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(54) **ALUMINUM PLATING SOLUTION,
METHOD FOR MANUFACTURING
ALUMINUM FILM, AND POROUS
ALUMINUM OBJECT**

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(57) **ABSTRACT**

Provided is an aluminum plating solution capable of continuously manufacturing an aluminum film, the surface of which is smooth and which has good elongation. The aluminum plating solution capable of electrodepositing aluminum on a surface of a base contains, as components, (A) an aluminum halide, (B) at least one compound selected from the group consisting of alkylimidazolium halides, alkyipyridinium halides, and urea compounds, and (C1) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds. The component (C1) has, as at least one side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms. A mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio. A concentration of the component (C1) is 1.0 g/L or more and 45 g/L or less.

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**ALUMINUM PLATING SOLUTION,
METHOD FOR MANUFACTURING
ALUMINUM FILM, AND POROUS
ALUMINUM OBJECT**

TECHNICAL FIELD

[0001] The present invention relates to an aluminum plating solution capable of manufacturing an aluminum film having good surface smoothness and good flexibility. The present invention further relates to a method for manufacturing an aluminum film, the method including using the aluminum plating solution, and a porous aluminum object obtained by using the aluminum plating solution.

BACKGROUND ART

[0002] Aluminum has many good characteristics such as electrical conductivity, corrosion resistance, light weight, and non-toxicity and is widely used in plating of, for example, metal products. However, aluminum has a high affinity to oxygen and has an oxidation-reduction potential lower than that of hydrogen. Thus, it is difficult to perform aluminum electroplating in an aqueous solution-based plating bath.

[0003] Therefore, a method using a molten-salt bath is employed as a method for performing aluminum electroplating. However, existing plating baths including molten salts need to be heated to a high temperature. Accordingly, when a resin product is electroplated with aluminum, there may be a problem in that the resin melts and electroplating cannot be performed.

[0004] In view of this problem, Japanese Unexamined Patent Application Publication No. 2012-144763 (Patent Literature 1) describes that an organic chloride salt such as 1-ethyl-3-methylimidazolium chloride (EMIC) or 1-butylpyridinium chloride (BPC) and aluminum chloride (AlCl_3) are mixed to prepare an aluminum plating bath that is liquid at room temperature, and that a surface of a resin molded body may be electroplated with aluminum using this plating bath.

[0005] In particular, the EMIC- AlCl_3 -based plating solution described in Patent Literature 1 has good solution properties and is very useful as an aluminum plating solution. Patent Literature 1 describes that a smooth aluminum film is formed by adding 1,10-phenanthroline to the aluminum plating solution so that the concentration of 1,10-phenanthroline becomes 0.25 to 7.0 g/L.

[0006] Regarding a porous metal object having a three-dimensional mesh-like structure, a porous aluminum object manufactured by the method described in Patent Literature 1 is very promising, for example, as an object that improves the capacity of the positive electrode of a lithium-ion battery. Since aluminum has good characteristics such as electrical conductivity, corrosion resistance, and light weight, currently, an aluminum foil, the surface of which is coated with an active material such as lithium cobalt oxide, is used as the positive electrode of a lithium-ion battery. By forming this positive electrode using a porous object formed of aluminum, the surface area is increased, and the inside of aluminum can also be filled with an active material. With this structure, even when the thickness of the electrode is increased, the utilization ratio of the active material does not decrease. Accordingly, the utilization ratio of the active

material per unit area improves, and the capacity of the positive electrode can be improved.

[0007] As described above, a porous aluminum object having a three-dimensional mesh-like structure is very useful. However, when such porous aluminum objects are continuously manufactured in large quantities by the method described in Patent Literature 1, the smoothness of the resulting aluminum film gradually decreases, and thus the plating solution needs to be replaced with a new one, as required.

In view of this problem, Japanese Unexamined Patent Application Publication No. 2014-058715 (Patent Literature 2) describes that it is effective to control the concentration of 1,10-phenanthroline monohydrate in an aluminum plating solution so as to be 0.05 g/L or more and 7.5 g/L or less.

CITATION LIST

Patent Literature

[0008] PTL 1: Japanese Unexamined Patent Application Publication No. 2012-144763

[0009] PTL 2: Japanese Unexamined Patent Application Publication No. 2014-058715

SUMMARY OF INVENTION

Technical Problem

[0010] As described in Patent Literature 1, smooth aluminum films can be continuously formed in large quantities by adding 1,10-phenanthroline monohydrate to an aluminum plating solution and performing aluminum plating while controlling the concentration of 1,10-phenanthroline monohydrate so as to be 0.05 g/L or more and 7.5 g/L or less. The aluminum films obtained in this manner are good in terms of smoothness to the extent that the surfaces thereof are mirror surfaces. However, the aluminum films are hard, have a high strength, and thus have a property of not being easily elongated.

[0011] In some applications of a porous aluminum object having a three-dimensional mesh-like structure, flexibility and elongation are required for an aluminum film, and thus the inventors of the present invention conducted examinations for providing flexibility to aluminum by applying heat to a porous aluminum object. In general, metals have a property of becoming soft as a result of heat treatment. However, the porous aluminum object obtained by the method described in Patent Literature 1 did not have flexibility even after heat treatment was performed.

[0012] Accordingly, it is an object of the present invention to provide an aluminum plating solution capable of continuously manufacturing an aluminum film, the surface of which is smooth and which has good elongation.

Solution to Problem

[0013] An aluminum plating solution according to an embodiment of the present invention is

(1) an aluminum plating solution capable of electrodepositing aluminum on a surface of a base,

[0014] the aluminum plating solution containing, as components:

(A) an aluminum halide;

(B) at least one compound selected from the group consisting of alkylimidazolium halides, alkylpyridinium halides, and urea compounds; and

(C1) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds,

[0015] in which the component (C1) has, as at least one side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms,

[0016] a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio, and

[0017] a concentration of the component (C1) is 1.0 g/L or more and 45 g/L or less.

[0018] In the aluminum plating solution described in (1) above, the term "side chain" in the component (C1) refers to a group bonded to a N atom, a P atom, or a S atom of each of the salts or the compounds.

[0019] An aluminum plating solution according to an embodiment of the present invention is

(2) an aluminum plating solution capable of electrodepositing aluminum on a surface of a base,

[0020] the aluminum plating solution containing, as components:

(A) an aluminum halide;

(B) at least one compound selected from the group consisting of alkylimidazolium halides, alkyipyridinium halides, and urea compounds;

(C2) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds; and

(D) at least one selected from the group consisting of alkyl halides, alkynes, alkenes, and alkanes,

[0021] in which the component (C2) has, as at least one side chain, a straight-chain or branched alkyl group having 1 or more and 36 or less carbon atoms,

[0022] the component (D) is a straight-chain or branched compound having 3 or more and 36 or less carbon atoms,

[0023] a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio,

[0024] a concentration of the component (C2) is 1.0 g/L or more and 45 g/L or less, and

[0025] a concentration of the component (D) is 0.5 g/L or more and 8.5 g/L or less.

[0026] In the aluminum plating solution described in (2) above, the term "side chain" in the component (C2) refers to a group bonded to a N atom, a P atom, or a S atom of each of the salts or the compounds.

Advantageous Effects of Invention

[0027] According to the present invention, it is possible to provide an aluminum plating solution capable of continuously manufacturing an aluminum film, the surface of which is smooth and which has good elongation.

DESCRIPTION OF EMBODIMENTS

Description of Embodiments of the Present Invention

[0028] First, embodiments of the present invention will be listed and described.

(1) An aluminum plating solution according to an embodiment of the present invention is

[0029] an aluminum plating solution capable of electrodepositing aluminum on a surface of a base,

[0030] the aluminum plating solution containing, as components:

(A) an aluminum halide;

(B) at least one compound selected from the group consisting of alkylimidazolium halides, alkyipyridinium halides, and urea compounds; and

(C1) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds,

[0031] in which the component (C1) has, as at least one side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms,

[0032] a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio, and

[0033] a concentration of the component (C1) is 1.0 g/L or more and 45 g/L or less.

[0034] According to the embodiment of the invention described in (1) above, it is possible to provide an aluminum plating capable of continuously manufacturing an aluminum film, the surface of which is smooth and which has good elongation.

(2) An aluminum plating solution according to an embodiment of the present invention is an aluminum plating solution capable of electrodepositing aluminum on a surface of a base,

[0035] the aluminum plating solution containing, as components:

(A) an aluminum halide;

(B) at least one compound selected from the group consisting of alkylimidazolium halides, alkyipyridinium halides, and urea compounds;

(C2) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds; and

(D) at least one selected from the group consisting of alkyl halides, alkynes, alkenes, and alkanes,

[0036] in which the component (C2) has, as at least one side chain, a straight-chain or branched alkyl group having 1 or more and 36 or less carbon atoms,

[0037] the component (D) is a straight-chain or branched compound having 3 or more and 36 or less carbon atoms,

[0038] a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio,

[0039] a concentration of the component (C2) is 1.0 g/L or more and 45 g/L or less, and

[0040] a concentration of the component (D) is 0.5 g/L or more and 8.5 g/L or less.

[0041] According to the embodiment of the invention described in (2) above, it is possible to provide, at a lower cost, an aluminum plating solution capable of continuously manufacturing an aluminum film, the surface of which is smooth and which has good elongation.

(3) In the aluminum plating solution described in (1) or (2) above, the component (A) is preferably aluminum chloride, and the component (B) is preferably 1-ethyl-3-methylimidazolium chloride.

[0042] According to the embodiment of the invention described in (3) above, it is possible to provide an aluminum plating solution capable of stably continuously obtaining an aluminum film having better surface smoothness.

(4) A method for manufacturing an aluminum film according to an embodiment of the present invention is a method for manufacturing an aluminum film, the method including electrodepositing aluminum on a surface of a base by using the aluminum plating solution according to any one of (1) to (3) above.

[0043] According to the embodiment of the invention described in (4) above, it is possible to provide a method for manufacturing an aluminum film having good surface smoothness and good elongation.

(5) A porous aluminum object according to an embodiment of the present invention is a porous aluminum object obtained by using the aluminum plating solution according to any one of (1) to (3) above, the porous aluminum object having a three-dimensional mesh-like structure and an elongation of 1.5% or more.

[0044] The porous aluminum object described in (5) above is soft and has good elongation and thus is a porous aluminum object that can be used in applications in which bending or vibration is applied.

[0045] The elongation of the porous aluminum object according to an embodiment of the present invention is affected by the coating weight of aluminum per unit area. Accordingly, the elongation is assumed to be an elongation when the coating weight of aluminum per unit area of the porous aluminum object is 100 g/m² or more and 180 g/m² or less, and the thickness is 0.95 mm or more and 1.05 mm or less.

[0046] The term “elongation” refers to an elongation measured when a tensile test is performed in accordance with JIS Z 2241 and refers to a ratio of the amount of displacement to the distance between marks (Gage Length: GL).

(6) In the porous aluminum object described in (5) above, a crystal grain size in a cross section of a skeleton is preferably 1 μm or more and 50 μm or less.

[0047] The porous aluminum object described in (6) above has a large crystal grain size and thus is a porous aluminum object that is soft and has good elongation.

(7) In the porous aluminum object described in (5) or (6) above, a content of aluminum carbide is preferably 0.8% by mass or less.

[0048] Regarding the porous aluminum object described in (7) above, since the content of aluminum carbide contained in an aluminum film is small, recrystallization of aluminum is allowed to proceed by heat treatment. Accordingly, a porous aluminum object including a softer aluminum film can be provided.

Details of Embodiments of the Present Invention

[0049] Specific examples of an aluminum plating solution, a method for manufacturing an aluminum film, and a porous aluminum object according to embodiments of the present invention will be described in more detail below. The present invention is not limited to these exemplifications but is defined by the claims. It is intended that the scope of the present invention includes the meaning of equivalents of the claims and all modifications within the scope of the claims.

[0050] In order to provide flexibility to porous aluminum objects obtained by using existing aluminum plating solutions, the inventors of the present invention performed heat treatment on the porous aluminum objects. However, it was found that even after the heat treatment, the properties of high strength and low elongation are maintained. The reason for this was examined in detail. According to the results, it

was found that recrystallization does not proceed because aluminum carbide is formed by the heat treatment at grain boundaries of crystals of aluminum. It was found that this aluminum carbide is derived from 1,10-phenanthroline taken in the aluminum film during the formation of the film.

<Aluminum Plating Solution>

[0051] In view of the above, as a result of intensive studies further conducted by the inventors of the present invention, it was found that the component (C1) is effective as an additive that contributes to the smoothness of an aluminum film.

[0052] Specifically, as described above, an aluminum plating solution according to an embodiment of the present invention is an aluminum plating solution obtained by mixing at least components (A) to (C1) below.

Component (A): an aluminum halide

Component (B): at least one compound selected from the group consisting of alkylimidazolium halides, alkylpyridinium halides, and urea compounds

Component (C1): at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds

[0053] The component (C1) has, as at least one side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms.

[0054] The aluminum plating solution according to an embodiment of the present invention may contain other components as unavoidable impurities. The aluminum plating solution may intentionally contain other components within a range that does not impair the effect of an aluminum film according to an embodiment of the present invention, the aluminum film being capable of forming an aluminum film having good smoothness and good elongation.

[0055] An aluminum halide that forms a molten salt at about 110° C. or less when mixed with the component (B) can be suitably used as the aluminum halide serving as the component (A). Examples thereof include aluminum chloride (AlCl₃), aluminum bromide (AlBr₃), and aluminum iodide (AlI₃). Among these, aluminum chloride is most preferable.

[0056] Similarly, an alkylimidazolium halide that forms a molten salt at about 110° C. or less when mixed with the component (A) can be suitably used as the alkylimidazolium halide serving as the component (B).

[0057] Examples thereof include imidazolium chlorides having alkyl groups (having 1 to 5 carbon atoms) at the 1- and 3-positions, imidazolium chlorides having alkyl groups (having 1 to 5 carbon atoms) at the 1-, 2-, and 3-positions, and imidazolium iodides having alkyl groups (having 1 to 5 carbon atoms) at the 1- and 3-positions.

[0058] More specifically, examples thereof include 1-ethyl-3-methylimidazolium chloride (EMIC), 1-butyl-3-methylimidazolium chloride (BMIC), and 1-methyl-3-propylimidazolium chloride (MPIC). Among these, 1-ethyl-3-methylimidazolium chloride (EMIC) can be most preferably used.

[0059] An alkylpyridinium halide that forms a molten salt at about 110° C. or less when mixed with the component (A) can be suitably used as the alkylpyridinium halide serving as the component (B).

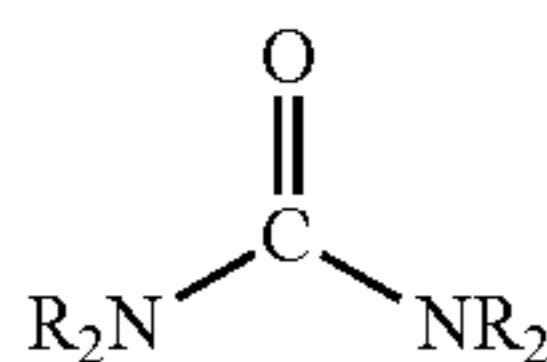
[0060] Examples thereof include 1-butylpyridinium chloride (BPC), 1-ethylpyridinium chloride (EPC), and 1-butyl-

3-methyl-pyridinium chloride (BMPC). Among these, 1-butylpyridinium chloride is most preferable.

[0061] The urea compound serving as the component (B) covers urea and derivatives thereof. A urea compound that forms a molten salt at about 110° C. or less when mixed with the component (A) can be suitably used as the urea compound serving as the component (B).

[0062] For example, compounds represented by formula (1) below are preferably used.

[Chem. 1]



Formula (1)

[0063] In formula (1), R each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, or a phenyl group, and R may be the same or different from each other.

[0064] Among the above urea compounds, urea and dimethylurea can be particularly preferably used.

[0065] In the aluminum plating solution, a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio. Thus, the aluminum plating solution suitable for electrodepositing an aluminum film on a surface of a base is obtained.

[0066] In the case where the proportion of the component (B) is assumed to be 1, when the molar ratio of the component (A) is less than 1, an electrodeposition reaction of aluminum does not occur. In the case where the proportion of the component (B) is assumed to be 1, when the molar ratio of the component (A) exceeds 3, aluminum chloride is deposited in the aluminum plating solution and is incorporated in the resulting aluminum film, and the quality of the film decreases.

[0067] The component (C1) is at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds. The component (C1) has, as at least one side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms, and other side chains are not particularly limited. Examples of the other side chains include hydrogen, groups having a benzene ring, and straight-chain or branched alkyl groups having 1 or more and 36 or less carbon atoms.

[0068] The alkyl group serving as at least one side chain of the component (C1) may be branched but is preferably a straight-chain alkyl group. A number of carbon atoms of 8 or more in the alkyl group can contribute to smoothness of the aluminum film. A number of carbon atoms of 36 or less in the alkyl group can prevent the viscosity of the aluminum plating solution from being excessively high. From the above viewpoints, the number of carbon atoms of the alkyl group serving as a side chain of the component (C1) is preferably 8 or more and 22 or less, and more preferably 12 or more and 18 or less.

[0069] When the component (C1) is a salt, the component (C1) is preferably a salt of a halogen. In particular, a salt of a chloride ion (Cl⁻), a bromide ion (Br), or an iodide ion (I) is preferable.

[0070] Specifically, examples of the component (C1) include stearylamine, dimethylstearylamine, N-docosyl-N-

methyl-1-docosanamine, dimethyldistearylammonium chloride, dodecyltrimethylammonium chloride, octyltrimethylammonium chloride, and tributyltetradecylphosphonium chloride.

[0071] When the concentration of the component (C1) in the aluminum plating solution is 1.0 g/L or more and 45 g/L or less, an aluminum film that is smooth and is good in terms of elongation can be formed. When the concentration of the component (C1) is less than 1.0 g/L, a sufficiently smooth aluminum film cannot be obtained. When the concentration of the component (C1) exceeds 45 g/L, the component (C1) is incorporated in the aluminum film. Consequently, the aluminum film becomes hard but is brittle and has low elongation. The concentration of the component (C1) is preferably 5 g/L or more and 25 g/L or less, and more preferably 7.5 g/L or more and 20 g/L or less.

[0072] When plating is performed for a long time using an aluminum plating solution containing the component (C1), the amount of the component (C1) decreases. Therefore, it is necessary to add the component (C1) to the aluminum plating solution, as required. In the case where the component (C1) is added to the aluminum plating solution, as described above, the concentration of the component (C1) in the aluminum plating solution is controlled to 1.0 g/L or more and 45 g/L or less.

[0073] The inventors of the present invention examined the reason why the amount of the component (C1) decreases from the aluminum plating solution. According to the results, the inventors of the present invention found that this is because a side chain of the component (C1), that is, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms is decomposed, though the decomposition occurs gradually. It was also found that the separated alkyl group is incorporated in the aluminum film and thereby contributes to the smoothness of the aluminum film.

[0074] As described above, when plating is performed for a long time using an aluminum plating solution containing the component (C1), the chain length of the alkyl group becomes gradually short, and a component having, as a side chain, an alkyl group having 7 or less carbon atoms accumulates. In this case, instead of the component (C1), a component (D) described below may be added to the aluminum plating solution. Note that the component (C1) in the aluminum plating solution at this time is changed to a component (C2) described below.

[0075] Specifically, an aluminum plating solution according to an embodiment of the present invention is an aluminum plating solution containing, in addition to the component (A) and the component (B), at least the component (C2) and the component (D) described below.

Component (C2): at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds

Component (D): at least one selected from the group consisting of alkyl halides, alkynes, alkenes, and alkanes

[0076] The component (C2) has, as at least one side chain, a straight-chain or branched alkyl group having 1 or more and 36 or less carbon atoms. The component (D) is a straight-chain or branched compound having 3 or more and 36 or less carbon atoms.

[0077] In the component (C2), a salt or compound having, as a side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms contributes to

smoothness and elongation of an aluminum film and further contributes to solubility of the component (D). In the component (C2), a salt or compound having, as a side chain, a straight-chain or branched alkyl group having 1 or more and 7 or less carbon atoms contributes to solubility of the component (D). That is, the component (D) can be easily dissolved by incorporating the component (C2) in the aluminum plating solution.

[0078] The component (C2) is at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds. The component (C2) has, as at least one side chain, a straight-chain or branched alkyl group having 1 or more and 36 or less carbon atoms, and other side chains are not particularly limited. Examples of the other side chains include hydrogen, groups having a benzene ring, and straight-chain or branched alkyl groups having 1 or more and 36 or less carbon atoms.

[0079] The alkyl group serving as at least one side chain of the component (C2) may be branched but is preferably a straight-chain alkyl group. A number of carbon atoms of 1 or more in the alkyl group can contribute to solubility of the component (D). A number of carbon atoms of 36 or less in the alkyl group can prevent the viscosity of the aluminum plating solution from being excessively high.

From the above viewpoints, the number of carbon atoms of the alkyl groups in the component (C2) is preferably 1 or more and 18 or less, and more preferably 3 or more and 12 or less.

[0080] When the component (C2) is a salt, the component (C2) is preferably a salt of a halogen. In particular, a salt of a chloride ion (Cl), a bromide ion (Br), or an iodide ion (I) is preferable.

[0081] Specifically, examples of the component (C2) include trimethylamine, trimethylphosphine, ethyl methyl sulfide, stearylamine, dimethylstearylamine, N-docosyl-N-methyl-1-docosanamine, dimethyldistearylammonium chloride, dodecyltrimethylammonium chloride, octyltrimethylammonium chloride, tetrabutylammonium chloride, tetrabutylphosphonium chloride, tributyltetradecylphosphonium chloride, and triethylphenylammonium chloride.

[0082] The concentration of the component (C2) in the aluminum plating solution is 1.0 g/L or more and 45 g/L or less. When the concentration of the component (C2) is less than 1.0 g/L, it is difficult to dissolve the component (D) in the aluminum plating solution. When the concentration of the component (C2) exceeds 45 g/L, the viscosity of the plating solution becomes excessively high.

[0083] The concentration of the component (C2) is preferably 5.0 g/L or more and 30 g/L or less, and more preferably 10 g/L or more and 15 g/L or less.

[0084] The component (D) is at least one selected from the group consisting of alkyl halides, alkynes, alkenes, and alkanes, all of which have 3 or more and 36 or less carbon atoms, and may have a straight-chain or branched structure. Since the component (D) has a low polarity, the component (D) is hardly soluble in an aluminum plating solution consisting of the component (A) and the component (B). However, when the aluminum plating solution contains the component (C2), the component (C2) functions as a surfactant and thus the component (D) is easily soluble in the aluminum plating solution. In addition, the component (D) is cheaper than the component (C1) and is easily available. Therefore, the aluminum plating solution according to an

embodiment of the present invention can be produced at a lower cost by adding the component (D) instead of the component (C1).

[0085] The component (D) is incorporated in an aluminum film when aluminum is electrodeposited on a surface of a base, and thereby contributes to smoothness of the aluminum film. However, since the component (D) has a very low thermal decomposition temperature and a very low boiling point, the component (D) is removed from the aluminum film at a temperature lower than a temperature at which aluminum carbide is formed when a resin serving as a base is removed by combustion. Therefore, unlike 1,10-phenanthroline, the component (D) does not remain in the aluminum film or does not form aluminum carbide.

[0086] When the component (D) is removed from the aluminum film, minute voids are formed in the aluminum film, though the number of the voids is small. Smoothness and elongation of the aluminum film are not decreased by these voids as long as the concentration of the component (D) in the aluminum plating solution is in the range of 0.5 g/L or more and 8.5 g/L or less.

[0087] A number of carbon atoms of 3 or more of the component (D) can contribute to smoothness of the aluminum film. A number of carbon atoms of 36 or less of the component (D) can prevent the viscosity of the aluminum plating solution from being excessively high. From the above viewpoints, the number of carbon atoms of the component (D) is preferably 5 or more and 24 or less, and more preferably 8 or more and 18 or less.

[0088] The component (D) is preferably liquid or solid at room temperature because the component (D) is easily dissolved in the aluminum plating solution.

[0089] The halogen atom contained in the alkyl halide is not particularly limited. However, for example, the halogen atom is preferably chlorine (Cl), bromine (Br), or iodine (I). The number of halogen atoms contained in the alkyl halide is not particularly limited and is preferably about 1 or more and about 2 or less.

[0090] The number of triple bonds contained in the alkyne is preferably 1 because alkyne molecules are unlikely to react with each other.

[0091] The number of double bonds contained in the alkene is preferably 1 because alkene molecules are unlikely to react with each other.

[0092] Specifically, examples of the component (D) include propane, butane, octane, pentane, tetradecane, octadecane, chloropropane, chlorobutane, lauryl chloride, stearyl chloride, pentene, hexene, decene, propyne, pentyne, and butyne.

[0093] In the aluminum plating solution containing the component (C2), when the concentration of the component (D) is 0.5 g/L or more and 8.5 g/L or less, an aluminum film that is smooth and is good in terms of elongation can be formed. When the concentration of the component (D) is less than 0.5 g/L, a sufficiently smooth aluminum film is not obtained in some cases. When the concentration of the component (D) exceeds 8.5 g/L, the number of voids formed in the aluminum film when a base is removed by combustion becomes excessively large. From the above viewpoints, the concentration of the component (D) is preferably 0.85 g/L or more and 4.5 g/L or less, and more preferably 1.0 g/L or more and 3.0 g/L or less.

[0094] As described above, since the component (D) is incorporated in the aluminum film, when aluminum plating

is performed for a long time, the amount of the component (D) in the aluminum plating solution gradually decreases. In the case where the amount of the component (D) in the aluminum plating solution is decreased, the component (D) is appropriately added so that the concentration of the component (D) becomes in the above ranges.

[0095] An aluminum film, the surface of which is smooth and which has good elongation, can be formed by using the aluminum plating solution according to an embodiment of the present invention.

<Method for Manufacturing Aluminum Film>

[0096] A method for manufacturing an aluminum film according to an embodiment of the present invention is a method for manufacturing an aluminum film, the method including electrodepositing aluminum on a surface of a base by using the aluminum plating solution according to an embodiment of the present invention.

[0097] In the method for manufacturing an aluminum film according to an embodiment of the present invention, in order to electrodeposit aluminum on a surface of a base in the electrolyte solution, an aluminum electrode (anode) is disposed in the electrolyte solution and electrical connection is established so that the base in the electrolyte solution acts as a cathode, and electricity is supplied.

[0098] In this case, aluminum is preferably electrodeposited on the surface of the base so that the current density becomes 0.5 A/dm² or more and 10.0 A/dm² or less. When the current density is in this range, an aluminum film having better smoothness can be obtained. The current density is more preferably 1.5 A/dm² or more and 6.0 A/dm² or less, and still more preferably 2.0 A/dm² or more and 4.0 A/dm² or less.

[0099] The electrodeposition of aluminum on a surface of a base is preferably performed while the temperature of the electrolyte solution is adjusted to 15° C. or more and 110° C. or less. By adjusting the temperature of the electrolyte solution to 15° C. or more, the viscosity of the electrolyte solution can be sufficiently reduced, and the electrodeposition efficiency of aluminum can be improved. By adjusting the temperature of the electrolyte solution to 110° C. or less, volatilization of the aluminum halide can be suppressed. The temperature of the electrolyte solution is more preferably 30° C. or more and 80° C. or less, and still more preferably 40° C. or more and 70° C. or less.

[0100] During the electrodeposition of aluminum on a surface of a base, the electrolyte solution may be stirred, if necessary.

[0101] According to the method for manufacturing an aluminum film according to an embodiment of the present invention, a smooth aluminum film whose surface has an arithmetic mean roughness (Ra) of about 0.2 μm or less can be manufactured.

[0102] The base is not particularly limited as long as the base has an application in which an aluminum film is formed on a surface thereof. For example, a copper plate, a steel strip, a copper wire, a steel wire, or a resin subjected to a conductive treatment can be used as the base. For example, a resin such as a polyurethane, melamine resin, polypropylene, or polyethylene that is subjected to a conductive treatment can be used as the resin subjected to a conductive treatment.

[0103] The resin serving as the base may have any shape. Use of a resin molded body having a three-dimensional

mesh-like structure is preferable because it is possible to finally produce a porous aluminum object having a three-dimensional mesh-like structure and exhibiting good properties in applications such as filters, catalyst supports, and electrodes for batteries. Use of a resin having a non-woven fabric shape can also finally provide a porous aluminum object having a porous structure. A porous aluminum object having a non-woven fabric shape and manufactured in this manner can also be preferably used in applications such as filters, catalyst supports, and electrodes for batteries.

[0104] Examples of the resin molded body having a three-dimensional mesh-like structure include foamed resin molded bodies manufactured by using, for example, a polyurethane or a melamine resin. Although the examples of the resin molded body are described as “foamed resin molded bodies”, resin molded bodies having any shape can be selected as long as the resin molded bodies have communicating pores (continuous pores). For example, non-woven fabric-like materials obtained by intertwining a fibrous resin such as polypropylene or polyethylene may also be used instead of the foamed resin molded bodies.

[0105] Hereinafter, a porous object having a three-dimensional mesh-like structure may be simply referred to as “porous object”.

[0106] The porosity of the porous object is preferably 80% or more and 98% or less. The pore diameter of the porous object is preferably 50 μm or more and 500 μm or less. Urethane foams and melamine foams can be preferably used as the foamed resin molded bodies because they have a high porosity, pores thereof have continuity, and they have good thermal degradability. Urethane foams are preferable from the viewpoint of, for example, the uniformity of pores and availability. Melamine foams are preferable from the viewpoint that a resin molded body having a small pore diameter is obtained. Foamed resin molded bodies formed of, for example, a urethane foam or a melamine foam often contain residues such as a foam stabilizer used in a foaming process and an unreacted monomer, and thus are preferably subjected to a washing treatment in advance.

[0107] The porosity of the porous object is defined by the following formula.

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

[0108] The pore diameter is determined by magnifying a surface of the porous object by means of, for example, a photomicrograph, counting the number of pores per inch (25.4 mm) as a cell number, and calculating an average value as mean pore diameter = 25.4 mm/cell number.

[0109] A resin molded body subjected to a conductive treatment is used as the resin molded body having a three-dimensional mesh-like structure.

[0110] The conductive treatment of a resin surface can be selected from methods including known methods. It is possible to employ a method including forming a metal layer formed of, for example, nickel by electroless plating or a gas-phase method, and a method including forming a metal or carbon layer using a conductive coating material.

[0111] By forming a metal layer on a resin surface by electroless plating or a gas-phase method, the electrical conductivity of the resin surface can be increased. On the other hand, although the conductive treatment of a resin surface by carbon coating is somewhat poor from the viewpoint of electrical conductivity, this conductive treat-

ment can be performed so that a metal other than aluminum is not mixed in the resulting aluminum structure after the formation of an aluminum film. Accordingly, a structure that is substantially formed of only aluminum as a metal can be manufactured. This method is also advantageous in that electrical conductivity can be imparted at a low cost.

[0112] In the case where the conductive treatment is performed by carbon coating, first, a carbon coating material serving as a conductive coating material is prepared. A suspension serving as the carbon coating material preferably contains a binder, a dispersant, and a dispersion medium, in addition to carbon particles.

[0113] When a resin molded body having a three-dimensional mesh-like structure is used, in order to uniformly apply carbon particles to the porous object, it is necessary that the suspension maintain a uniform suspension state. For this purpose, the suspension is preferably maintained at 20° C. to 40° C. By maintaining the temperature of the suspension at 20° C. or higher, a uniform suspension state can be maintained, it is possible to prevent only the binder from concentrating on the surface of the skeleton that forms a mesh-like structure of the porous object and forming a layer, and thus the carbon particles can be uniformly applied. Since the layer of the carbon particles that are uniformly applied in this manner is unlikely to separate, metal plating that strongly adheres to the layer can be formed. On the other hand, since the temperature of the suspension is 40° C. or less, evaporation of the dispersant can be suppressed. Accordingly, the suspension is not easily concentrated with the coating process time.

[0114] The carbon particles have a particle size of 0.01 to 5 μm, and preferably 0.01 to 0.5 μm. When the particle size is excessively large, the carbon particles may clog pores of the porous resin molded body or inhibit smooth plating. When the particle size is excessively small, it becomes difficult to ensure sufficient electrical conductivity.

<Porous Aluminum Object>

[0115] A porous aluminum object according to an embodiment of the present invention is a porous aluminum object having an elongation of 1.5% or more. A porous aluminum object obtained by a manufacturing method using a known aluminum plating solution has high strength and low elongation. In contrast, a porous aluminum object according to an embodiment of the present invention is a soft porous aluminum object having an elongation of 1.5% or more.

[0116] An elongation of 1.5% or more is preferable because the porous aluminum object is strong against bending and vibration, and thus the range of the application of the porous aluminum object is increased. Accordingly, the elongation of the porous aluminum object is preferably as high as possible. The elongation of the porous aluminum object is more preferably 1.8% or more, and still more preferably 2.5% or more. According to the method for manufacturing a porous aluminum object according to an embodiment of the present invention described below, a porous aluminum object having an elongation of about 1.5% or more and about 5.0% or less can be manufactured.

[0117] As described above, the elongation of the porous aluminum object is an elongation when the coating weight of aluminum per unit area of the porous aluminum object is 100 g/m² or more and 180 g/m² or less, and the thickness is

0.95 mm or more and 1.05 mm or less. The elongation of the porous aluminum object is measured by a tensile test specified in JIS Z 2241.

[0118] The crystal grain size in a cross section of the skeleton of the porous aluminum object is preferably 1 μm or more and 50 μm or less. A crystal grain size of 1 μm or more is preferable because the aluminum film becomes soft and the elongation of the porous aluminum object becomes 1.5% or more. On the other hand, a crystal grain size of 50 μm or less is preferable because it is possible to suppress a decrease in the strength due to an excessively soft porous aluminum object. From the above viewpoints, the crystal grain size in a cross section of the skeleton of the porous aluminum object is more preferably 1.5 μm or more and 25 μm or less, and still more preferably 2 μm or more and 15 μm or less.

[0119] By using the aluminum plating solution, a porous aluminum object having a relatively large crystal grain size can be obtained. Examples of the method for further increasing the crystal grain size include a method including heat-treating a porous aluminum object, a method including increasing a liquid temperature of an aluminum plating solution in manufacturing a porous aluminum object, and a method including decreasing the current density during plating.

[0120] The content of aluminum carbide in the porous aluminum object is preferably 0.8% by mass or less. In the porous aluminum object, a content of aluminum carbide of 0.8% by mass or less is preferable because the aluminum film becomes soft, and elongation of the porous aluminum object becomes 1.5% or more. The content of aluminum carbide in the porous aluminum object is more preferably 0.5% by mass or less, and still more preferably 0.3% by mass or less.

[0121] When a porous aluminum object is manufactured by using an aluminum plating solution according to an embodiment of the present invention, basically, during removal of a base by combustion, a component containing carbon is removed from an aluminum film at a temperature lower than a temperature at which aluminum carbide is formed. Therefore, the content of aluminum carbide in the porous aluminum object is 0% by mass. However, a carbon-containing component incorporated in an aluminum film may react with aluminum during removal of the base by combustion, and aluminum carbide may be formed in the aluminum film, though the amount of the carbon-containing component is very small. In addition, the component (B) may be incorporated in the aluminum film and may cause the formation of aluminum carbide.

(Method for Manufacturing Porous Aluminum Object)

[0122] The porous aluminum object can be manufactured through a step of forming, by molten-salt electrolytic plating, an aluminum film on a surface of a conductive resin molded body having a three-dimensional mesh-like structure to form a resin structure, and a step of removing the conductive resin molded body from the resin structure.

[0123] The steps will be described in detail below.

—Step of Forming Aluminum Film—

[0124] This step is a step of forming an aluminum film on a surface of a conductive resin molded body having a three-dimensional mesh-like structure by performing elec-

trolytic plating in a molten salt, that is, the aluminum plating liquid. The conductive resin molded body having a three-dimensional mesh-like structure may be the above-described resin molded body obtained by performing a conductive treatment on a surface of a resin molded body having a three-dimensional mesh-like structure.

[0125] By forming an aluminum film in the aluminum plating solution, an aluminum film having a large thickness can be uniformly formed even on a surface of a skeleton of a molded body having a complex skeleton structure, such as a conductive resin molded body having a three-dimensional mesh-like structure. In order to perform molten-salt electrolytic plating, the conductive resin molded body is allowed to act as a cathode and aluminum is allowed to act as an anode, and a direct current is applied in the aluminum plating solution.

[0126] Mixing of moisture and oxygen in the aluminum plating solution degrades the plating solution. Accordingly, the plating is preferably performed in an atmosphere of an inert gas such as nitrogen or argon and in a sealed environment.

[0127] The temperature of the aluminum plating solution may be 15° C. to 110° C. and is preferably 25° C. to 45° C. With the decrease in the temperature, a current density range in which plating can be performed becomes narrower, and it becomes more difficult to perform plating over the entire surface of the skeleton of the conductive resin molded body. Plating in a range of 110° C. or less can prevent the occurrence of a problem that the shape of the conductive resin molded body serving as a base is impaired.

[0128] Through the above step, it is possible to obtain a resin structure that has a surface formed of an aluminum film and that includes the conductive resin molded body as a core of the skeleton thereof

—Step of Removing Conductive Resin Molded Body—

[0129] The resin structure obtained as described above is heat-treated by heating, for example, in a nitrogen atmosphere or in air to a temperature equal to or more than 370° C. at which the resin is decomposed, and preferably equal to or more than 500° C. Thus, the resin and the conductive layer are burnt away to obtain a porous aluminum object. In this step, a carbon-containing component incorporated in the aluminum film can also be removed.

EXAMPLES

[0130] The present invention will now be described in more detail using Examples. These Examples are illustrative, and, for example, an aluminum plating solution of the present invention are not limited thereto. The scope of the present invention is defined by the claims and includes the meaning of equivalents of the claims and all modifications within the scope of the claims.

Example 1

(Aluminum Plating Solution)

[0131] Aluminum chloride (AlCl_3) was used as the component (A), and 1-ethyl-3-methylimidazolium chloride (EMIC) was used as the component (B). The component (A) and the component (B) were mixed so that the mixing ratio became 2:1 in terms of molar ratio to prepare a molten salt. Dimethyldistearylammonium chloride which is a reagent

(manufactured by Tokyo Chemical Industry Co., Ltd.) was added as the component (C1) to the molten salt so as to have a concentration of 15 g/L. Thus, an aluminum plating solution 1 was obtained.

(Formation of Aluminum Film)

[0132] A copper plate having a size of 20×40×1.0 mm was used as a base. In the aluminum plating solution 1 prepared above, the copper plate was connected on the cathode side of a rectifier, an aluminum plate (purity 99.99%) acting as a counter electrode was connected on the anode side thereof, and a voltage was applied to electrodeposit aluminum on a surface of the copper plate. The temperature of the aluminum plating solution 1 was controlled to 45° C., and the current density was controlled to 3.0 A/dm².

<Evaluation of Aluminum Film>

(Evaluation Methods)

[0133] Aluminum films were formed on surfaces of 50 copper plates by the same method as described above. A surface roughness (arithmetic mean roughness Ra) of each of the aluminum films was measured.

[0134] The surface roughness (arithmetic mean roughness Ra) was measured with a laser microscope manufactured by Keyence Corporation.

(Evaluation Results)

[0135] The average of the arithmetic mean roughness Ra of the surfaces of the aluminum films was 0.11 μm.

Example 2

<Preparation of Porous Aluminum Object>

(Formation of Aluminum Film on Base Surface)

[0136] Aluminum was electrodeposited on a surface of a base by using the aluminum plating solution 1 prepared in Example 1 to prepare a resin structure. A resin molded body having a three-dimensional mesh-like structure and subjected to a conductive treatment was used as the base. A urethane foam (100 mm×30 mm square) having a thickness of 1 mm, a porosity of 95%, and a number of pores (cell number) per inch of about 50 was used as the resin molded body. The conductive treatment was performed by immersing the urethane foam in a carbon suspension and drying the resulting urethane foam. The carbon suspension contained, as components, graphite and carbon black in an amount of 25%, a resin binder, a penetrant, and an antifoaming agent. The carbon black had a particle size of 0.5 μm.

[0137] The base was connected on the cathode side of a rectifier, and an aluminum plate (purity 99.99%) acting as a counter electrode was connected on the anode side thereof. The temperature of the aluminum plating solution 1 was controlled to 45° C., and the current density was controlled to 6.0 A/dm². The aluminum plating solution was stirred so that the rotation speed became 100 rpm.

(Removal of Base)

[0138] At the time when the coating weight of aluminum per unit area became 140 g/m², the resin structure was taken out from the aluminum plating solution 1. The resin struc-

ture was subjected to a water washing treatment and then heat-treated at 610° C. for 20 minutes in air. As a result, the base was burnt away, and a porous aluminum object 1 was obtained.

<Evaluation of Porous Aluminum Object>

(Evaluation Methods)

[0139] Fifteen porous aluminum objects 1 were prepared by the same method as described above. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects were measured.

[0140] The elongation of the each of the porous aluminum objects 1 was measured by performing a tensile test in accordance with JIS Z 2241. An Autograph manufactured by Shimadzu Corporation was used as a testing machine.

[0141] The crystal grain size of aluminum on a cross section of the skeleton was measured by cutting each of the porous aluminum objects 1 and then observing the cross section with a scanning electron microscope manufactured by Hitachi High-Technologies Corporation.

[0142] The amount of aluminum carbide contained in each of the porous aluminum objects 1 was measured using an X-ray diffractometer manufactured by Shimadzu Corporation.

(Evaluation Results)

[0143] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 1 was 1.8% at the lowest and 3.3% at the highest. The average of the elongation was 2.6%.

[0144] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 1 was 3.5 μm. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 1 was 0.35% by mass.

Example 3

[0145] An aluminum plating solution 2 was obtained as in Example 1 except that dodecyltrimethylammonium chloride which is a reagent (manufactured by Tokyo Chemical Industry Co., Ltd.) was used as the component (C1) in the aluminum plating solution, and the component (C1) was added so as to have a concentration of 20 g/L.

[0146] Fifteen porous aluminum objects 2 were prepared as in Example 2 except that the aluminum plating solution 2 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 2 were measured.

(Evaluation Results)

[0147] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 2 was 1.9% at the lowest and 2.8% at the highest. The average of the elongation was 2.3%.

[0148] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 2 was 3 μm. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 2 was 0.34% by mass.

Example 4

[0149] An aluminum plating solution 3 was obtained as in Example 1 except that octyltrimethylammonium chloride which is a reagent (manufactured by Tokyo Chemical Industry Co., Ltd.) was used as the component (C1) in the aluminum plating solution, and the component (C1) was added so as to have a concentration of 15 g/L.

[0150] Fifteen porous aluminum objects 3 were prepared as in Example 2 except that the aluminum plating solution 3 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 3 were measured.

(Evaluation Results)

[0151] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 3 was 1.6% at the lowest and 3.0% at the highest. The average of the elongation was 2.5%.

[0152] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 3 was 3.2 μm. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 3 was 0.37% by mass.

Example 5

[0153] An aluminum plating solution 4 was obtained as in Example 1 except that tributyltetradecylphosphonium chloride which is a reagent (manufactured by Kanto Chemical Co., Inc.) was used as the component (C1) in the aluminum plating solution, and the component (C1) was added so as to have a concentration of 5.0 g/L.

[0154] Fifteen porous aluminum objects 4 were prepared as in Example 2 except that the aluminum plating solution 4 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 4 were measured.

(Evaluation Results)

[0155] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 4 was 1.8% at the lowest and 3.4% at the highest. The average of the elongation was 2.8%.

[0156] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 4 was 3.5 μm. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 4 was 0.34% by mass.

Example 6

[0157] An aluminum plating solution 5 was obtained as in Example 1 except that dimethylstearylamine which is a reagent (manufactured by Tokyo Chemical Industry Co., Ltd.) was used as the component (C1) in the aluminum plating solution, and the component (C1) was added so as to have a concentration of was 15 g/L.

[0158] Fifteen porous aluminum objects 5 were prepared as in Example 2 except that the aluminum plating solution 5 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 5 were measured.

(Evaluation Results)

[0159] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 5 was 1.7% at the lowest and 2.8% at the highest. The average of the elongation was 2.2%.

[0160] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 5 was 4.0 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 5 was 0.28% by mass.

Example 7

[0161] An aluminum plating solution 6 was obtained as in Example 1 except that, in Example 1, the component (C1) was added so as to have a concentration of 1.0 g/L.

[0162] Fifteen porous aluminum objects 6 were prepared as in Example 2 except that the aluminum plating solution 6 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 6 were measured.

(Evaluation Results)

[0163] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 6 was 1.5% at the lowest and 2.7% even at the highest. The average of the elongation was 2.1%.

[0164] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 6 was 4.0 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 6 was 0.24% by mass.

Example 8

[0165] An aluminum plating solution 7 was obtained as in Example 1 except that, in Example 1, the component (C1) was added so as to have a concentration of 45 g/L.

[0166] Fifteen porous aluminum objects 7 were prepared as in Example 2 except that the aluminum plating solution 7 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 7 were measured.

(Evaluation Results)

[0167] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 7 was 1.9% at the lowest and 3.6% even at the highest. The average of the elongation was 2.7%.

[0168] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 7 was 3.2 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 7 was 0.39% by mass.

Comparative Example 1

[0169] An aluminum plating solution A was obtained as in Example 1 except that 1,10-phenanthroline monohydrate was used as the component (C1) in the aluminum plating solution, and the component (C1) was added so as to have a concentration of 0.5 g/L.

[0170] Fifteen porous aluminum objects A were prepared as in Example 2 except that the aluminum plating solution A was used. The elongation, the crystal grain size, and the

content of aluminum carbide of each of the porous aluminum objects A were measured.

(Evaluation Results)

[0171] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects A was 0.6% at the lowest and 1.2% even at the highest. The average of the elongation was 0.8%.

[0172] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects A was 1.0 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects A was 1.2% by mass.

Comparative Example 2

[0173] An aluminum plating solution B was obtained as in Example 1 except that, in Example 1, the component (C1) was added so as to have a concentration of 0.6 g/L.

[0174] Fifteen porous aluminum objects B were prepared as in Example 2 except that the aluminum plating solution B was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects B were measured.

(Evaluation Results)

[0175] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects B was 0.5% at the lowest and 1.3% even at the highest. The average of the elongation was 0.7%.

[0176] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects B was 4.0 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects B was 0.24% by mass.

Comparative Example 3

[0177] An aluminum plating solution C was obtained as in Example 1 except that, in Example 1, the component (C1) was added so as to have a concentration of 50 g/L.

[0178] Fifteen porous aluminum objects C were prepared as in Example 2 except that the aluminum plating solution C was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects C were measured.

(Evaluation Results)

[0179] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects C was 0.8% at the lowest and 1.2% even at the highest. The average of the elongation was 1.0%.

[0180] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects C was 1.2 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects C was 0.84% by mass.

Example 9

[0181] One liter of the aluminum plating solution 1 prepared in Example 1 was prepared, and a porous aluminum object was obtained as in Example 2. Aluminum plating was then performed for 42 hours while a current of 3.6 A was controlled to flow. At the time when the coating weight of

aluminum per unit area became 140 g/m^2 , the base was changed, and the aluminum plating was continued.

[0182] The elongation (ratio of amount of displacement to GL) of the porous aluminum object 2' obtained after 42 hours was measured. Twenty porous aluminum objects 2' were prepared by the same method as described above. The elongation of the porous aluminum objects 2' was 1.2% at the lowest. The elongation was decreased to 1.6% even at the highest. The average of the elongation became 1.3%.

[0183] The aluminum plating solution at this time was referred to as an aluminum plating solution 1', and components of the aluminum plating solution 1' were analyzed by liquid chromatography-mass spectroscopy (LC/MS). According to the results, it was confirmed that an alkyl group serving as a side chain of the component (C1) that was initially contained was shortened and changed to the component (C2) having, as a side chain, an alkyl group having 7 or less carbon atoms. The concentration of the component (C2) was 15 g/L.

(Aluminum Plating Solution)

[0184] Stearyl chloride (manufactured by Tokyo Chemical Industry Co., Ltd.) was added as the component (D) to the aluminum plating solution 1' so as to have a concentration of 1 g/L. Thus, an aluminum plating solution 8 was obtained.

<Preparation of Porous Aluminum Object>

[0185] Fifteen porous aluminum objects 8 were prepared as in Example 2 except that the aluminum plating solution 8 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 8 were measured.

(Evaluation Results)

[0186] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 8 was 2.0% at the lowest and 3.5% at the highest. The average of the elongation was 2.3%.

[0187] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 8 was $4.2 \mu\text{m}$. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 8 was 0.3% by mass.

Example 10

[0188] An aluminum plating solution 9 was obtained as in Example 9 except that the concentration of stearyl chloride serving as the component (D) was 8.3 g/L.

[0189] Fifteen porous aluminum objects 9 were prepared as in Example 2 except that the aluminum plating solution 9 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 9 were measured.

(Evaluation Results)

[0190] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 9 was 1.6% at the lowest and 2.5% at the highest. The average of the elongation was 1.8%.

[0191] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum

objects 9 was $3.2 \mu\text{m}$. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 9 was 0.6% by mass.

Example 11

[0192] An aluminum plating solution 10 was obtained as in Example 10 except that tetradecane (manufactured by Wako Pure Chemical Industries, Ltd.) was used as the component (D) in the aluminum plating solution, and the component (D) was added so as to have a concentration of 1 g/L.

[0193] Fifteen porous aluminum objects 10 were prepared as in Example 2 except that the aluminum plating solution 10 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 10 were measured.

(Evaluation Results)

[0194] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 10 was 2.5% at the lowest and 3.9% at the highest. The average of the elongation was 2.8%.

[0195] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 10 was $4.0 \mu\text{m}$. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 10 was 0.3% by mass.

Example 12

[0196] An aluminum plating solution 11 was obtained as in Example 10 except that decene (manufactured by Tokyo Chemical Industry Co., Ltd.) was used as the component (D) in the aluminum plating solution, and the component (D) was added so as to have a concentration of 0.8 g/L.

[0197] Fifteen porous aluminum objects 11 were prepared as in Example 2 except that the aluminum plating solution 11 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 11 were measured.

(Evaluation Results)

[0198] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 11 was 1.8% at the lowest and 2.8% at the highest. The average of the elongation was 2.2%.

[0199] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 11 was $3.6 \mu\text{m}$. Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 11 was 0.34% by mass.

Example 13

[0200] An aluminum plating solution 12 was obtained as in Example 10 except that dichlorooctane (manufactured by Tokyo Chemical Industry Co., Ltd.) was used as the component (D) in the aluminum plating solution, and the component (D) was added so as to have a concentration of 3.0 g/L.

[0201] Fifteen porous aluminum objects 12 were prepared as in Example 2 except that the aluminum plating solution 12 was used. The elongation, the crystal grain size, and the

content of aluminum carbide of each of the porous aluminum objects 12 were measured.

(Evaluation Results)

[0202] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 12 was 2.1% at the lowest and 2.8% at the highest. The average of the elongation was 2.4%.

[0203] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 12 was 6.0 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 12 was 0.52% by mass.

Example 14

[0204] An aluminum plating solution 13 was obtained as in Example 10 except that chloropropane (manufactured by Tokyo Chemical Industry Co., Ltd.) was used as the component (D) in the aluminum plating solution, and the component (D) was added so as to have a concentration of 3 g/L.

[0205] Fifteen porous aluminum objects 13 were prepared as in Example 2 except that the aluminum plating solution 13 was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects 13 were measured.

(Evaluation Results)

[0206] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects 13 was 1.7% at the lowest and 2.9% at the highest. The average of the elongation was 2.3%.

[0207] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects 13 was 12 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects 13 was 0.46% by mass.

Comparative Example 4

[0208] An aluminum plating solution D was obtained as in Example 9 except that, in Example 9, the component (D) was added so as to have a concentration of 0.3 g/L.

[0209] Fifteen porous aluminum objects D were prepared as in Example 2 except that the aluminum plating solution D was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects D were measured.

(Evaluation Results)

[0210] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects D was 0.8% at the lowest and 1.6% even at the highest. The average of the elongation was 1.1%.

[0211] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects D was 4.8 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects D was 0.12% by mass.

Comparative Example 5

[0212] An aluminum plating solution E was obtained as in Example 9 except that, in Example 9, the component (D) was added so as to have a concentration of 9 g/L.

[0213] Fifteen porous aluminum objects E were prepared as in Example 2 except that the aluminum plating solution E was used. The elongation, the crystal grain size, and the content of aluminum carbide of each of the porous aluminum objects E were measured.

(Evaluation Results)

[0214] The elongation (ratio of amount of displacement to GL) of the porous aluminum objects E was 1.2% at the lowest and 1.8% even at the highest. The average of the elongation was 1.4%.

[0215] The average crystal grain size of aluminum on the cross sections of the skeletons of the porous aluminum objects E was 0.6 μm . Furthermore, the amount of aluminum carbide contained in the porous aluminum objects E was 2.6% by mass.

1. An aluminum plating solution capable of electrodepositing aluminum on a surface of a base,

the aluminum plating solution comprising, as components:

(A) an aluminum halide;

(B) at least one compound selected from the group consisting of alkyimidazolium halides, alkylpyridinium halides, and urea compounds; and

(C1) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds,

wherein the component (C1) has, as at least one side chain, a straight-chain or branched alkyl group having 8 or more and 36 or less carbon atoms,

a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio, and

a concentration of the component (C1) is 1.0 g/L or more and 45 g/L or less.

2. An aluminum plating solution capable of electrodepositing aluminum on a surface of a base,

the aluminum plating solution comprising, as components:

(A) an aluminum halide;

(B) at least one compound selected from the group consisting of alkyimidazolium halides, alkylpyridinium halides, and urea compounds;

(C2) at least one selected from the group consisting of ammonium salts, phosphonium salts, sulfonium salts, amine compounds, phosphine compounds, and sulfide compounds; and

(D) at least one selected from the group consisting of alkyl halides, alkynes, alkenes, and alkanes,

wherein the component (C2) has, as at least one side chain, a straight-chain or branched alkyl group having 1 or more and 36 or less carbon atoms,

the component (D) is a straight-chain or branched compound having 3 or more and 36 or less carbon atoms,

a mixing ratio of the component (A) and the component (B) is in a range of 1:1 to 3:1 in terms of molar ratio,

a concentration of the component (C2) is 1.0 g/L or more and 45 g/L or less, and

a concentration of the component (D) is 0.5 g/L or more and 8.5 g/L or less.

3. The aluminum plating solution according to claim 1, wherein the component (A) is aluminum chloride, and the component (B) is 1-ethyl-3-methylimidazolium chloride.

4. A method for manufacturing an aluminum film, the method comprising electrodepositing aluminum on a surface of a base by using the aluminum plating solution according to claim 1.

5. A porous aluminum object obtained by using the aluminum plating solution according to claim 1, the porous aluminum object having a three-dimensional mesh-like structure and an elongation of 1.5% or more.

6. The porous aluminum object according to claim 5, wherein a crystal grain size in a cross section of a skeleton is 1 μm or more and 50 μm or less.

7. The porous aluminum object according to claim 5, wherein a content of aluminum carbide is 0.8% by mass or less.

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