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(54) **Microstructure and method of manufacturing the same**

(57) Disclosed is a method of manufacturing a microstructure, wherein an aluminum substrate surface is subjected at least to, in order, (A) an anodizing treatment for anodizing the aluminum substrate surface to form an anodized film bearing micropores; and (B) a heating treatment for heating the anodized film formed in the anodiz-

ing treatment (A) at a temperature of at least 50°C for at least 10 minutes, whereby the microstructure bearing the micropores at a surface of the anodized film. The method is capable of obtaining porous alumina membrane filters which are excellent in resistance to acids and alkalis with high filtration flow rate.

FIG. 1A

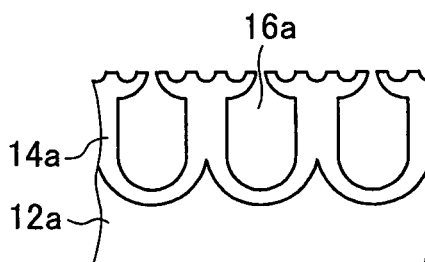


FIG. 1B

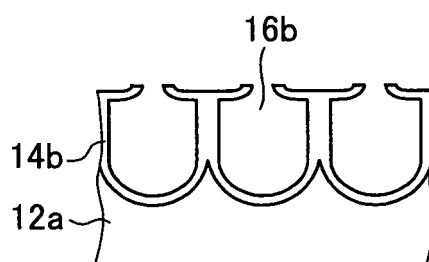


FIG. 1C

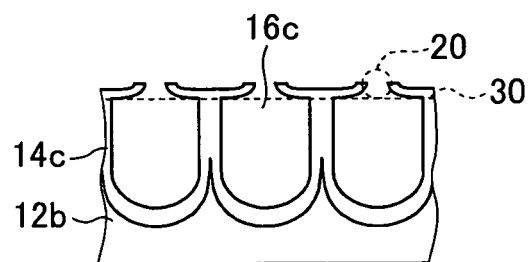
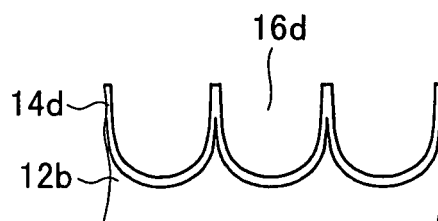


FIG. 1D



Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a microstructure and its manufacturing method. The invention also relates to a porous alumina membrane filter using the microstructure.

[0002] Membrane filters including organic membrane filters and inorganic membrane filters are commercialized in the field of microfiltration, and such organic membrane filters are actually widely used. In most of the organic membrane filters, pores are not separated from each other and the pore size distribution is relatively broad. Under these circumstances, researches for further improving the accuracy in the separation of a target substance which is the most important filter function have been made in various fields.

[0003] In order to solve such problems, a so-called track etching technique is known in which an organic film made of a polymer is irradiated with high energy particles generated in a nuclear reactor, and tracks of the particles through the organic film are etched to form micropores (see T. D. Brock, Membrane Filtration, Sci. Tech, Inc., Madison (1983)). According to the track etching technique, discrete micropores with a narrow pore size distribution are formed orthogonally to the organic film, but this technique suffered from the problem that the pore density, that is, porosity could not be increased to prevent overlapping pores from being generated due to incidence of particles on the film in an overlapping manner when forming tracks.

[0004] On the other hand, a porous alumina membrane filter making use of an anodized film of aluminum, such as the one described in Hideki Masuda, "New Technology of Porous Membranes Using Anodization" (ALTOPIA, July 1995) is known as the inorganic membrane filter. Aluminum is anodized in an acidic electrolytic solution to dispose discrete micropores having a narrow pore size distribution to achieve a high porosity, so a membrane filter with a high filtration flow rate per unit time can be produced at low cost.

[0005] However, improvements of the porous alumina membrane filter have been desired because of the fact that anodized film of aluminum is inferior in resistance to acids and alkalis.

SUMMARY OF THE INVENTION

[0006] It is therefore an object of the invention to provide a porous alumina membrane filter which is excellent in resistance to acids and alkalis and filtration flow rate.

[0007] Another object of the invention is to provide a microstructure appropriate for use in the porous alumina membrane filter.

[0008] Still another object of the invention is to provide a method of manufacturing the microstructure described above.

[0009] The inventors of the invention have made intensive studies to achieve the above objects and as a result completed the invention by forming a micropore-bearing anodized film and subjecting the formed anodized film to heating treatment.

[0010] Accordingly, the invention provides the following (i) to (iv).

(i) A method of manufacturing a microstructure, wherein an aluminum substrate surface is subjected at least to, in order,

(A) an anodizing treatment for anodizing the aluminum substrate surface to form an anodized film bearing micropores; and

(B) a heating treatment for heating the anodized film formed in the anodizing treatment (A) at a temperature of at least 50°C for at least 10 minutes, whereby the microstructure bearing the micropores at a surface of the anodized film is obtained.

(ii) The manufacturing method according to (i) above, wherein the anodized film obtained in the anodizing treatment (A) is further subjected to, in order,

(C) an aluminum removal treatment for removing aluminum from the anodized film obtained in the anodizing treatment (A); and

(D) a through micropore-forming treatment to make the micropores extend through the anodized film obtained in the anodizing treatment (A),

before being subjected to the heating treatment (B), whereby the microstructure obtained has the micropores extending through the anodized film.

(iii) A microstructure obtained by the manufacturing method according to (i) or (ii) above.

(iv) A microstructure comprising a micropore-bearing anodized film of aluminum, wherein the anodized film has a sulfur atom concentration of up to 3.2 wt%, a carbon atom concentration of up to 2.5 wt% and a phosphorus atom concentration of up to 1.0 wt%.

(v) The microstructure according to (iv) above which comprises through micropores.

(vi) The microstructure according to any one of (iii) to (v) above, wherein the micropores have a pore diameter variance of within 3% of average diameter.

(vii) The microstructure according to anyone of (iii) to (vi) above, wherein a degree of ordering of the micropores as defined by formula (1):

$$\text{Degree of Ordering (\%)} = B/A \times 100 \quad (1)$$

(wherein A represents a total number of micropores in a measurement region; and B represents a number of specific micropores in the measurement region for which, when a circle is drawn so as to be centered on a center of gravity of a specific micropore and so as to be of a smallest radius that is internally tangent to an edge of another micropore, the circle includes centers of gravity of six micropores other than the specific micropore) is at least 50%.

(viii) A porous alumina membrane filter using the microstructure according to any one of (iii) to (vii) above.

[0011] The present invention is capable of obtaining porous alumina membrane filters which are excellent in resistance to acids and alkalis with high filtration flow rate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] In the accompanying drawings:

FIGS. 1A to 1D are end views schematically showing an aluminum substrate and an anodized film formed on the aluminum substrate for use in illustrating the inventive method of manufacturing microstructures;

FIG. 2 is a partial cross-sectional view showing the state after the treatment (A);

FIG. 3 is a partial cross-sectional view showing the state after the treatment (C);

FIG. 4 is a partial cross-sectional view showing the state after the treatment (D); and

FIGS. 5A and 5B are views illustrating a method for calculating the degree of ordering of pores.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] The invention is described more fully below.

[0014] The invention provides a method of manufacturing a microstructure, wherein an aluminum substrate surface is subjected at least to, in order,

(A) an anodizing treatment for anodizing the aluminum substrate surface to form an anodized film bearing micropores; and

(B) a heating treatment for heating the anodized film formed in the anodizing treatment (A) at a temperature of at least 50°C for at least 10 minutes,

whereby the microstructure bearing the micropores at a surface of the anodized film is obtained.

<Aluminum Substrate>

[0015] The aluminum substrate is not subject to any particular limitation. Illustrative examples include pure aluminum plate; alloy plates composed primarily of aluminum and containing trace amounts of other elements; substrates made of low-purity aluminum (e.g., recycled material) on which high-purity aluminum has been vapor-deposited; substrates such as silicon wafers, quartz or glass whose surface has been covered with high-purity aluminum by a process such as vapor deposition or sputtering; and resin substrates on which aluminum has been laminated.

[0016] Of the aluminum substrate, the surface on which an anodized film is provided by anodizing treatment has an aluminum purity of preferably at least 99.5 wt%, more preferably at least 99.9 wt% and even more preferably at least 99.99 wt%. At an aluminum purity within the above range, the micropore arrangement will be sufficiently well-ordered.

[0017] It is preferable for the surface of the aluminum substrate to be subjected beforehand to degreasing treatment and mirror-like finishing treatment.

[0018] The microstructure obtained by the invention preferably has the aluminum substrate having been subjected to

heat treatment beforehand. Heat treatment will enhance the orderliness of the array of micropores.

<Heat Treatment>

[0019] Heat treatment is preferably carried out at a temperature of 200 to 350°C for a period of about 30 seconds to about 2 minutes. The orderliness of the array of micropores formed in the subsequently described anodizing treatment is enhanced in this way.

[0020] Following heat treatment, it is preferable to rapidly cool the aluminum substrate. The method of cooling is exemplified by a method involving direct immersion of the aluminum substrate in water or the like.

<Degreasing Treatment>

[0021] Degreasing treatment is carried out with a suitable substance such as an acid, alkali or organic solvent so as to dissolve and remove organic substances, including dust, grease and resins, adhering to the aluminum surface, and thereby prevent defects due to organic substances from arising in each of the subsequent treatments.

[0022] Known degreasers may be used in degreasing treatment. For example, degreasing treatment may be carried out using any of various commercially available degreasers by the prescribed method.

[0023] Preferred methods include the following: a method in which an organic solvent such as an alcohol (e.g., methanol), a ketone, benzene or a volatile oil is brought into contact with the aluminum surface at ambient temperature (organic solvent method); a method in which a liquid containing a surfactant such as soap or a neutral detergent is brought into contact with the aluminum surface at a temperature of from ambient temperature to 80°C, after which the surface is rinsed with water (surfactant method); a method in which an aqueous sulfuric acid solution having a concentration of 10 to 200 g/L is brought into contact with the aluminum surface at a temperature of from ambient temperature to 70°C for a period of 30 to 80 seconds, following which the surface is rinsed with water; a method in which an aqueous solution of sodium hydroxide having a concentration of 5 to 20 g/L is brought into contact with the aluminum surface at ambient temperature for about 30 seconds while electrolysis is carried out by passing a direct current through the aluminum surface as the cathode at a current density of 1 to 10 A/dm², following which the surface is brought into contact with an aqueous solution of nitric acid having a concentration of 100 to 500 g/L and thereby neutralized; a method in which any of various known anodizing electrolytic solutions is brought into contact with the aluminum surface at ambient temperature while electrolysis is carried out by passing a direct current at a current density of 1 to 10 A/dm² or an alternating current through the aluminum surface as the cathode; a method in which an aqueous alkali solution having a concentration of 10 to 200 g/L is brought into contact with the aluminum surface at 40 to 50°C for 15 to 60 seconds, following which the surface is brought into contact with an aqueous nitric acid solution having a concentration of 100 to 500 g/L and thereby neutralized; a method in which an emulsion prepared by mixing a surfactant, water or the like into an oil such as gas oil or kerosene is brought into contact with the aluminum surface at a temperature of from ambient temperature to 50°C, following which the surface is rinsed with water (emulsion degreasing method); and a method in which a mixed solution of, for example, sodium carbonate, a phosphate and a surfactant is brought into contact with the aluminum surface at a temperature of from ambient temperature to 50°C for 30 to 180 seconds, following which the surface is rinsed with water (phosphate method).

[0024] The method used for degreasing treatment is preferably one which may remove grease from the aluminum surface but causes substantially no aluminum dissolution. Hence, the organic solvent method, surfactant method, emulsion degreasing method and phosphate method are preferred.

<Mirror-Like Finishing Treatment>

[0025] Mirror-like finishing treatment is carried out to eliminate surface asperities of the aluminum substrate and improve the uniformity and reproducibility of grain-forming treatment by a process such as electrodeposition. Examples of surface asperities of the aluminum substrate include rolling streaks formed during rolling when the aluminum substrate has been produced by a process including rolling.

[0026] In the practice of the invention, mirror-like finishing treatment is not subject to any particular limitation, and may be carried out using any suitable method known in the art. Examples of suitable methods include mechanical polishing, chemical polishing, and electrolytic polishing.

[0027] Illustrative examples of suitable mechanical polishing methods include polishing with various commercial abrasive cloths, and methods that combine the use of various commercial abrasives (e.g., diamond, alumina) with buffing. More specifically, a method which is carried out with an abrasive while changing over time the abrasive used from one having coarser particles to one having finer particles is appropriately illustrated. In such a case, the final abrasive used is preferably one having a grit size of 1500. In this way, a glossiness of at least 50% (in the case of rolled aluminum, at least 50% in both the rolling direction and the transverse direction) can be achieved.

[0028] Examples of chemical polishing methods include various methods mentioned in the 6th edition of Aluminum Handbook (Japan Aluminum Association, 2001), pp. 164-165.

[0029] Preferred examples include phosphoric acid/nitric acid method, Alupol I method, Alupol V method, Alcoa R5 method, $\text{H}_3\text{PO}_4\text{-CH}_3\text{COOH-Cu}$ method and $\text{H}_3\text{PO}_4\text{-HNO}_3\text{-CH}_3\text{COOH}$ method. Of these, the phosphoric acid/nitric acid method, the $\text{H}_3\text{PO}_4\text{-CH}_3\text{COOH-Cu}$ method and the $\text{H}_3\text{PO}_4\text{-HNO}_3\text{-CH}_3\text{COOH}$ method are especially preferred.

[0030] With chemical polishing, a glossiness of at least 70% (in the case of rolled aluminum, at least 70% in both the rolling direction and the transverse direction) can be achieved.

[0031] Examples of electrolytic polishing methods include various methods mentioned in the 6th edition of Aluminum Handbook (Japan Aluminum Association, 2001), pp. 164-165.

[0032] A preferred example is the method described in US 2,708,655.

[0033] The method described in Jitsumu Hyomen Gijutsu (Practice of Surface Technology), Vol. 33, No. 3, pp. 32-38 (1986) is also preferred.

[0034] With electrolytic polishing, a glossiness of at least 70% (in the case of rolled aluminum, at least 70% in both the rolling direction and the transverse direction) can be achieved.

[0035] These methods may be suitably combined and used. In a preferred example, a method that uses an abrasive is carried out by changing over time the abrasive used from one having coarser particles to one having finer particles, following which electrolytic polishing is carried out.

[0036] Mirror-like finishing treatment enables a surface having, for example, a mean surface roughness R_a of 0.1 μm or less and a glossiness of at least 50% to be obtained. The mean surface roughness R_a is preferably 0.03 μm or less, and more preferably 0.02 μm or less. The glossiness is preferably at least 70%, and more preferably at least 80%.

[0037] The glossiness is the specular reflectance which can be determined in accordance with JIS Z8741-1997 (Method 3: 60° Specular Gloss) in a direction perpendicular to the rolling direction. Specifically, measurement is carried out using a variable-angle glossmeter (e.g., VG-1D, manufactured by Nippon Denshoku Industries Co., Ltd.) at an angle of incidence/reflection of 60° when the specular reflectance is 70% or less, and at an angle of incidence/reflection of 20° when the specular reflectance is more than 70%.

<Treatment (A): Micropore Formation through Anodization>

[0038] In the treatment (A), the aluminum substrate is anodized to form an anodized film having micropores on the aluminum substrate surface.

[0039] Any conventionally known method can be used for anodizing treatment. More specifically, a self-ordering method to be described below is preferably used.

[0040] The self-ordering method is a method which enhances the orderliness by using the regularly arranging nature of micropores in the anodized film and eliminating factors that may disturb an orderly arrangement. Specifically, an anodized film is formed on high-purity aluminum at a voltage appropriate for the type of electrolytic solution and at a low speed over an extended period of time (e.g., from several hours to well over ten hours).

[0041] In this method, because the pore diameter is dependent on the voltage, the desired pore diameter can be obtained to a certain degree by controlling the voltage.

[0042] Anodizing treatment to be described later may be carried out to form micropores by the self-ordering method, but it is preferable to carry out anodizing treatment, film removal treatment and re-anodizing treatment to be described later in this order.

<Anodizing Treatment>

[0043] The average flow rate in anodizing treatment is preferably 0.5 to 20.0 m/min, more preferably 1.0 to 15.0 m/min and even more preferably 2.0 to 10.0 m/min. Uniformity and high orderliness can be achieved by carrying out anodizing treatment at a flow rate within the above range.

[0044] The method of flowing the electrolytic solution under the condition described above is not subject to any particular limitation, and a method which uses a general stirring device such as a stirrer may be employed. Use of a stirrer capable of controlling the stirring speed in the digital display mode is preferable because the average flow rate can be controlled. An example of such stirring device includes a magnetic stirrer HS-50D (produced by As One Corporation).

[0045] Anodizing treatment may be carried out by, for example, a method that involves passing an electrical current through the aluminum substrate as the anode in a solution having an acid concentration of 0.01 to 5 mol/L. Solutions that may be used in anodizing treatment are preferably acid solutions. It is preferable to use sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid and amidosulfonic acid, and more preferably sulfuric acid, phosphoric acid and oxalic acid. These acids may be used singly or in combination of two or more.

[0046] The conditions for anodizing treatment vary depending on the electrolytic solution used, and thus cannot be strictly specified. However, it is generally preferable for the electrolyte concentration to be 0.01 to 5 mol/L, the temperature

of the solution to be -10 to 30°C, the current density to be 0.01 to 20 A/dm², the voltage to be 3 to 300 V, and the period of electrolysis to be 0.5 to 30 hours. It is more preferable for the electrolyte concentration to be 0.05 to 3 mol/L, the temperature of the solution to be -5 to 25°C, the current density to be 0.05 to 15 A/dm², the voltage to be 5 to 250 V, and the period of electrolysis to be 1 to 25 hours. It is particularly preferable for the electrolyte concentration to be 0.1 to 1 mol/L, the temperature of the solution to be 0 to 20°C, the current density to be 0.1 to 10 A/dm², the voltage to be 10 to 200 V, and the period of electrolysis to be 2 to 20 hours.

[0047] Anodizing treatment is carried out for a period of preferably 0.5 minute to 16 hours, more preferably 1 minute to 12 hours, and even more preferably 2 minutes to 8 hours.

[0048] In addition to a method in which anodizing treatment is carried out at a constant voltage, another method which involves changing the voltage continuously or intermittently may be used in anodizing treatment. In the latter case, it is preferable to gradually reduce the voltage. This method enables reduction of the resistance in the anodized film to make the formed micropores finer, and is therefore preferable in terms of improving uniformity particularly when sealing is carried out by electrodeposition.

[0049] The anodized film formed has a thickness of preferably 0.1 to 2,000 μm, more preferably 1 to 1,000 μm and even more preferably 10 to 500 μm.

[0050] The micropore diameter is preferably from 0.01 to 0.5 μm.

[0051] The average pore density is preferably from 50 to 1,500 pores/μm².

[0052] The micropores in the region having an area of 1 μm² preferably have a pore diameter variance of within 3% and more preferably within 2% of the average diameter. The average pore diameter and the variance can be determined by the following formulae:

$$\text{Average diameter: } \mu_x = (1/n) \sum X_i$$

$$\text{Variance: } \sigma^2 = (1/n) (\sum X_i^2) - \mu_x^2$$

$$\text{Variance/average diameter} = \sigma^2/\mu_x \leq 0.03$$

where X_i represents the diameter of one micropore measured in the region with an area of 1 μm².

[0053] The area ratio occupied by the micropores is preferably from 20 to 50%. The area ratio occupied by the micropores is defined as the proportion of the sum of the areas of the individual micropore openings to the area of the aluminum surface.

[0054] At the interface between the anodized film and the aluminum substrate, the micropores have a degree of ordering as defined by formula (1):

$$\text{Degree of Ordering (\%)} = B/A \times 100 \quad (1)$$

(wherein A represents a total number of micropores in a measurement region; and B represents a number of specific micropores in the measurement region for which, when a circle is drawn so as to be centered on a center of gravity of a specific micropore and so as to be of a smallest radius that is internally tangent to an edge of another micropore, the circle includes centers of gravity of six micropores other than the specific micropore) of preferably at least 10%, more preferably at least 15% and even more preferably at least 20%. The degree of ordering within such range enables the treatment time required for pore-ordering treatment and therefore total treatment time to be shortened.

[0055] The method of calculating the degree of ordering of the micropores is the same as that for the micropores in the microstructure to be described later except that the degree of ordering at the interface between the anodized film and the aluminum substrate is to be determined. This degree of ordering can be calculated after the bottoms of the micropores are bared by, for example, dissolving most of the anodized film in a mixed aqueous solution of phosphoric acid and chromic acid.

<Film Removal Treatment>

[0056] The anodized film may be subjected to heating treatment to be described below immediately after the anodized film has been formed on the aluminum substrate surface by anodizing treatment, but after anodizing treatment, film removal treatment and re-anodizing treatment may be carried out in this order before heating the anodized film.

[0057] Film removal treatment dissolves and removes at least part of the anodized film formed on the aluminum substrate surface by anodizing treatment.

[0058] The pore orderliness in the anodized film is increased toward the aluminum substrate, so ordered pits can be obtained by removing part of the anodized film through film removal treatment to bare its bottom portion remaining on the surface of the aluminum substrate. Therefore, film removal treatment does not dissolve aluminum but only the anodized film of alumina (aluminum oxide).

[0059] The solution for dissolving alumina is preferably an aqueous solution containing at least one selected from the group consisting of chromium compound, nitric acid, phosphoric acid, zirconium compound, titanium compound, lithium salt, cerium salt, magnesium salt, sodium silicofluoride, zinc fluoride, manganese compound, molybdenum compound, magnesium compound, barium compound and elemental halogen.

[0060] Examples of the chromium compound include chromium (III) oxide and chromium (VI) oxide.

[0061] Examples of the zirconium compound include ammonium fluorozirconate, zirconium fluoride and zirconium chloride.

[0062] Examples of the titanium compound include titanium oxide and titanium sulfide.

[0063] Examples of the lithium salt include lithium fluoride and lithium chloride.

[0064] Examples of the cerium salt include cerium fluoride and cerium chloride.

[0065] An example of the magnesium salt includes magnesium sulfide.

[0066] Examples of the manganese compound include sodium permanganate and calcium permanganate.

[0067] An example of the molybdenum compound includes sodium molybdate.

[0068] An example of the magnesium compound includes magnesium fluoride pentahydrate.

[0069] Examples of the barium compound include barium oxide, barium acetate, barium carbonate, barium chlorate, barium chloride, barium fluoride, barium iodide, barium lactate, barium oxalate, barium perchlorate, barium selenate, barium selenite, barium stearate, barium sulfite, barium titanate, barium hydroxide, barium nitrate and hydrates thereof. Of those barium compounds, barium oxide, barium acetate and barium carbonate are preferred and barium oxide is particularly preferred.

[0070] Examples of the elemental halogen include chlorine, fluorine and bromine.

[0071] The solution for dissolving aluminum is more preferably an acid-containing aqueous solution. Exemplary acids include sulfuric acid, phosphoric acid, nitric acid and hydrochloric acid, and a mixture of two or more acids may also be used.

[0072] The acid concentration is preferably at least 0.01 mol/L, more preferably at least 0.05 mol/L and even more preferably at least 0.1 mol/L. Although the upper limit is not particularly defined, in general, the acid concentration is preferably up to 10 mol/L and more preferably up to 5 mol/L. An unnecessarily high concentration is not economical and a higher acid concentration may cause dissolution of the aluminum substrate.

[0073] The solution for dissolving alumina preferably has a temperature of -10°C or higher and more preferably -5°C or higher and even more preferably 0°C or higher. Carrying out the treatment using a boiling aqueous solution destroys or disrupts the starting points for ordering. Hence, the aqueous solution is preferably used without being boiled.

[0074] The solution for dissolving alumina dissolves alumina, not aluminum. However, this solution may dissolve a small amount of aluminum as long as aluminum is not substantially dissolved.

[0075] Film removal treatment is carried out by bringing the aluminum substrate having the anodized film formed thereon into contact with the solution for dissolving alumina. The contacting method is not particularly limited and is exemplified by immersion and spraying. Of these, immersion is preferable.

[0076] Immersion is a treatment in which the aluminum substrate having the anodized film formed thereon is immersed in the solution for dissolving alumina. Immersion with stirring is preferable, because the treatment is uniformly carried out.

[0077] The aluminum substrate having the anodized film formed thereon is immersed in the solution for dissolving alumina for a period of preferably at least 10 minutes, more preferably at least 1 hour, even more preferably at least 3 hours, and most preferably at least 5 hours.

<Re-anodizing Treatment>

[0078] Film removal treatment serves to remove at least part of the anodized film to form ordered pits at the surface of the aluminum substrate, and the ordered pit-bearing aluminum substrate surface is subjected again to anodizing treatment to enable the anodized film with a higher degree of ordering of micropores to be formed.

[0079] Any known method may be used for anodizing treatment, but anodizing treatment is preferably carried out

under the same conditions as those defined in <Anodizing Treatment>.

[0080] Suitable use can also be made of a method in which the current is repeatedly turned on and off in an intermittent manner while keeping the dc voltage constant, and a method in which the current is repeatedly turned on and off while intermittently changing the dc voltage. Because these methods enable fine micropores to be formed at the anodized film, they are preferable for improving uniformity, particularly when sealing is carried out by electrodeposition.

[0081] Anodizing treatment at a low temperature achieves an ordered array of micropores and a uniform pore diameter.

[0082] On the other hand, anodizing treatment at a relatively high temperature may disturb the ordered array of micropores so that the pore diameter may vary within a specified range. The variations in the pore diameter may also be controlled based on the treatment time.

[0083] The anodized film formed by re-anodizing treatment preferably has a thickness of 0.1 to 1,000 μm , more preferably 1 to 500 μm , and even more preferably 10 to 500 μm .

[0084] The micropore diameter is preferably from 0.01 to 0.5 μm .

[0085] The average pore density is preferably from 50 to 1,500 pores/ μm^2 .

[0086] The micropore-bearing anodized film may be formed on the surface of the aluminum substrate by carrying out, in order, the treatment (A) including the following steps (1) to (4):

(1) a step of subjecting a surface of the aluminum substrate to a first anodizing treatment to form a micropore-bearing anodized film on the surface of the aluminum substrate;

(2) a step of partially dissolving the anodized film using an acid or alkali;

(3) a step of performing a second anodizing treatment to grow the micropores in their depth direction; and

(4) a step of removing a part of the anodized film above inflection points in cross section of the micropores. Step (1)

[0087] In Step (1), at least one surface of the aluminum substrate is anodized to form a micropore-bearing anodized film on the surface of the aluminum substrate.

[0088] Step (1) may be carried out in the same procedure as in the above-mentioned anodizing treatment.

[0089] FIG. 1A shows that an anodized film 14a bearing micropores 16a was formed on the surface of an aluminum substrate 12a in Step (1).

Step (2)

[0090] In Step (2), an acid or an alkali is used to partially dissolve the anodized film formed in Step (1). "Partially dissolve the anodized film" as used herein refers not to completely dissolving the anodized film formed in Step (1) but to partially dissolving the surface of the anodized film 14a and the interiors of the micropores 16a shown in FIG. 1A so that an anodized film 14b bearing micropores 16b remains on the aluminum substrate 12a as shown in FIG. 1B.

[0091] The amount of material dissolved from the anodized film is preferably in a range of 0.001 to 50 wt%, more preferably 0.005 to 30 wt% and even more preferably 0.01 to 15 wt% with respect to the whole anodized film. Within the above range, disordered array portions at the anodized film surface can be dissolved out to enhance the orderliness of the array of micropores. In addition, the anodized film remains at the micropore bottoms to enable the anodized film to keep having starting points for anodizing treatment to be performed in Step (3).

[0092] Step (2) is performed by bringing the anodized film formed on the aluminum substrate into contact with an aqueous acid solution or aqueous alkali solution. The contacting method is not particularly limited and is exemplified by immersion and spraying. Of these, immersion is preferable.

[0093] When Step (2) is to be performed with an aqueous acid solution, it is preferable to use an aqueous solution of an inorganic acid such as sulfuric acid, phosphoric acid, nitric acid or hydrochloric acid, or a mixture thereof. It is particularly preferable to use an aqueous solution containing no chromic acid in terms of its high degree of safety. It is desirable for the aqueous acid solution to have a concentration of 0.01 to 1 mol/L and a temperature of 25 to 60°C.

[0094] When Step (2) is to be performed with an aqueous alkali solution, it is preferable to use an aqueous solution of at least one alkali selected from the group consisting of sodium hydroxide, potassium hydroxide and lithium hydroxide. It is preferable for the aqueous alkali solution to have a concentration of 0.01 to 1 mol/L and a temperature of 20 to 35°C.

[0095] Specific examples of preferred solutions include a 40°C aqueous solution containing 0.5 mol/L of phosphoric acid, a 30°C aqueous solution containing 0.05 mol/L of sodium hydroxide, and a 30°C aqueous solution containing 0.05 mol/L of potassium hydroxide.

[0096] The aluminum substrate having the anodized film formed thereon is immersed in the aqueous acid solution or aqueous alkali solution for a period of preferably 8 to 120 minutes, more preferably 10 to 90 minutes, and even more preferably 15 to 60 minutes.

Step (3)

[0097] In Step (3), the aluminum substrate having thereon the anodized film partially dissolved in Step (2) is subjected to anodizing treatment again to grow the micropores in the depth direction.

[0098] As shown in FIG. 1C, anodizing treatment in Step (3) allows the oxidation of the aluminum substrate 12a shown in FIG. 1B to proceed to form on an aluminum substrate 12b an anodized film 14c that has micropores 16c grown in the depth direction more than the micropores 16b.

[0099] Anodizing treatment may be performed using a method known in the art, although it is preferably performed under the same conditions as the above-described self-ordering method.

[0100] Suitable use can also be made of a method in which the current is repeatedly turned on and off in an intermittent manner while keeping the dc voltage constant, and a method in which the current is repeatedly turned on and off while intermittently changing the dc voltage. Because these methods enable formation of fine micropores at the anodized film, they are preferable for improving uniformity, particularly when sealing is carried out by electrodeposition.

[0101] In the above method in which the voltage is intermittently changed, it is preferable to gradually reduce the voltage. It is possible in this way to lower the resistance in the anodized film, enabling uniformity to be achieved when electrodeposition is carried out later.

[0102] The thickness of the anodized film is preferably increased by 0.1 to 100 μm and more preferably 0.5 to 50 μm . Within the above range, the orderliness of the array of micropores can be more enhanced.

Step (4)

[0103] A part of the anodized film above inflection points 30 in cross section of the micropore 16c shown in FIG. 1C is removed in Step (4). As shown in FIG. 1C, the micropore 16c formed by the self-ordering method has an approximately direct tube shape in cross section except the upper part of the micropore 16c. In other words, the micropore 16c has in its upper part a portion which differs in cross-sectional shape from the other part of the micropore 16c. This portion is hereinafter referred to as the "different shape portion 20". In Step (4), a part of the anodized film above the inflection points 30 in cross section of the micropore 16c is removed to eliminate the different shape portion 20 in the upper part of the micropore 16c. The "inflection point" 30 as used herein refers to a point where the cross-sectional shape of the micropore 16c considerably changes from the main shape (approximately straight tube shape in this case), in other words, to a point where the shape continuity from the main shape (approximately straight tube shape) is lost in the cross section of the micropore 16c.

[0104] Removal of a part of the anodized film above the inflection points 30 in cross section of the micropore 16c provides a micropore 16d having an approximately straight tube shape as a whole as shown in FIG. 1D.

[0105] In Step (4), the cross sectional image of the anodized film 14c after the end of Step (3) may be taken by a field emission scanning electron microscope (FE-SEM) to specify the inflection points 30 in cross section of the micropore 16c so that a part of the anodized film above the inflection points 30 can be removed.

[0106] The micropore has the different shape portion mainly in the case where the anodized film 14a was newly formed on the aluminum substrate 12a as in Step (1). Therefore, the anodized film formed in Step (1) is removed in Step (4) in order to remove a part of the anodized film above the inflection points 30 in cross section of the micropore 16c to eliminate the different shape portion 20 in the upper part of the micropore 16c.

[0107] In the case where Steps (3) and (4) are repeatedly performed twice or more as will be described later, an anodized film 14d after the end of Step (4) from which the different shape portion 20 has been removed has the micropore 16d which is in an approximately straight tube shape as a whole, so that a micropore formed in Step (3) following Step (4) (Step (3')) has a new different shape portion in its upper part. Therefore, in Step (4) following Step (3') (Step (4')), it is necessary to remove the different shape portion newly formed in the upper part of the micropore in Step (3'), which requires removal of a part of the anodized film above the inflection points in cross section of the micropore formed in Step (3').

[0108] For example, polishing treatments such as mechanical polishing, chemical polishing and electrolytic polishing may be used to remove a part of the anodized film above the inflection points 30 in cross section of the micropores 16c. However, it is preferable to use a treatment in which the anodized film is dissolved using an acid or an alkali as in Step (2). In this case, the anodized film 14d which is thinner than the anodized film 14c shown in FIG. 1C is formed as shown in FIG. 1D.

[0109] In the case where an acid or an alkali is used to partially dissolve the anodized film in Step (4), the amount of material dissolved from the anodized film is not particularly limited and is preferably in a range of 0.01 to 30 wt% and more preferably 0.1 to 15 wt% with respect to the whole anodized film. Within the above range, disordered array portions at the anodized film surface can be dissolved out to enhance the orderliness of the array of micropores. In the case where Steps (3) and (4) are repeatedly performed twice or more, the anodized film can keep having starting points for one or more anodizing treatments to be performed in the second and any subsequent cycles.

[0110] In terms of enhancing the orderliness of the array of micropores, Steps (3) and (4) are repeatedly performed preferably twice or more, more preferably three times or more, and even more preferably four times or more.

[0111] In the case where these steps are repeatedly performed twice or more, the conditions in Steps (3) and (4) of the respective cycles may be the same or different. In terms of improving the degree of ordering, Step (3) is preferably performed by changing the voltage in each cycle. In this case, it is more preferable to gradually shift to higher voltage conditions in terms of improving the degree of ordering.

[0112] In the state shown in FIG. 1D, it is preferred for the average pore density to be 50 to 1,500 pores/ μm^2 and for the area ratio occupied by the micropores to be 20 to 50%.

<(B) Heating Treatment of Anodized Film Formed in (A)>

[0113] The anodized film formed in the procedure described above is heated at a temperature of 50°C or higher for at least 10 minutes. This heating treatment may be carried out by heating the aluminum substrate having the anodized film formed thereon under the conditions as described above.

[0114] The inventors of the invention have made intensive studies and as a result found that acid ions derived from an electrolytic solution used in anodizing treatment, a solution used in film removal treatment to dissolve alumina, and treatment solutions used in aluminum removal treatment and through micropore-forming treatment to be described below, for example, SO_4^{2-} in the case where sulfuric acid was used for the electrolytic solution may remain in the anodized film to impair the resistance to acids and alkalis of the anodized film.

[0115] By heating the anodized film formed in the procedure described above, such acid ions that may remain in the anodized film are removed. As a result, the anodized film has improved resistance to acids and alkalis. It is presumed that an acid ion remaining in the anodized film would dissolve in moisture remaining in the anodized film, and upon heating the anodized film, be removed along with evaporation of the moisture remaining in the anodized film.

[0116] A heating temperature of less than 50°C is not sufficient to implement the action of removing an acid ion that remains in the anodized film.

[0117] The heating temperature is preferably at least 150°C, more preferably at least 200°C and even more preferably at least 400°C.

[0118] Too high a heating temperature may deform the aluminum substrate having the anodized film formed thereon due to heat, so the heating temperature is preferably up to 800°C.

[0119] A heating time of less than 10 minutes is not sufficient to implement the action of removing an acid ion that remains in the anodized film.

[0120] The heating time is preferably at least 15 minutes, more preferably at least 30 minutes and even more preferably at least 1 hour.

[0121] Heating for 10 hours or more no longer contributes to the action of removing an acid ion remaining in the anodized film and is therefore not preferable in terms of yield and energy efficiency. Heating for 15 hours or more may cause the aluminum substrate having the anodized film formed thereon to be deformed by heat, although whether or not deformation may occur depends on the heating temperature.

[0122] It is preferred to rapidly cool the thus heated anodized film. An example of the cooling method includes a method which involves directly immersing the microstructure in water or the like.

[0123] In the case where the microstructure is to be used as a porous alumina membrane filter, the micropores must extend through the microstructure, that is, the microstructure must have through micropores.

[0124] In the case where the through micropore-bearing microstructure is obtained, in the microstructure-manufacturing method of the invention, the anodized film formed in the anodizing treatment (A) is preferably further subjected to, in order,

(C) an aluminum removal treatment for removing aluminum from the anodized film obtained in the anodizing treatment (A); and

(D) a through micropore-forming treatment to make the micropores extend through the anodized film obtained by the anodizing treatment (A),

before being subjected to the heating treatment (B).

<(C) Aluminum Removal Treatment>

[0125] FIG. 2 is a partial cross-sectional view showing the state after the treatment (A). As shown in FIG. 2, an anodized film 14 bearing micropores 16 is formed on the surface of an aluminum substrate 12.

[0126] Aluminum removal treatment serves to dissolve and remove the aluminum substrate 12 from the state shown in FIG. 2. FIG. 3 is a partial cross-sectional view showing the state after the treatment (C) and illustrates a microstructure

having the anodized film 14 bearing the micropores 16.

[0127] Therefore, a treatment solution that dissolves not alumina but aluminum is used in aluminum removal treatment.

[0128] The treatment solution is not particularly limited as long as the solution used dissolves not alumina but aluminum. Examples of the treatment solution that may be used include aqueous solutions of mercury chloride, a bromine/methanol mixture, a bromine/ethanol mixture, aqua regia and a hydrochloric acid/copper chloride mixture.

[0129] The concentration is preferably from 0.01 to 10 mol/L and more preferably from 0.05 to 5 mol/L.

[0130] The treatment temperature is preferably from -10°C to 80°C and more preferably 0°C to 60°C.

[0131] Aluminum removal treatment is carried out by bringing the aluminum substrate having the anodized film formed thereon into contact with the treatment solution described above. The contacting method is not particularly limited and is exemplified by immersion and spraying. Of these, immersion is preferable. The contacting time is preferably from 10 seconds to 5 hours and more preferably from 1 minute to 3 hours.

[0132] After aluminum removal treatment, the anodized film preferably has a thickness of 1 to 1,000 μm and more preferably 10 to 500 μm .

[0133] After aluminum removal treatment, the anodized film 14 is rinsed with water prior to the treatment (D) to be described later. Rinsing with water is preferably carried out at 30°C or lower in order to suppress the changes in the pore diameter of the micropores 16 due to hydration.

<(D) Through Micropore-Forming Treatment>

[0134] In through micropore-forming treatment, the anodized film 14 bearing the micropores 16 shown in FIG. 3 is partially dissolved by immersion in an aqueous acid solution or aqueous alkali solution. The anodized film 14 at the bottoms of the micropores 16 is thus removed to make the micropores 16 extend through the anodized film 14 (to form through micropores 18). FIG. 4 is a partial cross-sectional perspective view showing the state after through micropore-forming treatment and illustrates a microstructure having the anodized film 14 bearing the through micropores 18.

[0135] In FIG. 4, all the micropores in the anodized film 14 are the through micropores 18. Not all the micropores in the anodized film 14 may extend therethrough after the treatment (D), but in the case where the microstructure of the invention is used as a porous alumina membrane filter, it is preferable for 70% of the micropores in the anodized film to extend therethrough after the treatment (D).

[0136] When through micropore-forming treatment is to be carried out with an aqueous acid solution, it is preferable to use an aqueous solution of an inorganic acid such as sulfuric acid, phosphoric acid, nitric acid or hydrochloric acid, or a mixture thereof. It is preferable for the aqueous acid solution to have a concentration of 1 to 10 wt% and a temperature of 25 to 40°C.

[0137] When through micropore-forming treatment is to be carried out with an aqueous alkali solution, it is preferable to use an aqueous solution of at least one alkali selected from the group consisting of sodium hydroxide, potassium hydroxide and lithium hydroxide. It is preferable for the aqueous alkali solution to have a concentration of 0.1 to 5 wt% and a temperature of 20 to 35°C.

[0138] Specific examples of preferred solutions include a 40°C aqueous solution containing 50 g/L of phosphoric acid, a 30°C aqueous solution containing 0.5 g/L of sodium hydroxide, and a 30°C aqueous solution containing 0.5 g/L of potassium hydroxide.

[0139] The anodized film is immersed in the aqueous acid solution or aqueous alkali solution for a period of preferably 8 to 120 minutes, more preferably 10 to 90 minutes, and even more preferably 15 to 60 minutes.

[0140] After through micropore-forming treatment, the anodized film preferably has a thickness of 1 to 1,000 μm and more preferably 10 to 500 μm .

[0141] After through micropore-forming treatment, the anodized film 14 is rinsed with water prior to the treatment (B) described above. Rinsing with water is preferably carried out at 30°C or lower in order to suppress the changes in the pore diameter of the through micropores 18 due to hydration.

[0142] In the microstructure of the invention obtained by subjecting the aluminum substrate at least to, in order, the treatments (A) and (B), preferably the treatments (A), (C), (D) and (B), heating of the anodized film in the treatment (B) serves to remove acid ions remaining in the anodized film, that is, those derived from an electrolytic solution used in anodizing treatment, a solution used in film removal treatment to dissolve alumina, and treatment solutions used in aluminum removal treatment and through micropore-forming treatment, thus considerably lowering the concentrations of the elements derived from such acid ions.

[0143] Sulfuric acid, phosphoric acid or oxalic acid is particularly preferably used in anodizing treatment. Therefore, exemplary main acid ions that may remain in the anodized film include SO_4^{2-} , PO_3^{2-} , and $\text{C}_2\text{H}_5\text{COO}^-$, although they differ depending on the acids used in anodizing treatment and various other treatments. The anodized film of the microstructure of the invention has considerably reduced concentrations of the elements derived from such acid ions.

[0144] More specifically, the anodized film in the microstructure of the invention has a sulfur atom concentration of up to 3.2 wt%, a carbon atom concentration of up to 2.5 wt% and a phosphorus atom concentration of up to 1.0 wt%.

[0145] The atomic concentrations in the anodized film can be measured by, for example, electron probe microanalysis (EPMA) or X-ray photoelectron spectroscopy (ESCA).

[0146] In the microstructure of the invention, the micropores in the region having an area of $1 \mu\text{m}^2$ preferably have a pore diameter variance of within 3% and more preferably within 2% of the average diameter. The average diameter and the variance can be determined by the following formulae:

$$\text{Average diameter: } \mu_x = (1/n) \sum X_i$$

$$\text{Variance: } \sigma^2 = (1/n) (\sum X_i^2) - \mu_x^2$$

$$\text{Variance/average diameter} = \sigma^2/\mu_x \leq 0.03$$

where X_i represents the diameter of one micropore measured in the region with an area of $1 \mu\text{m}^2$.

[0147] The microstructure of the invention has the micropores with a degree of ordering as defined by formula (1):

$$\text{Degree of Ordering (\%)} = B/A \times 100 \quad (1)$$

(wherein A represents a total number of micropores in a measurement region; and B represents a number of specific micropores in the measurement region for which, when a circle is drawn so as to be centered on a center of gravity of a specific micropore and so as to be of a smallest radius that is internally tangent to an edge of another micropore, the circle includes centers of gravity of six micropores other than the specific micropore) of preferably at least 50%, more preferably at least 70% and even more preferably at least 80%.

[0148] FIGS. 5A and 5B are views illustrating a method for calculating the degree of ordering of pores. Formula (1) is explained more fully below in conjunction with FIGS. 5A and 5B.

[0149] With regard to a micropore 1 shown in FIG. 5A, when a circle 3 is drawn so as to be centered on the center of gravity of the micropore 1 and so as to be of the smallest radius that is internally tangent to the edge of another micropore (inscribed in a micropore 2), the interior of the circle 3 includes the centers of gravity of six micropores other than the micropore 1. Therefore, the micropore 1 is counted for B.

[0150] With regard to a micropore 4 shown in FIG. 5B, when a circle 6 is drawn so as to be centered on the center of gravity of the micropore 4 and so as to be of the smallest radius that is internally tangent to the edge of another micropore (inscribed in a micropore 5), the interior of the circle 6 includes the centers of gravity of five micropores other than the micropore 4. Therefore, the micropore 4 is not counted for B. With regard to a micropore 7 shown in FIG. 5B, when a circle 9 is drawn so as to be centered on the center of gravity of the micropore 7 and so as to be of the smallest radius that is internally tangent to the edge of another micropore (inscribed in a micropore 8), the interior of the circle 9 includes the centers of gravity of seven micropores other than the micropore 7. Therefore, the micropore 7 is not counted for B.

[0151] In addition, the microstructure of the invention is appropriate for use in a porous alumina membrane filter.

[0152] The microstructure of the invention may also support an organic compound, an inorganic compound or fine metal particles in the micropores of the anodized film according to the intended application.

EXAMPLES

[0153] Examples are given below by way of illustration and should not be construed as limiting the invention.

Example 1

1. Electrolytic Polishing Treatment

[0154] A high purity aluminum substrate (manufactured by Sumitomo Light Metal Industries, Ltd; purity, 99.99 wt%; thickness, 0.4 mm) was cut so as to enable anodizing treatment to be carried out over an area of 10 cm square. Electrolytic polishing was carried out in an electrolytic polishing solution of the composition indicated below, under the conditions

of a voltage of 25 V, a solution temperature of 65°C and a solution flow rate of 3.0 m/min. A carbon electrode and a GP0110-30R unit manufactured by Takasago, Ltd. were used for the cathode and the power supply, respectively. The flow rate of the electrolytic solution was measured using a vortex flow monitor FLM22-10PCW (manufactured by As One Corporation).

<Electrolytic Polishing Solution Composition>

[0155]

85 wt% Phosphoric acid (Wako Pure Chemical Industries, Ltd.)	660 mL
Pure water	160 mL
Sulfuric acid	150 mL
Ethylene glycol	30 mL

2. Treatment (A): Micropore Formation through Anodization

[0156] The steps (1) to (4) described above were carried out in this order for the treatment (A) to form a micropore-bearing anodized film on the surface of the aluminum substrate.

[0157] The sample polished as above was anodized in an electrolytic solution of 0.30 mol/L sulfuric acid for 1 hour under the conditions of a voltage of 25 V, a solution temperature of 15°C and a solution flow rate of 3.0 m/min. Then, the sample was immersed in a mixed aqueous solution of phosphoric acid and chromic acid having a concentration of 0.5 mol/L at 40°C for 20 minutes.

[0158] This treatment was repeated four times, after which the sample was anodized again in an electrolytic solution of 0.30 mol/L sulfuric acid for 5 hours under the conditions of a voltage of 25 V, a solution temperature of 15°C and a solution flow rate of 3.0 m/min, then immersed in a mixed aqueous solution of phosphoric acid and chromic acid having a concentration of 0.5 mol/L at 40°C for 20 minutes, thereby forming, on the surface of the aluminum substrate 12, the anodized film 14 having the micropores 16 of a straight tube shape arranged in a honeycomb pattern.

[0159] In both of anodizing treatment and re-anodizing treatment, Use was made of a stainless steel electrode as the cathode, GP0110-30R (Takasago, Ltd.) as the power supply, NeoCool BD36 (Yamato Scientific Co., Ltd.) as the cooling system, and Pairstirrer PS-100 (Tokyo Rikakikai Co., Ltd.) as the stirring and warming unit. The flow rate of the electrolytic solution was measured using the vortex flow monitor FLM22-10PCW (manufactured by As One Corporation).

3. (C) Aluminum Removal Treatment

[0160] The sample treated as above was immersed in an mercury chloride aqueous solution having a concentration of 2 mol/L at 20°C for 3 hours to dissolve and remove the aluminum substrate 12 to thereby prepare a microstructure shown in FIG. 3 in which the anodized film 14 had the micropores 16.

4. (D) Through Micropore-Forming Treatment

[0161] The sample treated as above was immersed in 5 wt% phosphoric acid at 30°C for 30 minutes to form through micropores to thereby prepare a microstructure shown in FIG. 4 in which the anodized film 14 had the through micropores 18.

5. (B) Heating Treatment

[0162] The microstructure shown in FIG. 4 as obtained above was subjected to heating treatment at a temperature of 400°C for 1 hour to obtain the microstructure of Example 1.

Example 2

[0163] Example 1 was repeated except that heating treatment (B) in Paragraph 5. above was carried out at a temperature of 200°C, thereby obtaining the microstructure of Example 2.

Example 3

[0164] Example 1 was repeated except that heating treatment (B) in Paragraph 5. above was carried out at a temper-

ature of 150°C, thereby obtaining the microstructure of Example 3.

Example 4

[0165] Example 1 was repeated except that an electrolytic solution of 0.50 mol/L oxalic acid was used in micropore formation through anodization (A) in Paragraph 2. above and the voltage was set to 40V, thereby obtaining the microstructure of Example 4.

Example 5

[0166] Example 1 was repeated except that an electrolytic solution of 0.30 mol/L phosphoric acid was used in micropore formation through anodization (A) in Paragraph 2. above, the voltage was set to 195 V, and a mixed aqueous solution of phosphoric acid and chromic acid having a concentration of 1.0 mol/L was used in film removal treatment, thereby obtaining the microstructure of Example 5.

Example 6

[0167] Example 3 was repeated except that heating treatment (B) in Paragraph 5. above was carried out for 30 minutes, thereby obtaining the microstructure of Example 6.

Example 7

[0168] Example 3 was repeated except that heating treatment (B) in Paragraph 5. above was carried out for 10 hours, thereby obtaining the microstructure of Example 7.

Comparative Example 1

[0169] Example 1 was repeated except that heating treatment (B) in Paragraph 5. above was not carried out, thereby obtaining the microstructure of Comparative Example 1.

Comparative Example 2

[0170] Example 4 was repeated except that heating treatment (B) in Paragraph 5. above was not carried out, thereby obtaining the microstructure of Comparative Example 2.

Comparative Example 3

[0171] Example 5 was repeated except that heating treatment (B) in Paragraph 5. above was not carried out, thereby obtaining the microstructure of Comparative Example 3.

Comparative Example 4

[0172] Example 1 was repeated except that heating treatment (B) in Paragraph 5. above was carried out at a temperature of 150°C for 5 minutes, thereby obtaining the microstructure of Comparative Example 4.

[0173] The microstructures in Examples 1 to 7 and Comparative Examples 1 to 4 were measured by electron probe microanalysis (EPMA) using an electron probe microanalyzer JXA-8800 (JEOL Ltd.) for the sulfur atom concentration, carbon atom concentration and phosphorus atom concentration in the anodized film under the conditions of an acceleration voltage of 20 kV, an irradiation current of 1×10^{-7} A, a dwelling time of 50 ms, a probe system of 0, and a magnification of 1,000X. The results are shown in Table 1.

[0174] The image of the surface of each of the microstructures in Examples 1 to 7 and Comparative Examples 1 to 4 was taken by FE-SEM at a magnification of 20,000X, and the average diameter and the diameter variance of arbitrary 300 micropores were determined at a field of view of $1 \mu\text{m} \times 1 \mu\text{m}$ by the following formulae:

$$\text{Average diameter: } \mu_x = (1/n) \sum X_i$$

$$\text{Variance: } \sigma^2 = (1/n) (\sum Xi^2) - \mu_x^2$$

$$\text{Variance/average diameter} = \sigma^2/\mu_x$$

where Xi represents the diameter of one micropore measured in the region with an area of 1 μm^2 . The results are shown in Table 1.

[0175] The image of the surface of each of the microstructures in Examples 1 to 7 and Comparative Examples 1 to 4 was taken by FE-SEM at a magnification of 20,000X and the degree of ordering as defined by formula (1):

$$\text{Degree of Ordering (\%)} = B/A \times 100 \quad (1)$$

(wherein A represents a total number of micropores in a measurement region; and B represents a number of specific micropores in the measurement region for which, when a circle is drawn so as to be centered on a center of gravity of a specific micropore and so as to be of a smallest radius that is internally tangent to an edge of another micropore, the circle includes centers of gravity of six micropores other than the specific micropore), was determined at a field of view of 1 $\mu\text{m} \times 1 \mu\text{m}$ using arbitrary 300 micropores. The results are shown in Table 1.

[0176] The microstructures in Examples 1 to 7 and Comparative Examples 1 to 4 were immersed at 20°C for 15 hours in aqueous hydrochloric acid solutions having pH adjusted to 0.05, 0.1, 1.0, and 2.0, respectively and aqueous sodium hydroxide solutions having pH adjusted to 11.0, 12.0, and 13.0, respectively. Following the immersion, the state of each microstructure was observed by FE-SEM. The results are shown in Table 1. The microstructure was rated as "Good" when there was no difference before and after the immersion, "Fair" when there was a change, and "Poor" when the immersion caused the microstructure to dissolve, respectively.

[0177] The microstructures in Examples 1 to 7 and Comparative Examples 1 to 4 were evaluated for their filtering property as the porous alumina membrane filter. More specifically, the filtration flow rate of pure water at 20°C at a drive pressure of 1.0 $\text{kgf}\cdot\text{cm}^{-2}$ for a filtration time of 0 to 100 minutes was determined. A larger value means that the microstructure serves as a filter with a higher filtering property. The results are shown in Table 1.

	EPMA evaluation (atomic concentration)			Micropore shape		pH resistance							Filtering property
	S[wt%]	C[wt%]	P[wt%]	Variance/ average diameter	Degree of ordering	0.05	0.1	1.0	2.0	11.0	12.0	13.0	Filtration flow rate [ml/cm ²]
EX1	2.1	0.0	0.0	2.5%	90%	Good	Good	Good	Good	Good	Good	Fair	100
EX2	2.6	0.0	0.0	2.5%	90%	Good	Good	Good	Good	Good	Good	Fair	100
EX3	3.2	0.0	0.0	2.5%	90%	Fair	Good	Good	Good	Good	Good	Poor	100
EX4	0.0	2.3	0.0	2.7%	88%	Good	Good	Good	Good	Good	Good	Fair	120
EX5	0.0	0.0	0.9	2.8%	85%	Good	Good	Good	Good	Good	Good	Fair	160
EX6	2.5	0.0	0.0	2.5%	90%	Fair	Good	Good	Good	Good	Good	Fair	100
EX7	2.0	0.0	0.0	2.5%	90%	Good	Good	Good	Good	Good	Good	Fair	100
CE1	3.4	0.0	0.0	2.5%	90%	Poor	Fair	Good	Good	Good	Good	Poor	100
CE2	0.0	2.6	0.0	2.7%	87%	Poor	Fair	Good	Good	Good	Good	Poor	120
CE3	0.0	0.0	1.2	2.8%	85%	Fair	Good	Good	Good	Good	Good	Poor	160
CE4	3.4	0.0	0.0	2.5%	90%	Poor	Fair	Good	Good	Good	Good	Poor	100

Claims

1. A method of manufacturing a microstructure, wherein an aluminum substrate surface is subjected at least to, in order,
 - (A) an anodizing treatment for anodizing the aluminum substrate surface to form an anodized film bearing micropores; and
 - (B) a heating treatment for heating the anodized film formed in the anodizing treatment (A) at a temperature of at least 50°C for at least 10 minutes, whereby the microstructure bearing the micropores at a surface of the anodized film is obtained.
2. The manufacturing method according to claim 1, wherein the anodized film obtained in the anodizing treatment (A) is further subjected to, in order,
 - (C) an aluminum removal treatment for removing aluminum from the anodized film obtained in the anodizing treatment (A); and
 - (D) a through micropore-forming treatment to make the micropores extend through the anodized film obtained in the anodizing treatment (A), before being subjected to the heating treatment (B), whereby the microstructure obtained has the micropores extending through the anodized film.
3. A microstructure obtained by the manufacturing method according to claim 1 or 2.
4. A microstructure comprising a micropore-bearing anodized film of aluminum, wherein the anodized film has a sulfur atom concentration of up to 3.2 wt%, a carbon atom concentration of up to 2.5 wt% and a phosphorus atom concentration of up to 1.0 wt%.
5. The microstructure according to claim 4 which comprises through micropores.
6. The microstructure according to any one of claims 3 to 5, wherein the micropores have a pore diameter variance of within 3% of average diameter.
7. The microstructure according to any one of claims 3 to 6, wherein a degree of ordering of the micropores as defined by formula (1):

$$\text{Degree of Ordering (\%)} = B/A \times 100 \quad (1)$$

(wherein A represents a total number of micropores in a measurement region; and B represents a number of specific micropores in the measurement region for which, when a circle is drawn so as to be centered on a center of gravity of a specific micropore and so as to be of a smallest radius that is internally tangent to an edge of another micropore, the circle includes centers of gravity of six micropores other than the specific micropore) is at least 50%.

8. A porous alumina membrane filter using the microstructure according to any one of claims 3 to 7.

FIG. 1A

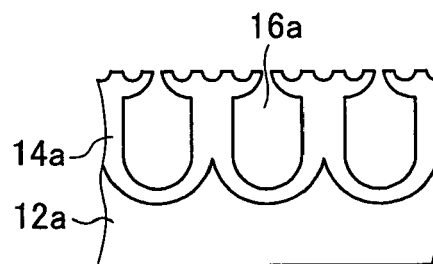


FIG. 1B

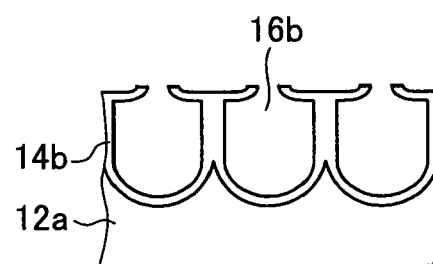


FIG. 1C

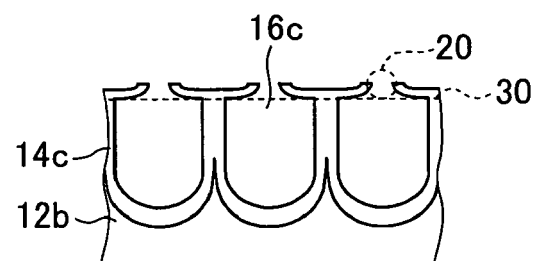


FIG. 1D

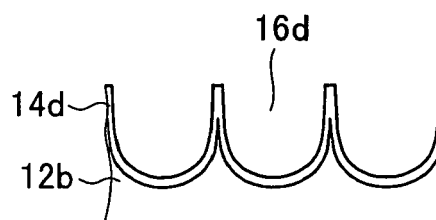


FIG. 2

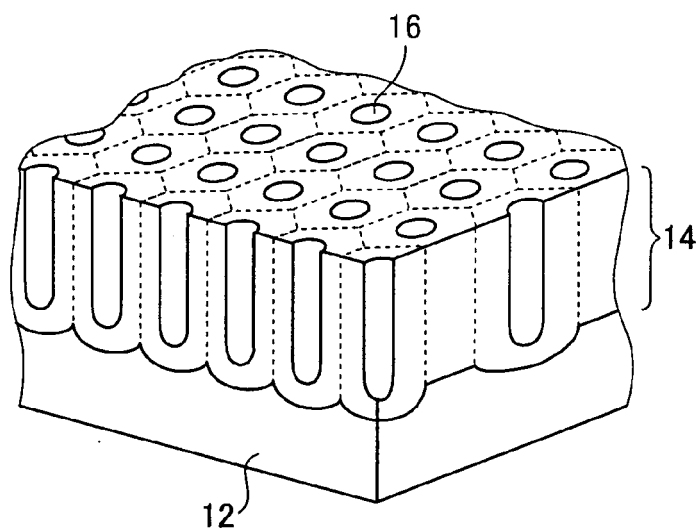


FIG. 3

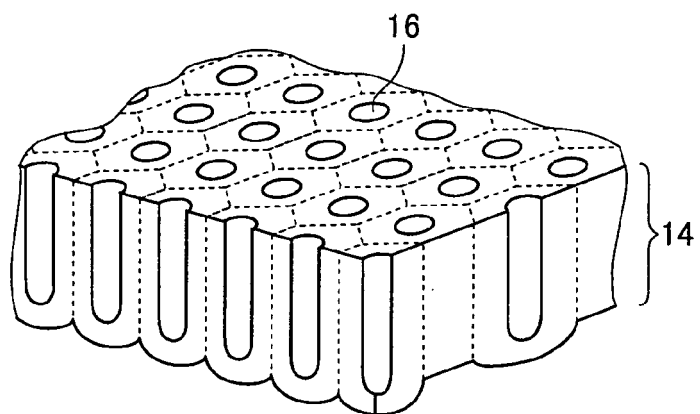


FIG. 4

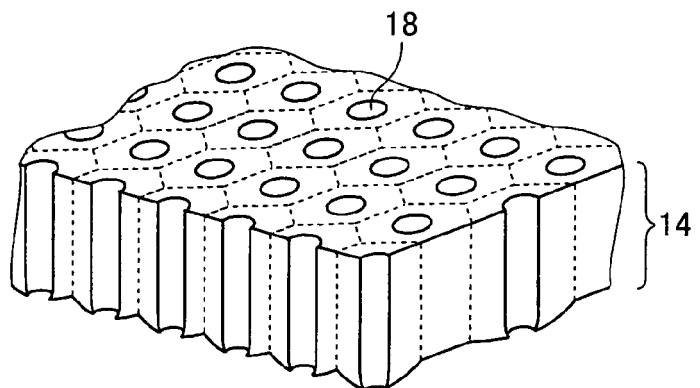


FIG. 5A

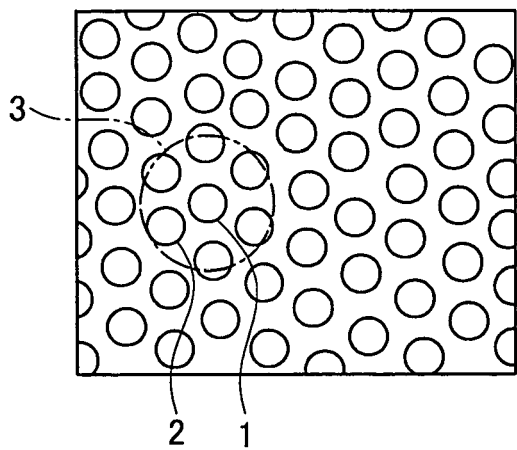
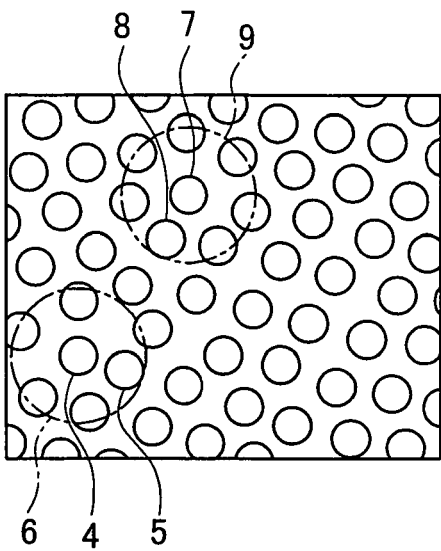


FIG. 5B





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2
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