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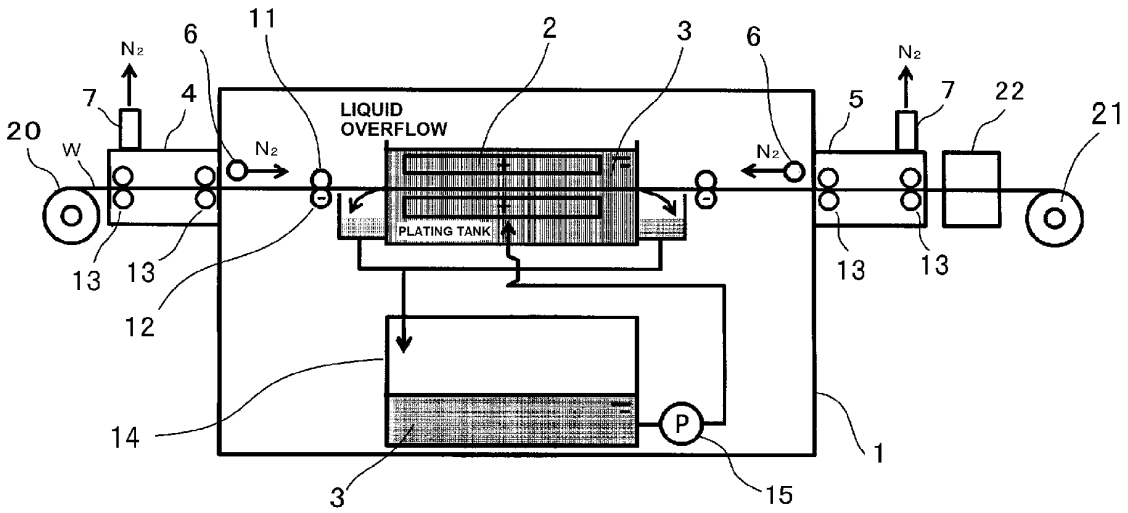
(54) ALUMINUM FILM MANUFACTURING METHOD AND MANUFACTURING DEVICE

(57) Provided are a manufacturing method and a manufacturing apparatus for an aluminum film in which moisture and oxygen do not intrude into a plating chamber. A manufacturing method for an aluminum film, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, includes a step of transferring the substrate W into a plating chamber 1 through a sealing chamber 4 disposed on the entrance side of the plating chamber; a step of electrodepositing an aluminum film on the surface of the substrate W in the plating chamber 1; and a step of transferring the substrate having the aluminum film electrodeposited thereon from the plating chamber 1 through a sealing chamber 5 disposed on the exit side of the plating chamber 1, in which an inert gas is supplied into the plating chamber such that the plating chamber has a positive pressure relative to outside air, and the inert gas is forcibly discharged from an inert gas exhaust pipe 7 provided on each of the two sealing chambers.

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(Cont. next page)

FIG. 1


N2
6
11
2
3
6
N2
7
4
LIQUID
OVERFLOW
5
7
22
21
20
W
N2
N2
PLATING TANK
13
13
12
13
13
14
P
1
3
15

Description

Technical Field

[0001] The present invention relates to a manufacturing method and a manufacturing apparatus for an aluminum film in which a surface of a long, porous resin substrate is electroplated with aluminum to form an aluminum film on the substrate.

Background Art

[0002] Aluminum is passivated by the formation of a dense oxide film on its surface to exhibit excellent corrosion resistance. Therefore, corrosion resistance is enhanced by plating surfaces of steel strips and the like with aluminum.

[0003] For example, in order to perform aluminum plating on surfaces of a steel strip, first, the steel strip is continuously supplied to a plating chamber, passed around a conductor roll, and made to travel between anodes immersed in a plating solution inside the plating chamber. At this moment, the steel strip itself is electrically connected such that it acts as a cathode. Therefore, electrolysis occurs between the steel strip, which is the cathode, and the anodes, and aluminum is electrodeposited on the surfaces of the steel strip to achieve aluminum plating. The direction of the steel strip travelling in the plating solution is changed by a turn roll, and then, the steel strip travels upward. In this case, plating is also performed between the cathode and the anodes. After the aluminum-plated steel strip leaves the plating chamber, it is passed around another conductor roll and taken out of the system (refer to Patent Literature 1 and 2).

[0004] Furthermore, an aluminum porous body having a three-dimensional mesh-like structure is a promising material for improving the capacity of a positive electrode of a lithium-ion battery. Currently, by utilizing excellent characteristics of aluminum, such as electrical conductivity, corrosion resistance, and lightweight properties, an aluminum foil whose surface is coated with an active material, such as lithium cobalt oxide, is used as the positive electrode of a lithium-ion battery. By forming the positive electrode using a porous body composed of aluminum, the surface area can be increased and the inside of the aluminum porous body can also be filled with the active material. Thereby, even if the thickness of the electrode is increased, the active material utilization ratio does not decrease, and the active material utilization ratio per unit area is improved, enabling improvement in the capacity of the positive electrode.

[0005] The present applicant has proposed, as a manufacturing method for such an aluminum porous body, a method of electroplating a resin molded body having a three-dimensional mesh-like structure with aluminum (refer to Patent Literature 3). The existing aluminum molten salt bath needs to be heated to a high temperature. Therefore, when an attempt is made to electroplate the surface of a resin molded body with aluminum, the resin cannot endure the high temperature and melts, which is a problem. However, according to the method described in Patent Literature 2, by mixing an organic chloride salt, such as 1-ethyl-3-methylimidazolium chloride (EMIC) or 1-butylpyridinium chloride (BPC), and aluminum chloride ($AlCl_3$), an aluminum bath that is liquid at room temperature is formed, and it becomes possible to electroplate a resin molded body with aluminum. In particular, an EMIC-$AlCl_3$-based solution exhibits good liquid characteristics and is useful as an aluminum plating solution.

[0006] In a continuous electroplating apparatus in which a molten salt is used as a plating solution, when the molten salt which is a plating solution comes into contact with air, it reacts with and absorbs moisture in air to generate reaction products. As a result, functions required of a plating solution are impaired. In particular, when a chloride-based molten salt is used for aluminum-based plating, the molten salt reacts with moisture in air to form hydrogen chloride, causing problems, such as a deterioration in the working environment and corrosion of components of a plating apparatus. Furthermore, since metallic aluminum is very apt to be oxidized, the aluminum film formed on the surface of a substrate also reacts with a small amount of dissolved oxygen contained in the plating solution to form aluminum oxide. When such reactions occur simultaneously with growth of a plating film, aluminum crystal grains are changed, resulting in problems such as a decrease in the mechanical strength of the plating film and a degradation in electrical conductivity.

[0007] Accordingly, in a continuous electroplating apparatus in which a molten salt is used as a plating solution, as shown in Fig. 7, sealing chambers 4 and 5, each provided with two pairs of seal rolls, are disposed in an entrance section and an exit section of a plating chamber 1 for a long sheet W (hereinafter also referred to as the "work piece"), and thereby, plating is carried out in a closed system completely blocked off from outside air (refer to Patent Literature 4).

Citation List

Patent Literature

[0008]

PTL 1: Japanese Unexamined Patent Application Publication No. 5-222599

PTL2: Japanese Unexamined Patent Application Publication No. 5-186892
PTL 3: Japanese Unexamined Patent Application Publication No. 2012-007233
PTL 4: Japanese Unexamined Patent Application Publication No. 2000-87287

Summary of Invention

Technical Problem

[0009] The present inventors have produced an aluminum film manufacturing apparatus, such as the one shown in Fig. 7, which includes a plating chamber 1 and sealing chambers 4 and 5 disposed in a work piece entrance section and a work piece exit section of the plating chamber 1, each of the sealing chambers 4 and 5 having two pairs of seal rolls and being filled with N_2 gas. Using this apparatus, in which in order to further ensure that moisture and oxygen do not enter the plating chamber from outside air, the N_2 gas pressure in the plating chamber is set to a positive pressure, a resin molded body having a three-dimensional mesh-like structure has been electroplated with aluminum. As a result, it has been found that slight amounts of moisture and oxygen still intrude into the electrolysis chamber, which is a problem.
[0010] In view of the problem described above, an object of the present invention is to provide a manufacturing method and a manufacturing apparatus for an aluminum film in which moisture and oxygen do not intrude into a plating chamber.

Solution to Problem

[0011] The present inventors have performed thorough studies in order to solve the problem described above, and have found that, by providing sealing chambers on the substrate entrance side and substrate exit side of a plating chamber, supplying an inert gas into the plating chamber such that the plating chamber has a positive pressure relative to outside air, and forcibly discharging the inert gas from an inert gas exhaust pipe provided on each of the two sealing chambers, it is possible to prevent intrusion of moisture into the plating chamber. Thus, the present invention has been accomplished.
[0012] In order to solve the problem described above, the present invention employs the following features.
[0013] That is, a manufacturing method for an aluminum film according to the present invention, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, includes a step of transferring the substrate into a plating chamber through a sealing chamber disposed on the entrance side of the plating chamber; a step of electrodepositing an aluminum film on the surface of the substrate in the plating chamber; and a step of transferring the substrate having the aluminum film electrodeposited thereon from the plating chamber through a sealing chamber disposed on the exit side of the plating chamber, in which an inert gas is supplied into the plating chamber such that the plating chamber has a positive pressure relative to outside air, and the inert gas is forcibly discharged from an inert gas exhaust pipe provided on each of the two sealing chambers.
[0014] In another aspect of the present invention, a manufacturing apparatus for an aluminum film, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, includes a plating chamber; a sealing chamber disposed on the substrate entrance side of the plating chamber and a sealing chamber disposed on the substrate exit side of the plating chamber; an inert gas supply pipe which is provided on the plating chamber and supplies an inert gas into the plating chamber; and an inert gas exhaust pipe which is provided on each of the two sealing chambers and forcibly discharges the inert gas in the sealing chamber.

Advantageous Effects of Invention

[0015] According to the present invention, in a manufacturing method and a manufacturing apparatus for an aluminum film in which aluminum is electrodeposited on a substrate using a molten salt electrolytic solution, it is possible to reliably prevent moisture and oxygen from intruding into a plating chamber.

Brief Description of Drawings

[0016]

[Fig. 1] Figure 1 is a diagram showing an example of an aluminum film manufacturing apparatus according to an embodiment of the present invention.
[Fig. 2] Figure 2 is a diagram showing an example of an aluminum film manufacturing apparatus according to an embodiment of the present invention.
[Fig. 3] Figure 3 is a diagram showing an example of an aluminum film manufacturing apparatus according to an embodiment of the present invention.

[Fig. 4] Figure 4 is a diagram showing an example of an aluminum film manufacturing apparatus according to an embodiment of the present invention.
[Fig. 5] Figure 5 is a diagram showing an example of an aluminum film manufacturing apparatus according to an embodiment of the present invention.
[Fig. 6] Figure 6 is a diagram showing an example of a structure of a sealing chamber used in an embodiment of the present invention.
[Fig. 7] Figure 7 is a diagram showing an aluminum film manufacturing apparatus which does not have the features of the present invention.
[Fig. 8] Figure 8 is a flowchart showing a production process of an aluminum porous body.
[Fig. 9] Figure 9 includes cross-sectional schematic views illustrating the production process of an aluminum porous body.
[Fig. 10] Figure 10 is a diagram illustrating an example of a step of continuously imparting electrical conductivity to surfaces of a resin porous body using an electrically conductive coating material.
[Fig. 11] Figure 11 is a diagram showing a metal porous body having a three-dimensional mesh-like structure including interconnected pores.

Description of Embodiments

[0017] First, contents of embodiments of the present invention will be enumerated and described.

(1) A manufacturing method for an aluminum film according to an embodiment of the present invention, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, includes
a step of transferring the substrate into a plating chamber through a sealing chamber disposed on the entrance side of the plating chamber;
a step of electrodepositing an aluminum film on the surface of the substrate in the plating chamber; and
a step of transferring the substrate having the aluminum film electrodeposited thereon from the plating chamber through a sealing chamber disposed on the exit side of the plating chamber,
in which an inert gas is supplied into the plating chamber such that the plating chamber has a positive pressure relative to outside air, and
the inert gas is forcibly discharged from an inert gas exhaust pipe provided on each of the two sealing chambers.
According to this embodiment, by forcibly discharging moisture and oxygen that have intruded into the sealing chambers by means of an inert gas stream, it is possible to reliably prevent intrusion of moisture and oxygen in outside air into the plating chamber. Therefore, a high-quality aluminum plating film can be obtained, and generation of harmful substances, such as hydrogen chloride, can be prevented.
(2) A manufacturing method for an aluminum film according to an embodiment of the present invention is the manufacturing method for an aluminum film stated in (1) above, in which the inert gas exhaust pipe is provided at the substrate entrance side in the sealing chamber disposed on the entrance side, and the inert gas exhaust pipe is provided at the substrate exit side in the sealing chamber disposed on the exit side.
According to this embodiment, moisture and oxygen intruding from outside into each of the sealing chamber can be discharged together with the inert gas before they intrude into the plating chamber.
(3) A manufacturing method for an aluminum film according to an embodiment of the present invention is the manufacturing method for an aluminum film stated in (1) or (2) above, in which an inert gas supply pipe that supplies an inert gas is further provided on each of the two sealing chambers.
According to this embodiment, since the flow rate of the inert gas in each of the sealing chambers can be increased, it is possible to more reliably prevent intrusion of moisture and oxygen into the plating chamber.
(4) A manufacturing method for an aluminum film according to an embodiment of the present invention is the manufacturing method for an aluminum film stated in (3) above, in which the inert gas supply pipe is provided at the substrate exit side in the sealing chamber disposed on the entrance side, and the inert gas supply pipe is provided at the substrate entrance side in the sealing chamber disposed on the exit side.
According to this embodiment, since the flow rate of the inert gas moving from the plating chamber side toward the exhaust pipe side in each of the sealing chambers can be further increased, it is possible to more reliably prevent intrusion of moisture and oxygen into the plating chamber.
(5) A manufacturing method for an aluminum film according to an embodiment of the present invention is the manufacturing method for an aluminum film stated in any one of (1) to (4) above, in which the substrate entrance and the substrate exit of each of the two sealing chambers are sealed with seal rolls.
According to this embodiment, since the outside air intrusion prevention effect by means of seal rolls is obtained, it is possible to further reliably prevent intrusion of moisture and oxygen into the plating chamber.

(6) A manufacturing apparatus for an aluminum film according to an embodiment of the present invention, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, includes
a plating chamber;
a sealing chamber disposed on the substrate entrance side of the plating chamber and a sealing chamber disposed on the substrate exit side of the plating chamber;
an inert gas supply pipe which is provided on the plating chamber and supplies an inert gas into the plating chamber; and
an inert gas exhaust pipe which is provided on each of the two sealing chambers and forcibly discharges the inert gas in the sealing chamber.

[0018] According to this embodiment, by forcibly discharging moisture and oxygen that have intruded into the sealing chambers by means of an inert gas stream, it is possible to reliably prevent intrusion of moisture and oxygen in outside air into the plating chamber. Therefore, a high-quality aluminum plating film can be obtained, and generation of harmful substances, such as hydrogen chloride, can be prevented.

[0019] Note that, in order to prevent the plating solution from mixing with moisture and oxygen, it is necessary to constantly supply the inert gas into the plating chamber or the sealing chambers and forcibly discharge the inert gas in the sealing chambers regardless of the presence or absence of a substrate transferred into the plating chamber. The reasons for this are to prevent a phenomenon in which, when moisture is mixed into the plating solution, the plating solution and moisture react with each other to form reaction products and functions required of a plating solution are impaired, and to prevent a phenomenon in which, when oxygen is mixed into the plating solution, the aluminum film formed during plating reacts with a small amount of dissolved oxygen contained in the plating solution to form aluminum oxide.

[0020] A manufacturing method and a manufacturing apparatus for an aluminum film according to the present invention will be described in detail.

[0021] It is intended that the scope of the present invention is determined not by this but by appended claims, and includes all variations of the equivalent meanings and ranges to the claims.

[0022] In the case where an aluminum film is formed by plating on an ordinary substrate, moisture can be sufficiently blocked by a sealing chamber provided with seal rolls only. However, in the case where a resin molded body having a three-dimensional mesh-like structure (hereinafter, also referred to as the "resin porous body") is electroplated with aluminum, seal rolls alone do not provide a sufficient moisture blocking effect.

[0023] The reason for this is assumed to be that the resin molded body placed between seal rolls is porous with interconnected pores, and moisture and oxygen held in the interconnected pores are introduced into the plating chamber. The other reason for this is assumed to be that because of the concentration gradient between the concentration of moisture and oxygen in the nitrogen atmosphere in the plating chamber and the concentration of moisture or oxygen in outside air, moisture and oxygen pass through the interconnected pores and diffuse into the plating chamber.

[0024] In particular, in the case where a rinsing device is provided at the downstream side of the exit side sealing chamber in order to remove the plating solution remaining on the surface of the substrate having an aluminum film formed thereon, it is assumed that moisture intrudes into the plating chamber because of the phenomenon described above.

[0025] Accordingly, the present inventors have configured an apparatus such that sealing chambers are disposed on the entrance side and the exit side of a plating chamber containing a plating solution, an exhaust pipe is provided on each of the sealing chambers, and by forcibly discharging an inert gas blowing off from the plating chamber through the exhaust pipe, a gas stream is formed in the sealing chamber. Consequently, it has been possible to prevent intrusion of moisture and oxygen into the plating chamber.

[0026] A description will be made on the general outline of steps of producing an aluminum film by electroplating a resin molded body having a three-dimensional mesh-like structure (hereinafter, also referred to as the "resin porous body") with aluminum, and also a detailed description will be made on a specific structure of a sealing chamber in the present invention.

(General outline of production process of aluminum film)

[0027] In a manufacturing apparatus for an aluminum film according to the present invention, a substrate is transferred into a plating solution contained in a plating chamber, and aluminum is electrodeposited on the substrate to form an aluminum film on the substrate.

[0028] Figure 8 is a flowchart showing a production process of an aluminum porous body. Furthermore, Fig. 9, which corresponds to the flowchart, includes schematic views illustrating the state in which, using, as a core, a porous resin substrate (hereinafter, may be referred to as the "resin porous body") serving as a substrate, an aluminum film is formed.

With reference to the two drawings, the flow of the entire production process will be described.

[0029] First, preparation of a resin porous body 101 is performed. Figure 9(a) is an enlarged schematic view showing a surface of a resin porous body having interconnected pores, as an example of a resin porous body. Pores are formed with a resin porous body 31 serving as a skeleton. Next, impartment of electrical conductivity to the surface of the resin porous body 102 is performed. By way of this step, as shown in Fig. 9(b), a conductive layer 32 composed of an electric conductor is thinly formed on the surface of the resin porous body 1.

[0030] Subsequently, aluminum plating in a molten salt 103 is performed to form an aluminum film 33 on the surface of the resin porous body provided with the conductive layer (Fig. 9(c)). Thereby, an aluminum structure which includes the resin porous body serving as a substrate and the aluminum film 33 formed on the surface thereof is obtained. As necessary, removal of the substrate resin 104 from the aluminum structure is performed.

[0031] By causing the resin porous body 31 to disappear by decomposition or the like, an aluminum porous body 33 in which a metal layer only remains can be obtained (Fig. 9(d)).

[0032] The individual steps will be described in order below.

(Preparation of porous resin substrate)

[0033] A resin porous body having a three-dimensional mesh-like structure and interconnected pores is prepared. As the material for the resin porous body, any resin can be selected. For example, a resin foam molded body of polyurethane, melamine, polypropylene, polyethylene, or the like can be used. Although expressed as the resin foam molded body, a resin molded body having any shape can be selected as long as it has continuous pores (interconnected pores). For example, a body having a nonwoven fabric-like shape in which resin fibers are entangled with each other can be used instead of the resin foam molded body. Preferably, the resin foam molded body has a porosity of 80% to 98% and a pore diameter of 50 to 500 μm. A urethane foam and a melamine foam have a high porosity, an interconnecting property of pores, and excellent heat decomposability, and thus can be suitably used as a resin foam molded body.

[0034] A urethane foam is preferable in terms of uniformity of pores, availability, and the like, and a melamine foam is preferable in terms of being able to obtain pores having a small pore diameter.

[0035] In many cases, the resin porous body has residues, such as a foaming agent and unreacted monomers, in the foam production process, and it is preferable to carry out cleaning treatment for the subsequent steps. The substrate resin, which serves as a skeleton, forms a three-dimensional meshes, and thus, as a whole, continuous pores are formed. In the skeleton of the urethane foam, a cross section perpendicular to the direction in which the skeleton extends has a substantially triangular shape. Herein, the porosity is defined by the following formula:

$$\text{Porosity} = (1 - (\text{weight of resin porous body [g]}/(\text{volume of resin porous body [cm}^3\text{]} \times \text{material density}))) \times 100\ [\%]$$

[0036] Furthermore, the pore diameter is determined by a method in which a magnified surface of a resin porous body is obtained by a photomicroscope or the like, the number of pores per inch (25.4 mm) is calculated as the number of cells, and an average value is obtained by the formula: average pore diameter = 25.4 mm/number of cells.

(Impartment of electrical conductivity to surface of resin porous body)

[0037] In order to perform electroplating, the surface of the resin porous body is subjected to electrical conductivity-imparting treatment in advance. In the present invention, electrical conductivity-imparting treatment is carried out by applying an electrically conductive coating material containing electrically conductive particles of carbon or the like to the surface of the resin porous body.

[0038] First, a carbon coating material as an electrically conductive coating material is prepared. A suspension as the electrically conductive coating material preferably contains carbon particles, a binder, a dispersant, and a dispersion medium. In order to perform application of electrically conductive particles uniformly, the suspension needs to maintain a uniformly suspended state. Accordingly, the suspension is preferably maintained at 20°C to 40°C. The reason for this is that, when the temperature of the suspension is lower than 20 °C, the uniformly suspended state is lost, and a layer is formed such that only the binder is concentrated on the surface of the skeleton constituting the mesh-like structure of the resin porous body. In this case, the layer of carbon particles applied is easily peeled off, and it is difficult to form firmly adhering metal plating. On the other hand, when the temperature of the suspension exceeds 40°C, the amount of evaporation of the dispersion medium is large, the suspension becomes concentrated as application treatment time passes, and the carbon coating amount is likely to change. Furthermore, the particle size of carbon particles is 0.01 to 5 μm, and preferably 0.01 to 0.5 μm. When the particle size is large, the particles may clog pores of the resin porous

body or block smooth plating. When the particle size is excessively small, it is difficult to secure sufficient electrical conductivity.

[0039] Application of carbon particles to a resin porous body can be performed by immersing the target resin porous body in the suspension, followed by squeezing and drying.

[0040] Figure 10 is a schematic diagram showing an example of a structure of treatment equipment that imparts electrical conductivity to a strip-shaped resin porous body serving as a skeleton, which is one example of a practical production process. As shown in the drawing, the equipment includes a supply bobbin 52 that supplies a long substrate resin (hereinafter also referred to as the "strip-shaped resin") 51, a tank 55 that contains an electrically conductive coating material suspension 54, a pair of squeezing rolls 57 placed above the tank 55, a plurality of hot air nozzles 56 disposed on the sides of the travelling strip-shaped resin 51 in an opposing manner, and a take-up bobbin 58 that takes up the treated strip-shaped resin 51. Furthermore, deflector rolls 53 for guiding the strip-shaped resin 51 are appropriately placed. In the equipment having the structure described above, the strip-shaped resin 51 having a three-dimensional mesh-like structure is unwound from the supply bobbin 52, guided by a deflector roll 53, and immersed in the suspension 54 in the tank 55. The strip-shaped resin 51 immersed in the suspension 54 in the tank 55 is directed upward and travels between the squeezing rolls 57 located above the surface of the suspension 54. At this stage, the distance between the squeezing rolls 57 is smaller than the thickness of the strip-shaped resin 51, and the strip-shaped resin 51 is compressed. Consequently, the excess suspension impregnated in the strip-shaped resin 51 is squeezed out and returns back into the tank 55.

[0041] Subsequently, the travelling direction of the strip-shaped resin 51 is changed again. Then, the dispersion medium and the like of the suspension are removed by hot air jetted from the hot air nozzles 56 including a plurality of nozzles, and after the strip-shaped resin 51 is thoroughly dried, it is taken up by the take-up bobbin 58. Note that the temperature of hot air jetted from the hot air nozzles 56 is preferably in the range of 40°C to 80°C. By using such equipment, electrical conductivity-imparting treatment can be carried out automatically and continuously, and it is possible to form a skeleton having a mesh-like structure free from clogging and provided with a uniform conductive layer. Therefore, the subsequent step of metal plating can be smoothly performed.

(Formation of aluminum film: molten salt plating)

[0042] Next, electrolytic plating is performed in a molten salt to form an aluminum film on the surface of the resin porous body.

[0043] By performing aluminum plating in a molten salt bath, it is possible to form a thick aluminum film uniformly, in particular, on the surface of a complex skeleton structure, such as a resin porous body having a three-dimensional mesh-like structure.

[0044] Using the resin porous body the surface of which has been imparted with electrical conductivity as a cathode and aluminum as an anode, a DC current is applied in the molten salt.

[0045] Furthermore, as the molten salt, an organic molten salt which is a eutectic salt of an organic halide and an aluminum halide or an inorganic molten salt which is a eutectic salt of an alkali metal halide and an aluminum halide can be used. When a bath of an organic molten salt which melts at a relatively low temperature is used, the resin porous body serving as a substrate can be plated without being decomposed, thus being preferable. As the organic halide, an imidazolium salt, a pyridinium salt, or the like can be used. Specifically, 1-ethyl-3-methylimidazolium chloride (EMIC) and butylpyridinium chloride (BPC) are preferable.

[0046] When moisture or oxygen is mixed into a molten salt, the molten salt is degraded. Therefore, preferably, plating is performed in an inert gas atmosphere, such as nitrogen or argon, and under a sealed environment.

[0047] As the molten salt bath, a nitrogen-containing molten salt bath is preferable, and in particular, an imidazolium salt bath is preferably used. In the case where a salt that melts at a high temperature is used as the molten salt, dissolution into the molten salt or decomposition of the resin proceeds faster than growth of a plating film, and it is not possible to form a plating film on the surface of the resin porous body. An imidazolium salt bath can be used even at a relatively low temperature without affecting the resin. As the imidazolium salt, a salt containing an imidazolium cation having alkyl groups at the 1-and 3-positions is preferably used. In particular, an aluminum chloride-1-ethyl-3-methylimidazolium chloride ($AlCl_3$-EMIC)-based molten salt is most preferably used because it has high stability and is unlikely to decompose. It is possible to perform plating on a urethane foam, a melamine foam, or the like. The temperature of the molten salt bath is 10°C to 100°C, and preferably 25°C to 45°C. As the temperature decreases, the current density range in which plating can be performed narrows, and it becomes difficult to perform plating over the entire surface of the resin porous body. At a high temperature exceeding 100°C, a problem of deformation of the resin porous body is likely to occur.

[0048] In molten salt aluminum plating onto a surface of a metal, for the purpose of improving smoothness of the plating surface, addition of an additive, such as xylene, benzene, toluene, or 1,10-phenanthroline, to $AlCl_3$-EMIC has been reported. The present inventors have found that, in particular, in the case where aluminum plating is performed on a resin porous body having a three-dimensional mesh-like structure, addition of 1,10-phenanthroline exhibits particular

effects in forming an aluminum porous body. That is, a first feature obtained is that the aluminum skeleton constituting the porous body is unlikely to break, and a second feature obtained is that it is possible to perform plating in which the difference in plating thickness between the surface portion and the interior portion of the porous body is small.

[0049] On the other hand, it is also possible to use an inorganic salt bath as the molten salt within a range that the resin is not dissolved or the like. The inorganic salt bath is typically an $AlCl_3$-XCl (X: alkali metal) binary salt system or multicomponent salt system. In such an inorganic salt bath, although the melting temperature is generally high compared with organic salt baths, such as an imidazolium salt bath, environmental conditions, such as moisture and oxygen, are less limited, and low-cost practical implementation is generally possible. In the case where the resin is a melamine foam, use at a high temperature is possible compared with a urethane foam, and an inorganic salt bath at 60°C to 150°C is used.

(Plating apparatus)

[0050] Figure 1 shows an example of an aluminum film manufacturing apparatus according to an embodiment of the present invention.

[0051] The aluminum film manufacturing apparatus includes a plating chamber 1, an entrance side sealing chamber 4 disposed on the substrate entrance side of the plating chamber 1, and an exit side sealing chamber 5 disposed on the substrate exit side of the plating chamber 1.

[0052] A substrate W (hereinafter, also referred to as the "work piece") unwound from a supply bobbin 20 that sends the substrate passes through the entrance side sealing chamber 4 and is transferred into the plating chamber 1. The work piece W on which an aluminum film has been formed in the plating chamber 1 passes through the exit side sealing chamber 5, is water-washed in a rinsing device 22, and then is taken up by a take-up bobbin 21.

- Plating chamber -

[0053] As shown in Fig. 1, the plating chamber 1 contains an anode 2 and a plating solution 3. The plating chamber 1 is provided with inert gas supply pipes 6 for supplying an inert gas into the plating chamber 1. Thereby, the inside of the plating chamber is in an inert gas atmosphere and has a positive pressure relative to outside air. The inert gas may be a gas that does not react with the molten salt, such as nitrogen gas or argon gas, and use of nitrogen is preferable from the viewpoint of costs.

[0054] A case where nitrogen gas is used as the inert gas will be described below.

[0055] As the plating chamber 1, any existing plating chamber can be used, and a system in which power supply is performed in the liquid or a system in which power supply is performed outside the liquid may be used.

[0056] Although Fig. 1 shows a plating chamber in which the substrate is transferred in the horizontal direction in the plating chamber, it may be possible to use a type of plating chamber in which an aluminum film is formed while transferring a work piece along the circumferential surface of a transfer drum.

- Entrance side sealing chamber and exit side sealing chamber -

[0057] Figure 1 shows sealing chambers according to an embodiment of the present invention.

[0058] A nitrogen gas exhaust pipe 7 is provided on each of the sealing chambers 4 and 5, and by forcibly discharging the nitrogen gas blowing off from the plating chamber 1 through the nitrogen gas exhaust pipe 7, a nitrogen gas stream is formed in each of the sealing chambers 4 and 5. The nitrogen gas exhaust pipes 7 are preferably disposed at positions far from the plating chamber. That is, in the entrance side sealing chamber, the nitrogen gas exhaust pipe 7 is preferably disposed at a position close to the substrate entrance, and in the exit side sealing chamber, the nitrogen gas exhaust pipe 7 is preferably disposed at a position close to the substrate exit. By disposing the nitrogen gas exhaust pipes 7 at the positions described above, a gas stream that flows from the plating chamber 1 to the substrate entrance is formed in the entrance side sealing chamber, and a gas stream that flows from the plating chamber 1 to the substrate exits side is formed in the exit side sealing chamber. Therefore, the effect of preventing moisture and oxygen from intruding into the plating chamber is increased.

[0059] Figures 2 and 3 show sealing chambers according to other embodiments of the present invention.

[0060] In the examples shown in Figs. 2 and 3, a nitrogen gas supply pipe 8 is provided on each of the sealing chambers 4 and 5.

[0061] By supplying nitrogen gas from the nitrogen gas supply pipe 8, the flow rate of the gas stream formed in each of the sealing chambers 4 and 5 increases, and the effect of preventing moisture and oxygen from intruding into the plating chamber is further increased.

[0062] The nitrogen gas supplied by the nitrogen gas supply pipe 8 is preferably blown to the work piece in an inclined manner with respect to the work piece. By supplying the nitrogen gas in such a manner, a gas stream moving from the plating chamber 1 side toward the nitrogen gas exhaust pipe 7 side is likely to be formed, and moisture and oxygen

present in pores of the work piece W are replaced by the nitrogen gas and expelled from the work piece. The moisture and oxygen expelled from the work piece are carried off by the gas stream in the sealing chamber and discharged from the exhaust pipe 7.

[0063] Figures 4 and 5 show sealing chambers according to other embodiments of the present invention.

[0064] In the example shown in Fig. 4, two pairs of seal rolls 9 are provided on each of the sealing chambers 4 and 5 of the example shown in Fig. 1, and in the example shown in Fig. 5, two pairs of seal rolls 9 are provided on each of the sealing chambers 4 and 5 of the example shown in Fig. 2.

[0065] By providing such seal rolls on the sealing chambers, it is possible to more effectively prevent moisture and oxygen from intruding into the plating chamber.

[0066] In the example shown in Fig. 6, a seal plate (sealing material) 10 for preventing intrusion of outside air is provided at the substrate entrance of the sealing chamber 4. The seal plate is arranged such that the ends thereof are in contact with surfaces of a work piece W, and thereby, outside air is prevented from intruding from the substrate entrance. The seal plate can be composed of a material that does not damage the surfaces of the work piece, and is preferably composed of a flexible material. Furthermore, a similar seal plate (sealing material) 10 for preventing intrusion of outside air is also provided at the substrate exit of the sealing chamber 5.

(Cleaning)

[0067] A plated aluminum structure in which an aluminum film is formed on the surface of the resin porous body is subjected to nitrogen blow to remove the plating solution sufficiently, and then cleaning is performed to obtain an aluminum porous body.

[0068] As a cleaning liquid, although water is usually used, an organic solvent may be used.

[0069] Through the steps described above, an aluminum structure (aluminum porous body) including the resin porous body as a core of the skeleton is obtained. This aluminum structure may be used as a resin-metal composite depending on the intended use, such as for various filters and catalyst carriers. In the case where the aluminum structure is used as a metal structure without including the resin owing to usage environment constraints or the like, the resin may be removed. The removal of the resin can be performed by any method, such as decomposition (dissolution) by an organic solvent, a molten salt, or supercritical water, or decomposition by heating. The method of decomposition by high-temperature heating is simple and easy, but causes oxidation of aluminum. Unlike nickel or the like, aluminum is difficult to be subjected to reduction treatment once it is oxidized. Consequently, for example in the case of use as an electrode material for a battery or the like, electrical conductivity is lost due to oxidation, and therefore, the method of decomposition by high-temperature heating cannot be used.

[0070] Accordingly, it is desirable to use a method in which the resin is removed by decomposition by heating in a molten salt, which will be described below, so as to prevent oxidation of aluminum.

(Removal of resin: decomposition by heating in molten salt)

[0071] Decomposition by heating in a molten salt is performed by a method described below. The resin porous body provided with the aluminum film on the surface thereof is immersed in a molten salt, and heating is performed while applying a negative potential to the aluminum film to decompose the resin porous body. When a negative potential is applied in a state in which the resin porous body is immersed in the molten salt, it is possible to decompose the resin porous body without oxidizing aluminum. The heating temperature may be appropriately selected in accordance with the type of resin porous body. It is necessary to carry out treatment at a temperature lower than the melting point (660°C) of aluminum so as not to melt aluminum. A preferred temperature range is 500°C to 600°C. Furthermore, the magnitude of the negative potential to be applied is on the negative side with respect to the reduction potential of aluminum and on the positive side with respect to the reduction potential of cations in the molten salt.

[0072] The molten salt used in the decomposition by heating of the resin may be a halide salt of an alkali metal or alkaline earth metal such that the aluminum electrode potential becomes base. Specifically, preferably, the molten salt contains one or more selected from the group consisting of lithium chloride (LiCl), potassium chloride (KCl), sodium chloride (NaCl), and aluminum chloride ($AlCl_3$). By such a method, it is possible to obtain an aluminum porous body having interconnected pores and having a thin oxide layer on the surface thereof with a low oxygen content.

EXAMPLES

[0073] The present invention will be described in more detail below on the basis of examples. However, the examples are merely illustrative and the present invention are not limited thereto. It is intended that the scope of the present invention is determined by appended claims, and includes all variations of the equivalent meanings and ranges to the claims.

[Example 1]

[0074] Using an aluminum film manufacturing apparatus shown in Fig. 1 according to an embodiment of the present invention, an aluminum plating film was formed on a porous resin substrate. Plating conditions were set as described below.

(Porous resin substrate)

[0075] As a substrate, a urethane foam having a width of 1 m, a thickness of 1 mm, a porosity of 95% by volume, and a number of pores (cells) per inch of about 50 was prepared. By immersing the urethane foam in a carbon suspension, followed by drying, electrical conductivity was imparted thereto. The carbon suspension was composed of 17% by mass of graphite and carbon black and 7% by mass of a resin binder, and further included a penetrant and an antifoamer. The particle size of the carbon black was 0.5 μm.

(Sealing chambers)

[0076] Each of the entrance side sealing chamber 4 and the exit side sealing chamber had a length of 500 mm and a height of 200 mm.

[0077] The gas in each of the sealing chambers was sucked off and forcibly discharged from the exhaust pipe 7.

(Plating chamber)

[0078] Nitrogen gas was supplied from two nitrogen gas supply pipes 6 of the plating chamber 1 at a flow rate of 4.0 m^3/min in total.

(Plating conditions)

[0079] Plating conditions were set as follows:

Composition of plating solution: $AlCl_3$/EMIC = 2 mol/l mol
Applied current: 1,000 A
Work piece: urethane foam (thickness 1 mm, width 1,000 mm, pore diameter 0.5 mm)
Work piece speed: 150 mm/min
Immersion length of work piece: 2 m

(Evaluation)

[0080] After the plating apparatus was operated for 24 hours, the atmosphere gas (nitrogen gas) in the plating chamber was collected by suction with an air pump, which was defined as a [sampling gas 1], and the atmosphere gas in the vicinity of the supply bobbin in a room where the plating apparatus was stored (hereinafter referred to as the "general room") was collected by suction with an air pump, which was defined as a [sampling gas 2].

[0081] Regarding the [sampling gas 1], the dew point and the oxygen concentration were analyzed with a dew point meter (capacitance type) and an oxygen concentration meter, respectively.

[0082] Furthermore, regarding the [sampling gas 2], the hydrogen chloride concentration was analyzed with a hydrogen chloride concentration meter.

[0083] The analysis results are shown in Table 1.

[Example 2]

[0084] A plating apparatus was operated and sampling gases were collected as in Example 1 except that an aluminum film manufacturing apparatus provided with seal rolls 9 shown in Fig. 4 according to an embodiment of the present invention was used, and nitrogen gas was supplied from two nitrogen gas supply pipes 6 of the plating chamber 1 at a flow rate of 3.5 m^3/min in total.

[0085] The analysis results for the sampling gases are shown in Table 1.

[Example 3]

[0086] A plating apparatus was operated and sampling gases were collected as in Example 1 except that, in Example

1, the seal plate 10 shown in Fig. 6 was disposed on each of the substrate entrance side of the sealing chamber 4 and the substrate exit side of the sealing chamber 5, and nitrogen gas was supplied from two nitrogen gas supply pipes 6 of the plating chamber at a flow rate of 3.5 m^3/min in total.

[0087] The analysis results for the sampling gases are shown in Table 1.

[Example 4]

[0088] A plating apparatus was operated and sampling gases were collected as in Example 1 except that an aluminum film manufacturing apparatus shown in Fig. 2 according to an embodiment of the present invention was used, nitrogen gas was supplied from two nitrogen gas supply pipes 6 of the plating chamber 1 at a flow rate of 3.3 m^3/min in total, and nitrogen gas was supplied from nitrogen gas supply pipes 8 of the sealing chambers 4 and 5 at a flow rate of 0.2 m^3/min in total.

[0089] The analysis results for the sampling gases are shown in Table 1.

[Example 5]

[0090] A plating apparatus was operated and sampling gases were collected as in Example 1 except that an aluminum film manufacturing apparatus provided with seal rolls 9 shown in Fig. 5 according to an embodiment of the present invention was used, nitrogen gas was supplied from two nitrogen gas supply pipes 6 of the plating chamber 1 at a flow rate of 3.0 m^3/min in total, and nitrogen gas was supplied from nitrogen gas supply pipes 8 of the sealing chambers 4 and 5 at a flow rate of 0.2 m^3/min in total.

[0091] The analysis results for the sampling gases are shown in Table 1.

[Comparative Example 1]

[0092] A plating apparatus was operated and sampling gases were collected as in Example 1 except that, in Example 1, the gas in each of the sealing chamber 4 and 5 was not forcibly discharged from the nitrogen gas exhaust pipe 7.

[0093] The analysis results for the sampling gases are shown in Table 1.

[Comparative Example 2]

[0094] A plating apparatus was operated and sampling gases were collected as in Example 2 except that, in Example 2, the gas in each of the sealing chamber 4 and 5 was not forcibly discharged from the nitrogen gas exhaust pipe 7.

[0095] The analysis results for the sampling gases are shown in Table 1.

[Comparative Example 3]

[0096] A plating apparatus was operated and sampling gases were collected as in Example 3 except that, in Example 3, the gas in each of the sealing chamber 4 and 5 was not forcibly discharged from the nitrogen gas exhaust pipe 7.

[0097] The analysis results for the sampling gases are shown in Table 1.

[Comparative Example 4]

[0098] A plating apparatus was operated and sampling gases were collected as in Example 4 except that, in Example 4, the gas in each of the sealing chamber 4 and 5 was not forcibly discharged from the nitrogen gas exhaust pipe 7.

[0099] The analysis results for the sampling gases are shown in Table 1.

[0100] A plating chamber oxygen concentration of less than 0.5% is considered to be within an acceptable range.

[0101] A plating chamber dew point of lower than -30°C is considered to be within an acceptable range.

[0102] When the HCl concentration is less than 0.1 ppm, it is considered that there is no leakage.

[Table 1]

	Conditions in sealing chambers				Conditions in plating chamber	Evaluation results		
	Discharging	Seal rolls	Seal plates	N_2 flow rate total [m^3/min]	N_2 flow rate total [m^3/min]	HCl leakage to general room	Plating chamber oxygen concentration [vol%]	Plating chamber dew point [°C]
Example 1	Performed	Absent	Absent	0	4.0	None	0.40%	-34°C
Example 2	Performed	Present	Absent	0	3.5	None	0.20%	-40°C
Example 3	Performed	Absent	Present	0	3.5	None	0.20%	-39°C
Example 4	Performed	Absent	Absent	0.2	3.3	None	0.20%	-42°C
Example 5	Performed	Present	Present	0.2	3.0	None	0.10%	-46°C
Comparative Example 1	Not performed	Absent	Absent	0	4.0	Occurred	19.50%	+9.5°C
Comparative Example 2	Not performed	Present	Absent	0	3.5	Occurred	0.80%	-28°C
Comparative Example 3	Not performed	Absent	Present	0	3.5	Occurred	1.00%	-25°C
Comparative Example 4	Not performed	Absent	Absent	0.2	3.3	Occurred	0.70%	-39°C

Reference Signs List

[0103]

1	plating chamber
2	anode
3	plating solution
4	entrance side sealing chamber
5	exit side sealing chamber
6	inert gas (nitrogen gas) supply pipe
7	inert gas (nitrogen gas) exhaust pipe
8	inert gas (nitrogen gas) supply pipe
9	seal roll
10	seal plate
11	hold-down roll
12	power supply roll
13	transfer roll
14	storage tank
15	pump
20	supply bobbin
21	take-up bobbin
22	rinsing device
31	resin porous body
32	conductive layer
33	aluminum film
51	long, porous resin substrate (strip-shaped resin)
52	supply bobbin
53	deflector roll
54	electrically conductive coating material suspension
55	tank
56	hot air nozzle

57 squeezing roll

58 take-up bobbin

W work piece

Claims

1. A manufacturing method for an aluminum film, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, comprising:

   a step of transferring the substrate into a plating chamber through a sealing chamber disposed on the entrance side of the plating chamber;
   a step of electrodepositing an aluminum film on the surface of the substrate in the plating chamber; and
   a step of transferring the substrate having the aluminum film electrodeposited thereon from the plating chamber through a sealing chamber disposed on the exit side of the plating chamber,

   wherein an inert gas is supplied into the plating chamber such that the plating chamber has a positive pressure relative to outside air, and
   the inert gas is forcibly discharged from an inert gas exhaust pipe provided on each of the two sealing chambers.

2. The manufacturing method for an aluminum film according to Claim 1, wherein the inert gas exhaust pipe is provided at the substrate entrance side in the sealing chamber disposed on the entrance side, and
   the inert gas exhaust pipe is provided at the substrate exit side in the sealing chamber disposed on the exit side.

3. The manufacturing method for an aluminum film according to Claim 1 or 2, wherein an inert gas supply pipe that supplies an inert gas is further provided on each of the two sealing chambers.

4. The manufacturing method for an aluminum film according to Claim 3, wherein the inert gas supply pipe is provided at the substrate exit side in the sealing chamber disposed on the entrance side, and the inert gas supply pipe is provided at the substrate entrance side in the sealing chamber disposed on the exit side.

5. The manufacturing method for an aluminum film according to any one of Claims 1 to 4, wherein the substrate entrance and the substrate exit of each of the two sealing chambers are sealed with seal rolls.

6. A manufacturing apparatus for an aluminum film, in which aluminum is electrodeposited on a surface of a long, porous resin substrate imparted with electrical conductivity in a molten salt electrolytic solution, comprising:

   a plating chamber;
   a sealing chamber disposed on the substrate entrance side of the plating chamber and a sealing chamber disposed on the substrate exit side of the plating chamber;
   an inert gas supply pipe which is provided on the plating chamber and supplies an inert gas into the plating chamber; and
   an inert gas exhaust pipe which is provided on each of the two sealing chambers and forcibly discharges the inert gas in the sealing chamber.

FIG. 1

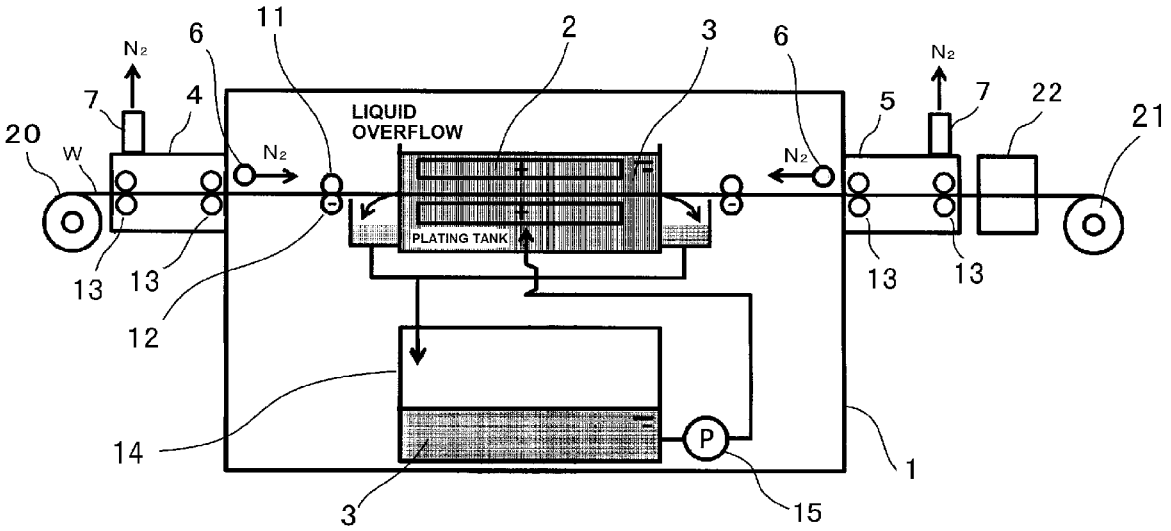

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FIG. 2

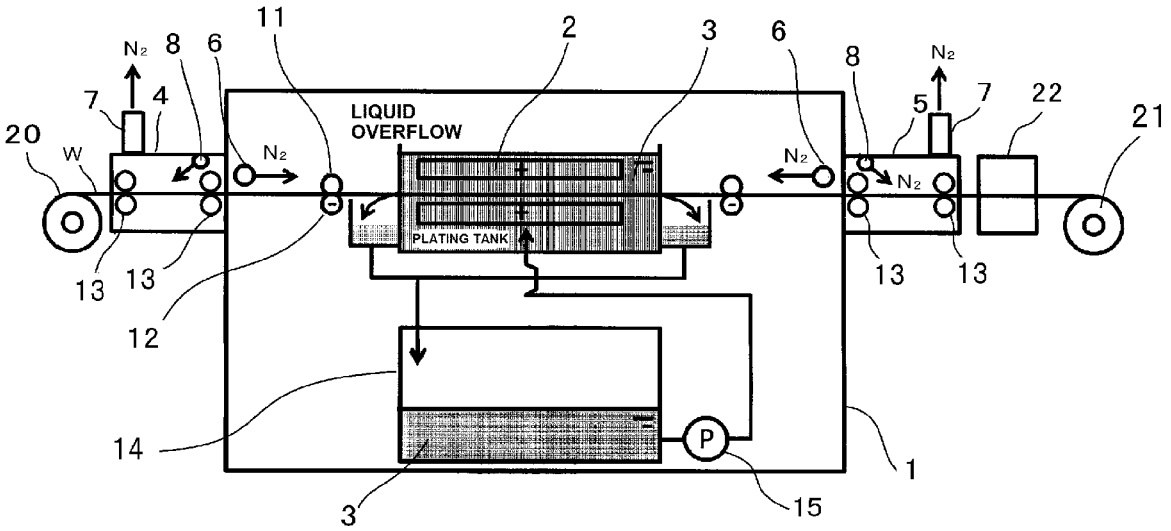

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FIG. 3

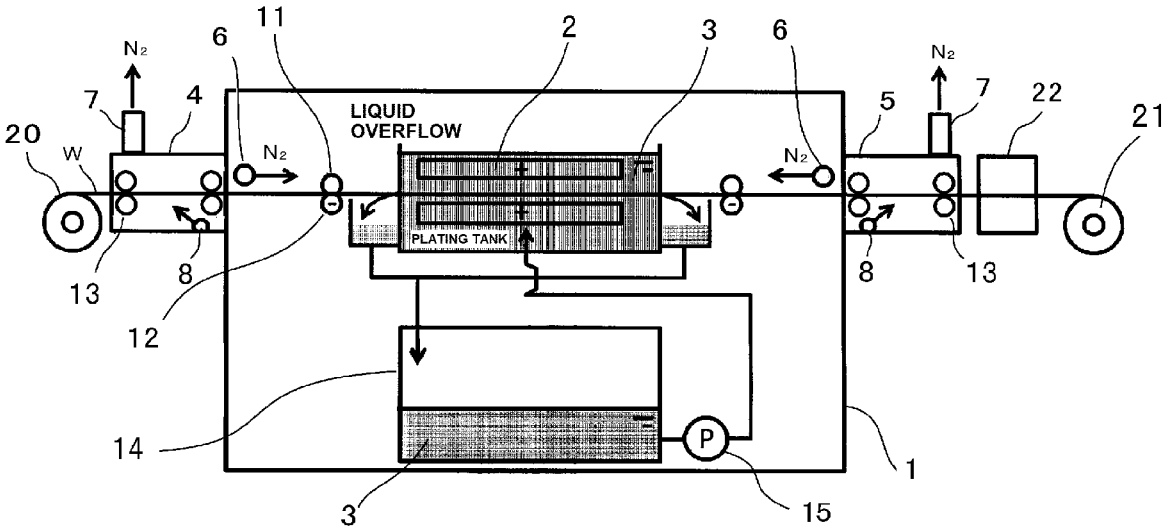

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FIG. 4

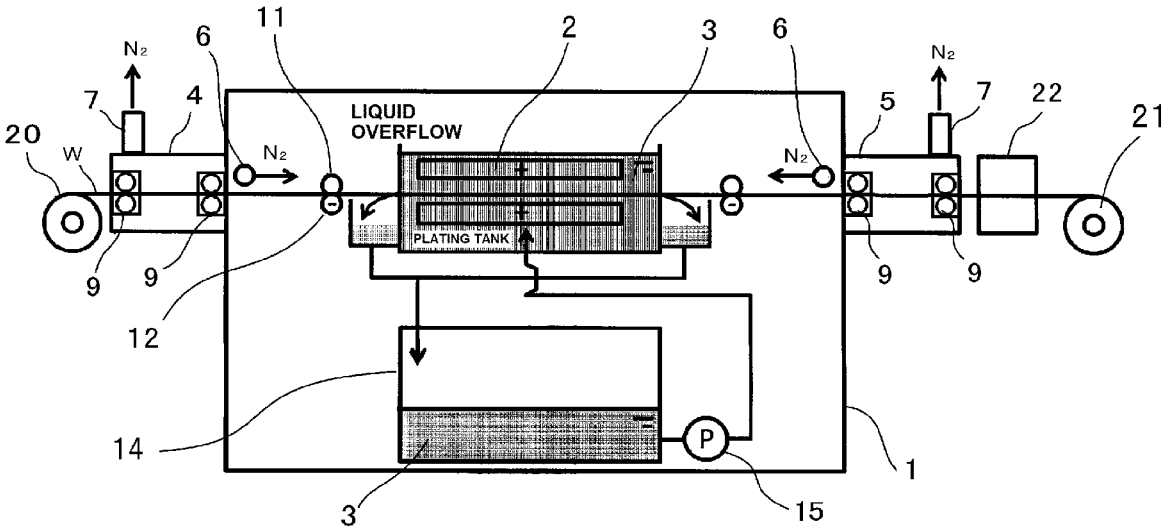

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FIG. 5

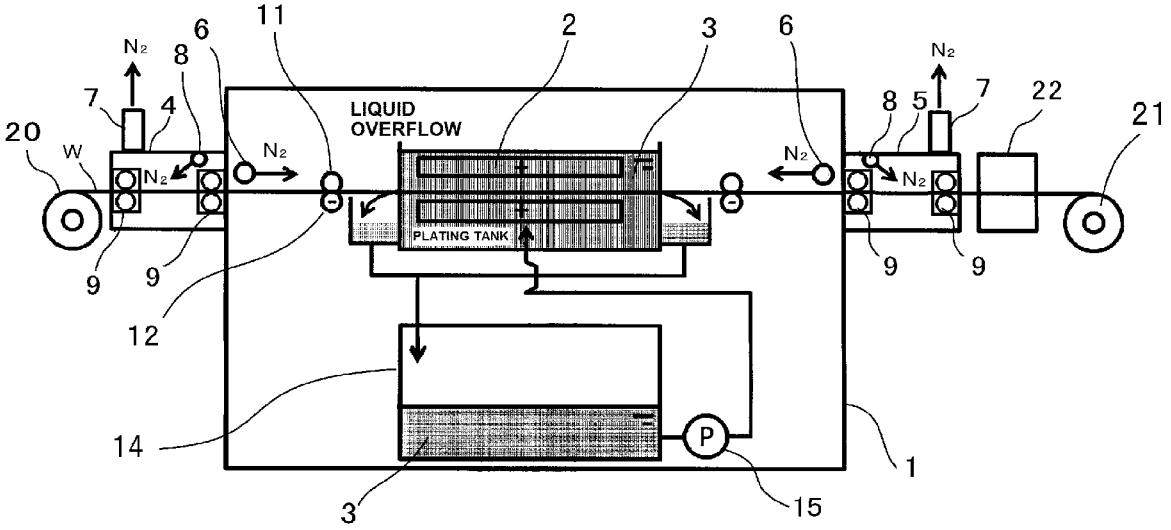

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FIG. 6

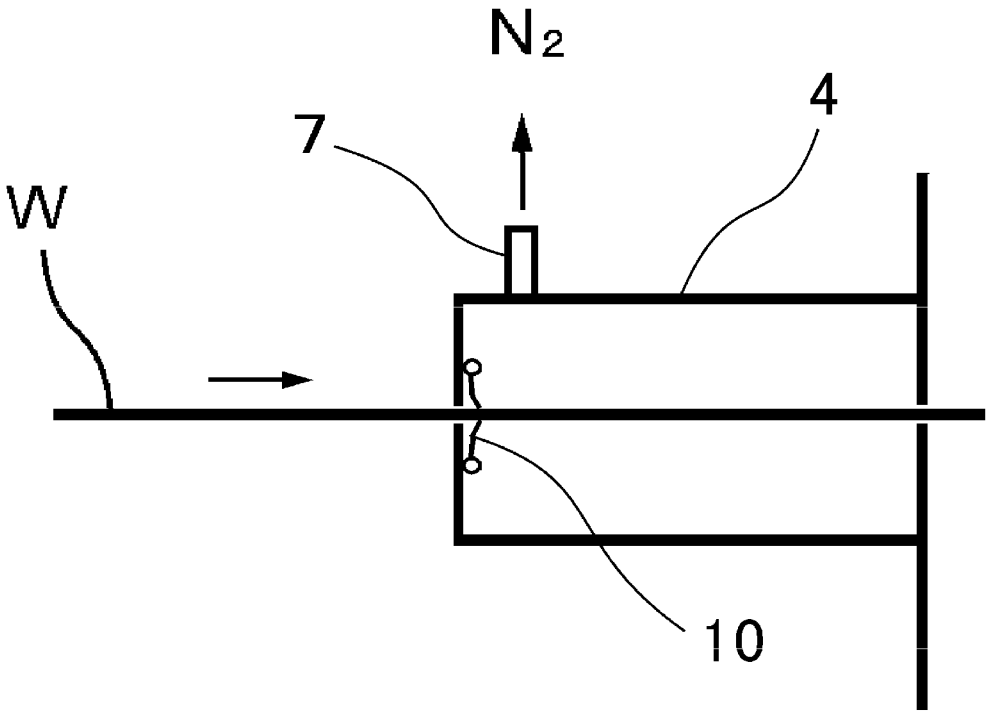

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FIG. 7

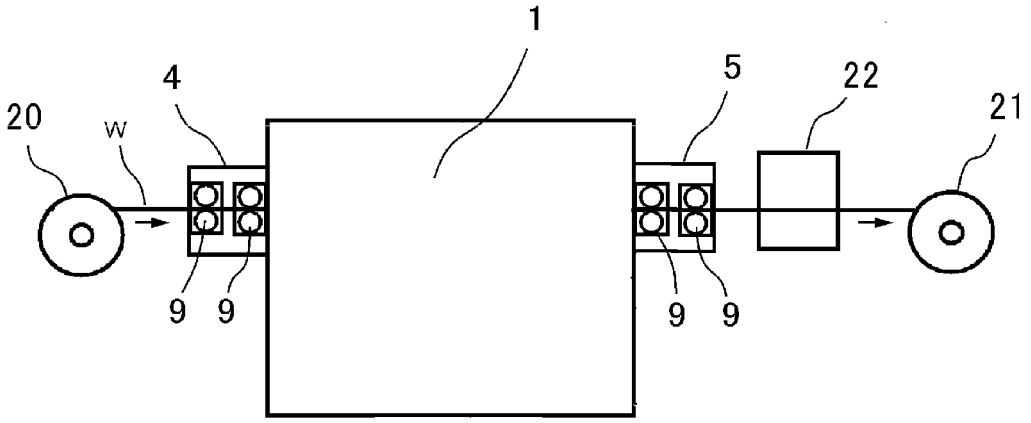

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FIG. 8

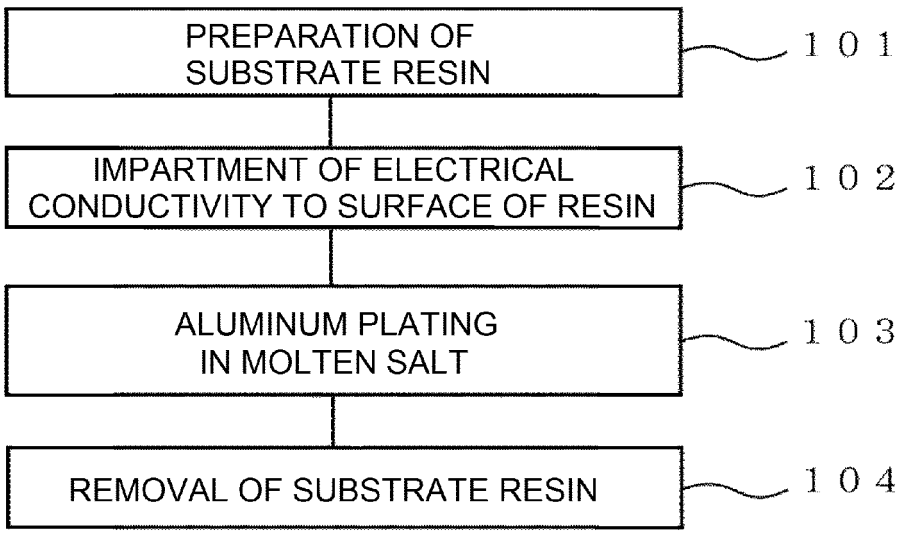

PREPARATION OF SUBSTRATE RESIN
101
IMPARTMENT OF ELECTRICAL CONDUCTIVITY TO SURFACE OF RESIN
102
ALUMINUM PLATING IN MOLTEN SALT
103
REMOVAL OF SUBSTRATE RESIN
104

FIG. 9

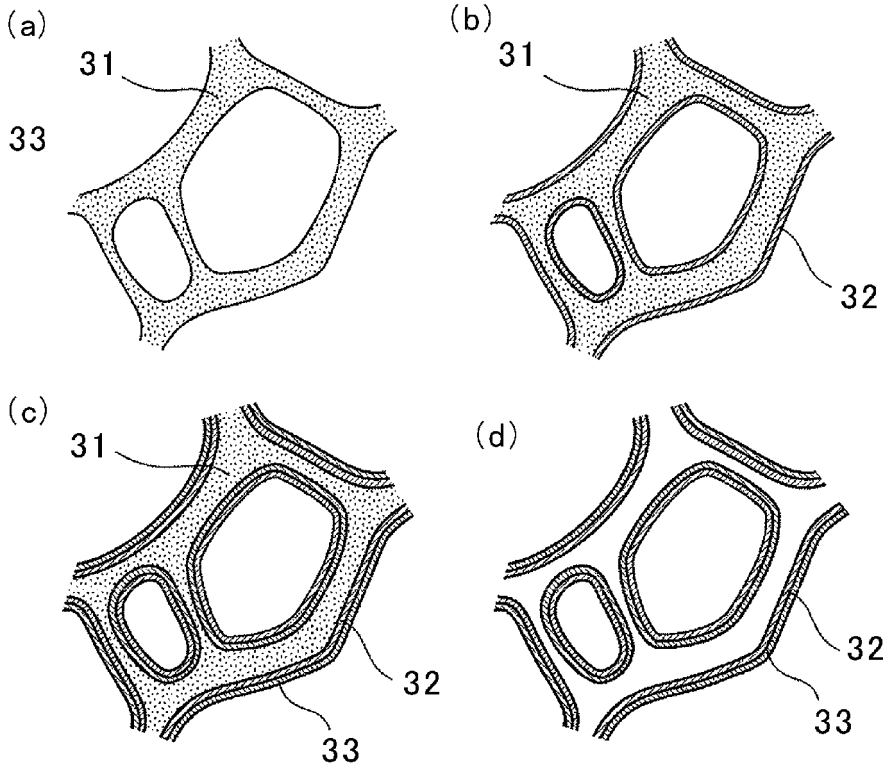


FIG. 10

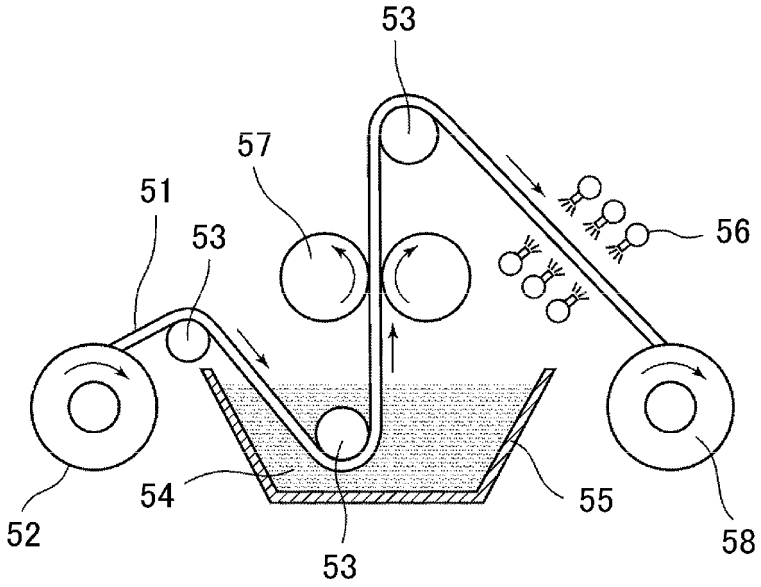
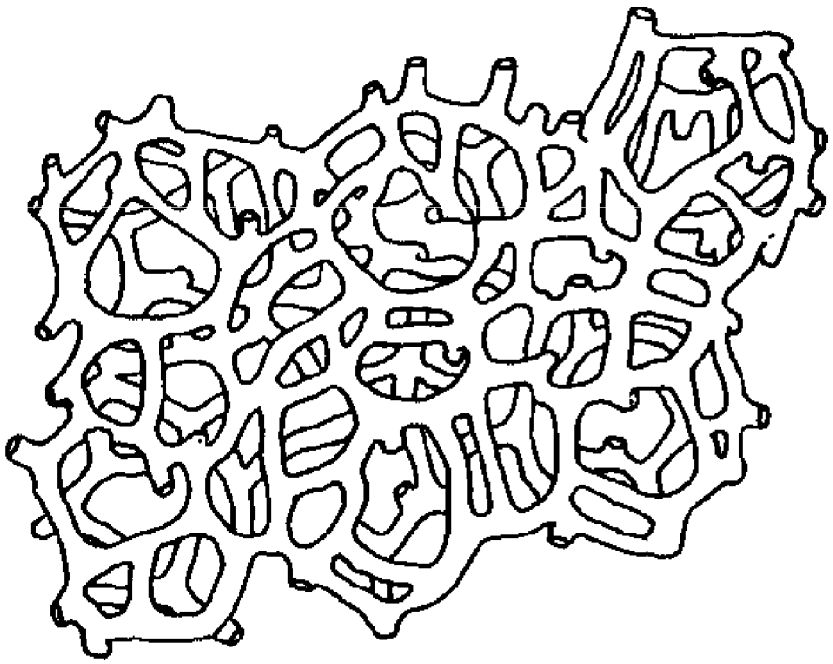


FIG. 11



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/051983

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/08(2006.01)i, *C25D1/00*(2006.01)i, *C25D3/66*(2006.01)i, *C25D7/06*(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, C25D1/00, C25D3/66, C25D7/06

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 1996-2015
Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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 A	JP 2012-255185 A (Sumitomo Electric Industries, Ltd.), 27 December 2012 (27.12.2012), claims; paragraphs [0025], [0030], [0037]; fig. 5, 7 (Family: none)	1,2,6 3-5
A	JP 4-329898 A (Sumitomo Metal Industries, Ltd.), 18 November 1992 (18.11.1992), claims; fig. 2 (Family: none)	1-6
A	JP 2002-30480 A (Casio Micronics Co., Ltd.), 31 January 2002 (31.01.2002), paragraphs [0011], [0018], [0019]; fig. 1 (Family: none)	1-6

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

* Special categories of cited documents:
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"P" document published prior to the international filing date but later than the priority date claimed
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 April 2015 (06.04.15)	21 April 2015 (21.04.15)
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) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/051983

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 61-213389 A (Sumitomo Metal Industries, Ltd.), 22 September 1986 (22.09.1986), claims; fig. 1 (Family: none)	1-6
A	JP 3-17292 A (Nisshin Steel Co., Ltd.), 25 January 1991 (25.01.1991), claims; fig. 1 (Family: none)	1-6

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 5222599 A **[0008]**
- JP 5186892 A **[0008]**
- JP 2012007233 A **[0008]**
- JP 2000087287 A **[0008]**