are enumerated.

[1] A conductive material of the present disclosure includes: a base material that is conductive at least at a surface thereof; and a titanium film on the surface of the base material, the titanium film having an average film thickness

of not less than 1 μm and not more than 300 μm.

According to the above conductive material, a conductive material is provided that has a thin titanium film on its surface, the titanium film having little unevenness in film thickness.

[2] In the above conductive material, when the thickness of the titanium film is measured at each of arbitrary five spots on the surface of the conductive material, the maximum thickness and the minimum thickness of the titanium film measured at each of the arbitrary five spots are preferably within ±50% of the average film thickness. Thus, a conductive material is provided that has a smooth titanium film with little unevenness in film thickness.

[3] In the above conductive material, the titanium film preferably includes: a titanium layer; and a titanium alloy layer containing an alloy of a metal contained in the base material and titanium, with the titanium alloy layer being disposed between the titanium layer and the base material. In this case, the stress generated between the titanium film and the base material is relaxed, and thus the titanium film is not easily peeled off.

[4] A method for manufacturing a conductive material of the present disclosure is a method for manufacturing the above conductive material, the method including: a molten salt bath formation step of preparing a molten salt bath that contains KF, KCl, and K_2TiF_6; a dissolving step of supplying Ti to the molten salt bath to dissolve Ti in the molten salt bath; and an electrolyzing step of performing molten salt electrolysis using a cathode and an anode provided in the molten salt bath in which Ti is dissolved, to electrodeposit Ti on a surface of the cathode. In the dissolving step, Ti is supplied in at least a minimum amount necessary for Ti^{4+} in the molten salt bath to become Ti^{3+} by a comproportionation reaction expressed by Formula (1) below:

$$\text{Formula (1):} \qquad 3Ti^{4+} + \text{Ti metal} \rightarrow 4Ti^{3+}.$$

In the electrolyzing step, a base material that is conductive at least at a surface thereof is used as the cathode.

According to the above method for manufacturing the conductive material, a conductive material is manufactured that has a thin titanium film on its surface, the titanium film having little unevenness in film thickness.

[5] In the above method for manufacturing the conductive material, the molar mixing ratio of KF and KCl is preferably 10 : 90 to 90 : 10. Thus, the above conductive material can be manufactured in a molten salt bath that is lower in temperature than a molten salt of KF alone.

[6] In the above method for manufacturing the conductive material, the K_2TiF_6 content in the molten salt bath is preferably not less than 0.1 mol%. Thus, the above conductive material can be stably manufactured.

[7] In the above method for manufacturing the conductive material, Ti to be supplied in the dissolving step is preferably a titanium sponge. Thus, the comproportionation reaction of Ti can be facilitated in the dissolving step. Note that the titanium sponge refers to a porous titanium metal having a porosity rate of not less than 1%. The porosity rate of the titanium sponge is calculated by the following formula:

$$100 - (\text{the volume calculated from the mass}) / (\text{the apparent volume}) \times 100.$$

[8] In the above method for manufacturing the conductive material, the anode is preferably made of Ti. Thus, a titanium film can be stably and continuously electrodeposited on the surface of the cathode.

[Details of Embodiment]

[0016] An Embodiment of the present disclosure is described hereinafter in detail. Note that the present embodiment is not limited to the description but is defined by the terms of the claims. It is intended that the present embodiment encompasses any modification within the meaning and scope equivalent to the terms of the claims.

<Conductive Material>

[0017] Fig. 1 is a schematic cross-sectional view showing an example conductive material in an embodiment. As shown in Fig. 1, a conductive material 10 includes a base material 11 that is conductive at least at its surface, and a titanium film 12 on the surface of base material 11, titanium film 12 having an average film thickness of not less than 1 μm and not more than 300 μm.

(Base Material)

[0018] Base material 11 is simply required to be conductive at least at its surface. Examples of base material 11 include: a metal that can be used with titanium film 12 formed on its surface; and a conductive sintered material.

Specifically, nickel, iron, SUS304, molybdenum, tungsten, copper, carbon or the like can be preferably used.

[0019] The shape of base material 11 is not particularly limited. For example, base material 11 may have a flat-plate shape, a bar shape, a cylindrical shape, or a complex three-dimensional shape. According to a method for manufacturing the conductive material described later, titanium film 12 can be easily formed on the surface of base material 11 even if base material 11 has a complex three-dimensional shape.

(Titanium Film)

[0020] Titanium film 12 is disposed on the surface of base material 11. Specifically, titanium film 12 covers the surface of base material 11. Titanium film 12 may cover the surface of base material 11 in whole or in part. Titanium film 12 has an average film thickness of not less than 1 μm and not more than 300 μm. The average film thickness of titanium film 12 is measured in the following way.

[0021] Fig. 2 is a conceptual diagram for illustrating a method for measuring the average film thickness of the titanium film. As shown in Fig. 2, first, conductive material 10 is arbitrarily and equally divided into areas, and five spots (area 1 to area 5) are selected as measurement spots. Then, the cross section of titanium film 12 at each area is observed with a scanning electron microscope (SEM). The magnifying power of the SEM is set in such a way that titanium film 12 in its entirety in the thickness direction can be observed and that the thickness can be enlarged as much as possible in one field of view. For each area, three spots are observed with different fields of view.

[0022] As an example, Fig. 2 shows a conceptual diagram obtained from the observation of three fields of view (field of view 1 to field of view 3) in area 1. In each field of view, a maximum thickness dmax at the portion where titanium film 12 is maximum in thickness, and a minimum thickness dmin at the portion where titanium film 12 is minimum in thickness are measured. The thickness of titanium film 12 refers to the dimension of titanium film 12 extending in the vertical direction from substrate 11. Thus, maximum thickness dmax of the field of view of each of the three spots, and minimum thickness dmin of the field of view of each of the three spots are determined for area 1. In the same manner as area 1, maximum thickness dmax and minimum thickness dmin in the field of view of each of the three spots are measured for area 2 to area 5. The average value of all of 15 maximum thicknesses dmax and 15 minimum thicknesses dmin measured as described above is defined as the average film thickness of the titanium film.

[0023] Titanium film 12 having an average film thickness of not less than 1 μm exhibits good corrosion resistance and good heat resistance. Titanium film 12 having an average film thickness of not more than 300 μm eliminates excessive formation of titanium film 12 on the surface of base material 11, thus providing low-cost conductive material 10 with titanium film 12. From these viewpoints, the average film thickness of titanium film 12 is more preferably not less than 5 μm and not more than 200 μm, still more preferably not less than 15 μm and not more than 100 μm.

[0024] Titanium film 12 is preferably a smooth film with little unevenness in film thickness. Such a smooth titanium film 12 with little unevenness in film thickness does not have a portion where the film thickness is extremely small. Thus, conductive material 10 has better corrosion resistance and heat resistance.

[0025] Smooth titanium film 12 with little unevenness in film thickness refers to a film such that: when the thickness of titanium film 12 is measured at arbitrary five spots on the surface of conductive material 10, each (all) of maximum thicknesses dmax and minimum thicknesses dmin of titanium film 12 measured at the arbitrary five spots is within ±50% of the average film thickness. That is, it refers to a film such that all of 15 maximum thicknesses dmax and 15 minimum thicknesses dmin measured in the above-described method for measuring the average film thickness of titanium film 12 are within ±50% of the average film thickness.

[0026] Referring back to Fig. 1, titanium film 12 preferably includes a titanium layer 12a and a titanium alloy layer 12b, with titanium alloy layer 12b being disposed between titanium layer 12a and base material 11. More specifically, titanium film 12 preferably includes a configuration where titanium alloy layer 12b and titanium layer 12a are stacked in this order from the base material 11 side.

[0027] Titanium layer 12a is a layer consisting of only titanium (which may include, however, inevitable impurities). Titanium alloy layer 12b is made of an alloy of the metal contained in base material 11 and titanium (which may include, however, inevitable impurities). The metal contained in base material 11 refers to a metal that is conductive at least at its surface.

[0028] As described later, conductive material 10 is manufactured by plating the surface of base material 11 with titanium. Since the plating with titanium is performed in a molten salt bath at a high temperature of about 650°C, rapid cooling of conductive material 10 after the plating causes a great stress due to the difference in coefficient of thermal expansion between titanium and base material 11. If titanium film 12 is configured with titanium layer 12a on the surface side and titanium alloy layer 12b on the base material 11 side, titanium alloy layer 12b relaxes the stress. Thus, titanium film 12 can be prevented from peeling off base material 11.

[0029] The thickness of titanium alloy layer 12b, though not particularly limited, is preferably not less than 0.1 μm and not more than 20 μm, for example. Titanium alloy layer 12b having a thickness of not less than 0.1 μm can more reliably prevent the peeling-off of titanium film 12. Titanium alloy layer 12b having a thickness of not more than 20 μm does not impair the functions of pure titanium (i.e., the functions derived from titanium layer 12a). From these viewpoints, the thickness of titanium alloy layer 12b is more preferably not less than 0.5 μm and not more than 15 μm, still more preferably not less than 1 μm and not more than 10 μm.

[0030] If base material 11 is made of nickel for example, titanium alloy layer 12b is preferably composed of three layers. Specifically, titanium alloy layer 12b and titanium layer 12a are preferably formed in this order on the surface of base material 11 made of Ni, where titanium alloy layer 12b is composed of: a composite layer 2bc of $TiNi_3$ and Ni; a composite layer 2bb of TiNi and $TiNi_3$; and a composite layer 2ba of Ti_2Ni and TiNi, which are stacked in this order. This case provides a buffering function for relaxing the stress generated between titanium film 12 and base material 11.

[0031] Alternatively, base material 11 made of iron, SUS304, copper, carbon or the like may be plated with titanium film 12. Thus, titanium film 12 containing titanium alloy layer 12b on the base material side can be formed.

<Method for Manufacturing Conductive Material>

[0032] A method for manufacturing a conductive material in the present embodiment includes: a molten salt bath formation step of preparing a molten salt bath that contains KF, KCl, and K_2TiF_6; a dissolving step of dissolving Ti in the molten salt bath; and an electrolyzing step of performing molten salt electrolysis using a cathode and an anode provided in the molten salt bath in which Ti is dissolved, so as to electrodeposit Ti on the surface of the cathode. The steps are described in detail hereinafter.

Molten Salt Bath Formation Step

[0033] The molten salt bath formation step is a step of preparing a molten salt bath that contains KF, KCl, and K_2TiF_6.

[0034] KF-KCl eutectic molten salt is lower in melting point than a molten salt of KF alone or a molten salt of KCl alone, and is easily soluble in water. Therefore, KF-KCl eutectic molten salt used as a molten salt bath has excellent water washability. If a molten salt bath of KF-KCl eutectic molten salt with K_2TiF_6 added is used for Ti electroplating, a smooth titanium film can be electrodeposited on the surface of the base material.

[0035] The molar mixing ratio of KF and KCl is preferably 10 : 90 to 90 : 10. A KF content of not less than 10 mol% in KF-KCl enables a smooth titanium film to be electrodeposited on the surface of the base material. A KF content of not more than 90 mol% in KF-KCl enables the melting point to be lower than that of a molten salt of KF alone. From these viewpoints, the molar mixing ratio of KF and KCl is more preferably 20 : 80 to 80 : 20, still more preferably 40 : 60 to 60 : 40.

[0036] By adding K_2TiF_6 to the above KF-KCl eutectic molten salt, a molten salt bath can be prepared that enables electrodeposition of a titanium film on the surface of the base material. The timing of adding K_2TiF_6 is not particularly limited: KF, KCl, and K_2TiF_6 may be mixed first and then heated to obtain a molten salt bath; or K_2TiF_6 may be added to KF-KCl eutectic molten salt to obtain a molten salt bath.

[0037] The K_2TiF_6 content in the molten salt bath is preferably not less than 0.1 mol%. A K_2TiF_6 content of not less than 0.1 mol% can provide a molten salt bath that enables efficient electrodeposition of Ti on the surface of the base material.

Dissolving Step

[0038] The dissolving step is a step of supplying Ti to the molten salt bath prepared by the molten salt bath formation step, so as to dissolve Ti in the molten salt bath. The amount of Ti to be supplied may be at least the minimum amount necessary for Ti^{4+} in the molten salt bath to become Ti^{3+} by a comproportionation reaction expressed by the Formula (1) below.

$$\text{Formula (1):} \qquad 3Ti^{4+} + \text{Ti metal} \rightarrow 4Ti^{3+}$$

[0039] By dissolving sufficient Ti in the molten salt bath in advance, electrodeposited Ti is prevented from dissolving in the molten salt bath in the subsequent electrolyzing step. Thus, according to the method for manufacturing a conductive material in the present embodiment, a thin titanium film with little unevenness in film thickness can be formed on the surface of the base material.

[0040] The amount of Ti to be supplied to the molten salt bath is more preferably not less than two times, still more preferably not less than three times the above minimum necessary amount. For example, Ti is supplied preferably in such a large amount as to precipitate without fully dissolving in the molten salt bath.

[0041] Although the form of Ti to be supplied is not particularly limited, a titanium sponge, a finest possible titanium powder or the like is preferably used. A titanium sponge having a higher porosity rate has a larger specific surface area and is thus easier to dissolve in the molten salt bath. Accordingly, the titanium sponge preferably has a porosity rate of not less than 20%, more preferably not less than 40%. The upper limit of the porosity rate, though not particularly defined here, could be about 85% from the viewpoint of easiness of handling, manufacturability and the like.

Electrolyzing Step

[0042] The electrolyzing step is a step of performing molten salt electrolysis using a cathode and an anode provided in the molten salt bath in which Ti is dissolved. The molten salt electrolysis of the molten salt bath in which Ti is dissolved causes electrodeposition of Ti. Thus, a thin titanium film with little unevenness in film thickness can be formed on the surface of the cathode.

(Cathode)

[0043] As the cathode, the base material included in the conductive material to be manufactured may be used, since a titanium film is formed on the surface of the cathode as described above. The base material is simply required to be conductive at least at its surface, and may be the one included in the conductive material according to the present embodiment described above. If the base material is made of a material to be alloyed with titanium, a titanium alloy layer can be produced on the base material side of the titanium film. If, on the other hand, a high-purity titanium film (i.e., a titanium film consisting of only a titanium layer) is to be formed without a titanium alloy layer, a material that cannot be alloyed with Ti in the molten salt bath may be used as the base material (cathode).

(Anode)

[0044] The anode may be made of any conductive material, such as glassy carbon and titanium for example. From the viewpoint of stable and continuous manufacture of the titanium film, the anode made of Ti is preferably used.

(Other Conditions)

[0045] The atmosphere in which the molten salt electrolysis is performed may be a nonoxidative atmosphere that does not form a compound with titanium. For example, the molten salt electrolysis may be performed with an inert gas (e.g. argon gas) filling or circulating in a glove box.

[0046] The current density for the molten salt electrolysis may be, for example, not less than 10 mA/cm^2 and not more than 500 mA/cm^2, though not particularly limited. A current density of not less than 10 mA/cm^2 enables stable formation of a titanium film on the surface of the cathode. With a current density of not more than 500 mA/cm^2, the diffusion of the titanium ion in the molten salt bath is not a rate-limiting factor, and thus the resulting titanium film can be prevented from being blackened. From these viewpoints, the current density is more preferably not less than 50 mA/cm^2 and not more than 250 mA/cm^2, still more preferably not less than 100 mA/cm^2 and not more than 200 mA/cm^2.

[0047] In the electrolyzing step, the temperature of the molten salt bath is preferably not less than 650°C and not more than 850°C. The molten salt bath at a temperature of not less than 650°C can be maintained in a liquid state, thus enabling stable molten salt electrolysis. The molten salt bath at the temperature of not more than 850°C can suppress evaporation of its components and thus can be prevented from losing stability. From these viewpoints, the temperature of the molten salt bath is more preferably not less than 650°C and not more than 750°C, still more preferably not less than 650°C and not more than 700°C.

[0048] The length of time for the molten salt electrolysis, though not particularly limited, may be a length of time with which an intended titanium film is satisfactorily formed.

EXAMPLES

[0049] The present embodiment is described in more detail hereinafter with reference to examples. The examples are by way of illustration only, and the conductive material and the manufacturing method thereof in the present disclosure are not limited to the examples.

(Example 1)

Molten Salt Bath Formation Step

[0050] KCl, KF, and K_2TiF_6 were mixed, with the molar mixing ratio of KCl and KF being 55 : 45, and the concentration of K_2TiF_6 being 0.1 mol%. The mixture was heated to 650°C to produce a molten salt bath.

Dissolving Step

[0051] 13 mg of titanium sponge per 1 g of the molten salt bath was added to and sufficiently dissolved in the molten salt bath produced in the above-described molten salt bath formation step. As the titanium sponge, the one having a porosity rate of 50% was used. Some of the titanium sponge that was unable to dissolve in the molten salt bath precipitated.

Electrolyzing Step

[0052] Molten salt electrolysis was performed in a glove box with an Ar flow atmosphere. A Ni plate of 0.5 cm × 2.5 cm × 0.1 mmt was used as a cathode, and a Ti bar was used as an anode. A Pt wire was used as a pseudo-reference electrode. A voltage was applied to the cathode and the anode for molten salt electrolysis in such a way that the current density was 25 mA/cm^2. The electric potential of the pseudo-reference electrode was calibrated with the electric potential of metallic K electrochemically precipitated on the Pt wire (K^+/K electric potential). As a result, titanium was electrodeposited on the surface of the cathode Ni plate, and a conductive material having a titanium film was obtained.

Water Washing

[0053] After the electrolyzing step, the conductive material was washed with water. The salt that adhered to the surface of the conductive material was highly soluble in water and was easily removed. Through the above-described steps, conductive material No. 1 having a titanium film was obtained.

(Example 2)

[0054] Conductive material No. 2 was produced in the same manner as Example 1 except that the current density was set to 100 mA/cm^2.

(Example 3)

[0055] Conductive material No. 3 was produced in the same manner as Example 1 except that the concentration of K_2TiF_6 was set to 2.0 mol%.

(Example 4)

[0056] Conductive material No. 4 was produced in the same manner as Example 3 except that the current density was set to 100 mA/cm^2.

(Example 5)

[0057] Conductive material No. 5 was produced in the same manner as Example 3 except that the current density was set to 150 mA/cm^2.

(Example 6)

[0058] Conductive material No. 6 was produced in the same manner as Example 3 except that the current density was set to 200 mA/cm^2.

(Comparative Example 1)

[0059] Conductive material No. 7 was produced in the same manner as Example 1 except that the dissolving step was not performed and that the current density was set to 150 mA/cm^2.

(Comparative Example 2)

[0060] Conductive material No. 8 was produced in the same manner as Comparative Example 1 except that the concentration of K_2TiF_6 was set to 2.0 mol% and that the current density was set to 100 mA/cm^2.

(Comparative Example 3)

[0061] Conductive material No. 9 was produced in the same manner as Comparative Example 2 except that the current density was set to 150 mA/cm^2.

(Comparative Example 4)

[0062] Conductive material No. 10 was produced in the same manner as Comparative Example 2 except that the current density was set to 200 mA/cm^2.

(Comparative Example 5)

[0063] Conductive material No. 11 was produced in the same manner as Comparative Example 1 except that the concentration of K_2TiF_6 was set to 5.0 mol%.

Evaluation

[0064] Conductive materials No. 1 to No. 11 were evaluated as follows.

<Appearance of Titanium Film>

[0065] The appearance of the film formed on the surface of the base material of each of conductive materials No. 1 to No. 11 was visually observed. Further, the presence or absence of titanium in the film was examined by the X-ray diffraction (XRD). The results are shown in Table 1 below.

[Table 1]

	Current Density (mA/cm^2)	K_2TiF_6 Concentration (mol%)	Appearance	Presence or Absence of Titanium
Conductive Material No. 1	25	0.1	Silvery white plating film adhered	Titanium detected
Conductive Material No. 2	100	0.1	Silvery white plating film adhered	Titanium detected
Conductive Material No. 3	25	2.0	Silvery white plating film adhered	Titanium detected
Conductive Material No. 4	100	2.0	Silvery white plating film adhered	Titanium detected
Conductive Material No. 5	150	2.0	Silvery white plating film adhered	Titanium detected
Conductive Material No. 6	200	2.0	Silvery white plating film adhered	Titanium detected
Conductive Material No. 7	150	0.1	Black plating film adhered	No titanium detected
Conductive Material No. 8	100	2.0	Black plating film adhered	No titanium detected
Conductive Material No. 9	150	2.0	Black plating film adhered	No titanium detected
Conductive Material No. 10	200	2.0	Black plating film adhered	No titanium detected
Conductive Material No. 11	150	5.0	Black plating film adhered	No titanium detected

[0066] As shown in Table 1, in each of conductive materials No. 1 to No. 6, a silvery white titanium film was observed on the surface of the base material which is a Ni plate. In each of conductive materials No. 7 to No. 11, on the other hand, a black film was formed on the surface of the Ni plate and titanium was not detected by the XRD

<Average Film Thickness of Titanium Film>

[0067] Maximum thickness dmax and minimum thickness dmin of the obtained titanium film of conductive material No. 1 were measured in accordance with the above-described method. The results are shown in Table 2.

[Table 2]

	Field of View 1		Field of View 2		Field of View 3	
	Maximum Thickness (μm)	Minimum Thickness (μm)	Maximum Thickness (μm)	Minimum Thickness (μm)	Maximum Thickness (μm)	Minimum Thickness (μm)
Area 1	42	25	38	22	36	21
Area 2	41	23	36	20	35	21
Area 3	40	22	35	18	33	20
Area 4	42	25	37	23	31	22
Area 5	41	24	36	17	30	19

[0068] The results of Table 2 show that the average film thickness of the titanium film of conductive material No. 1 was 29 μm, and that all the maximum thicknesses dmax and minimum thicknesses dmin were within ±50% of the average film thickness. Similarly, measurement was performed also for each of conductive materials No. 2 to No. 6, and the average film thickness and the film thickness distribution were calculated. The results are shown in Table 3. Note that the film thickness distribution refers to the range of the percentages of 15 maximum thicknesses dmax and 15 minimum thicknesses dmin to the average film thickness.

[Table 3]

	Average Film Thickness (μm)	Film Thickness Distribution (%)
Conductive Material No. 1	29	59~145
Conductive Material No. 2	24	55~146
Conductive Material No. 3	30	65~138
Conductive Material No. 4	31	67~135
Conductive Material No. 5	31	66~138
Conductive Material No. 6	30	62~141

<SEM/EDX Photograph>

[0069] Fig. 3 and Fig. 4 respectively show photographs, secondary electron images, of a surface and a cross section of conductive material No. 5, observed with a Schottky field emission scanning electron microscope (SEM) "JSM-7600F" manufactured by JEOL Ltd. Further, Fig. 5 is a photograph, a reflected electron image, of a cross section of conductive material No. 5, observed with a scanning electron microscope (SEM). The conductive material was embedded in a resin and the cross section was polished by mechanical polishing and by a cross section polisher.

[0070] Composition analysis was performed for conductive material No. 5 by the energy dispersive X-ray spectrometry (EDX spectrometry). The EDX spectrometry was performed by the point analysis at the center of each alloy layer in the thickness direction using an energy dispersive X-ray spectrometry (EDX, X-Max80 Premium manufactured by Oxford Instruments), with an accelerating voltage of 10 kV.

[0071] As shown in Fig. 3 and Fig. 4, titanium film 2 having a smooth surface was observed. Further, titanium alloy layer 2b was observed on the base material side of titanium film 2, i.e., between titanium layer 2a and Ni base material 1. Peeling-off of titanium film 2 from Ni base material 1 was not observed.

[0072] As shown in Fig. 5, titanium alloy layer 2b had a structure with three layers: composite layer 2bc of $TiNi_3$ and Ni; composite layer 2bb of TiNi and $TiNi_3$; and composite layer 2ba of Ti_2Ni and TiNi, in this order from the side adjacent to Ni base material 1. Further, the total thickness of titanium alloy layer 2b was about 3 μm, with composite layer 2bc of $TiNi_3$ and Ni being the thickest, composite layer 2bb of TiNi and $TiNi_3$ being the second thickest, composite layer 2ba of Ti_2Ni and TiNi being the thinnest.

REFERENCE SIGNS LIST

[0073] 10: conductive material; 11: base material; 12: titanium film; 12a: titanium layer; 12b: titanium alloy layer; 1: Ni base material; 2: titanium film; 2a: titanium layer; 2b: titanium alloy layer; 2ba: composite layer of Ti_2Ni and TiNi; 2bb: composite layer of TiNi and $TiNi_3$; 2bc: composite layer of $TiNi_3$ and Ni

Claims

1. A conductive material comprising:

   a base material that is conductive at least at a surface thereof; and
   a titanium film on the surface of the base material, the titanium film having an average film thickness of not less than 1 μm and not more than 300 μm.

2. The conductive material according to claim 1, wherein, when a thickness of the titanium film is measured at each of arbitrary five spots on a surface of the conductive material, a maximum thickness and a minimum thickness of the titanium film measured at each of the arbitrary five spots are within ±50% of the average film thickness.

3. The conductive material according to claim 1 or 2, wherein
   the titanium film includes:

   a titanium layer; and
   a titanium alloy layer containing an alloy of a metal contained in the base material and titanium, and

   the titanium alloy layer is disposed between the titanium layer and the base material.

4. A method for manufacturing the conductive material according to any one of claims 1 to 3, the method comprising:

   a molten salt bath formation step of preparing a molten salt bath that contains KF, KCl, and K_2TiF_6;
   a dissolving step of supplying Ti to the molten salt bath to dissolve the Ti in the molten salt bath; and
   an electrolyzing step of performing molten salt electrolysis using a cathode and an anode provided in the molten salt bath in which the Ti is dissolved, to electrodeposit Ti on a surface of the cathode,
   in the dissolving step, Ti being supplied in at least a minimum amount necessary for Ti^{4+} in the molten salt bath to become Ti^{3+} by a comproportionation reaction expressed by Formula (1) below,

   $$\text{Formula (1):} \quad 3Ti^{4+} + \text{Ti metal} \rightarrow 4Ti^{3+},$$

   in the electrolyzing step, a base material that is conductive at least at a surface thereof being used as the cathode.

5. The method for manufacturing the conductive material according to claim 4, wherein a molar mixing ratio of the KF and the KCl is 10 : 90 to 90 : 10.

6. The method for manufacturing the conductive material according to claim 4 or 5, wherein a K_2TiF_6 content in the molten salt bath is not less than 0.1 mol%.

7. The method for manufacturing the conductive material according to any one of claims 4 to 6, wherein the Ti to be

supplied in the dissolving step is a titanium sponge.

8. The method for manufacturing the conductive material according to any one of claims 4 to 7, wherein the anode is made of Ti.

FIG.1

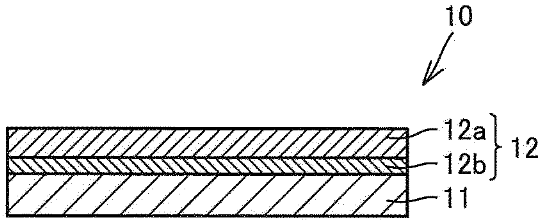
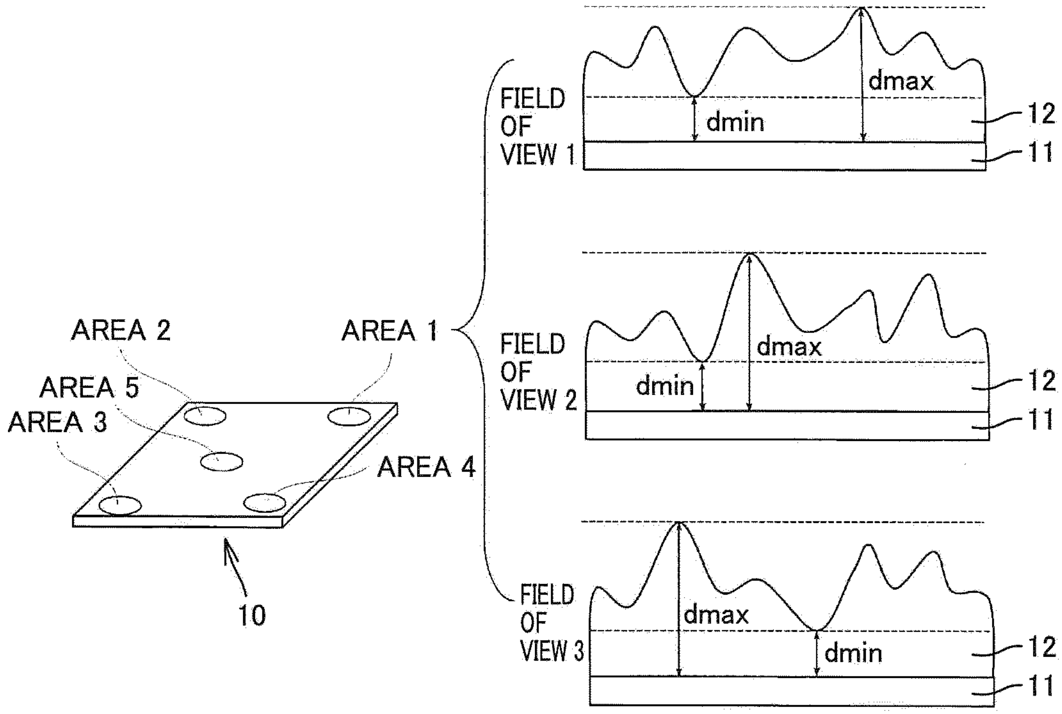

10
12a
12b
12
11

FIG.2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AREA 1
AREA 5
AREA 3
AREA 4
10
FIELD OF VIEW 1
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dmin
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11
FIELD OF VIEW 2
dmax
dmin
12
11
FIELD OF VIEW 3
dmax
dmin
12
11

FIG.3

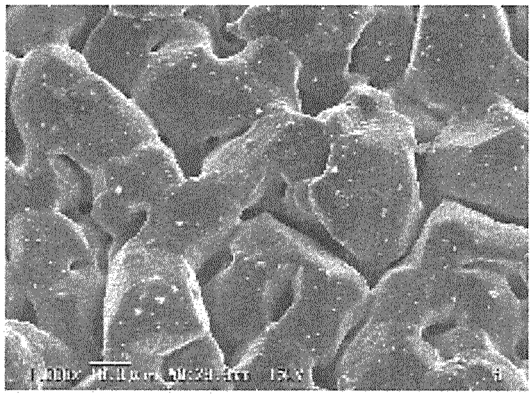
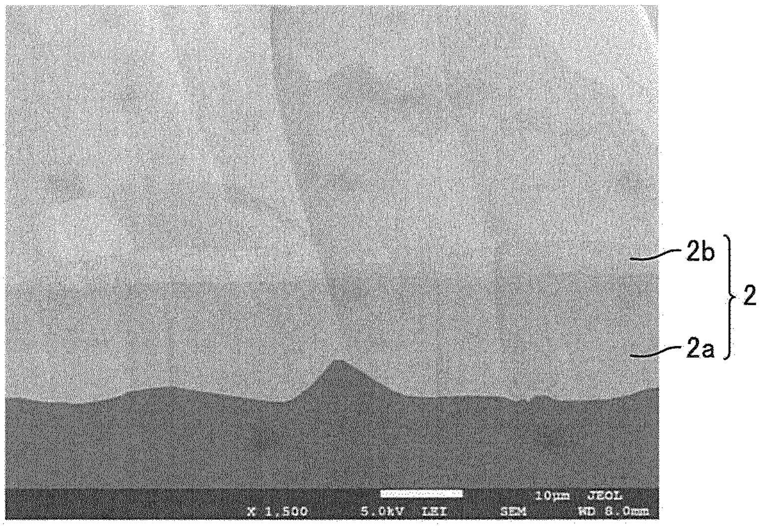


FIG.4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2a
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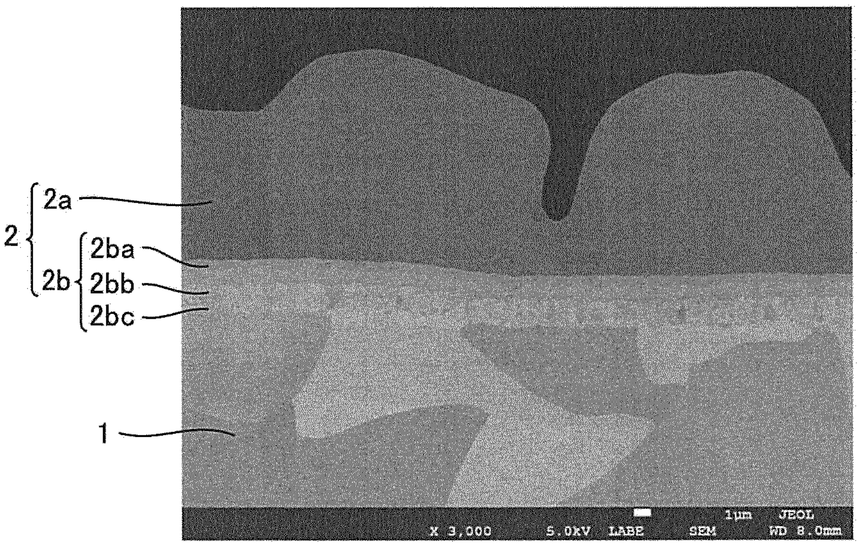
X 1,500 5.0kV LEI SEM WD 8.0mm

FIG.5


2a
2
2ba
2b
2bb
2bc
1
1μm JEOL
X 3,000 5.0kV LABE SEM WD 8.0mm

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/007520

A. CLASSIFICATION OF SUBJECT MATTER
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)
C25D3/66

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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.
X Y	JP 8-246130 A (NKK Corp.), 24 September 1996 (24.09.1996), claim 1 (Family: none)	1 2
Y	JP 1-31990 A (Nisshin Steel Co., Ltd.), 02 February 1989 (02.02.1989), examples (Family: none)	2
A	JP 4-173996 A (Tokin Corp.), 22 June 1992 (22.06.1992), (Family: none)	3-8

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search 13 March 2017 (13.03.17)	Date of mailing of the international search report 18 April 2017 (18.04.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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

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- JP 9071890 A **[0004] [0005]**

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- **YANG SONG.** The Cathodic Behavior of Ti(III) Ion in a NaCl-2CsCl Melt. *Metallurgical and Materials Transactions B,* February 2016, vol. 47B, 804-810 **[0006]**