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(71) Applicant: **Kabushiki Kaisha Toyota Chuo Kenkyusho**
Nagakute-shi, Aichi 480-1192 (JP)

(72) Inventors:
• **Ohta, Riichiro**
Nagakute-shi, Aichi 480-1192 (JP)
• **Koga, Tomoyuki**
Nagakute-shi, Aichi 480-1192 (JP)
• **Ohwaki, Takeshi**
Nagakute-shi, Aichi 480-1192 (JP)
• **Okamoto, Atsuto**
Nagakute-shi, Aichi 480-1192 (JP)

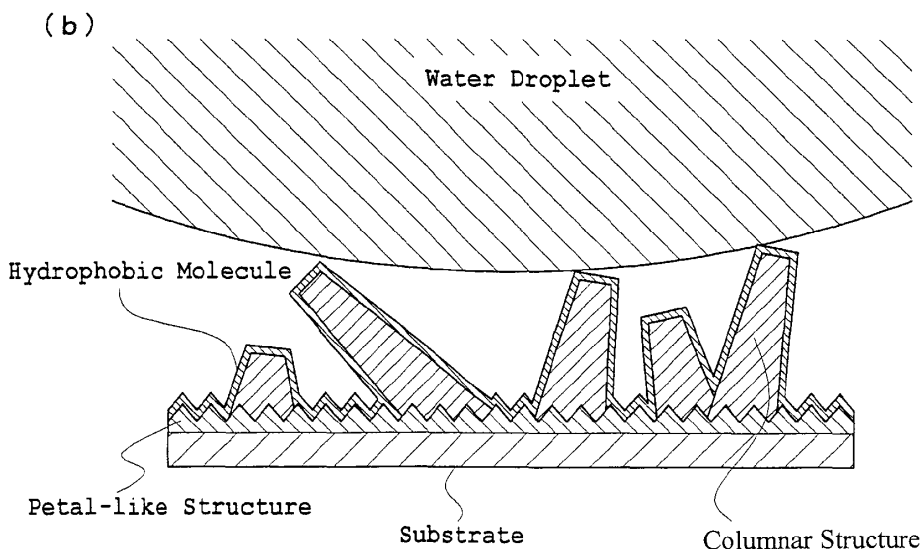
(74) Representative: **Kramer - Barske - Schmidtchen**
Landsberger Strasse 300
80687 München (DE)

(54) **Hydrophobic material and production process thereof**

(57) A hydrophobic material includes a substrate, a fine uneven structure formed on a surface of the substrate, and a hydrophobic molecule covering a surface of the fine uneven structure. The fine uneven structure includes a petal-like structure formed of an aggregate of a plurality of plate-like particles and a columnar structure formed of columnar particles, in which a length from a surface of the substrate to the tip of the columnar structure is longer than a length from the surface of the sub-

strate to the tip of the petal-like structure. The hydrophobic material is obtained by forming a fine uneven structure including a petal-like structure formed of an aggregate of a plurality of plate-like particles and a columnar structure formed of columnar particles on a surface of a substrate, in which a length from a surface of the substrate to a tip of the columnar structure is longer than a length from the surface of the substrate to a tip of the petal-like structure, and covering a surface of the fine uneven structure with a hydrophobic molecule.

[Fig. 1]



Description

FIELD OF THE INVENTION

[0001] The present invention relates to a hydrophobic material and a production process thereof, and more particularly to a hydrophobic material in which a super hydrophobic layer having extremely high hydrophobicity is formed on a surface of a substrate, and a production process thereof.

BACKGROUND OF THE INVENTION

[0002] Super hydrophobicity refers to a phenomenon that water droplets contact the surface of a material at a contact angle of 150° or more. When the surface of a material has super hydrophobicity, water droplets on the surface of the material become spherical and slide on the surface. It has been contemplated to apply a material including the super hydrophobicity to the body of a vehicle which requires the reduction in washing costs, the hull of a high speed vessel which requires the reduction in water friction, the external wall of a house which requires anti-contamination, rain gear or clothing which requires waterproof property, a heat exchanger or an antenna of a cold district, which requires the prevention of frost formation, and the like.

[0003] Various proposals have been made in the related art about a hydrophobic material having the super hydrophobicity.

For example, Patent Document 1 discloses a super hydrophobic aluminum foil with the coating film of a condensate of hexyltrimethoxysilane which does not include fluorine or a condensate of heptadecafluorodecyltrimethoxysilane which includes fluorine directly provided on the surface of the hot water-treated metal aluminum foil.

The document describes that:

- (1) when the metal aluminum foil is subjected to hot-water treatment, nanosheets are grown on the metal aluminum foil in a vertical direction; and
- (2) when heptadecafluorodecyltrimethoxysilane is coated on the metal aluminum foil, super hydrophobicity is exhibited.

[0004] Further, Patent Document 2 discloses a scroll vacuum pump, in which (1) the surface of a fixed scroll and a rotary scroll consisting of aluminum casting is subjected to anodic oxidation treatment,

- (2) polytetrafluoroethylene is impregnated in fine pores of the anodic oxidized layer,
- (3) the aluminum casting is immersed in a boiling sodium carbonate aqueous solution to form an aluminum hydrate layer having fine unevenness on the surface of the anodic oxidized layer, and
- (4) a fluorine compound layer is formed on the surface of the aluminum hydrate layer.

The document describes that the surface of the aluminum casting has super hydrophobicity by this treatment.

[0005] In addition, Patent Document 3 discloses a method of sputtering Al on a glass substrate to 140 nm thick, putting the glass substrate into ion exchanged water, and leaving the glass substrate to stand as it is at 90°C for 60 minutes. The document describes that a nanosheet structure is formed on the glass substrate by the method.

[0006] Furthermore, Non-Patent Document 1, which does not relate to a hydrophobic material, but discloses a method of immersing an yttria-stabilized tetragonal zirconia substrate in a suspension (70°C) which is prepared by dispersing an AlN powder in water, lifting the substrate after a predetermined time has elapsed, and drying the substrate.

The document describes that:

- (1) when the substrate is maintained in the suspension for 15 minutes, the lamellar of boehmite completely covers the surface of the substrate; and
- (2) when the substrate is maintained in the suspension for four hours, large bayerite particles are precipitated.

[0007] As described in Patent Documents 1 and 2, when fine unevenness is formed on the surface and the unevenness surface is covered with a fluorine-based compound having high hydrophobicity, super hydrophobicity is exhibited. However, in order to apply the hydrophobic material to various uses, it is required to further improve its hydrophobicity.

[Citation List]

[Patent Document]

[0008]

[Patent Document 1] Japanese Patent Application Laid-Open No. 2008-104936

[Patent Document 2] Japanese Patent Application Laid-Open No. 2005-315142

[Patent Document 3] Japanese Patent Application Laid-Open No. 2008-266709

[Non-Patent Document]

[0009]

[Non-Patent Document 1] K. Krnel et al., Journal of the American Ceramic Society, 92(10) 2451-2454(2009)

SUMMARY OF THE INVENTION

[0010] A problem to be solved by the present invention is to provide a novel hydrophobic material provided with super hydrophobicity and a production process thereof.

[0011] In order to solve the problem, the gist of the hydrophobic material according to the present invention is to include the following constitutions.

(1) The hydrophobic material includes:

- a substrate;
- a fine uneven structure formed on a surface of the substrate; and
- a hydrophobic molecule covering a surface of the fine uneven structure.

(2) The fine uneven structure includes:

- a petal-like structure formed of an aggregate of a plurality of plate-like particles; and
- a columnar structure formed of columnar particles, and
- the length from the surface of the substrate to a tip of the columnar structure is longer than a length from the surface of the substrate to a tip of the petal-like structure.

[0012] The gist of the production process of the hydrophobic material according to the present invention is to include the following constitutions.

(1) an unevenness step of forming a fine uneven structure including a petal-like structure formed of an aggregate of a plurality of plate-like particles and a columnar structure formed of columnar particles on a surface of a substrate, in which a length from the surface of the substrate to a tip of the columnar structure is longer than a length from the surface of the substrate to a tip of the petal-like structure to obtain a fine uneven substrate, and

(2) a covering step of covering a surface of the fine uneven structure with a hydrophobic molecule to obtain a hydrophobic molecule-covered fine uneven substrate.

[0013] When the surface of the substrate is subjected to predetermined treatment, a fine uneven structure including a fine petal-like structure and a coarse columnar structure may be formed. When the surface of the fine uneven structure is covered with a hydrophobic molecule, excellent super hydrophobicity is exhibited, compared to the case in which the surface of the substrate including only a fine petal-like structure is covered with a hydrophobic molecule.

This is thought to be because the contact area between water droplets and a fine uneven structure decreases and the area of the interface between droplets and an air layer, which is formed between the projections increases, by combining the petal-like structure with the columnar structure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

FIG. 1(a) is a schematic cross-sectional view of a hydrophobic material in the related art, and FIG. 1(b) is a schematic cross-sectional view of a hydrophobic material according to the present invention;

FIG. 2 is a view illustrating the relationship between the time and the moving distance during a dynamic sliding test conducted by inclining the surface of samples after covering with the hydrophobic molecule prepared in Example 2 and Comparative Example 2 by 2° from the horizontal direction;

FIG. 3 is a view illustrating the relationship between the time and the moving distance during a dynamic sliding test conducted by inclining the surface of samples after covering with the hydrophobic molecule prepared in Example 2 and Comparative Example 2 by 1° from the horizontal direction;

[0015]

FIG. 4 is FESEM images on the surface of a sample before covering with the hydrophobic molecule, which is prepared in Example 1 ((a) a low-magnification image, (b) an intermediate-magnification image, (c) a high-magnification image of the petal-like structure, and (d) a high-magnification image of the columnar structure);

FIG. 5 is FESEM images on the surface of a sample after covering with the hydrophobic molecule, which is prepared in Example 1 ((a) a low-magnification image, (b) an intermediate-magnification image, (c) a high-magnification image of the petal-like structure, and (d) a high-magnification image of the columnar structure);

[0016]

FIG. 6 is FESEM images on the surface of a sample before covering with the hydrophobic molecule, which is prepared in Comparative Example 1 ((a) a low-magnification image and (b) a high-magnification image of the petal-like structure);

FIG. 7 is FESEM images on the surface of a sample after covering with the hydrophobic molecule, which is prepared in Comparative Example 1 ((a) a low-magnification image and (b) a high-magnification image of the petal-like structure);

FIG. 8 is FESEM images observed by inclining the surface of the sample by 45° before covering with the hydrophobic molecule, which is prepared in Example 1 ((a) a low-magnification image and (b) a high-magnification image); and

FIG. 9 is X-ray diffraction patterns of an Al substrate in Example 1 (TEA-added water) an Al substrate in Comparative Example 1 (only water), and an Al substrate (untreated Al) which is subjected to only chemical polishing and is not subjected to fine uneven treatment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] Hereinafter, an embodiment of the present invention will be described in detail.

[1. Hydrophobic Material]

[0018] The hydrophobic material according to the present invention includes the following constitutions:

(1) The hydrophobic material includes:

- a substrate;
- a fine uneven structure formed on a surface of the substrate; and
- a hydrophobic molecule covering a surface of the fine uneven structure, and

(2) The fine uneven structure includes

- a petal-like structure formed of an aggregate of a plurality of plate-like particles; and
- a columnar structure formed of columnar particles,

wherein a length from a surface of the substrate to the tip of the columnar structure is longer than length from the surface of the substrate to the tip of the petal-like structure.

[1.1. Substrate]

[0019] The shape of the substrate is not particularly limited and may be arbitrarily selected according to the purpose. Examples of the shape of the substrate include a plate, a rod, a tube, a honeycomb, a fiber, a foil, a powder, a porous body and the like.

[0020] The material for the substrate is not particularly limited, and an appropriate material may be selected according

to the method of forming a fine uneven structure to be described below, the use of the hydrophobic material and the like. Examples of the material for the substrate include:

- (1) a metal material such as aluminum, an aluminum alloy, iron, an iron alloy, magnesium, a magnesium alloy, nickel, a nickel alloy, titanium, a titanium alloy, cobalt, a cobalt alloy and the like;
- (2) ceramics such as zeolite, zirconia, hydroxyapatite, alumina, silica, titania, barium titanate and the like;
- (3) a carbon material such as amorphous carbon, diamond-like carbon, diamond, graphite, carbon nanotubes, graphene and the like;
- (4) a polymer material such as polyvinyl alcohol, polyethylene terephthalate, polyethylene glycol, polycarbonate, polyacrylonitrile, polyethylene and the like; and
- (5) a semiconductor material such as silicon, germanium, gallium arsenide, gallium phosphide, gallium nitride, silicon carbide and the like.

[0021] In addition, when a fine uneven structure is formed by using a hot-water treatment method to be described below, an aluminum-containing material is preferably used as the substrate.

The "aluminum-containing material" refers to a material which includes Al as a significant component and may elute Al having an amount sufficient to precipitate boehmite and bayerite on the surface of the material by hot-water treatment under the coexistence of an amine-based molecule.

Examples of the aluminum-containing material include aluminum, an aluminum alloy, aluminum nitride, aluminum gallium nitride and the like.

[1.2. Fine Uneven Structure]

[0022] A fine uneven structure is formed on the surface of a substrate. The fine uneven structure may be formed on the entire surface of the substrate, or may be formed on only a portion which requires super hydrophobicity in the surface of a substrate.

The "fine uneven structure" refers to a structure including a fine petal-like structure and a coarse columnar structure.

[0023] The "petal-like structure" refers to a structure formed of an aggregate of a plurality of plate-like particles. Individual plate-like particles are facing random directions in the surface of the substrate. That is, the petal-like structure refers to a structure in which fine plate-like particles having a nanometer-sized thickness are densely packed like petals. The petal-like structure is formed in a region in which at least a columnar structure is not formed in the surface of the substrate. Further, according to the preparation method of the fine uneven structure, a petal-like structure may be further formed on the surface of the columnar structure in some cases.

The size of plate-like particles constituting the petal-like structure varies depending on the preparation method of the petal-like structure, but in order to obtain high hydrophobicity, the thickness of plate-like particles is preferably from 0.3 nm to 50 nm.

[0024] The "columnar structure" refers to a structure formed of columnar particles. For columnar particles, the diameters of one end and the other end thereof may not be the same as each other. The length (L_1) from the surface of the substrate to the tip of the columnar structure needs to be longer than the length (L_2) from the surface of the substrate to the tip of the petal-like structure. In other words, in order to exhibit super hydrophobicity, at least one end of the columnar structure needs to be at a position spaced apart from the tip of petal-like structure formed on the surface of the substrate. The bigger the difference between the size of the columnar structure and the size of the petal-like structure is, the higher the hydrophobicity becomes. In order to obtain high hydrophobicity, L_1 is longer than L_2 by preferably two-folds or more, more preferably five-folds or more, and even more preferably ten-folds or more.

The size of columnar particles constituting the columnar structure varies depending on the preparation method of the columnar structure, but in order to obtain high hydrophobicity, the columnar particles preferably have a diameter of 0.4 nm or more and a length of 50 nm or more. Herein, the "diameter of columnar particles" refers to a maximum length of the cross-section in a vertical direction to the axis direction of columnar particles. The columnar particles need not be a cylinder. For example, when the cross-section of the columnar particles is a regular square, the diameter of the columnar particles refers to the diagonal length of the regular square.

[0025] The upper limit of the diameter of the columnar structure which may exhibit super hydrophobicity varies depending on the size of water droplets which contact the surface thereof. Even though the diameter of the columnar structure is large, when water droplets are sufficiently larger than the columnar structure, super hydrophobicity may be exhibited. For this reason, the diameter of the columnar structure may be appropriately adjusted depending on the size of water droplets to be a target in accordance with the use of the hydrophobic material.

The number density of the columnar structure may also be appropriately optimized depending on the size of water droplets to be a target in accordance with the use of the hydrophobic material.

However, when the columnar structure is bayerite and uses the preparation method of the present invention, it is tech-

nically difficult to obtain a columnar structure having a diameter of 1 mm or more.

Further, when the columnar structure is carbon, it is technically difficult to obtain a columnar structure formed of monolayered carbon nanotubes and having a diameter of 0.4 nm or less.

Even when the length of the columnar structure is longer than necessary, there is no difference in obtaining super hydrophobicity, and thus there is no substantial advantage. When the columnar structure is bayerite and uses the method according to the present invention, it is technically difficult to obtain a columnar structure having a length of 1 mm or more.

[0026] In the fine uneven structure, it is preferred that coarse columnar particles having a size from submicron to micron are discretely formed on the surface of the substrate and a fine petal-like structure having a nanometer-size is formed in the gap thereof. The columnar structure may be formed directly on the surface of the substrate in some cases, or may be formed on the petal-like structure to be a basis in some cases.

Individual columnar particles usually are facing random directions, and thus an angle formed by the axis direction of the columnar particles and the surface of the substrate varies for each particle. That is, there are columnar particles grown almost vertically to the surface of the substrate, and there are columnar particles grown almost in parallel to the surface of the substrate.

[0027] The material constituting the petal-like structure and the columnar structure is not particularly limited, and various materials may be used depending on the formation method thereof.

Examples of the material constituting the petal-like structure include boehmite, carbon, nickel hydroxide and the like.

Examples of the material constituting the columnar structure include bayerite, carbon and the like.

[0028] The combination of materials constituting the petal-like structure and the columnar structure is not particularly limited, and various combinations may be selected depending on the formation method thereof.

For example, when an aluminum-containing material is subjected to hot-water treatment under the coexistence of an amine-based molecule, or when a suspension prepared by dispersing an AlN powder in water is coated on the surface of the substrate, the petal-like structure is formed of boehmite and the columnar structure is formed of bayerite.

Examples of other material combinations (petal-like structure, columnar structure) include (carbon nanowall, carbon nanofiber), (carbon nanowall, carbon nanotube) and the like.

[0029] When the hydrophobic molecule is a molecule including a polar functional group (B) to be described below, the polar functional group (B) has high adsorptivity to:

(1) the surface of metal oxide; or

(2) the surface of a metal material, a polymer material, a ceramic material or a carbon material having a polar functional group (A) consisting of a silanol group, a functional group that forms a silanol group by hydrolysis, a hydroxyl group, a phosphoric acid group, a carboxyl group, a sulfo group, an aldehyde group, an amino group and the like or a salt thereof on the surface.

For this reason, when the whole of the fine uneven structure or at least the surface thereof is formed of a metal oxide or a material having the polar functional group (A), the hydrophobic molecule may be fixed on the surface of the fine uneven structure by interaction between the polar functional group (B) and the surface of the fine uneven structure.

However, in order to strongly bond the hydrophobic molecule with the fine uneven structure, it is preferred that the formation of covalent bond between them is accelerated by heat treatment or a chemical reaction using a catalyst.

[1.3. Hydrophobic Molecule]

[1.3.1. Definition]

[0030] The surface of the fine uneven structure is covered with a hydrophobic molecule. The hydrophobic molecule may be only physically adsorbed on the surface of the fine uneven structure in some cases, or may be chemically bonded to the surface of the fine uneven structure through the polar functional group (B) in some cases.

The "hydrophobic molecule" refers to a molecule in which when a flat surface is densely covered with the molecule and droplets are added dropwise thereto, an angle (static contact angle of water droplet) formed by the surface thereof and water droplets is 90° or more.

The hydrophobic molecule may be a molecule including only a moiety that contributes to hydrophobic property, or a molecule further including the polar functional group (B) that may form a chemical bond between the molecule and the surface of the fine uneven structure, in addition to the moiety. The polar functional group (B) may only react with a metal oxide or the polar functional group (A) which is present on the surface of the fine uneven structure, and need not always be the same functional group as the polar functional group (A).

[0031] Even a hydrophobic molecule that does not include the polar functional group (B) may be physically adsorbed on the surface of a substrate to form a coating film when the molecule has a high molecular weight and exists as a solid around at room temperature. However, the coating film has a weak interaction with the substrate, and thus the mechanical

durability thereof is extremely low. On the contrary, when the fine uneven structure is chemically bonded to the hydrophobic molecule through the polar functional group (B), hydrophobicity may be sustained over a long period.

[0032] As the hydrophobic molecule, molecules including a fluoroalkyl group (Rf) and molecules including a hydrocarbon group are known. The hydrophobicity of a hydrophobic molecule including Rf is higher than that of a hydrophobic molecule including a hydrocarbon group. Furthermore, the hydrophobic molecule including Rf has high hydrophobicity as the number of carbons in Rf increases.

[0033] Further, examples of the polar functional group (B) include:

- (1) silanol group, or a functional group that forms a silanol group by hydrolysis (for example, a chlorosilane group, a methoxy silane group, an ethoxy silane group and the like) (hereinafter, these groups are also referred to as "a silanol-based functional group");
- (2) a hydroxyl group, a phosphoric acid group, a carboxyl group, a sulfo group, an aldehyde group and an amino group;
- (3) salts of (1) or (2).

Among them, the silanol-based functional group or a salt thereof may form a strong bond with a substrate and thus is suitable as the polar functional group (B).

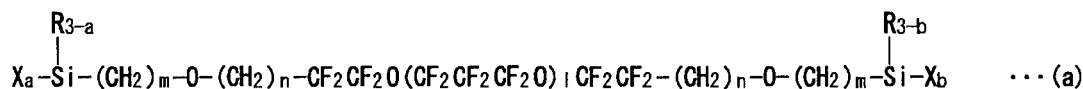
[1.3.2. Specific Examples]

[0034] Specific examples of the hydrophobic molecule include the followings. These hydrophobic molecules may be used either alone or in combination of two or more thereof.

[1.3.2.1. Hydrophobic Molecule Including Silanol-Based Functional Group]

[0035] A first specific example is a molecule represented by the following Formula (a) as a hydrophobic molecule including a silanol-based functional group.

[Chem. 1]



where, R: a monovalent hydrocarbon having from 1 to 8 carbon atoms,

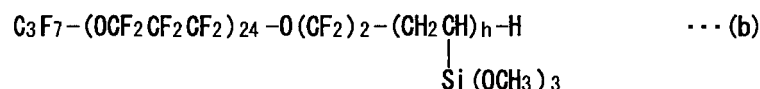
X: -OR (R is an alkyl group), -OH or a halogen atom,

l: an integer of 0 or higher, m: an integer from 1 to 5, n: an integer from 0 to 2, and a and b: 2 or 3.

[0036] The molecular weight of a hydrophobic molecule represented by Formula (a) varies depending on the number of carbons of R or the number (l, m, n) of repetitions of the repeating unit, but is usually in a range from 2,000 to 3,000. The molecule represented by Formula (a) is commercially available.

[0037] A second specific example is a molecule represented by the following Formula (b) as a hydrophobic molecule including a silanol-based functional group.

[Chem. 2]



where, h: an integer from 1 to 10.

[0038] The hydrophobic molecule represented by Formula (b) exhibits hydrophobicity higher than that of the hydrophobic molecule represented by Formula (a). The hydrophobic molecule represented by Formula (b) is commercially available.

[0039] A third specific example is a molecule including an Rf having 8 carbon atoms or more (hereinafter referred to as "hydrophobic molecule (c)") as a hydrophobic molecule including a silanol-based functional group.

Examples of the hydrophobic molecule (c) include (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-1-triethoxysilane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-1-trimethoxysilane and the like.

[0040] The hydrophobic molecule (c) has been frequently used until now in the preparation of a hydrophobic surface, in that a silanol-based functional group easily reacts with the surface of a substrate.

However, environmental pollution or toxicity to an animal or a human body caused by these molecules has become a problem. For example, in animal experiments using mice, it has recently been confirmed that (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-1-triethoxysilane causes damage to the lung (Reference Document 1). For this reason, for example, a ban on the use of the molecule and molecules similar thereto in Denmark is described in a document written in the Stockholm Conference on Persistent Organic Pollutants (POPs) (Reference Documents 2 and 3).

Reference Document 1: "Lung Damage in Mice after Inhalation of Nanofilm Spray Products: The Role of Perfluorination and Free Hydroxyl Groups," Asger W. Norggad, Søren T. Larsen, Maria Hammer, Steen S. Poulsen, Keld A. Jensen, Gunnar D. Nielsen, Peder Wolkoff; Toxicological Science 116(1), 216-224 (2010).

Reference Document 2: Report of the Persistent Organic Pollutants Review Committee on the work of its sixth meeting, Addendum, Guidance on alternatives to perfluorooctane sulfonate and its derivatives, 14 October 2011.

Reference Document 3: Milijostyrelsen, Pressemeldelser, Nanospray, 16 April 2010.

[0041] In addition, there is concern that the perfluorooctanoic acid (PFOA), whose hazardousness has been concerned in the related art, is produced as a by-product produced during the preparation of these molecules or a decomposition product produced from products covered with these molecules. Herein, the hazardousness refers to remaining in a living body and bioaccumulation. When the number of carbons in R_f is 8 or higher, the bioaccumulation potential is considered to be high.

[0042] On the contrary, molecules represented by Formulas (a) and (b) exhibit high hydrophobicity and do not generate molecules including an R_f having 8 carbon atoms or more even when these molecules are decomposed, and thus the bioaccumulation potential is low. For this reason, molecules represented by Formulas (a) and (b) are suitable as a hydrophobic molecule. The molecules represented by Formulas (a) and (b) may be used either alone or in combination of two or more thereof.

[0043] The hydrophobic molecule including a silanol-based functional group may be prepared by using, as a raw material, an ethylene-based hydrophobic molecule that is a hydrophobic molecule having a carbon-carbon double bond, or an acetylene-based hydrophobic molecule that is a hydrophobic molecule having a carbon-carbon triple bond.

For example, a hydrophobic molecule including a chlorosilane group may be prepared by reacting an ethylene-based hydrophobic molecule with trichlorosilane.

For example, a hydrophobic molecule including a methoxysilane group may be prepared by reacting an ethylene-based hydrophobic molecule with trimethoxysilane.

For example, a hydrophobic molecule including an ethoxysilane group may be prepared by reacting an ethylene-based hydrophobic molecule with triethoxysilane.

As a catalyst which allows these reactions to proceed, a platinum-based catalyst such as C₈H₁₈OSi₂Pt (Karstedt catalyst), H₂PtCl₆ (Speyer catalyst) and the like, a nickel-based catalyst, a palladium-based catalyst, a ruthenium-based catalyst, and the like may be used.

[1.3.2.2. Hydrophobic Molecule Including Polar Functional Groups Other Than Silanol-Based Functional Group]

[0044] Specific examples of a hydrophobic molecule including polar functional groups other than a silanol-based functional group include:

(1) ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA) as a hydrophobic molecule including an ammonium salt of a carboxyl group;

(2) N-methyl perfluorobutane sulfonamidoethanol (N-MeFBSE) as a hydrophobic molecule including a hydroxyl group;

(3) N-ethyl perfluorobutane sulfonamidoethanol (N-EtFBSE) as a hydrophobic molecule including a hydroxyl group; and

(4) perfluoropolyether (PFPE) including a hydroxyl group at one end or both ends of the molecular chain thereof as a hydrophobic molecule including a hydroxyl group.

These are commercially available. Further, a hydrophobic molecule including another polar functional group may be prepared by a known method using a compound having a similar molecular structure as a starting material.

[1.3.2.3. Hydrophobic Molecule Which Does Not Include Polar Functional Group]

[0045] Specific examples of a hydrophobic molecule which does not include a polar functional group include PFPE including a fluorocarbon group at both ends of the molecular chain thereof, and the like.

These are commercially available or may be prepared by a known method using a compound having a similar molecular structure as a starting material.

[1.3.3. Chemical Bond]

[0046] When a hydrophobic molecule includes the polar functional group (B), the hydrophobic molecule may be a molecule that may only cover the surface of the fine uneven structure physically, or a molecule in which a chemical bond is formed between the surface of the fine uneven structure and the polar functional group (B).

The method of forming the chemical bond will be described below.

[2. Production Process of Hydrophobic Material]

[0047] The production process of the hydrophobic material according to the present invention includes a fine unevenness step and a covering step. The production process of the hydrophobic material may further include a bonding step.

[2.1. Unevenness Step]

[0048] The unevenness step is a step of forming a fine uneven structure including a petal-like structure formed of an aggregate of a plurality of plate-like particles and a columnar structure formed of columnar particles on a surface of the substrate, in which a length from a surface of the substrate to a tip of the columnar structure is longer than a length from the surface of the substrate to a tip of the petal-like structure, thereby obtaining a fine uneven substrate.

The method of forming the fine uneven structure is not particularly limited, and an appropriate method may be selected according to the material constituting the substrate and the material constituting the fine uneven structure. Specific examples thereof include the following methods.

[2.1.1. Specific Example 1]

[0049] A first method is a method (hot-water treatment method) of immersing a substrate in a solution including water and an amine-based molecule at a temperature from 60°C to 300°C when the substrate is an aluminum-containing material. By this method, it is possible to form a fine uneven structure including a petal-like structure formed of boehmite and a columnar structure formed of bayerite on the surface of the substrate formed of the aluminum-containing material.

[0050] The "amine-based molecule" refers to:

(a) ammonia; or

(b) a molecule (for example, triethylamine, triethanolamine, trimethylamine and the like) in which the all or some of hydrogen in ammonia is substituted with a hydrocarbon group.

When the aluminum-containing material is subjected to hot-water treatment with only water, a fine uneven structure including only a petal-like structure is formed. Meanwhile, when the aluminum-containing material is subjected to hot-water treatment under the coexistence of an amine-based molecule, a fine uneven structure including both a petal-like structure and a columnar structure may be formed.

[0051] The content of the amine-based molecule included in an aqueous solution is not particularly limited, and may be arbitrarily selected according to the purpose. In general, as the content of the amine-based molecule increases, a fine uneven structure may be formed by treatment at a lower temperature and/or for a shorter period.

[0052] When the hot-water treatment temperature is extremely low, the precipitation rate of boehmite or bayerite is reduced, thereby making it difficult to form the fine uneven structure within a practical time. Therefore, the hot-water treatment temperature needs to be 60°C or more. The hot-water treatment temperature is more preferably 80°C or more, and even more preferably 100°C or more.

Meanwhile, when the hot-water treatment temperature is increased more than necessary, there is concern that deformation or crack and the like of the substrate may occur. The equipment costs are also increased. Therefore, the hot-water treatment temperature needs to be 300°C or less.

The time for the hot-water treatment is sufficient as long as it is time during which a desired fine uneven structure is formed. In general, as the hot-water treatment temperature is increased, a fine uneven structure may be formed for a shorter period.

Further, when the hot-water treatment temperature exceeds the boiling point of an aqueous solution, it is necessary to perform the hot-water treatment in a hermetically sealed container.

[0053] When the aluminum-containing material is subjected to hot-water treatment under the coexistence of amine, a fine uneven structure including both a petal-like structure and a columnar structure is obtained. This is thought to be based on the following reasons.

That is, boehmite and bayerite are known to be formed during hydro-thermal sealing of an anodic oxidation coating film. In this treatment, in general, boehmite is formed by treatment at about 80°C or higher, while bayerite is formed by treatment at about 80°C or lower.

[0054] Even in the present invention, it is thought that bayerite is formed at a temperature lower than that of boehmite, and it is presumed that boehmite is precipitated when kept at a high temperature, and then bayerite is precipitated during the cooling.

Both a petal-like structure and a columnar structure are formed by adding an amine-based molecule to a treatment solution during the hot-water treatment. This is thought to be because the etching of an aluminum-containing substrate is accelerated, and thus the amount of Al-containing ions in the treatment solution is increased compared to the case of only water. That is, it is presumed that the amount of remaining Al-containing ions which are not precipitated as boehmite when kept at a high temperature is increased by the addition of an amine-based molecule, and thus these ions are precipitated as bayerite in the cooling process.

[0055] On the contrary, only a petal-like structure is formed by hot-water treatment with only water. This is thought to be because the amount of Al-containing ions eluting in the treatment solution is small. That is, the Al-containing ions necessary for growing boehmite are present in the treatment solution, but most of the Al-containing ions are precipitated as boehmite when kept at a high temperature. As a result, it is presumed that Al-containing ions are not present in the solution in an amount necessary for growing bayerite during the cooling.

Although the reason that bayerite becomes a columnar structure is not clearly explained, it is presumed that:

- (1) a form derived from the crystal structure of bayerite is formed; or
- (2) the amine-based molecule acts as a surfactant.

[2.1.1. Specific Example 2]

[0056] A second method is a method of dispersing AlN in water to prepare a suspension, immersing a substrate in the suspension heated at a predetermined temperature (for example, 70°C), lifting the substrate after a predetermined time has elapsed, and drying the substrate (see Non-Patent Document 1).

By this method, it is possible to form a fine uneven structure including a petal-like structure formed of boehmite and a columnar structure formed of bayerite on the surface of the substrate. The method is advantageous in that a fine uneven structure formed of boehmite and bayerite may be formed even on a substrate formed of a material other than the aluminum-containing material.

[2.1.1. Specific Example 3]

[0057] A third method is a method of forming a petal-like structure and a columnar structure separately. In this case, any structure may be formed in advance as long as it is possible to form a fine uneven structure. The method is advantageous in that the combination of materials constituting the petal-like structure and materials constituting the columnar structure may be arbitrarily selected. Furthermore, depending on the preparation method, the petal-like structure may be formed on the surface of the columnar structure as well as on the surface of the substrate in some cases.

[0058] Examples of the method of preparing the petal-like structure include:

- (1) a method of subjecting an aluminum-containing material to hot-water treatment under an environment in which only water is present;
- (2) a plasma chemical vapor deposition (CVD) method or a high speed and high pressure CVD method of using a raw material including carbon to form a petal-like structure (also referred to as carbon nanowall or Graphene Flower (registered trademark)) formed of a monolayer or multilayer graphenes (see, for example, Japanese Patent No. 4762945);
- (3) a method of heating an aqueous solution including a nickel salt, ethylenediamine and sodium hydroxide to form a petal-like structure formed of nickel hydroxide (see, for example, "Self-Assembled Hollow Spheres of β -Ni(OH)₂ and Their Derived Nanomaterials," Shengmao Zhang, Hua Chun Zeng; Chemistry of Materials 21,871-883(2009)), and the like.

[0059] Further, examples of the method of preparing the columnar structure include:

(1) a method of using, as a template, a substrate having a plurality of fine pores with a diameter of 100 nm or more and a depth of 100 nm or more to fill fine pores with a material constituting a columnar structure and transfer the material in the fine pores on the surface of the substrate;

(2) a method of preparing a columnar structure formed of carbon nanofibers by a plasma-assisted chemical vapor deposition method using a carbon source (for example, a hydrocarbon gas such as methane and the like) on a silicon substrate in which a nickel catalyst in the form of particle or thin film is supported;

(3) a method of preparing a columnar structure formed of carbon nanotubes by densely supporting a fine catalyst (for example, an Fe-Ti-O-based catalyst) on the surface of a substrate, introducing a carbon source into the surface of the substrate, and thermally decomposing the carbon source.

Examples of the method of preparing a substrate having a plurality of fine pores include:

(a) a method of etching a flat substrate by focused ion beam; and

(b) a method of forming a porous alumite layer by anodic oxidation of an aluminum substrate.

Examples of the method of filling fine pores of a substrate with a material include:

(a) a method of using a template as an electrode to electrodeposit a metal in fine pores; and

(b) a method of impregnating a metal alkoxide-based raw material in fine pores and polycondensing the metal alkoxide-based raw material in the fine pores.

[0060] When the surface of the fine uneven structure thus-formed is not formed of a metal oxide or a material having a polar functional group (A), it is preferred that the surface of the fine uneven structure is oxidized or the polar functional group (A) is introduced into the surface of the fine uneven structure. The method of introducing the polar functional group (A) is not particularly limited, and a known method may be used.

[0061] When the fine uneven structure is formed of boehmite and bayerite, the treatment of introducing a functional group is not always necessary, and a hydroxyl group derived from the chemical structure thereof is already included on the surface thereof.

For example, when the fine uneven structure is formed of boehmite and bayerite, in order to introduce an amino group into the surface thereof, the fine even structure may be heated while being brought into contact with a gas including an ammonium molecule or may be brought into contact with ammonia plasma.

For example, when the fine even structure is formed of carbon, in order to introduce a hydroxyl group into the surface thereof, the fine uneven structure may be irradiated with ultraviolet light while being brought into contact with a gas including an oxygen molecule or steam.

For example, when the fine uneven structure is formed of carbon, in order to introduce an amino group into the surface thereof, the fine uneven structure may be brought into contact with ammonia plasma.

[2.1.4. Specific Example 4]

[0062] A fourth method is a method of preparing a petal-like structure and a columnar structure simultaneously.

For example, a pattern including two regions of a region in which a nickel catalyst is present on a silicon substrate and the other region in which the surface of the silicon substrate is exposed is formed. When performing plasma CVD using a carbon source on a substrate including the pattern, it is possible to grow a columnar structure formed of carbon nanofibers in a nickel catalyst region, and to grow a petal-like structure formed of carbon nanowalls in a region in which the surface of the substrate is exposed.

[2.2. Covering Step]

[0063] The covering step is a step of covering the surface of the fine uneven structure with a hydrophobic molecule to obtain a hydrophobic molecule-covered unevenness substrate.

Details on the hydrophobic molecule are the same as those described above, and thus the description thereof will be omitted.

The method of covering the hydrophobic molecule is not particularly limited, and various methods may be used. Typically, the covering with the hydrophobic molecule is performed by dissolving the hydrophobic molecule in a suitable solvent to prepare a solution, coating the solution on the surface of the fine uneven structure, and volatilizing the solvent. By the method, a coating film of the hydrophobic molecule may be formed on the surface of the fine uneven structure. Examples of the coating method of the solution include coating by a brush, dipping, spin coat, sink and the like.

[2.3. Bonding Step]

[0064] The bonding step is a step of forming a chemical bond between the surface of the fine uneven structure and the polar functional group (B) after the covering step, in the case where at least the surface of the fine uneven structure is formed of a metal oxide or a material having a polar functional group (A) and a hydrophobic molecule includes a polar functional group (B) that may form a chemical bond between the molecule and the surface of the fine uneven structure. Super hydrophobicity is exhibited by only physically adsorbing the hydrophobic molecule on the surface of the fine uneven structure. However, durability is low in the case where the hydrophobic molecule is only physically adsorbed. For this reason, when the hydrophobic molecule includes the polar functional group (B) and the surface of the fine uneven structure is in a state capable of being bonded to the polar functional group (B), it is preferred that the surface of the fine uneven structure is covered with the hydrophobic molecule, and then treatment of forming a chemical bond between the fine uneven structure and the polar functional group (B) is performed.

[0065] The treatment for forming a chemical bond varies depending on the kind of polar functional group (B) or the surface state of the fine uneven structure.

For example, when the polar functional group (B) is a silanol-based functional group and at least the surface of the fine uneven structure is formed of a metal oxide or a material having a polar functional group (A), the hydrophobic molecule-covered fine uneven substrate may be heated. When the substrate is heated, the hydrophobic molecule is bonded to the surface of the fine uneven structure through a silanol-based functional group.

In this case, when the heating temperature is too low, the reaction rate becomes slow, and the bonding becomes insufficient. Therefore, the heating temperature is preferably 50°C or more.

Meanwhile, when the heating temperature is too high, the hydrophobic molecule may be decomposed. Therefore, the heating temperature is preferably 300°C or lower.

[0066] Even in the case of between other polar functional groups, it is possible to bond the hydrophobic molecule on the surface of the fine uneven structure by allowing a dehydration and condensation reaction and the like between the polar functional groups to proceed while adjusting the heating temperature or using a catalyst.

[3. Effects of Hydrophobic Material and Production Process Thereof]

[0067] FIG. 1(a) illustrates a schematic cross-sectional view of a hydrophobic material in the related art. In addition, FIG. 1(b) illustrates a schematic cross-sectional view of a hydrophobic material according to the present invention.

As described in Patent Document 1, when a substrate formed of a metal aluminum foil is subjected to hot-water treatment, a petal-like structure, in which nanosheets formed of boehmite on the surface of the substrate are grown in a vertical direction, is obtained, as illustrated in FIG. 1(a). When a hydrophobic molecule (for example, short-chain Rf polymer such as heptadecafluorodecyltrimethoxysilane and the like) is coated on the petal-like structure, the surface of the substrate exhibits super hydrophobicity. Water droplets on the surface of the substrate are ideally supported in the vicinity of the vertex of the fine petal-like structure, and the distance from the valley of the petal-like structure to the droplet is short.

[0068] On the contrary, when the surface of the substrate is subjected to predetermined treatment, it is possible to form a fine uneven structure including a fine (for example, a size of nanometer) petal-like structure and a coarse (for example, a size from submicron to micron) columnar structure, as illustrated in FIG. 1(b). When the surface of the fine uneven structure is coated with a hydrophobic molecule, the surface of the substrate exhibits super hydrophobicity. Furthermore, the hydrophobic material including the fine uneven structure exhibits excellent super hydrophobicity, compared to a hydrophobic material in the related art including only a petal-like structure.

This is thought to be because Water droplets on the surface of the substrate are ideally supported in the vicinity of the vertex of the coarse columnar structure, as illustrated in FIG. 1(b), and thus the distance from the valley of the petal-like structure to the water droplet becomes elongated. That is, water droplets on the surface of the substrate, which are hydrophobic and have a fine uneven structure, are brought into contact with the projections of the fine uneven structure in terms of the microscopic scale, and an air layer is formed between the projections. Herein, the smaller the contact area between water droplets and the projections becomes, that is, the larger the area of the interface between the air layer formed between the projections and water droplets becomes, the larger the contact angle with water droplets becomes. The fact that hydrophobicity is further improved by combining the petal-like structure with the columnar structure is thought to be because the contact area between water droplets and a fine uneven structure is decreased, and the area of the interface between an air layer formed between the projections and droplets is increased.

[0069] Frost is formed by attaching steam in the atmosphere to the surface of the substrate, then growing the steam into somewhat large water droplets by further introducing other steam in the atmosphere, passing the water droplets through a super-cooling state, and then freezing the water droplets.

When the super hydrophobic film is applied for preventing frost on the surface of the substrate from being formed, it is necessary to remove water droplets from the surface of the substrate by external wind or water slipping effects before

water droplets aggregating on the surface of the substrate are frozen. When the surface of the substrate includes a smooth region without the petal-like structure at the lower portion of the columnar structure or between the columnar structures, and is coated with a hydrophobic molecule, super hydrophobicity is not expressed in the smooth region. As a result, it is difficult for water droplets to be removed by external wind or water slipping effects. For this reason, water droplets are grown up to the micrometer scale and then frozen, and thus frost is generated.

[0070] Meanwhile, super hydrophobicity is exhibited up to the nanometer scale on the petal-like structure by combining the columnar structure with the petal-like structure. Therefore, water droplets may be removed by external wind or water slipping effects in the early stage before the water droplets are grown to a large size and frozen.

Further, when small droplets slide, some of the small droplets may aggregate on the fine uneven structure and grow to large water droplets to the micrometer scale or more in some cases, while not being removed from the fine uneven structure. In contrast, a combination of the columnar structure and the petal-like structure also has excellent super hydrophobicity against these large water droplets, compared to the structural body formed only of the petal-like structure due to effects of expanding the area of the interface between the air layer/the water droplets by the above-described columnar structure.

As described above, when the hydrophobic material is a composite of the columnar structure and the petal-like structure, and the entire surface thereof is covered with a hydrophobic molecule, the material has excellent super hydrophobicity against water droplets having a size in a wide range from the nanometer scale to the micrometer scale or more.

[Examples]

(Examples 1 and 2, Comparative Examples 1 and 2)

[1. Preparation of Sample]

[1.1. Examples 1 and 2]

[1.1.1. Chemical Polishing of Aluminum Substrate]

[0071] An aluminum substrate is immersed in a polishing solution (concentrated phosphoric acid: 95% by volume, concentrated nitric acid: 5 % by volume, and urea: 30 g/L) heated to about 85°C from 5 minutes to 10 minutes.

[1.1.2. Hot-Water Treatment]

[0072] The chemically polished aluminum substrate and a triethylamine aqueous solution (triethylamine: 5% by volume, pure water: 95% by volume) are enclosed in a hermetically sealed container, and then the container is heated at 120°C for three hours.

[1.1.3. Covering of Hydrophobic Molecule]

[0073] KY-130 (manufactured by Shin-Etsu Chemical Co., Ltd.) is dissolved in Novec 7200 (manufactured by Sumitomo 3M Limited) to prepare a solution having a polymer concentration: 0.2% by weight. It is described in Japanese Patent Application Laid-Open No. 2009-109612 that the polymer included in KY-130 has a chemical structure represented by Formula (a).

Subsequently, the fine uneven substrate manufactured in [1.1.2.] is immersed in the solution for one minute, and then the substrate is lifted from the solution at a pulling rate: 20 cm/min. Thereafter, the sample is subjected to heat treatment at 150°C (Example 1).

[0074] OPTOOL DSX (manufactured by DAIKIN INDUSTRIES, Ltd.) is dissolved in perfluorohexane to prepare a solution having a polymer concentration: 0.1% by weight. It is described in Japanese Patent Application Laid-Open No. 2009-109612 that the polymer included in OPTOOL DSX has a chemical structure represented by Formula (b).

Subsequently, the fine uneven substrate manufactured in [1.1.2.] is immersed in the solution for one minute, and then the substrate is lifted from the solution at a pulling rate: 20 cm/min. Thereafter, the sample is subjected to heat treatment at 150°C (Example 2).

[1.2. Comparative Examples 1 and 2]

[1.2.1. Chemical Polishing of Aluminum Substrate]

[0075] The aluminum substrate is subjected to chemical polishing in the same manner as in Example 1.

[1.2.2. Hot-Water Treatment]

[0076] The aluminum substrate subjected to chemical polishing and pure water are enclosed in a hermetically sealed container, and the container is heated at 120°C for three hours.

[1.2.3. Covering of Hydrophobic Molecule]

[0077] The surface of the fine uneven substrate manufactured in [1.2.2.] is covered with a hydrophobic molecule represented by Formula (a) in the same manner as in Example 1 (Comparative Example 1).

In addition, the surface of the fine uneven substrate manufactured in [1.2.2.] is covered with a hydrophobic molecule represented by Formula (b) in the same manner as in Example 2 (Comparative Example 2).

[2. Test Method and Result]

[2.1. Evaluation of Contact Angle of Water Droplet]

[0078] For the samples after coating with the hydrophobic molecule prepared in Example 1 and Comparative Example 1, 15 μ L of water droplet is dropped on the surface of the sample to measure an angle formed by the surface and the water droplet.

The contact angle on the sample prepared in Comparative Example 1 is 130°. Meanwhile, the contact angle of water droplet on the sample prepared in Example 1 is 150° or more, indicating super hydrophobicity.

For the samples prepared in Example 2 and Comparative Example 2, the contact angles of water droplet in both the samples are 150° or more, indicating super hydrophobicity. In addition, even at the contact angles (each angle of advance and angle of sweepback) when a water droplet is discharged and sucked from a syringe needle on the surface of the sample, a significant difference between both the samples is not found.

[2.2 Measurement of Dynamic Sliding]

[0079] For the samples after covering with hydrophobic molecules prepared in Example 2 and Comparative Example 2, 2 μ L of a water droplet while kept in a syringe is attached to the surface of the sample which had been in advance inclined by 1° or 2° from the horizontal direction. Thereafter, the water droplet is detached from the syringe by lifting the syringe. Immediately after being detached from the syringe, the water droplet begins to slide on the surface of the sample. The time after detaching the syringe from the water droplet and the moving distance of the water droplet are checked.

[0080] FIG. 2 illustrates the relationship between the time and the moving distance during a dynamic sliding test conducted by inclining the surface of a sample after covering with the hydrophobic molecule prepared in Example 2 and Comparative Example 2 by 2° from the horizontal direction. FIG. 3 illustrates the relationship between the time and the moving distance during a dynamic sliding test conducted by inclining the surface of a sample after covering with the hydrophobic molecule prepared in Example 2 and Comparative Example 2 by 1° from the horizontal direction.

Even in the measurement at any inclined angle, the acceleration of the water droplet during the sliding is high and the water droplet slides fast in the sample in Example 2, compared to the sample in Comparative Example 2.

[2.3. FESEM Observation]

[0081] For the samples before and after coating with the hydrophobic molecule prepared in Example 1 and in Comparative Example 1, each of the surface shapes thereof is observed by a field emission-type scanning electron microscope (FESEM).

FIGS. 4 and 5 each illustrate FESEM images of the surface of the samples before and after covering with the hydrophobic molecule prepared in Example 1. FIGS. 6 and 7 each illustrate FESEM images of the surface of the samples before and after covering with the hydrophobic molecule prepared in Comparative Example 1. Furthermore, FIG. 8 illustrates FESEM images observed by inclining the surface of the sample before covering with the hydrophobic molecule prepared in Example 1 by 45°.

[0082] When a fine uneven structure is prepared with only water, only a petal-like structure is formed, as illustrated in FIG. 6. Meanwhile, when a fine uneven structure is prepared with a triethylamine aqueous solution, a coarse columnar structure is grown along with a petal-like structure, as illustrated in FIG. 4. Some of the coarse columnar structures are grown vertically to the substrate plane and some are obliquely inclined or are also lying on the substrate plane, and thus the growth direction thereof is random.

From the comparison of FESEM images (FIG. 4) before coating with the hydrophobic molecule and FESEM images (FIG. 5) after coating with the hydrophobic molecule, no significant difference in these forms is found at the magnification

used in the observation. At least in the scale of several tens of nm or more, it is seen that the petal-like structure and the columnar structure are not changed by covering with the hydrophobic molecule.

This point also applies to Comparative Example 1, and it is seen from the comparison of FIGS. 6 and 7 that there is no change in the petal-like structure before and after covering with the hydrophobic molecule.

[2.4. XRD]

[0083] For the samples before covering with the hydrophobic molecules prepared in Example 1 and Comparative Example 1, each of the crystal structures that the fine uneven structure had is analyzed by X-ray diffraction (XRD). FIG. 9 illustrates X-ray diffraction patterns of an Al substrate in Example 1 (TEA-added water), an Al substrate in Comparative Example 1 (only water), and an Al substrate (untreated Al) which is subjected to only chemical polishing and is not subjected to fine uneven treatment.

In the sample prepared in Comparative Example 1, a diffraction pattern belonging to boehmite and a diffraction pattern belonging to aluminum of the substrate appear. In the sample prepared in Example 1, along with a diffraction pattern belonging to boehmite and a diffraction pattern belonging to aluminum of the substrate, a diffraction pattern belonging to bayerite also appears.

[2.5. XPS]

[0084] For the fine uneven substrate prepared in Example 1 (without the covering with a hydrophobic molecule), the hydrophobic molecule-covered fine uneven substrates prepared in Example 1 and Example 2 (with the covering with a hydrophobic molecule), and the fine uneven substrate prepared in Comparative Example 1 (without the covering with a hydrophobic molecule), surface analysis is performed by X-ray photoelectron spectroscopy (XPS). The results are shown in Table 1.

In the fine uneven substrates prepared in Example 1 and Comparative Example 1 (without covering), aluminum, oxygen and carbon are detected. Carbon is derived from the adsorption of contaminated organic materials because boehmite or bayerite easily adsorbs organic molecules in the air and is easily contaminated.

In the hydrophobic molecule-covered fine uneven substrates prepared in Example 1 and Example 2 (with covering), the concentration of fluorine, silicon and carbon derived from the covered hydrophobic molecule is higher than that of the fine uneven substrate which is not covered with hydrophobic molecules. Even in the sample covered with any hydrophobic molecular film, the thickness of the hydrophobic molecular films is below the XPS detection depth (from several nm to several tens of nm) in that aluminum consisting of a basis is detected.

[0085]

[Table 1]

		Concentration of elements (at%)					
		C	N	O	F	Al	Si
Comparative Example 1	Without covering	4.88	0.12	65.94	0.68	28.39	0.00
Example 1	Without covering	6.03	0.13	66.81	0.84	26.17	0.00
	with covering	13.06	0.14	45.15	23.49	17.62	0.54
Example 2	with covering	16.07	0.10	39.66	26.06	17.33	0.79

[0086] As described above, the examples of the present invention has been described in detail, but the present invention is not limited to the Examples in any way, and various modifications may be made within a scope not departing from the gist of the present invention.

[0087] The hydrophobic material and the production process thereof according to the present invention may be used in the body of a vehicle, the hull of a high speed vessel, the external wall of a house, rain gear, clothing, a heat exchanger, an antenna and the like.

Claims

1. A hydrophobic material comprising the following constitutions:

(1) the hydrophobic material including:

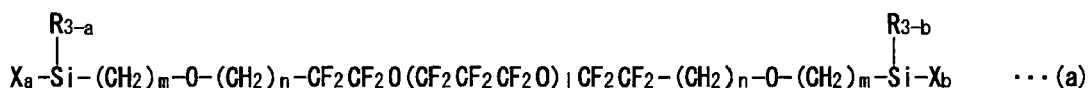
a substrate,
a fine uneven structure formed on a surface of the substrate; and
a hydrophobic molecule covering a surface of the fine uneven structure, and

(2) the fine uneven structure including:

a petal-like structure formed of an aggregate of a plurality of plate-like particles; and
a columnar structure formed of columnar particles,
wherein a length from the surface of the substrate to a tip of the columnar structure is longer than a length from the surface of the substrate to a tip of the petal-like structure.

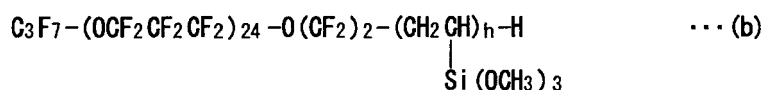
2. The hydrophobic material according to claim 1,
wherein the fine uneven structure is formed of a metal oxide or a material including a polar functional group (A) at least on the surface thereof,
the hydrophobic molecule includes a polar functional group (B) capable of forming a chemical bond with the surface of the fine uneven structure, and
the hydrophobic material is obtained by covering the surface of the fine uneven structure with the hydrophobic molecule and forming a chemical bond of the surface of the fine uneven structure with the polar functional group (B).
3. The hydrophobic material according to claim 1,
wherein the petal-like structure is formed of boehmite and
the columnar structure is formed of bayerite.
4. The hydrophobic material according to claim 1, wherein the hydrophobic molecule includes one or more selected from the group of molecules represented by the following Formula (a) and Formula (b).

[Chem. 1]



where, R: a monovalent hydrocarbon having from 1 to 8 carbon atoms,
X: -OR (R is an alkyl group), -OH or a halogen atom,
l: an integer of 0 or higher, m: an integer from 1 to 5, n: an integer from 0 to 2, and a and b: 2 or 3, and

[Chem. 2]



where, h: an integer from 1 to 10.

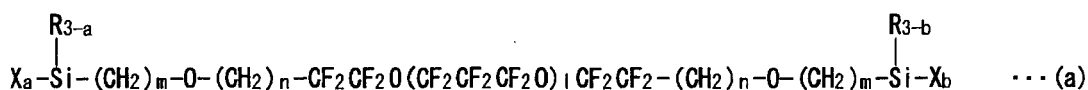
5. The hydrophobic material according to claim 1, wherein the substrate is formed of an aluminum-containing material.
6. A process of producing a hydrophobic material comprising:

(1) an unevenness step of forming a fine uneven structure including a petal-like structure formed of an aggregate of a plurality of plate-like particles and a columnar structure formed of columnar particles on a surface of a substrate, wherein a length from the surface of the substrate to a tip of the columnar structure is longer than a length from the surface of the substrate to a tip of the petal-like structure to obtain a fine uneven substrate, and

(2) a covering step of covering a surface of the fine uneven structure with a hydrophobic molecule to obtain a hydrophobic molecule-covered fine uneven substrate.

7. The process of producing a hydrophobic material according to claim 6, wherein the substrate is formed of an aluminum-containing material and the unevenness step is a hot-water treatment step of forming the fine uneven structure on the surface of the substrate by immersing the substrate in a solution including water and an amine-based molecule at a temperature from 60°C to 300°C to obtain the fine uneven substrate.
8. The process of producing a hydrophobic material according to claim 7, wherein the amine-based molecule is trimethyl amine.
9. The process of producing a hydrophobic material according to claim 6, wherein the fine uneven structure is formed of a metal oxide or a material including a polar functional group (A) at least on the surface thereof, the hydrophobic molecule includes a polar functional group (B) capable of forming a chemical bond with the surface of the fine uneven structure, and the method further comprising a bonding step of forming a chemical bond of the surface of the fine uneven structure with the polar functional group (B) after the covering step.
10. The process of producing a hydrophobic material according to claim 6, wherein the hydrophobic molecule includes one or more selected from the group of molecules represented by the following Formula (a) and Formula (b).

[Chem. 3]

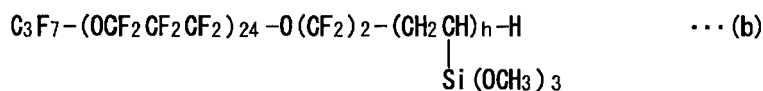


where, R: a monovalent hydrocarbon having from 1 to 8 carbon atoms,

X: -OR (R is an alkyl group), -OH or a halogen atom,

l: an integer of 0 or higher, m: an integer from 1 to 5, n: an integer from 0 to 2, and a and b: 2 or 3, and

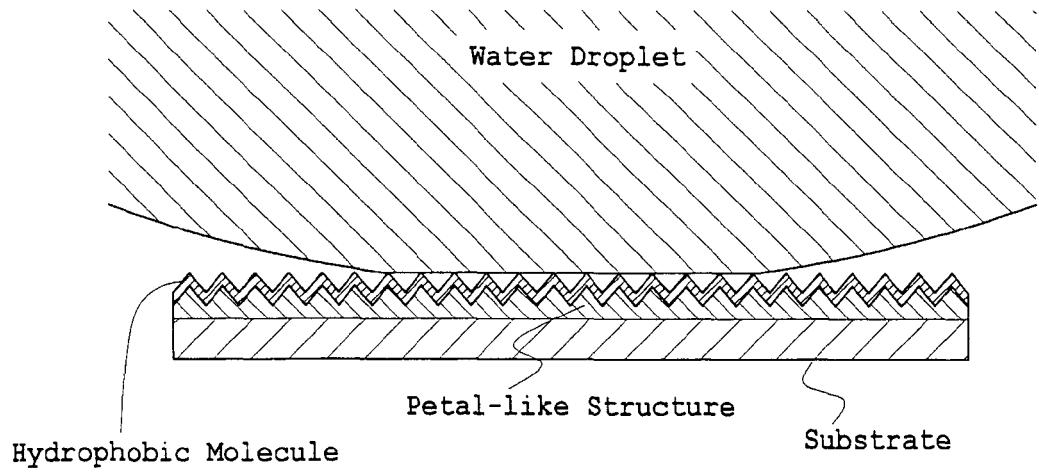
[Chem. 4]



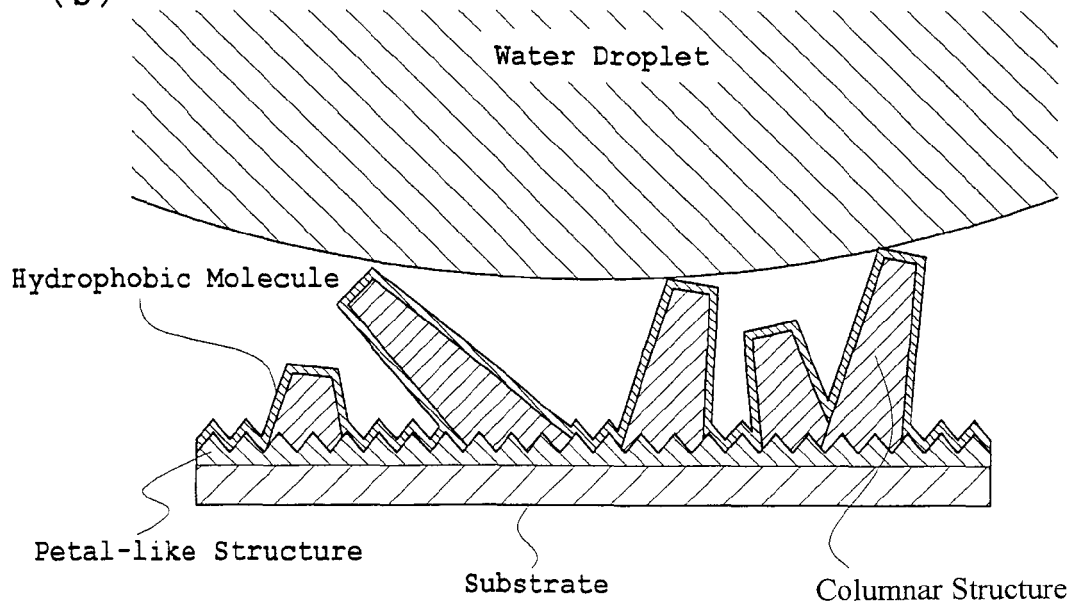
where, h: an integer from 1 to 10.

[Fig. 1]

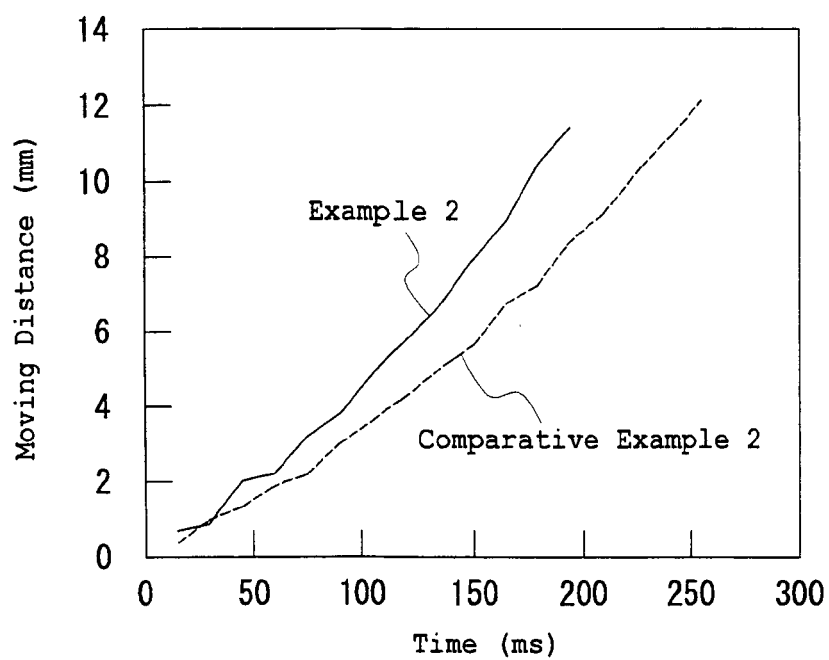
(a)



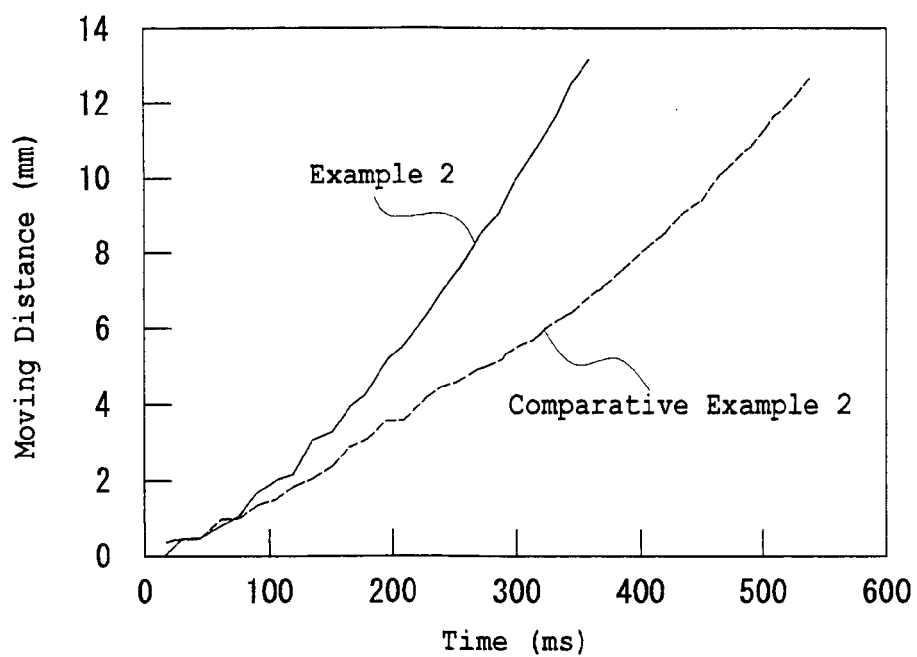
(b)



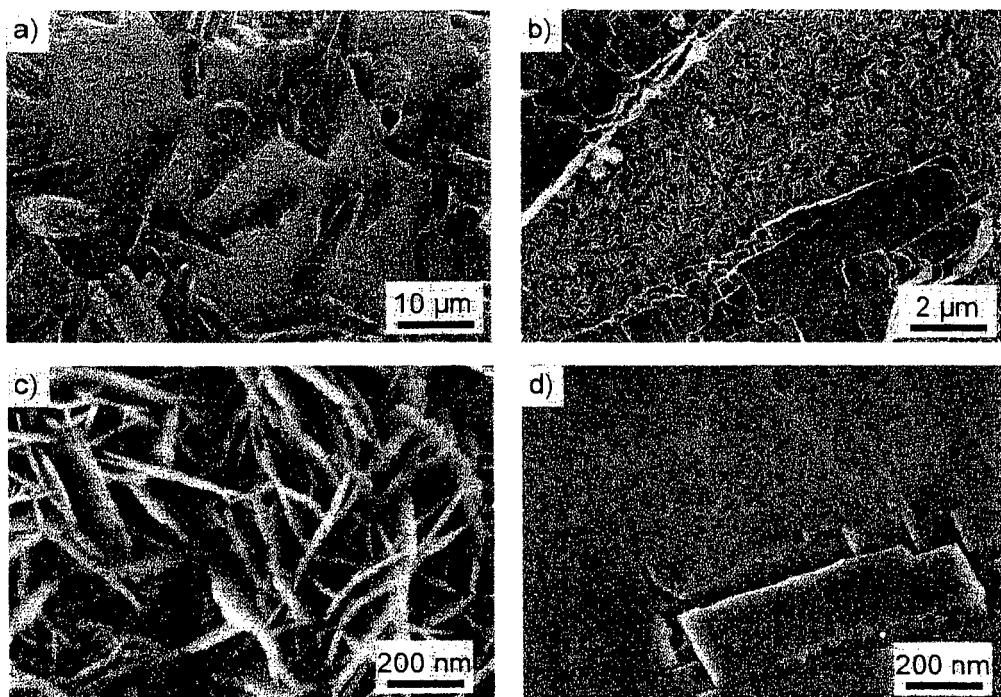
[Fig. 2]



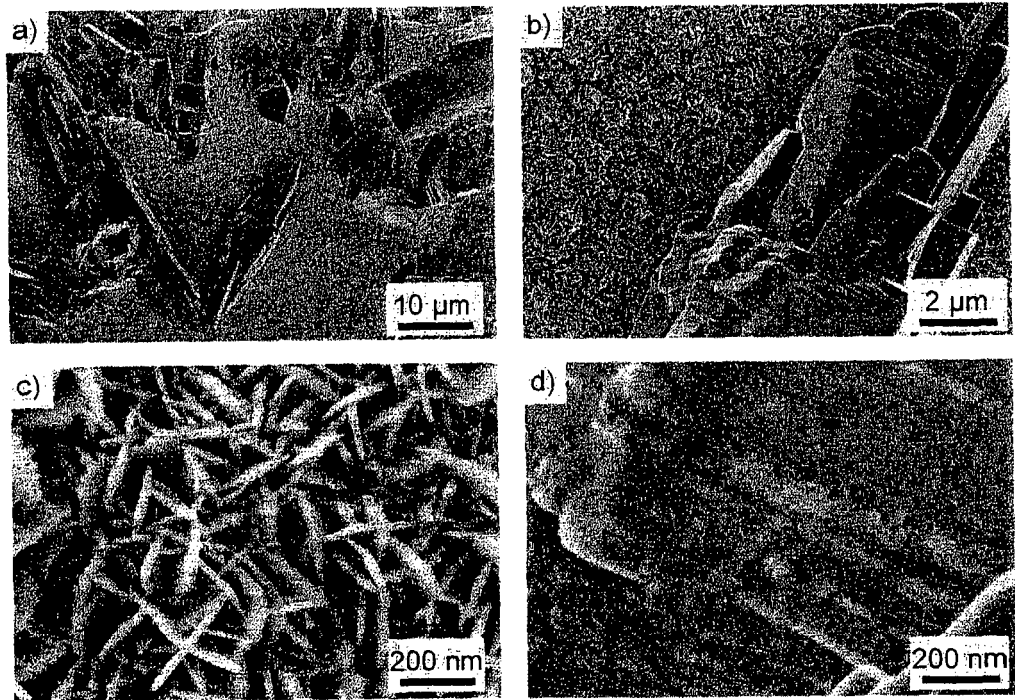
[Fig. 3]



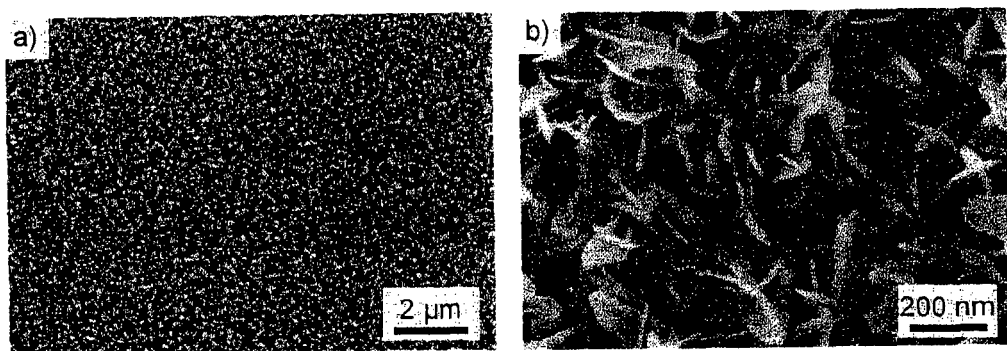
[Fig. 4]



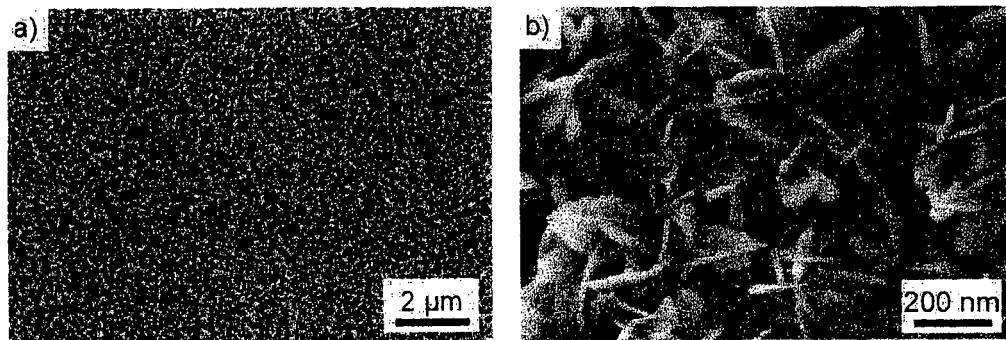
[Fig. 5]



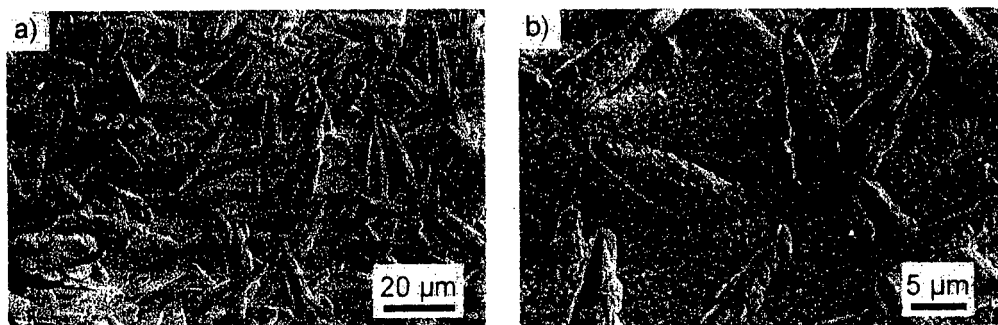
[Fig. 6]



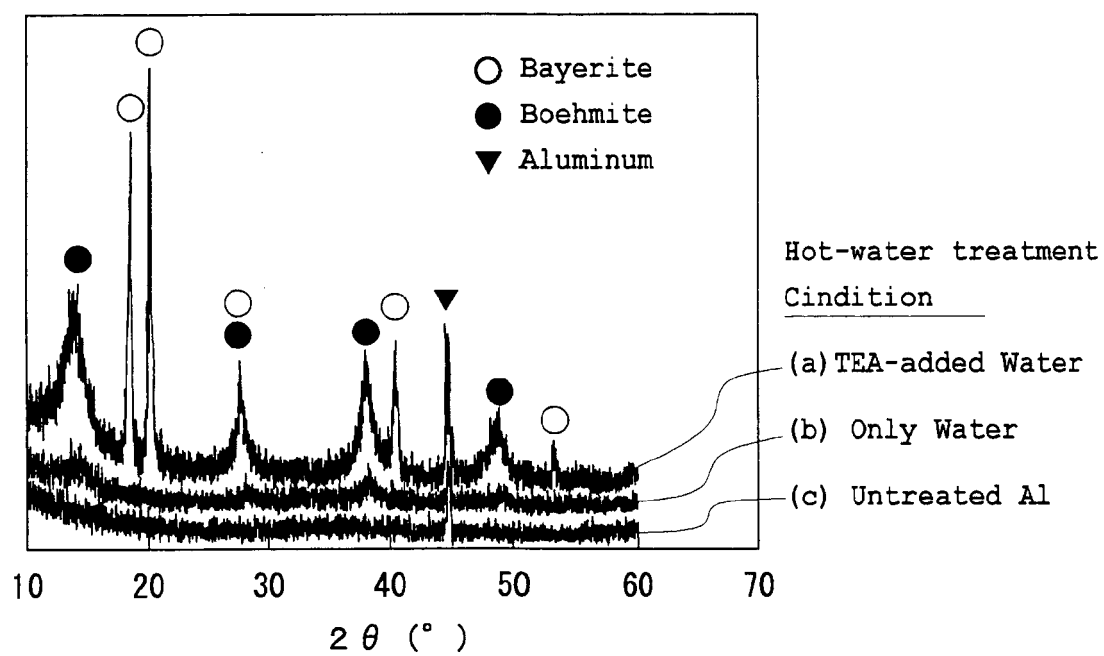
[Fig. 7]



[Fig. 8]



[Fig. 9]



REFERENCES CITED IN THE DESCRIPTION

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