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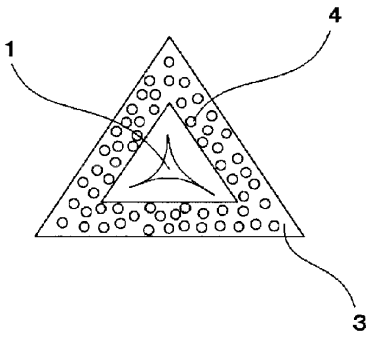
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(54) **METHOD FOR PRODUCING NICKEL ALLOY POROUS BODY**

(57) A method for producing a nickel alloy porous body includes a step of applying a coating material that contains a nickel alloy powder of nickel and an added metal, the nickel alloy powder having a volume-average particle size of 10 μm or less, onto a surface of a skeleton of a resin formed body having a three-dimensional mesh-like structure; a step of plating with nickel the surface of the skeleton of the resin formed body onto which the coating material has been applied; a step of removing the resin formed body; and a step of diffusing the added metal into the nickel by a heat treatment.

FIG. 1C



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Description

Technical Field

[0001] The present invention relates to a method for producing a nickel alloy porous body that is usable, for example, as a current collector for a battery, filter, or catalyst carrier, that is excellent in terms of strength and toughness, and that is produced at a low cost and from a wide range of materials.

Background Art

[0002] Porous metal bodies have been used in various applications, such as current collectors for batteries, filters, and catalyst carriers. Accordingly, there are many known documents regarding production techniques for porous metal bodies, as described below.

[0003] Japanese Unexamined Patent Application Publication No. 7-150270 (PTL 1) proposes a porous metal body having high strength, which is obtained by applying a coating material containing reinforcing fine particles of an oxide, carbide, or nitride of an element selected from Groups II to VI of the periodic table onto a surface of a skeleton of a three-dimensional mesh-like resin having interconnected pores; forming a metal plating layer of a Ni alloy or Cu alloy on the coating film of the coating material; and dispersing the fine particles in the metal plating layer by performing a heat treatment. However, since the reinforcing fine particles are dispersed in the metal plating layer which is a base layer, the porous metal body has low elongation at break although its breaking strength is high. The porous metal body is vulnerable to processing that involves plastic deformation, such as bending or pressing, and breaks when subjected to such processing, which is a problem.

[0004] Japanese Examined Patent Application Publication No. 38-17554 (PTL 2), Japanese Unexamined Patent Application Publication No. 9-017432 (PTL 3), and Japanese Unexamined Patent Application Publication No. 2001-226723 (PTL 4) each propose a porous metal body which is obtained by applying or spraying a slurry composed of a metal or metal oxide powder and a resin onto a three-dimensional mesh-like resin, followed by drying, and performing a sintering treatment. However, in the porous metal body produced by the sintering process, since the skeleton is formed by sintering between metal or metal oxide powder particles, even if the powder particle size is decreased, voids occur in considerable numbers in the skeleton in cross section. As a result, even when a body having high breaking strength is obtained by designing a single metal or alloy species, since the elongation at break is low, the body is vulnerable to processing that involves plastic deformation, such as bending or pressing, and breaks when subjected to such processing, which is a problem, as in the case described above.

[0005] Japanese Unexamined Patent Application Publication No. 8-013129 (PTL 5) and Japanese Unexamined Patent Application Publication No. 8-232003 (PTL 6) each propose a porous metal body obtained by a diffusion coating process in which a Ni porous body formed by a plating process, with a three-dimensional mesh-like resin to which conductivity has been imparted being used as a substrate, is buried in powder of Cr or Al and NH_4Cl, and is subjected to a heat treatment in an Ar or H_2 gas atmosphere. However, the low productivity of the diffusion coating process results in a high cost, and the element capable of forming an alloy with the Ni porous body is limited to Cr and Al, all of which are problems.

[0006] Japanese Unexamined Patent Application Publication No. 2013-133504 (PTL 7) proposes a method for producing a porous body in which, when an electrical conduction treatment is performed on a surface of a resin formed body having a three-dimensional mesh-like structure, a carbon coating material to which a metal powder has been added is applied to the surface, and then electroplating with a desired metal and a heat treatment are performed, thereby obtaining a homogeneous alloy porous body.

Citation List

Patent Literature

[0007]

PTL 1: Japanese Unexamined Patent Application Publication No. 7-150270
PTL 2: Japanese Examined Patent Application Publication No. 38-17554
PTL 3: Japanese Unexamined Patent Application Publication No. 9-017432
PTL4: Japanese Unexamined Patent Application Publication No. 2001-226723
PTL 5: Japanese Unexamined Patent Application Publication No. 8-013129
PTL 6: Japanese Unexamined Patent Application Publication No. 8-232003
PTL 7: Japanese Unexamined Patent Application Publication No. 2013-133504

Summary of Invention

Technical Problem

[0008] According to the method described in PTL 7, it is possible to produce a porous metal body that is suitable for use, for example, as a current collector for a battery, filter, or catalyst carrier, that is excellent in terms of strength and toughness, and that is produced at a low cost and from a wide range of materials.

[0009] However, as a result of diligent studies by the present inventors, it has been found that in the method described in PTL 7, in the case where the content of the metal added is small (e.g., about 5% by mass or less), there is room for improvement from the viewpoint of facilitating control of the concentration. As a result of further studies on this matter, it has been found that, when the resin formed body is removed by burning, some metal particles remain on the surface of the resin formed body and are not incorporated in the metal plating layer. In such a phenomenon, the contraction of the resin formed body on which metal particles are held proceeds faster than the diffusion of metal particles into the metal plating layer, and some metal particles separate from the metal plating layer without being diffused and remain on the inner surface of the skeleton. In particular, the phenomenon is markedly observed in the heat treatment of Cr-based oxide particles.

[0010] The phenomenon described above will be described in detail with reference to Figs. 3A to 3C.

[0011] Figs. 3A to 3C are schematic diagrams, each showing a cross section of a skeleton of a resin formed body during a production step when a porous metal body is produced by the method described in PTL 7.

[0012] First, in order to perform an electrical conduction treatment on the surface of a resin formed body 1, a carbon coating material containing a metal powder 2 is applied onto the surface of the resin formed body 1 (refer to Fig. 3A). Thereby, the surface of the resin formed body 1 is made conductive. Subsequently, coating with a desired metal is performed by electrolytic plating. Thereby, as shown in Fig. 3B, a metal plating layer 3 is formed on the surface of the resin formed body 1. Subsequently, in order to remove the resin formed body 1, a heat treatment is performed. In this process, a phenomenon is observed in which, as shown in Fig. 3C, the resin formed body 1 contracts, and some of the metal particles 2 which have been adhering to the surface of the resin formed body 1 remain adhering to the resin formed body 1 and are not incorporated in the metal plating layer 3.

[0013] This necessitates that metal particles should be added in an amount larger than that required for the desired alloy concentration of the porous metal body.

[0014] Accordingly, it is an object of the present invention to provide a method for producing a nickel alloy porous body, in which, even in the case where the concentration of the metal added to nickel is low, control of the concentration is facilitated, and the added metal can be uniformly diffused into the porous body.

Solution to Problem

[0015] A method for producing a nickel alloy porous body according to an embodiment of the present invention is as follows:

(1) A method for producing a nickel alloy porous body includes:

a step of applying a coating material that contains a nickel alloy powder of nickel and an added metal onto a surface of a skeleton of a resin formed body having a three-dimensional mesh-like structure;
a step of plating with nickel the surface of the skeleton of the resin formed body onto which the coating material has been applied;
a step of removing the resin formed body; and
a step of diffusing the added metal into the nickel by a heat treatment.

Advantageous Effects of Invention

[0016] According to the invention, it is possible to provide a method for producing a nickel alloy porous body, in which, even in the case where the concentration of the metal added to nickel is low, control of the concentration is facilitated, and the added metal can be uniformly diffused into the porous body.

Brief Description of Drawings

[0017]

[Fig. 1A] Figure 1A is a schematic diagram showing a cross section of a skeleton in a state in which a coating

material is applied onto the surface of the skeleton of a resin formed body in a method for producing a nickel alloy porous body according to an embodiment of the present invention.

[Fig. 1B] Figure 1B is a schematic diagram showing a cross section of a skeleton in a state in which the surface of the skeleton of the resin formed body is plated with nickel in the method for producing a nickel alloy porous body according to the embodiment of the present invention.

[Fig. 1C] Figure 1C is a schematic diagram showing a cross section of a skeleton in a step of removing the resin formed body in the method for producing a nickel alloy porous body according to the embodiment of the present invention.

[Fig. 2A] Figure 2A is a photograph showing a cross section of a skeleton of a nickel alloy porous body 1 produced in Example 1 when observed with an electron microscope.

[Fig. 2B] Figure 2B is a photograph showing a cross section of a skeleton of a nickel alloy porous body 2 produced in Example 1 when observed with an electron microscope.

[Fig. 2C] Figure 2C is a photograph showing a cross section of a skeleton of a nickel alloy porous body 3 produced in Example 1 when observed with an electron microscope.

[Fig. 2D] Figure 2D is a photograph showing a cross section of a skeleton of a nickel alloy porous body 4 produced in Example 1 when observed with an electron microscope.

[Fig. 2E] Figure 2E is a photograph showing a cross section of a skeleton of a nickel alloy porous body 9 produced in Comparative Example 1 when observed with an electron microscope.

[Fig. 2F] Figure 2F is a photograph showing a cross section of a skeleton of a nickel alloy porous body 10 produced in Comparative Example 1 when observed with an electron microscope.

[Fig. 2G] Figure 2G is photograph showing a cross section of a skeleton of a nickel alloy porous body 11 produced in Comparative Example 1 when observed with an electron microscope.

[Fig. 2H] Figure 2H is photograph showing a cross section of a skeleton of a nickel alloy porous body 12 produced in Comparative Example 1 when observed with an electron microscope.

[Fig. 3A] Figure 3A is a schematic diagram showing a cross section of a skeleton in a state in which a coating material is applied onto the surface of the skeleton of a resin formed body in an existing method for producing an alloy porous body.

[Fig. 3B] Figure 3B is a schematic diagram showing a cross section of a skeleton in a state in which the surface of the skeleton of the resin formed body is plated with nickel in the existing method for producing an alloy porous body.

[Fig. 3C] Figure 3C is a schematic diagram showing a cross section of a skeleton in a step of removing the resin formed body in the existing method for producing an alloy porous body.

[Fig. 4] Figure 4 is a schematic diagram showing an existing water decomposition device.

[Fig. 5] Figure 5 is a schematic diagram showing a water decomposition device which uses porous metal bodies according to an embodiment of the present invention. Description of Embodiments

[Description of embodiments of the present invention]

[0018] First, the embodiments of the present invention will be enumerated and described below.

(1) A method for producing a nickel alloy porous body according to an embodiment of the present invention includes:

a step of applying a coating material that contains a nickel alloy powder of nickel and an added metal onto a surface of a skeleton of a resin formed body having a three-dimensional mesh-like structure;
a step of plating with nickel the surface of the skeleton of the resin formed body onto which the coating material has been applied;
a step of removing the resin formed body; and
a step of diffusing the added metal into the nickel by a heat treatment.

According to the invention described in (1), it is possible to provide a method for producing a nickel alloy porous body, in which, even in the case where the concentration of the metal added to nickel is low, control of the concentration is facilitated, and the added metal can be uniformly diffused into the porous body.

(2) In the method for producing a nickel alloy porous body according to (1), preferably, the added metal is at least one metal selected from the group consisting of Cr, Sn, Co, Cu, Al, Ti, Mn, Fe, Mo, and W.

According to the invention described in (2), at least one added metal selected from the group consisting of Al, Ti, Cr, Mn, Fe, Co, Cu, Mo, Sn, and W can be uniformly distributed in the nickel porous body, and the concentration thereof can be easily controlled.

(3) In the method for producing a nickel alloy porous body according to (1) or (2), preferably, at least a surface of

the nickel alloy powder is oxidized.

According to the invention described in (3), by decreasing the particle size of the nickel alloy powder, the added metal can be easily diffused into the nickel layer.

(4) In the method for producing a nickel alloy porous body according to any one of (1) to (3), preferably, the coating material that contains the nickel alloy powder further contains a carbon powder.

According to the invention described in (4), the conductivity of the surface of the resin formed body is improved, and nickel plating can be performed easily.

[Detailed description of embodiments of the present invention]

[0019] Specific examples of a method for producing a nickel alloy porous body according to the embodiments of the present invention will be described in detail below. The present invention is not limited to the examples, but is defined by the appended claims, and is intended to include all modifications within the meaning and scope equivalent to those of the claims.

[0020] A method for producing a nickel alloy porous body according to an embodiment of the present invention will be described in detail with reference to Figs. 1A to 1C.

[0021] Figures 1A to 1C are schematic diagrams, each showing a cross section of a skeleton of a resin formed body during a production step when a nickel alloy porous body is produced by the method for producing a nickel alloy porous body according to the embodiment of the present invention.

[0022] First, a resin formed body 1 serving as a base for a nickel alloy porous body is prepared. In order to impart conductivity to a surface of a skeleton of the resin formed body 1, a coating material containing a conductive powder is applied onto the surface of the skeleton of the resin formed body 1. As the conductive powder, an alloy powder 4 including a metal to be added to a nickel porous body and nickel is used (refer to Fig. 1A). Subsequently, a nickel plating layer 3 is formed on the surface of the skeleton of the resin formed body 1. Since the surface of the skeleton of the resin formed body 1 is conductive, the nickel plating layer 3 can be formed by electrolytic plating. Thereby, as shown in Fig. 1B, a layer composed of the nickel alloy powder 4 and the nickel plating layer 3 are formed.

[0023] Then, a heat treatment is performed in order to remove the resin formed body. At this time, the nickel alloy powder 4 on the surface of the skeleton of the resin formed body rapidly starts to diffuse into the nickel plating layer 3. Therefore, when the resin formed body 1 starts to contract, the nickel alloy powder 4 does not move without adhering to the surface of the resin formed body 1, but remains incorporated in the nickel plating layer 1 (refer to Fig. 1C).

[0024] That is, in the existing method, some particles of the metal powder on the surface of the skeleton of the resin formed body are pulled to the surface of the skeleton of the resin formed body before starting to diffuse into the metal plating layer, and are not incorporated in the metal plating layer (refer to Fig. 3C). Such a phenomenon does not occur in the method for producing a nickel alloy porous body according to the embodiment of the present invention, and all of the nickel alloy powder can be effectively used.

[0025] As described above, the method for producing a nickel alloy porous body according to the embodiment of the present invention includes a step of applying a coating material that contains a nickel alloy powder onto a surface of a skeleton of a resin formed body, a step of performing nickel plating, a step of removing the resin formed body, and a step of diffusing the nickel alloy powder into nickel.

[0026] Each of the steps will be described in detail below.

(Step of applying coating material that contains nickel alloy powder)

- Resin formed body -

[0027] As the resin formed body having a three-dimensional mesh-like structure, a resin foam, nonwoven fabric, felt, woven fabric, or the like can be used. As necessary, these may be used in combination. Furthermore, the material that constitutes the resin formed body is not particularly limited, but is preferably a material that can be plated with a metal and then can be removed by a burning treatment. Furthermore, from the viewpoint of handling of the resin formed body, in particular, in a sheet-shaped body, a material having high rigidity may break, and therefore, a material having flexibility is preferable.

[0028] In the method for producing a nickel alloy porous body according to the embodiment of the present invention, it is preferable to use a resin foam as the resin formed body having a three-dimensional mesh-like structure. The resin foam may be a known or commercially available resin foam as long as it is porous. Examples thereof include a urethane foam and a styrene foam. Among these, in particular, a urethane foam is preferable from the viewpoint of a high porosity. The thickness, porosity, and average pore size of the resin foam are not particularly limited and can be appropriately determined depending on the application.

- Nickel alloy powder -

[0029] A nickel alloy powder having a volume-average particle size of 10 μm or less is used for performing an electrical conduction treatment on the surface of the skeleton of the resin formed body. In order to produce a coating material by adding the nickel alloy powder into a binder or solvent, the nickel alloy powder preferably has a smaller volume-average particle size, and more preferably has a volume-average particle size of 3 μm or less. Furthermore, the volume-average particle size may be appropriately selected in accordance with the diameter of the skeleton of a resin formed body to be used.

[0030] In the nickel alloy powder, the added metal that forms an alloy with nickel is not particularly limited, and a desired metal may be selected in accordance with the intended use. For example, it is preferable to use at least one metal selected from the group consisting of Cr, Sn, Co, Cu, Al, Ti, Mn, Fe, Mo, and W.

[0031] In the method for producing a nickel alloy porous body according to the embodiment of the present invention, the nickel alloy powder may be a powder in which nickel and an added metal form a completely homogeneous alloy, or may be a mixed-type powder, a core-shell type powder, or a composite-type powder. In the present invention, all of these types of powder are referred to as the nickel alloy powder.

[0032] The term "mixed-type powder" refers to a powder in which a plurality of single particles of an added metal are present inside a nickel particle, or a powder in which a layer-shaped added metal is present inside a nickel particle. Furthermore, the term "core-shell type powder" refers to a powder in which the surface of a single particle of an added metal is coated with nickel.

[0033] The term "composite-type powder" refers to, for example, a powder which has a core-shell structure composed of an added metal and a nickel alloy, or a powder having a core-shell structure in which a particle-shaped or layer-shaped added metal is partially present.

[0034] In any of the nickel alloy powders, a powder in which most of the surfaces of nickel alloy particles are made of nickel or a homogeneous nickel alloy is used so that the nickel alloy particles can be easily diffused into the nickel plating layer.

[0035] Such a nickel alloy powder can be obtained by a disintegration process for disintegrating a nickel alloy, an atomization process, or the like.

[0036] Preferably, at least a surface of the nickel alloy powder is oxidized.

[0037] In the case where a nickel alloy powder is produced by disintegrating an alloy of nickel and an added metal, a nickel alloy, i.e., a starting material, in an oxidized state is more likely to be disintegrated, and it is possible to obtain a nickel alloy powder having a smaller volume-average particle size. By using such a nickel alloy powder having a small particle size, the added metal can be easily diffused into nickel. Furthermore, regarding the nickel alloy powder obtained by disintegrating the nickel alloy in an oxidized state, at least a surface of the nickel alloy powder is in an oxidized state, and the oxidized metal can be reduced in a heat treatment step in which the added metal is diffused into nickel. Alternatively, it may be possible to perform, separately, a step of reducing metal oxides by carrying out a heat treatment in a reducing atmosphere.

- Carbon powder -

[0038] In the case where at least a surface of the nickel alloy powder is oxidized and the nickel alloy powder is not a conductive powder, preferably, a carbon powder is further added to the coating material. Thereby, the conductivity of the coating material can be enhanced. The volume-average particle size of the carbon powder is preferably 10 μm or less, and more preferably 3 μm or less, as in the nickel alloy porous body. Furthermore, the volume-average particle size may be appropriately selected in accordance with the diameter of the skeleton of a resin formed body.

[0039] Examples of the material of the carbon powder include crystalline graphite and amorphous carbon black. Among these, graphite is particularly preferable from the viewpoint that, in general, graphite tends to have a small particle size.

- Coating material -

[0040] A conductive coating material can be produced by adding the nickel alloy powder and, if necessary, a carbon powder to a binder, followed by mixing.

[0041] In order to perform an electrical conduction treatment on the surface of the resin formed body, the coating material may to be applied onto the surface of the skeleton of the resin formed body. The method of applying the coating material is not particularly limited and, for example, an immersion method or an application method by using a brush or the like may be used. Thereby, a conductive coating layer is formed on the surface of the skeleton of the resin formed body.

[0042] The conductive coating layer may be continuously formed on the surface of the skeleton of the resin formed body. Furthermore, the coating weight of the conductive coating layer is not particularly limited, and is usually about 0.1 to 300 g/m^2, and preferably about 1 to 100 g/m^2.

(Step of performing nickel plating)

[0043] In the step of performing nickel plating, a known plating process can be used, and an electroplating process is preferably used. Instead of the electroplating treatment, if the thickness of a plating film is increased by an electroless plating treatment and/or a sputtering treatment, it may not be necessary to perform an electroplating treatment. However, this is not desirable from the viewpoint of productivity and cost. For this reason, as described above, by employing a method in which a resin formed body is subjected to an electrical conduction treatment, and then a nickel plating layer is formed by an electroplating process, a nickel alloy porous body can be produced with high productivity and at a low cost. Furthermore, it is possible to obtain a highly stable nickel alloy porous body in which the skeleton, in cross section, has a void ratio of less than 1%.

[0044] Furthermore, the plating layer may have a multi-layered structure, and in such a case, a nickel plating layer is formed as a first plating layer. Thereby, the nickel alloy particles can be easily diffused into the nickel plating layer. A metal plating layer may be appropriately formed on the nickel plating layer in accordance with the intended use.

[0045] The nickel plating layer may be formed on the conductive coating layer to such an extent that the conductive coating layer is not exposed. The coating weight of the nickel plating layer is not particularly limited, and may be appropriately selected in accordance with the thickness of the nickel alloy porous body. In order to achieve both strength and a porosity, the coating weight per 1 mm thickness may be usually about 100 to 600 g/m^2, and is more preferably about 200 to 500 g/m^2.

(Step of removing resin formed body)

[0046] By subjecting the composite body of resin and metal obtained through the foregoing steps to a heat treatment in the air, the resin formed body can be removed.

[0047] The heat treatment temperature is preferably 700°C to 1,200°C. When the heat treatment temperature is 700°C or higher, the resin formed body can be removed and the nickel alloy powder can be easily diffused into the nickel plating layer. When the heat treatment temperature is 1,200°C or lower, nickel can be suppressed from being excessively oxidized. From these viewpoints, the heat treatment temperature is more preferably 750°C to 1,100°C, and still more preferably 800°C to 1,050°C.

[0048] Furthermore, the heat treatment time may be appropriately changed depending on the heat treatment temperature. For example, in the case where the heat treatment is performed at 800°C, the resin formed body can be satisfactorily removed in about 10 to 30 minutes.

(Step of diffusing added metal by heat treatment)

[0049] This step is carried out to more uniformly diffuse the added metal incorporated in the nickel plating layer.

[0050] The heat treatment temperature and the heat treatment time may be appropriately selected in accordance with the metal added. For example, in the case where a nickel alloy porous body is produced by using a nickel-chromium alloy powder or nickel-tungsten powder, the heat treatment may be performed at 1,100°C for 30 minutes or more. In the case where an alloy powder of nickel and tin, cobalt, copper, aluminum, titanium, manganese, iron, or molybdenum is used, the heat treatment may be performed at 1,000°C for 15 minutes or more.

[0051] Furthermore, when the heat treatment is performed in a reducing atmosphere by using H_2 gas or the like, the nickel alloy powder or nickel alloy oxide powder and the nickel plating layer can be reduced. The carbon powder contained in the conductive coating layer serves as a strong reducing agent at high temperatures to reduce the nickel alloy powder or nickel alloy oxide powder and the nickel plating layer.

[0052] Furthermore, the heat treatment at the optimal temperature for the optimum period of time suitable for the added metal species allows reduction of the nickel alloy (decrease in the oxygen concentration in the metal) with the carbon powder when used, alloy formation due to thermal diffusion, and coarsening of crystal grains. As a result, the strength and roughness of the nickel alloy porous body are improved, and it is possible to obtain a strong nickel alloy porous body that does not break even when subjected to processing that involves plastic deformation, such as bending or pressing.

EXAMPLES

[0053] The present invention will be described in more detail below on the basis of examples. However, the examples are merely illustrative and the porous metal body of the present invention is not limited thereto. The scope of the present invention is defined by the appended claims, and includes all modifications within the meaning and scope equivalent to those of the claims.

[Example 1]

(Electrical conduction treatment of resin formed body)

[0054] First, as resin formed bodies having a three-dimensional mesh-like structure, polyurethane foam sheets (pore size 0.45 mm) with a thickness of 1.5 mm were prepared. Subsequently, 100 g of graphite with a volume-average particle size of 10 μm, 20 g of carbon black with a volume-average particle size of 0.1 μm, and 100 g of a nickel alloy oxide powder with a volume-average particle size shown in Table 1 were dispersed in 0.5 L of a 10% aqueous solution of an acrylic ester resin, and a viscous coating material was produced at this composition ratio.

[0055] As the nickel alloy oxide powder, a nickel-chromium alloy oxide powder, a nickel-cobalt alloy oxide powder, a nickel-tin alloy oxide powder, and a nickel-copper alloy oxide powder was used. The nickel alloy oxide powders were obtained by oxidizing the corresponding nickel alloy powders and used by disintegrating and classifying the oxidized powders so that the volume-average particle size was 0.5 to 1.5 μm.

[0056] Subsequently, each of the polyurethane foam sheets was continuously immersed in the coating material and squeezed with rolls, followed by drying. In such a manner, the polyurethane foam sheet was subjected to an electrical conduction treatment. Thereby, a conductive coating layer was formed on the surface of the resin formed body having a three-dimensional mesh-like structure. The viscosity of the conductive coating material was adjusted with a thickener, and the coating weight of the coating material was set to be 20 g/m^2 in terms of alloy powder. The coating weight is shown in Table 1.

(Nickel plating step)

[0057] A nickel plating layer was formed by electroplating with 300 g/m^2 on the surface of the skeleton of the resin formed body having a three-dimensional mesh-like structure which had been subjected to the electrical conduction treatment. As the plating solution, a nickel sulfamate plating solution was used.

(Step of removing the resin formed body)

[0058] By performing a heat treatment in the air at 800°C for 15 minutes, the resin formed body was removed by burning. The oxidized porous metal body was reduced by performing a heat treatment in a reducing hydrogen atmosphere at 1,000°C for 15 minutes.

(Step of diffusing added metal)

[0059] By performing a heat treatment in a hydrogen atmosphere at 1,100°C for 30 minutes, the added metal was sufficiently diffused into nickel.

[0060] In such a manner, nickel alloy porous bodies 1 to 4 were produced.

<Evaluation>

[0061] Figures 2A to 2D show the results of observation, by an electron microscope (SEM), of cross sections of skeletons of the nickel alloy porous bodies 1 to 4 obtained as described above. As shown in Figs. 2A to 2D, in each of the nickel alloy porous bodies 1 to 4, it has been confirmed that the added metal particles do not remain on the inner surface of the skeleton of the nickel alloy porous body and that the added metal is uniformly diffused into nickel.

[Example 2]

[0062] Nickel alloy porous bodies 5 to 8 were produced as in Example 1 except that, instead of the nickel-chromium alloy oxide powder, the nickel-cobalt alloy oxide powder, the nickel-tin alloy oxide powder, and the nickel-copper alloy oxide powder, a nickel-chromium alloy powder, a nickel-cobalt alloy powder, a nickel-tin alloy powder, and a nickel-copper alloy powder were used. The volume-average particle size and coating weight of the nickel alloy powders are shown in Table 1.

[0063] Cross sections of skeletons of the nickel alloy porous bodies 5 to 8 were observed by an electron microscope as in Example 1. As a result, it was confirmed that the added metal particles do not remain on the inner surface of the skeleton of the nickel alloy porous body and that the added metal is uniformly diffused into nickel.

[Comparative Example 1]

[0064] Nickel alloy porous bodies 9 to 12 were produced as in Example 1 except that, instead of the nickel-chromium alloy oxide powder, the nickel-cobalt alloy oxide powder, the nickel-tin alloy oxide powder, and the nickel-copper alloy oxide powder, a chromium oxide powder, a cobalt oxide powder, a tin oxide powder, and a copper oxide powder were used. The metal oxide powders were obtained by oxidizing the corresponding metal powders and used by disintegrating and classifying the oxidized powders. The volume-average particle size and coating weight of the oxidized metal powders are shown in Table 1.

[0065] Figures 2E to 2H show the results of observation, by an electron microscope, of cross sections of skeletons of the nickel alloy porous bodies 9 to 12, as in Example 1. As shown in Figs. 2E to 2H, in each of the porous metal bodies 9 to 12, it has been confirmed that some of the added metal particles remain on the inner surface of the skeleton of the nickel alloy porous body.

[Comparative Example 2]

[0066] Nickel alloy porous bodies 13 to 16 were produced as in Example 1 except that, instead of the nickel-chromium alloy oxide powder, the nickel-cobalt alloy oxide powder, the nickel-tin alloy oxide powder, and the nickel-copper alloy oxide powder, a chromium powder, a cobalt powder, a tin powder, and a copper powder were used.

[0067] Cross sections of skeletons of the nickel alloy porous bodies 13 to 16 were observed by an electron microscope as in Example 1. As a result, it was confirmed that some of the added metal particles remain on the inner surface of the skeleton of the nickel alloy porous body.

[Table 1]

Nickel alloy porous body No.	Powder			Added metal content in nickel alloy porous body (mass%)
	Kind	Volume-average particle size (μm)	Coating weight (g/m^2) in terms of metal	
1	Nickel-chromium alloy oxide	0.5	21	3.4
2	Nickel-cobalt alloy oxide	0.7	19	3.1
3	Nickel-tin alloy oxide	0.6	20	3.2
4	Nickel-copper alloy oxide	1.1	22	3.5
5	Nickel-chromium alloy	1.5	23	3.5
6	Nickel-cobalt alloy	1.8	21	3.4
7	Nickel-tin alloy	1.5	20	3.3
8	Nickel-copper alloy	2.3	24	3.7
9	Chromium oxide	0.5	20	3.2
10	Cobalt oxide	0.5	23	3.7
11	Tin oxide	0.6	19	3.1
12	Copper oxide	1.4	18	2.9
13	Chromium	1.4	21	3.3
14	Cobalt	1.5	23	3.7
15	Tin	1.7	20	3.3

(continued)

Nickel alloy porous body No.	Powder			Added metal content in nickel alloy porous body (mass%)
	Kind	Volume-average particle size (μm)	Coating weight (g/m^2) in terms of metal	
16	Copper	2.2	21	3.4

[0068] Besides being used for fuel cells, porous metal bodies which are nickel alloy porous bodies according to the present invention can also be suitably used for the production of hydrogen by water electrolysis.

[0069] Figure 4 is a schematic diagram showing an existing water decomposition device. Current collectors 6 are disposed on both sides of an ion permeable membrane 5. The ion permeable membrane 5 allows mainly hydrogen or oxygen to permeate therethrough. The current collectors 6 each have a gas channel, which is made of a corrugated stainless steel plate, carbon structure having grooves, or the like, on the side thereof in contact with the ion permeable membrane. Steam is introduced into one of the gas channels. For example, hydrogen ions generated from decomposition pass through the ion permeable membrane 5 and are discharged from the gas channel on the opposite side, and oxygen generated from decomposition, together with steam that has not been decomposed, is discharged as is.

[0070] Figure 5 is a schematic diagram showing a water decomposition device which uses porous metal bodies according to an embodiment of the present invention. The water decomposition device has the same structure as that of the existing water decomposition device shown in Fig. 4 except that gas channels are made of porous metal bodies 7. By using current collectors 6 whose gas channels are made of porous metal bodies 7 in such a manner, hydrogen can be efficiently produced by water decomposition compared with the existing device.

(1) In an alkaline electrolysis method, an anode and a cathode are immersed in a strongly alkaline aqueous solution, and water is electrolyzed by applying a voltage. By using a porous metal body as an electrode, the contact area between water and the electrode increases, and the efficiency of water electrolysis can be enhanced. The pore size of the porous metal body is preferably 100 to 5,000 μm. When the pore size is less than 100 μm, removal of bubbles of generated hydrogen/oxygen becomes unsatisfactory, and the area of contact between water and the electrode decreases, resulting in a decrease in efficiency. Furthermore, when the pore size is more than 5,000 μm, the surface area of the electrode decreases, resulting in a decrease in efficiency. From the same viewpoint, the pore size is more preferably 400 to 4,000 μm.

Since a larger electrode area may cause deflection or the like, the thickness and metal content of the porous metal body can be appropriately selected in accordance with the scale of equipment. In order to secure both removal of bubbles and a sufficient surface area, a plurality of porous metal bodies having different pore sizes may be combined for use.

(2) In a PEM method, water is electrolyzed by using a solid polymer electrolyte membrane. An anode and a cathode are placed on both surfaces of the solid polymer electrolyte membrane, and by applying a voltage while feeding water to the anode side, hydrogen ions are generated by electrolysis of water. The hydrogen ions are transported through the solid polymer electrolyte membrane to the cathode side, and are taken out as hydrogen at the cathode side. The operating temperature is about 100°C. The PEM electrolysis device has the same structure as that of a solid polymer-type fuel cell which produces electricity from hydrogen and oxygen and discharges water, but is operated in a completely reverse manner. Since the anode side and the cathode side are completely separated from each other, hydrogen with a high purity can be taken out, which is advantageous. In each of the anode and the cathode, since it is necessary to pass water/hydrogen gas through an electrode, a conductive porous body is required as the electrode.

The porous metal body according to the present invention has a high porosity and good electrical conductivity, and therefore, can be suitably used for PEM water electrolysis as well as suitably used for a solid polymer-type fuel cell. The pore size of the porous metal body is preferably 100 to 5,000 μm. When the pore size is less than 100 μm, removal of bubbles of generated hydrogen/oxygen becomes unsatisfactory, and the area of contact between water and the solid polymer electrolyte decreases, resulting in a decrease in efficiency. Furthermore, when the pore size is more than 5,000 μm, water retention is poor, and water passes through the porous metal body before fully reacting, resulting in a decrease in efficiency. From the same viewpoint, the pore size is more preferably 400 to 4,000 μm.

The thickness and metal content of the porous metal body can be appropriately selected in accordance with the scale of equipment. When the porosity is excessively small, the pressure loss during feeding of water increases. Therefore, the thickness and metal content are preferably adjusted so that the porosity is 30% or more. Furthermore, in this method, since the electrical conduction between the solid polymer electrolyte and the electrode is performed

by pressure bonding, it is necessary to adjust the metal content such that the increase in electrical resistance due to deformation/creeping during application of pressure is within a range that causes no problem in practical use. The metal content is preferably 400 g/m^2 or more. Additionally, in order to secure the porosity and to achieve electrical connection, a plurality of porous metal bodies having different pore sizes may combined for use.

(3) In an SOEC method, water is electrolyzed by using a solid oxide electrolyte membrane, and the structure is different depending on whether the electrolyte membrane is protonically conductive or oxygen ion-conductive. In an oxygen ion-conductive membrane, since hydrogen is generated at the cathode side into which steam is fed, the hydrogen purity decreases. Therefore, from the viewpoint of hydrogen production, a protonically conductive membrane is preferable. An anode and a cathode are placed on both sides of a protonically conductive membrane, and by applying a voltage while introducing steam to the anode side, hydrogen ions are generated by electrolysis of water. The hydrogen ions are transported through the solid oxide electrolyte membrane to the cathode side, and hydrogen alone is taken out at the cathode side. The operating temperature is about 600°C to 800°C. The SOEC electrolysis device has the same structure as that of a solid oxide fuel cell which produces electricity from hydrogen and oxygen and discharges water, but is operated in a completely reverse manner. In each of the anode and the cathode, since it is necessary to pass steam/hydrogen gas through an electrode, a porous body that is conductive and that can withstand a high-temperature oxidizing atmosphere, in particular, at the anode side is required as the electrode.

[0071] The porous metal body according to the present invention has a high porosity, good electrical conductivity, high oxidation resistance, and high heat resistance, and therefore, can be suitably used for SOEC water electrolysis as well as suitably used for a solid oxide fuel cell. It is preferable to use a Ni alloy to which a metal having high oxidation resistance, such as Cr, is added for the electrode on the side subjected to an oxidizing atmosphere. The pore size of the porous metal body is preferably 100 to 5,000 μm. When the pore size is less than 100 μm, flow of steam or generated hydrogen becomes unsatisfactory, and the area of contact between steam and the solid oxide electrolyte decreases, resulting in a decrease in efficiency. Furthermore, when the pore size is more than 5,000 μm, since the pressure loss excessively decreases, steam passes through the porous metal body before fully reacting, resulting in a decrease in efficiency. From the same viewpoint, the pore size is more preferably 400 to 4,000 μm.

[0072] The thickness and metal content of the porous metal body can be appropriately selected in accordance with the scale of equipment. When the porosity is excessively small, the pressure loss during feeding of steam increases. Therefore, the thickness and metal content are preferably adjusted so that the porosity is 30% or more. Furthermore, in this method, since the electrical connection between the solid oxide electrolyte and the electrode is performed by pressure bonding, it is necessary to adjust the metal content such that the increase in electrical resistance due to deformation/creeping during application of pressure is within a range that causes no problem in practical use. The metal content is preferably 400 g/m^2 or more. Additionally, in order to secure the porosity and to achieve electrical connection, a plurality of porous metal bodies having different pore sizes may combined for use.

- Appendixes -

(Water decomposition device)

[0073] A water decomposition device including:

a current collector including a nickel alloy porous body,
the nickel alloy porous body being produced through a step of applying a coating material that contains a nickel alloy powder of nickel and an added metal onto a surface of a skeleton of a resin formed body having a three-dimensional mesh-like structure, a step of plating with nickel the surface of the skeleton of the resin formed body onto which the coating material has been applied, a step of removing the resin formed body, and a step of diffusing the added metal into the nickel by a heat treatment; and
an ion permeable membrane having the current collector on each of two sides thereof.

(Water decomposition method)

[0074] A water decomposition method including:

a step of preparing a current collector including a nickel alloy porous body,
the nickel alloy porous body being produced through a step of applying a coating material that contains a nickel alloy powder of nickel and an added metal onto a surface of a skeleton of a resin formed body having a three-dimensional mesh-like structure, a step of plating with nickel the surface of the skeleton of the resin formed body

onto which the coating material has been applied, a step of removing the resin formed body, and a step of diffusing the added metal into the nickel by a heat treatment;
a step of forming an ion permeable membrane having the current collector on each of two sides thereof; and
a step of introducing steam into the current collector and taking out hydrogen that has passed through the ion permeable membrane.

Industrial Applicability

[0075] Nickel alloy porous bodies according to the present invention have excellent mechanical properties and high corrosion resistance and can be produced at a reduced cost. Therefore, the nickel alloy porous bodies can be suitably used as current collectors for secondary batteries, such as lithium-ion batteries, capacitors, and fuel cells, and water decomposition devices.

Reference Signs List

[0076]

1 cross section of resin formed body
2 metal powder
3 nickel plating layer
4 alloy powder
5 ion permeable membrane
6 current collector
7 porous metal body

Claims

1. A method for producing a nickel alloy porous body comprising:

a step of applying a coating material that contains a nickel alloy powder of nickel and an added metal onto a surface of a skeleton of a resin formed body having a three-dimensional mesh-like structure;
a step of plating with nickel the surface of the skeleton of the resin formed body onto which the coating material has been applied;
a step of removing the resin formed body; and
a step of diffusing the added metal into the nickel by a heat treatment.

2. The method for producing a nickel alloy porous body according to Claim 1, wherein the added metal is at least one metal selected from the group consisting of Cr, Sn, Co, Cu, Al, Ti, Mn, Fe, Mo, and W.

3. The method for producing a nickel alloy porous body according to Claim 1 or 2, wherein at least a surface of the nickel alloy powder is oxidized.

4. The method for producing a nickel alloy porous body according to any one of Claims 1 to 3, wherein the coating material that contains the nickel alloy powder further contains a carbon powder.

FIG. 1A

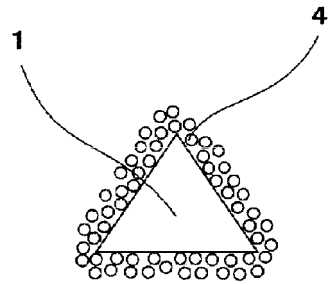


FIG. 1B

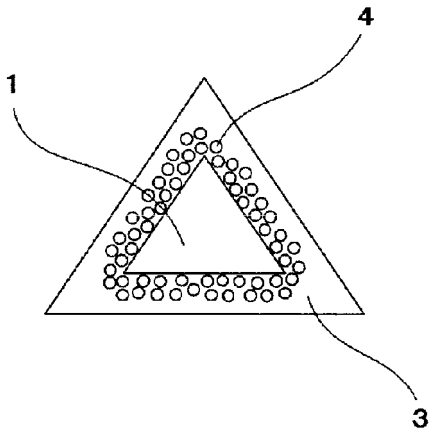


FIG. 1C

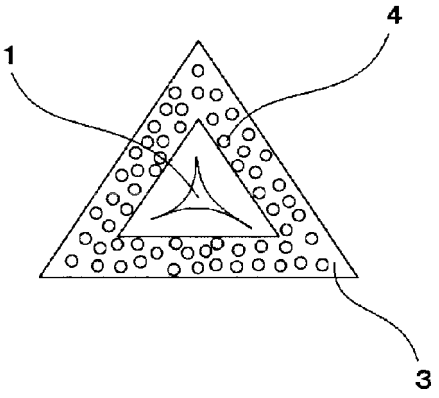


FIG. 2A

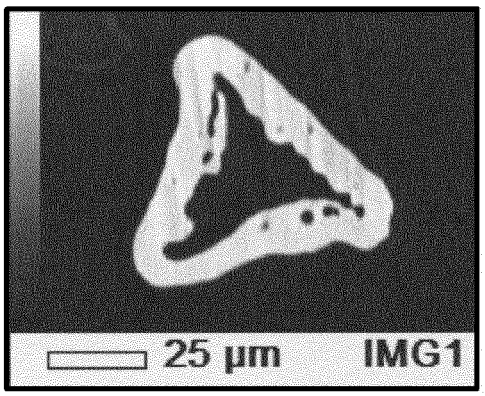


FIG. 2B

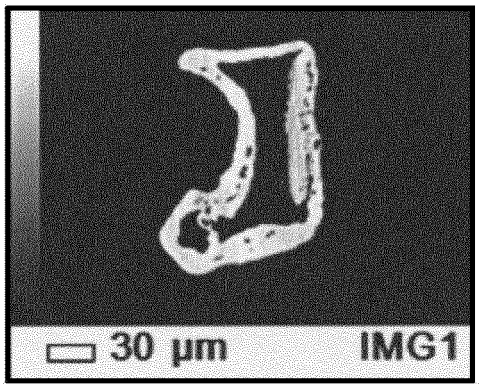


FIG. 2C

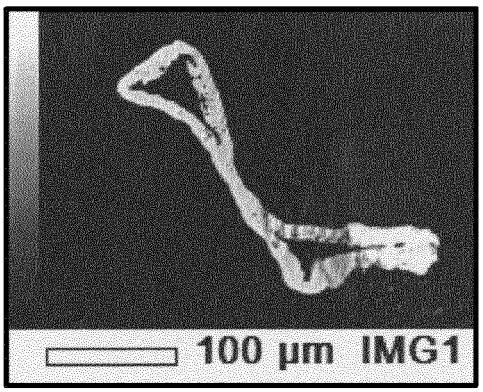


FIG. 2D

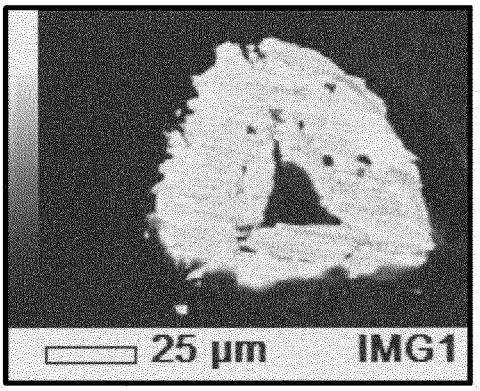


FIG. 2E

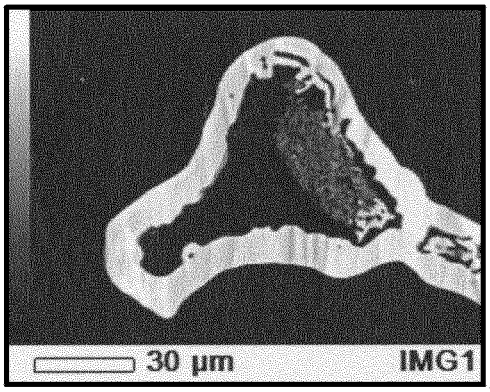


FIG. 2F

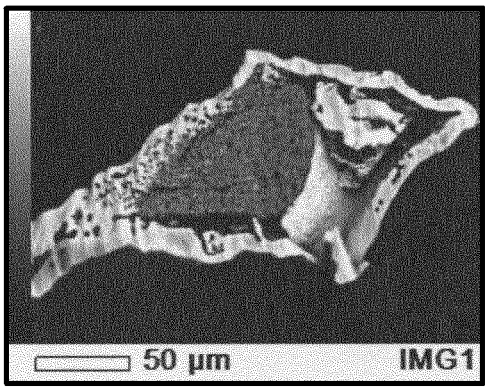


FIG. 2G

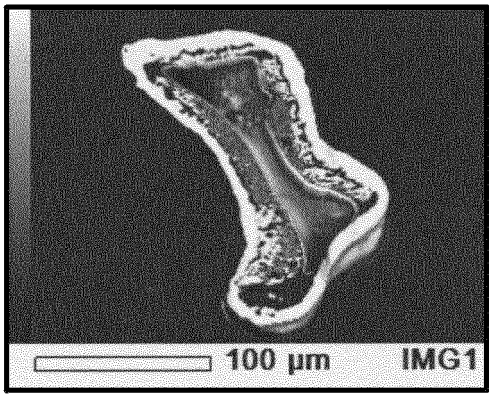


FIG. 2H

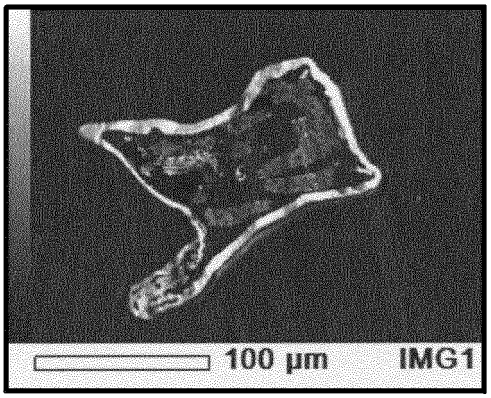


FIG. 3A

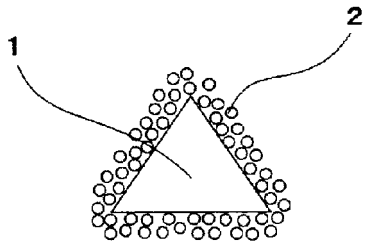


FIG. 3B

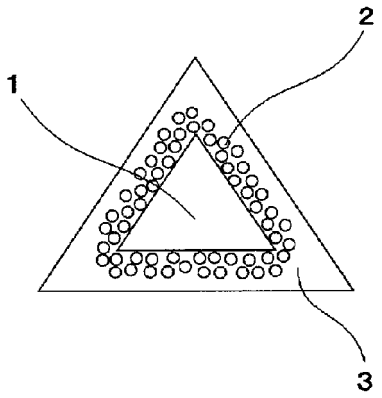


FIG. 3C

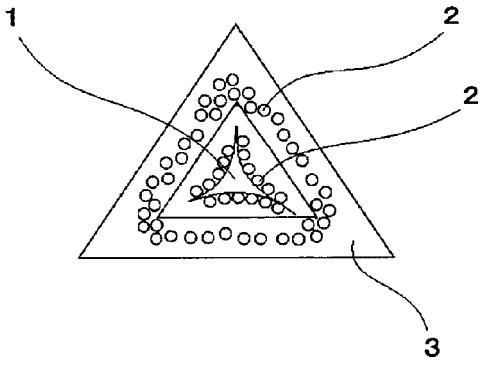


FIG. 4

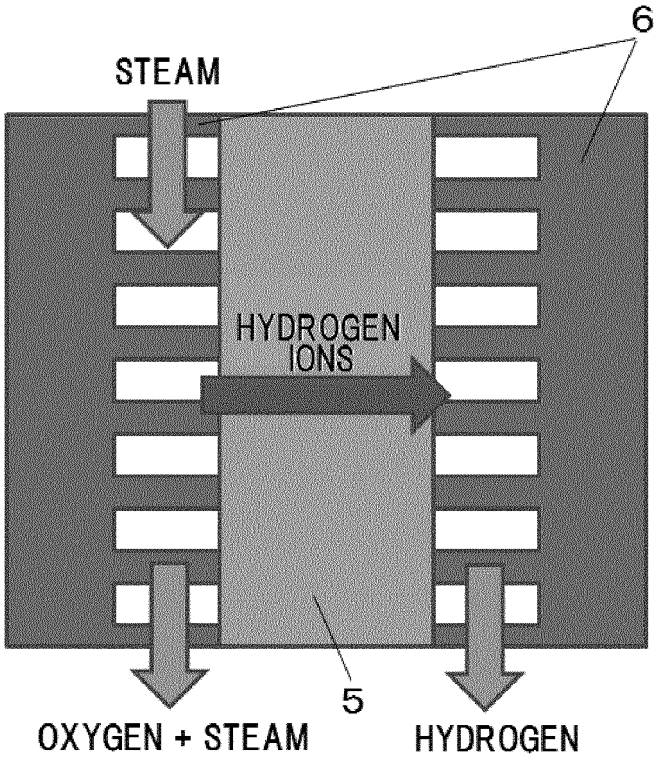
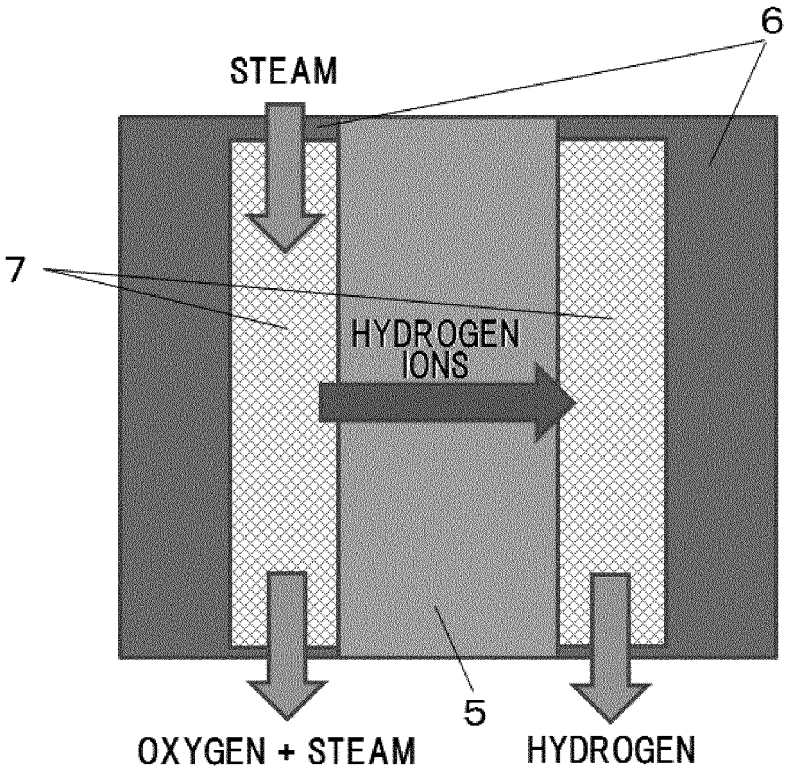

6
STEAM
HYDROGEN
IONS
5
OXYGEN + STEAM
HYDROGEN

FIG. 5


6
STEAM
7
HYDROGEN
IONS
5
OXYGEN + STEAM
HYDROGEN

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/051784

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/08(2006.01)i, *B22F1/00*(2006.01)i, *C22C1/08*(2006.01)i, *C25D5/50*(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)
C25D1/08, B22F1/00, C22C1/08, C25D5/50

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 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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	JP 2013-133504 A (Sumitomo Electric Toyama Co., Ltd.), 08 July 2013 (08.07.2013), claims 1 to 8; paragraphs [0001], [0012] to [0031]; fig. 1, 2 & US 2014/0335441 A1 paragraphs [0001], [0014] to [0056]; fig. 1, 2 & WO 2013/099532 A1 & DE 112012005501 T & CN 104024484 A & KR 10-2014-0109885 A	1-4
Y	JP 2003-147570 A (Sumitomo Electric Industries, Ltd.), 21 May 2003 (21.05.2003), claims 1, 5, 6; paragraph [0022] (Family: none)	1-4

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 February 2016 (23.02.16)	08 March 2016 (08.03.16)
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)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/051784

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 7-150270 A (Sumitomo Electric Industries, Ltd.), 13 June 1995 (13.06.1995), entire text (Family: none)	1-4

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 9017432 A **[0004] [0007]**
- JP 2001226723 A **[0004] [0007]**
- JP 8013129 A **[0005] [0007]**
- JP 8232003 A **[0005] [0007]**
- JP 2013133504 A **[0006] [0007]**