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(54) Title: METHOD OF MANUFACTURING ALUMINUM MATERIAL FOR ELECTROLYTIC CAPACITOR ELECTRODES, ALUMINUM MATERIAL FOR ELECTROLYTIC CAPACITOR ELECTRODES, ANODE MATERIAL FOR ALUMINUM ELECTROLYTIC CAPACITORS, AND ALUMINUM ELECTROLYTIC CAPACITORS

(57) Abstract: A method for manufacturing an aluminum material for electrolytic capacitor electrodes of the present invention, comprising the steps of heating an aluminum material in an oxidative atmosphere, removing the surface layer of the aluminum material by washing the heated aluminum material and subjecting the washed aluminum material obtained by washing to final annealing.



WO 2005/078751 A1

DESCRIPTION**METHOD OF MANUFACTURING ALUMINUM MATERIAL FOR ELECTROLYTIC
CAPACITOR ELECTRODES, ALUMINUM MATERIAL FOR ELECTROLYTIC
CAPACITOR ELECTRODES, ANODE MATERIAL FOR ALUMINUM ELECTROLYTIC
CAPACITORS, AND ALUMINUM ELECTROLYTIC CAPACITORS**

Priority is claimed to Japanese Patent Application No. 2004-040328, filed on February 17, 2004, Japanese Patent Application No.2004-304717, filed on October 19, 2004, Japanese Patent Application No.2004-316592, filed on October 29, 2004, Japanese Patent Application No.2004-348837, filed on December 1, 2004, Japanese Patent Application No.2004-377539, filed on December 27, 2004, U.S. Provisional Application No.60/614,328, filed on September 30, 2004, U.S. Provisional Application No.60/621,067, filed on October 25, 2004, and U.S. Provisional Application No.60/629,971, filed on November 23, 2004, the disclosure of which are incorporated by reference in their entireties.

Cross Reference to Related Applications

This application is an application filed under 35 U.S.C. §111(a) claiming the benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of Provisional Application No. 60/614,328, filed on September 30, 2004, U.S. Provisional Application No.60/621,067, filed on October 25, 2004, and U.S. Provisional Application

No.60/629,971, filed on November 23, 2004 pursuant to 35 U.S.C.§111(b).

Technical Field

The present invention relates to a method of manufacturing aluminum material for electrolytic capacitor electrodes, aluminum material for electrolytic capacitor electrodes, anode material for aluminum electrolytic capacitors, and aluminum electrolytic capacitors.

In this description, the term "aluminum" is used as aluminum and alloys thereof, and aluminum material includes a foil, a plate, and products thereof.

Background Art

Aluminum material generally used as electrode material for aluminum electrolytic capacitors is treated by an electrochemical, or a chemical etching to expand effective surface area of aluminum material in order to enhance capacitance.

In manufacturing aluminum material for electrolytic capacitor anode, where tunnel structure pits are generated by direct current etching to grow cube texture of aluminum, in general, intermediate annealing is performed in mid-course of a cold rolling process, and after performing finish cold rolling (rolling with low reduction in thickness), aluminum material is subjected to final annealing at around 500° C in an inert atmosphere or in vacuum (e.g. Patent Document 1).

Moreover, as described in Patent Document 2, tensile strain application instead of finish cold rolling can also grow the cubic texture of aluminum.

Etching characteristics of aluminum material obtained by final annealing depends greatly on the characteristics of aluminum prior to annealing. For the uniformity of the characteristics on the surface layer of aluminum material, therefore, it has been considering that aluminum is washed with aluminum soluble liquids in mid-course of cold rolling or after cold rolling.

According to Patent Document 3, after an aluminum plate in thickness (t) is reduced by cold rolling to a thickness satisfying $3.3 t_0 \leq t \leq 20 t_0$ (t_0 is a final thickness of aluminum), the surface is washed and dissolved with alkaline aqueous solution or acid aqueous solution, subsequently is subjected to cold rolling. This method of manufacturing aluminum foil for electrolytic capacitors prevents the formation of a thick oxide layer.

According to Patent Document 4, is disclosed a method that makes an oxide layer on the surface of aluminum foil after annealing become thin, and also it dissolve and remove easily in an etching solution, by the method comprising: a process of removing a surface layer of aluminum foil; after the removing, a heat-oxidation process at a temperature of 40 to 350° C, a dew point of 0 to 80° C, for 30 to 1,800 sec; and after the heat-oxidation, an annealing process in a non-oxidative atmosphere. Also, as a means of removing the surface layer of aluminum foil, is disclosed washing with an alkaline solution such as sodium hydroxide or the like,

and with an acid solution.

Patent Document 5 describes a method of manufacturing aluminum foil for electrolytic capacitor electrodes, the method is that using a pure aluminum material of 99.96 to 99.98% in purity, intermediate annealing is performed at a temperature of 200 to 500° C, for not less than 1 hr, and in a course after the intermediate annealing before final annealing, the surface layer of aluminum foil is removed no less than 0.1 μm in a thickness direction.

Patent Document 6 describes a method of manufacturing aluminum foil for electrolytic capacitor electrodes, the method is that cold rolled aluminum foil of 99.99% or more in purity, containing impurities for expanding effective surface area, is performed in a first step of annealing at a temperature of 250° C to 530° C, then the surface layer of aluminum foil is removed to give final annealing at higher than 500° C. According to Patent Document 6, an average Fe content of aluminum foil surface layer having a ratio of less than 2.0 to that of inside may provide an aluminum foil for electrolytic capacitor electrodes to obtain capacitors with a large capacitance.

Patent Document 1: Japanese Examined Patent Publication No. 11242 (1979)

Patent Document 2: WO 2004/ 003248 A1

Patent Document 3: Japanese Unexamined Patent Publication No.257137 (1991)

Patent Document 4: Japanese Unexamined Patent Publication No.

201673 (1995)

Patent Document 5: Japanese Unexamined Patent Publication No.

81945 (1998)

Patent Document 6: Japanese Unexamined Patent Publication No.

210561 (2001)

However, when surface layer is removed chemically, because of unevenness in corrosion resistance of aluminum material surface prior to the removal of the surface layer, it is difficult to remove the surface layer uniformly, so that there has been a limit to enhance capacitance.

By the technique described in Patent Document 3, because of the unevenness of aluminum material surface layer prior to washing, the aluminum material surface layer dissolves unevenly, it was insufficient to obtain improved etching characteristics of aluminum material after final annealing.

By the technique described in Patent Document 4, although heat-oxidation prior to annealing contributes to the evenness of aluminum material surface layer, the characteristics of aluminum material surface layer prior to removing is uneven, thereby the surface after washing is affected, therefore it was insufficient to improve the evenness by the heat-oxidation and there was a limit to enhance the etching characteristics.

Furthermore, characteristics of oxidized surface of aluminum material after intermediate annealing is changed by an atmosphere in the intermediate annealing, which affects greatly

a surface layer removing afterwards, but there was no description on intermediate annealing atmosphere in the Patent Document 5. As well as a case of removing surface layer after intermediate annealing before finish cold rolling, in a case where surface layer is removed after performing sequentially intermediate annealing and finish cold rolling, since rolling reduction is lower in finish cold rolling than that in cold rolling prior to intermediate annealing, the atmosphere in the intermediate annealing affects greatly a solubility of surface layer by a chemical forming after the finish cold rolling.

In Patent Document 6, there is no description on atmosphere in a first step of annealing before surface layer removing, no consideration is taken on such the method in the present invention that provides the uniform removing of the surface layer after being heated in an oxidative atmosphere.

In the light of this technical background, the present invention was achieved to overcome the problem in the art, that is, in the conventional manufacturing method for aluminum material for electrolytic capacitor, upon solving the surface layer of aluminum material by washing, its dissolution is not uniform, and gives an insufficient etching characteristics of the aluminum material obtained after final annealing. It is an object of the present invention to provide a method of manufacturing aluminum material for electrolytic capacitor electrodes with excellent etching characteristics, aluminum material for electrolytic capacitor electrodes, a method of manufacturing electrode

material for electrolytic capacitors, and aluminum electrolytic capacitors. Other objects of the present invention will become apparent from following embodiments of the present invention.

SUMMARY OF THE INVENTION

In order to achieve the aforementioned objects, the present invention provides a following means:

(1) A method for manufacturing an aluminum material for electrolytic capacitor electrodes including the steps of hot-rolling, cold-rolling and final annealing, comprising the steps of: heating an aluminum material in oxidative atmosphere after the hot-rolling and before commencing final annealing; removing the surface layer of the aluminum material by washing after the heating; and subjecting the washed aluminum material to the final annealing.

(2) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to aforementioned Item 1, wherein heating of the aluminum material in oxidative atmosphere and removing of the surface layer by washing are conducted after finishing the cold-rolling.

(3) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 1 or 2, wherein a cleaning liquid used for washing is an alkaline aqueous solution.

(4) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned

Item 1 or 2, wherein the cleaning liquid used for washing is an acid aqueous solution.

(5) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Items 1 or 2, wherein the aluminum material is sequentially washed by alkaline aqueous solution and by acid aqueous solution.

(6) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Items 3 or 5, wherein an alkali in alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate (Na_3PO_4) and sodium carbonate.

(7) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 4 or 5, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and phosphorus-containing acid.

(8) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 7, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

quantity of removal D (nm) = $E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3)$,

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm^3 is the density of aluminum.

(9) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 8, wherein the heating temperature in the oxidative atmosphere is within the range of 50 to 400 °C.

(10) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 9, wherein the heating time in the oxidative atmosphere is not less than 3 sec, and not more than 72 hr.

(11) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 10, wherein the oxygen concentration in the oxidative atmosphere during heating is 0.1 volume % or more.

(12) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 11, further comprising the step of degreasing the aluminum material before heating the aluminum material in the oxidative atmosphere, or after heating the aluminum material in the oxidative atmosphere before washing the surface layer of the aluminum material.

(13) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 12, wherein the aluminum material is degreased by using an

organic solvent.

(14) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 12, wherein the aluminum material is degreased by using water added with a surfactant.

(15) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 1, wherein the aluminum material is subjected to an intermediate annealing during the cold-rolling and subjected to finish cold-rolling after intermediate annealing; wherein the intermediate annealing is conducted in oxidative atmosphere, and the removing of the surface layer of the aluminum material by washing is conducted after intermediate annealing.

(16) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 15, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the finish cold-rolling before the final annealing.

(17) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 15, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the intermediate annealing before the finish cold-rolling.

(18) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 17, wherein the oxygen concentration

in the oxidative atmosphere during the intermediate annealing is 0.1 volume % or more.

(19) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 18, wherein the aluminum material is subjected to the intermediate annealing in oxidative atmosphere at a temperature not less than 200 °C, and not more than 320 °C.

(20) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 19, wherein the cleaning liquid used for washing is alkaline aqueous solution.

(21) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 19, wherein the cleaning liquid used for washing is acid aqueous solution.

(22) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 19, wherein the aluminum material is sequentially washed by alkaline aqueous solution and acid aqueous solution.

(23) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 20 to 22, wherein an alkali in alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary

phosphate and sodium carbonate.

(24) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 21 or 22, wherein an acid in acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and phosphorus-containing acid.

(25) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 24, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal } D \text{ (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 \text{ (g/cm}^3\text{)},$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

(26) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 15 to 25, further comprising the step of degreasing the aluminum material after the cold-rolling before the intermediate annealing, before the final annealing.

(27) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 26, wherein the aluminum material is degreased by using an organic solvent.

(28) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 26, wherein the aluminum material is degreased by using water added with a surfactant.

(29) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 1, wherein the aluminum material is subjected to an intermediate annealing during the cold-rolling and subjected to a finish cold-rolling after the intermediate annealing; wherein the intermediate annealing is conducted in an oxidative atmosphere, and the heating of the aluminum material in the oxidative atmosphere and the removing of the surface layer by washing are conducted after the finish cold-rolling.

(30) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 29, comprising the step of removing the surface of the aluminum material by washing the aluminum material after the intermediate annealing and before the finish cold-rolling.

(31) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 29 or 30, wherein the cleaning liquid used for washing is the alkaline aqueous solution.

(32) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 or 30, wherein the cleaning liquid used for washing is acid aqueous solution.

(33) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 or 30, wherein the aluminum material is sequentially washed by alkaline aqueous solution and acid aqueous solution.

(34) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 31 to 33, wherein an alkali in alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

(35) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 32 or 33, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and phosphorus-containing acid.

(36) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 to 35, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in oxidative atmosphere after finish cold-rolling is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

quantity of removal D (nm) = $E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3)$,

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

(37) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 to 36, wherein the heating temperature in the oxidative atmosphere after the finish cold-rolling is within the range of 50 to 400 °C.

(38) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 37, wherein the heating time in the oxidative atmosphere after the finish cold-rolling is not less than 3 sec, and not more than 72 hr.

(39) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 to 38, wherein aluminum material is subjected to the intermediate annealing in the oxidative atmosphere at a temperature not less than 200 °C, and not more than 320 °C.

(40) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 to 39, wherein the oxygen concentration in the oxidative atmosphere during heating after the finish cold-rolling is 0.1 volume % or more.

(41) The method for manufacturing an aluminum material for

electrolytic capacitor electrodes according to any one of the aforementioned Items 29 to 40, wherein the oxygen concentration in the oxidative atmosphere during the intermediate annealing is 0.1 volume % or more.

(42) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 29 to 41, further comprising the step of degreasing the aluminum material before the intermediate annealing after the cold-rolling, before finally removing the surface layer of the aluminum material by washing the aluminum material.

(43) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 42, wherein the aluminum material is degreased by using an organic solvent.

(44) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 42, wherein the aluminum material is degreased by using water containing a surfactant.

(45) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 1, wherein the aluminum material is subjected to an intermediate annealing after the cold-rolling and tensile-strained after the intermediate annealing and before commencing the final annealing; and the heating of the aluminum material in the oxidative atmosphere and the removing of the

surface layer of the aluminum material by washing are conducted after giving the tensile strain.

(46) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 45, wherein the cleaning liquid used for washing is the alkaline aqueous solution.

(47) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 45, wherein the cleaning liquid used for washing is the acid aqueous solution.

(48) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 45, wherein the aluminum material is sequentially washed by the alkaline aqueous solution and the acid aqueous solution.

(49) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 46 to 48, wherein an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

(50) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 47 or 48, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and phosphorus-containing acid.

(51) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 45 to 50, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal D (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3),$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

(52) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 45 to 51, wherein the heating temperature in the oxidative atmosphere is within the range of 50 to 400 °C.

(53) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 52, wherein the heating time in the oxidative atmosphere is not less than 3 sec, and not more than 72 hr.

(54) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 45 to 53, wherein the oxygen concentration in the oxidative atmosphere during heating is 0.1 volume % or more.

(55) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned

Item 1, wherein the aluminum material is subjected to an intermediate annealing in oxidative atmosphere after cold-rolling and tensile strained after the intermediate annealing and before commencing the final annealing; and the removing of the surface layer of the aluminum material by washing is conducted at least one time after the intermediate annealing.

(56) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 55, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the tensile strain application before the final annealing.

(57) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 55, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the intermediate annealing before the tensile strain application.

(58) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 57, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the tensile strain application before the final annealing, after heating the aluminum material in the oxidative atmosphere.

(59) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 58, wherein the cleaning liquid used for washing is alkaline aqueous solution.

(60) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 58, wherein the cleaning liquid used for washing is the acid aqueous solution.

(61) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 58, wherein the aluminum material is sequentially washed by alkaline aqueous solution and acid aqueous solution.

(62) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 59 to 61, wherein an alkali in alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

(63) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 60 or 61, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and a phosphor element.

(64) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 63, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere after

intermediate annealing is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal D (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3),$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

(65) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 57 to 64, wherein the heating temperature in the oxidative atmosphere after the tensile strain application is within the range of 50 to 400 °C.

(66) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 65, wherein the heating time in the oxidative atmosphere after the tensile strain application is not less than 3 sec, and not more than 72 hr.

(67) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 66, wherein the intermediate annealing in the oxidative atmosphere is performed at a temperature not less than 200 °C, and not more than 300 °C.

(68) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 67, wherein the oxygen concentration in the oxidative atmosphere during heating after the tensile strain

application is 0.1 volume % or more.

(69) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 55 to 67, wherein the oxygen concentration in the oxidative atmosphere during the intermediate annealing is 0.1 volume % or more.

(70) The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 69, wherein the aluminum material is subjected to the final annealing in inert gas atmosphere.

(71) A method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 70, wherein the aluminum material is subjected to the final annealing at a temperature not less than 450 °C, and not more than 600 °C.

(72) A method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of the aforementioned Items 1 to 71, wherein the aluminum purity of the aluminum material is 99.9 mass % or more.

(73) The aluminum material for electrolytic capacitor electrodes manufactured by the method according to any one of the aforementioned Items 1 to 72.

(74) The aluminum material for electrolytic capacitor electrodes according to the aforementioned Item 73, wherein the aluminum material is an anode material for middle or high voltages.

(75) The method for manufacturing an electrode material for

electrolytic capacitors, comprising the step of etching the aluminum material manufactured by any one of the aforementioned Items 1 to 72.

(76) The method for manufacturing an electrode material for electrolytic capacitors according to the aforementioned Item 75, further comprising the step of performing formation of the dielectric by anodizing after etching.

(77) The method for manufacturing an electrode material for electrolytic capacitors according to the aforementioned Item 75 or 76, wherein at least a part of the etching is DC electrolytic etching.

(78) The anode material for aluminum electrolytic capacitors manufactured by the method according to any one of the aforementioned Items 75 to 77.

(79) The aluminum electrolytic capacitor comprising the aluminum electrode material manufactured by the method according to any one of the aforementioned Items 75 to 77 as electrode materials.

The invention according to the aforementioned Item 1 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics by a method wherein aluminum material is heated in the oxidative atmosphere, thereafter, the surface layer of aluminum material is removed by washing, which can solve aluminum material uniformly upon washing, and then is subjected to final annealing.

The invention according to the aforementioned Item 2 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics by a method wherein after cold rolling, aluminum material is heated in oxidative atmosphere, thereafter, the surface layer of aluminum material is removed by washing, which can solve aluminum material uniformly upon washing, and is subjected to final annealing.

The invention according to the aforementioned Item 3 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an alkaline aqueous solution.

The invention according to the aforementioned Item 4 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an acid aqueous solution.

The invention according to the aforementioned Item 5 provides that the surface layer of aluminum material can be removed reliably by washing because the washing is performed sequentially with an alkaline aqueous solution and an acid aqueous solution.

The invention according to the aforementioned Item 6 provides that the surface layer can be removed more effectively because an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate (Na_3PO_4), and sodium carbonate.

The invention according to the aforementioned Item 7 provides that the surface layer can be removed more effectively because an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphorus-containing acid.

The invention according to the aforementioned Item 8 provides that an enhancement effect of capacitance can be surely obtained by uniform dissolution of aluminum material because the average removed amount of aluminum material surface layer by washing is not less than 1nm, and not more than 500 nm per one side of aluminum material in the removed amount D (nm).

The invention according to the aforementioned Item 9 provides that while an excess thickening of oxide layer on aluminum material surface layer is suppressed, sufficient oxidization can be performed, then the surface layer can dissolve uniformly upon surface layer removing by washing, because the heating temperature in the oxidative atmosphere is 50 to 400 °C.

The invention according to the aforementioned Item 10 provides that while an excess thickening of oxide layer on aluminum material surface layer is suppressed, sufficient oxidization can be performed, then the surface layer can dissolve uniformly upon surface layer removing by washing, because the heating time is not less than 3 sec, and not more than 72 hr.

The invention according to the aforementioned Item 11 provides that the surface layer of aluminum material can dissolve uniformly because the oxygen density of heating atmosphere in the

oxidative atmosphere is not less than 0.1 volume%.

The invention according to the aforementioned Item 12 provides aluminum material for electrolytic capacitor electrodes with better performances by a method where degreasing is performed before heating in the oxidative atmosphere, or before washing the surface layer of aluminum material after heating in the oxidative atmosphere, which can remove oils adhered to the surface layer of aluminum material.

The invention according to the aforementioned Item 13 provides that degreasing can be performed reliably because the degreasing is performed with an organic solvent.

The invention according to the aforementioned Item 14 provides that degreasing can be performed reliably because the degreasing is performed with water containing a surfactant.

The invention according to the aforementioned Item 15 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics resulting in a large capacitance by a method wherein the intermediate annealing is preformed in the oxidative atmosphere, and the surface layer of aluminum material is removed by washing in a process after the intermediate annealing prior to final annealing, which can solve aluminum material uniformly upon washing; and final annealing is preformed.

The invention according to the aforementioned Item 16 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics resulting in a large

capacitance by a method wherein the surface layer removing of aluminum material by washing is performed after finish cold rolling before final annealing, which can solve aluminum material uniformly upon washing; and the final annealing is performed.

The invention according to the aforementioned Item 17 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics resulting in a large capacitance by a method wherein the surface layer removing of aluminum material by washing is performed after intermediate annealing before finish cold rolling, which can solve aluminum material uniformly upon washing; and final annealing is performed.

The invention according to the aforementioned Item 18 provides sufficient oxidization of aluminum material surface layer because the oxygen density of the oxidative atmosphere in intermediate annealing is not less than 0.1 volume%.

The invention according to the aforementioned Item 19 provides aluminum material for electrolytic capacitor electrodes with a stable excellent etching characteristics by a method where the intermediate annealing is performed in the oxidative atmosphere at a temperature of not lower than 200° C, and not higher than 320° C, which allows a sufficient texture to grow preferentially recrystallized grain with a cubic orientation in final annealing.

The invention according to the aforementioned Item 20 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is

an alkaline aqueous solution.

The invention according to the aforementioned Item 21 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an acid aqueous solution.

The invention according to the aforementioned Item 22 provides that the surface layer of aluminum material can be removed more reliably by washing because the washing is performed sequentially with an alkaline aqueous solution and an acid aqueous solution.

The invention according to the aforementioned Item 23 provides that the surface layer can be removed more effectively because an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate.

The invention according to the aforementioned Item 24 provides that the surface layer of aluminum can be removed more effectively because an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorous.

The invention according to the aforementioned Item 25 provides that the enhancement effect of capacitance can be surely obtained by uniform dissolution of aluminum material because the average removed amount of aluminum material surface layer by washing is not less than 1nm, and not more than 500 nm per one

side of aluminum material.

The invention according to the aforementioned Item 26 provides aluminum material for electrolytic capacitor electrodes with better performances by a method wherein the degreasing is performed, after cold rolling before intermediate annealing, in a process prior to final annealing, which can remove oil adhered to the surface layer of aluminum material.

The invention according to the aforementioned Item 27 provides that degreasing can be performed reliably because the degreasing is performed with an organic solvent.

The invention according to the aforementioned Item 28 provides that degreasing can be performed reliably because the degreasing is performed with water containing a surfactant.

The invention according to the aforementioned Item 29 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics resulting in a large capacitance by a method wherein intermediate annealing in the oxidative atmosphere, finish cold rolling are preformed and further heated in the oxidative atmosphere, thereafter the surface layer of aluminum material is removed by washing, which can solve aluminum material uniformly upon washing; and then the final annealing is preformed.

The invention according to the aforementioned Item 30 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics resulting in a large capacitance by a method wherein the intermediate annealing in the

oxidative atmosphere, surface layer removing of aluminum material by washing, finish cold rolling are performed, and further heated in oxidative atmosphere, thereafter the surface layer of aluminum material is removed by washing, which can solve aluminum material uniformly upon washing; and then final annealing is preformed.

The invention according to the aforementioned Item 31 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an alkaline aqueous solution.

The invention according to the aforementioned Item 32 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an acid aqueous solution.

The invention according to the aforementioned Item 33 provides that the surface layer of aluminum material can be removed more reliably because the washing is performed sequentially with an alkaline aqueous solution and an acid aqueous solution.

The invention according to the aforementioned Item 34 provides that the surface layer can be removed more effectively because an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate.

The invention according to the aforementioned Item 35 provides that the surface layer can be removed more effectively because an acid in the acid aqueous solution is one or more acid

selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorous.

The invention according to the aforementioned Item 36 provides that the enhancement effect of capacitance can be surely obtained by uniform dissolution of aluminum material because the average removed amount of aluminum material surface layer by washing, after heating in oxidative atmosphere, performing after a finish cold rolling, is not less than 1nm, and not more than 500 nm per one side of aluminum material.

The invention according to the aforementioned Item 37 provides that while an excess thickening of oxide layer on aluminum material surface layer is suppressed, sufficient oxidization can be performed, then the surface layer of aluminum material can dissolve uniformly upon surface layer removing by washing, because the heating temperature in the oxidative atmosphere after finish cold rolling is 50 to 400 °C.

The invention according to the aforementioned Item 38 provides that while useless energy consumption is suppressed, sufficient oxidization on aluminum material surface layer can be performed, then the surface layer of aluminum material can dissolve uniformly upon surface layer removing by washing, because the heating time in oxidative atmosphere after finish cold rolling is not less than 3 sec, and not more than 72 hr.

The invention according to the aforementioned Item 39 provides aluminum material for electrolytic capacitor electrodes with a stable excellent etching characteristics by a method where

the intermediate annealing is performed in the oxidative atmosphere at a temperature of higher than 200°C, and lower than 320°C, which allows a sufficient texture to grow preferentially recrystallized grain with a cubic orientation in final annealing.

The invention according to the aforementioned Item 40 provides sufficient oxidization on aluminum material surface layer because the oxygen density of heating atmosphere in the oxidative atmosphere, performing after finish cold rolling, is not less than 0.1 volume%.

The invention according to the aforementioned Item 41 provides sufficient oxidization on aluminum material surface layer because the oxygen density of heating atmosphere in oxidative atmosphere in intermediate annealing is not less than 0.1 volume%.

The invention according to the aforementioned Item 42 provides aluminum material for electrolytic capacitor electrodes with better performances by a method wherein the degreasing is performed, after cold rolling before intermediate annealing, in a process prior to surface layer removing of aluminum material by last washing, which can remove oils adhered to the surface layer of aluminum material.

The invention according to the aforementioned Item 43 provides that degreasing can be performed reliably because the degreasing is performed with an organic solvent.

The invention according to the aforementioned Item 44 provides that degreasing can be performed reliably because the degreasing is performed with water containing a surfactant.

The invention according to the aforementioned Item 45 provides aluminum material for electrolytic capacitor electrodes with an excellent characteristics resulting in a large capacitance by performing final annealing, after tensile strain application in a course of hot rolling and cold rolling, then intermediate annealing, thereafter before the start of final annealing, wherein after the tensile strain application, aluminum material is heated in oxidative atmosphere before final annealing, thereafter the surface layer of aluminum material is removed by washing, which can solve aluminum material uniformly upon washing; and then the final annealing is performed..

The invention according to the aforementioned Item 46 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an alkaline aqueous solution.

The invention according to the aforementioned Item 47 provides that the surface layer of aluminum material can be removed reliably because the cleaning liquid for washing is an acid aqueous solution.

The invention according to the aforementioned Item 48 provides that the surface layer can be removed more reliably because the washing is performed sequentially with an alkaline aqueous solution and an acid aqueous solution.

The invention according to the aforementioned Item 49 provides that the surface layer can be removed more effectively because an alkali in the alkaline aqueous solution is one or more

alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate.

The invention according to the aforementioned Item 50 provides that the surface layer can be removed more effectively because an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorous.

The invention according to the aforementioned Item 51 provides that the enhancement effect of capacitance can be surely obtained by uniform dissolution of aluminum material because the average removed amount of aluminum material surface layer by washing, after heating in oxidative atmosphere, is not less than 1nm, and not more than 500 nm per one side of aluminum material.

The invention according to the aforementioned Item 52 provides that while an excess thickening of oxide layer on aluminum material surface layer is suppressed, sufficient oxidization can be performed, then the surface layer can dissolve uniformly upon surface layer removing by washing, because the heating temperature in the oxidative atmosphere is 50 to 400 °C.

The invention according to the aforementioned Item 53 provides that while useless energy consumption is suppressed, sufficient oxidization on aluminum material surface layer can be performed, then the surface layer can dissolve uniformly upon surface layer removing by washing, because the heating time in the oxidative atmosphere is not less than 3 sec, and not more than

72 hr.

The invention according to the aforementioned Item 54 provides sufficient oxidization on aluminum material surface layer because the oxygen density of heating atmosphere in the oxidative atmosphere is not less than 0.1 volume%.

The invention according to the aforementioned Item 55 provides aluminum material for electrolytic capacitor electrodes with an excellent characteristics resulting in a large capacitance by performing tensile strain application and final annealing, in a course of hot rolling and cold rolling, then intermediate annealing, thereafter before the start of final annealing, wherein the intermediate annealing is performed in the oxidative atmosphere, thereafter at least one time of surface layer removing of aluminum material by washing is performed in a process prior to final annealing, which can solve aluminum material uniformly upon washing; and then the final annealing is performed.

The invention according to the aforementioned Item 56 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristics resulting in a large capacitance by a method wherein the surface layer removing of aluminum material by washing is performed after tensile stain application before final annealing, which can solve aluminum material uniformly upon washing; and then the final annealing is performed.

The invention according to the aforementioned Item 57 provides aluminum material for electrolytic capacitor electrodes

with an excellent etching characteristics resulting in a large capacitance by a method wherein the surface layer removing of aluminum material by washing is performed after intermediate annealing before tensile stain giving, which can solve aluminum material uniformly upon washing; and then the final annealing is performed.

The invention according to the aforementioned Item 58 provides aluminum material for electrolytic capacitor electrodes with an excellent characteristics by a method wherein after the tensile strain application prior to final annealing, the surface layer removing of aluminum material by washing is performed after heating aluminum material in oxidative atmosphere, which gives aluminum material the uniform solubility of surface layer upon washing, by intermediate annealing in the oxidative atmosphere and heating in the oxidative atmosphere.

The invention according to the aforementioned Item 59 provides that the surface layer of aluminum material can be removed reliably by washing because the cleaning liquid for washing is an alkaline aqueous solution.

The invention according to the aforementioned Item 60 provides that the surface layer of aluminum material can be removed reliably because the cleaning liquid for washing is an acid aqueous solution.

The invention according to the aforementioned Item 61 provides that the surface layer of aluminum material can be removed more reliably because the washing is performed sequentially with

an alkaline aqueous solution and an acid aqueous solution.

The invention according to the aforementioned Item 62 provides that the surface layer can be removed more effectively because an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate.

The invention according to the aforementioned Item 63 provides that the surface layer can be removed more effectively because an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorous.

The invention according to the aforementioned Item 64 provides that the enhancement effect of capacitance can be surely obtained by uniform dissolution of aluminum material because the average removed amount of aluminum material surface layer by washing, after heating in the oxidative atmosphere, is not less than 1nm, and not more than 500 nm per one side of aluminum material.

The invention according to the aforementioned Item 65 provides that while the excess thickening of oxide layer on aluminum material surface layer is suppressed, sufficient oxidization can be performed, which can solve the surface layer uniformly upon surface layer removing by washing afterwards, because the heating temperature in the oxidative atmosphere, performing after tensile strain application, is 50 to 400 °C.

The invention according to the aforementioned Item 66

provides that while useless energy consumption is suppressed, sufficient oxidization on aluminum material surface layer can be performed, which can solve the surface layer of aluminum material uniformly upon surface layer removing by washing afterward, because the heating time in the oxidative atmosphere, performing after tensile strain application, is not less than 3 sec, and not more than 72 hr.

The invention according to the aforementioned Item 67 provides that solubility of aluminum material surface layer becomes uniform because the intermediate annealing is performed in the oxidative atmosphere at a temperature of higher than 200° C, and lower than 300° C.

The invention according to the aforementioned Item 68 provides sufficient oxidization on aluminum material surface layer because the oxygen density of heating atmosphere in the oxidative atmosphere, performing after tensile strain application, is not less than 0.1 volume%.

The invention according to the aforementioned Item 69 provides sufficient oxidization on aluminum material surface layer because the oxygen density of heating atmosphere in the oxidative atmosphere, performing in intermediate annealing, is not less than 0.1 volume%.

The invention according to the aforementioned Item 70 provides that the thickening of oxide layer on aluminum material surface layer can be suppressed, and the effect of surface layer removing is exerted effectively by heating aluminum material in

the oxidative atmosphere and washing because the final annealing is performed in an inert gas atmosphere.

The invention according to the aforementioned Item 71 provides that aluminum material surface layer generating uniform etch-pits can be obtained because the final annealing is performed at a temperature of higher than 450°C, and lower than 600°C.

The invention according to the aforementioned Item 72 provides that the deterioration of etching characteristic resulting from too much impurity can be prevented because the aluminum purity of aluminum material is not less than 99.9 weight%.

The invention according to the aforementioned Item 73 provides aluminum material for electrolytic capacitor electrodes with an excellent etching characteristic.

The invention according to the aforementioned Item 74 provides anode material for a middle or high voltage with an excellent etching characteristic.

The invention according to the aforementioned Item 75 provides manufacturing of electrode material for electrolytic capacitors with a large capacitance by etching.

The invention according to the aforementioned Item 76 provides manufacturing of electrode material for suitable electrolytic capacitors as anode material because the formation of dielectric by anodizing is performed after etching.

The invention according to the aforementioned Item 77 provides that a large number of deep and thick tunnel structure pits can be generated by at least a part of the etching being

performed by a direct current electrolytic etching, and the effect is exerted efficiently by the heating in the oxidative atmosphere and surface layer removing by washing.

The invention according to the aforementioned Item 78 provides anode material for aluminum electrolytic capacitors with a large capacitance.

The invention according to the aforementioned Item 79 provides aluminum electrolytic capacitors with a large capacitance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventor of this application has found that heating of aluminum material in the oxidative atmosphere prior to removal of the surface layer of aluminum material by washing could uniformly dissolve the surface layer of aluminum material during washing, and generate uniform etch pits when electrolytic etching is provided to the aluminum material to be subsequently obtained after final annealing, thus significantly improving etching characteristic.

The inventor has also found that in a method of manufacturing aluminum material for electrolytic capacitors through sequential implementation of cold rolling, intermediate annealing, finish cold rolling, and final annealing on aluminum material, when intermediate annealing is carried out in the oxidative atmosphere and the surface layer of aluminum material is removed by washing in a process following the intermediate annealing and preceding

final annealing, solubility of the surface layer of aluminum material becomes uniform due to oxidation of the aluminum material by intermediate annealing in the oxidative atmosphere, and thus etching characteristic of the aluminum material after final annealing significantly improves.

The inventor of this application has also found that when a surface layer of aluminum material is dissolved by washing and subject to final annealing, after aluminum material is subject to intermediate annealing in oxidative atmosphere following cold rolling and is heated in oxidative atmosphere following finish cold rolling, because of oxidation of the aluminum material caused by intermediate annealing in the oxidative atmosphere and heating in oxidative atmosphere after finish cold rolling, solubility of the surface layer of aluminum material becomes uniform, and thus etching characteristic of the aluminum material after final annealing significantly improves.

The inventor has also found that when a surface layer of aluminum material is dissolved by washing and subjected to final annealing after it is given tensile strain following intermediate annealing and further heated in oxidative atmosphere, because of oxidation of the aluminum material by heating in the oxidative atmosphere after provision of tensile strain completes, solubility of the surface layer of aluminum material becomes uniform and thus etching characteristic of the aluminum material after final annealing significantly improves.

In addition, the inventor has found that in manufacture of

aluminum material for electrolytic capacitors wherein hot and cold rolling are conducted followed by intermediate annealing, tensile strain is given in the period after intermediate annealing and before start of final annealing, and then final annealing is conducted, wherein if said intermediate annealing is conducted in the oxidative atmosphere and a surface layer of aluminum material is removed by washing in a process following intermediate annealing and preceding final annealing, because of oxidation of the aluminum material by intermediate annealing in the oxidative atmosphere, solubility of the surface layer of aluminum material in washing to be subsequently done becomes uniform, and thus etching characteristic of the aluminum material after final annealing significantly improves. In addition, sequential implementation of heating in the oxidative atmosphere, removal of a surface layer of aluminum material by washing, and final annealing after intermediate annealing in the oxidative atmosphere and addition of tensile strain can effect better etching characteristic because of heating in the oxidative atmosphere following addition of tensile strain, in addition to intermediate annealing in the oxidative atmosphere.

As described above, addition of tensile strain is the process to be conducted in place of finish cold rolling so that cubic texture of aluminum can be developed in final annealing. However, as appropriate tensile strain has a lower processing rate than that of finish cold rolling (refer to Patent Document 1 and Patent Document 2), it can provide more uniform solubility of a surface

layer of aluminum material and better improvement of etching characteristic, compared with the case in which the surface layer of aluminum material is removed by washing after finish cold rolling.

In the following, we describe a method of manufacturing aluminum material for electrolytic capacitors in detail.

[Purity of Aluminum Material]

Purity of aluminum material is not specifically limited if it falls within the grade for electrolytic capacitors. However, preferably, the purity would be not less than 99.9 mass %, and specifically, not less than 99.95 mass % more preferably. In this invention, purity of aluminum material shall be a value of 100 mass % minus total concentration of Fe, Si and Cu (mass %).

Pb segregates on a surface layer of aluminum material during final annealing and has a considerable effect on generation of etch pits. When a tunnel-like etch pit is generated by direct current (DC) etching method, in some etching method, etch pit dispersibility is poor if there is too little Pb, while large amount of surface dissolution of aluminum material is caused by etching if there is too much Pb. Thus, the aluminum material may contain moderate amounts of Pb, as necessary. We can recommend that adjustment be made, for instance, so that aluminum material contains Pb of 0.00002 to 0.0002 mass %.

[Manufacturing process according on a First Embodiment (Till end

of final annealing)]

In this embodiment, manufacture of aluminum material, although it is not defined, takes place in the order of adjustment of soluble components/slab casting, hot rolling, cold rolling, intermediate annealing, cold rolling including finish cold rolling (rolling of low rolling reduction), and final annealing. Prior to final annealing, after being heated in oxidative atmosphere, the surface layer of aluminum material is removed by washing. It would be preferable to conduct heating in the oxidative atmosphere following cold rolling and to remove a surface layer of aluminum material by washing. In addition, in order to increase fraction of cube orientation after final annealing, intermediate annealing should be conducted, as necessary.

The heating in the oxidative atmosphere and removal of surface layer of aluminum material by washing may be carried out once, respectively, or heating and removal by washing may be alternately carried out several times.

The heating in the oxidative atmosphere is conducted by atmosphere heating rather than contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark. Hence, this invention has adopted atmosphere heating.

As a method of heating in the oxidative atmosphere, ventilation heating, radiation heating, etc. can be exemplified. In addition, shape of aluminum material to be heated is not

specifically defined. The aluminum material wound around the coil may be batch heated or it may be wound around the coil, after the coil is rewound and it is continuously heated.

Preferably, heating temperature of the aluminum material in the oxidative atmosphere would be 50 to 400° C. When the heating temperature is less than 50° C, oxidation of the surface layer of aluminum material may not be adequate and the aluminum material may not dissolve uniformly when the surface layer thereof is removed. When the heating temperature exceeds 400° C, oxide film of the surface layer of aluminum material will be thick, which deteriorates solubility of the aluminum material and makes it difficult to dissolve the aluminum material in uniform manner. Particularly preferable heating temperature would be 70 to 350° C, and 70 to 240° C, in particular.

Preferably, the heating time would be not less than 3 seconds and not more than 72 hr. If heating time is less than 3 seconds, the surface layer of aluminum material may not be oxidized adequately and the aluminum material may not dissolve uniformly when the surface layer thereof is removed. When the heating time exceeds 72 hr, dissolving uniformity during removal of the surface layer of aluminum material becomes almost flat, and thus cost will be higher due to energy consumption during heating. Preferable heating time, in particular, would be not less than 10 seconds and not more than 48 hr, and particularly, not less than 70 seconds and not more than 48 hr.

For the heating temperature and time in the oxidative

atmosphere, appropriate conditions should be selected, depending on a heating method. For example, when aluminum material is heated in the condition being wound up as a coil, it would be preferably heated at 50 to 240°C for 30 min to 72 hr, and more preferably at 70 to 240°C for 1 to 48 hr. In addition, when aluminum material unwound from a coil or sheet-cut aluminum material is heated, the heating time t (hour) would be preferably $10/(1.44 \times x^{1.5}) \leq t \leq 72$, where x is the heating temperature (°C). It would be more preferably $10/(1.44 \times x^{1.5}) \leq t \leq 48$.

Preferably, oxygen concentration in the oxidative atmosphere during heating of aluminum material in the oxidative atmosphere would be not less than 0.1 volume %. If the oxygen concentration is less than 0.1 volume %, the surface of aluminum material may not be adequately oxidized when it is heated. Preferably, the oxygen concentration would be not less than 1 volume %, in particular. More preferably, it would be not less than 5 volume %, in particular, and air can be preferably used as the oxidative atmosphere.

Although cleaning liquid to be used in removing a surface layer of aluminum material by washing is not specifically defined, alkaline solution or acid solution may be used. The surface layer may be removed by using either alkaline solution or acid solution, or it may be washed with acid solution after being removed with alkaline solution.

As alkali, sodium hydroxide, calcium hydroxide, potassium

hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate may be exemplified, and one or more alkali selected from the above alkalis may be used as cleaning liquid by being dissolved in water.

As acid, one or more acid selected from those including hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorus element shall be used. As acids including phosphorus element, orthophosphoric acid (hereafter referred to as phosphoric acid), pyrophosphoric acid, metaphosphoric acid, and polyphosphoric acid may be exemplified. In addition, as acid to be used in removing the surface layer of aluminum material, perchloric acid and hypochlorous acid may be used.

The removal amount of the surface layer of aluminum material may be adjusted by keeping at an appropriate level concentration of alkalis or acids, temperature of alkaline or acid aqueous solution, and contact time of the aluminum material with alkaline or acid aqueous solution. In addition, in order to enhance cleaning effect of the surface layer of aluminum material, a surfactant or a chelating agent may be added to the cleaning liquid.

The removal amount of the surface layer of aluminum material by washing is a mean value, and would be preferably not less than 1 mm and not more than 500nm per side of the aluminum material. If the removal amount of the surface layer is less than 1 mm, removal of the oxide film on the surface layer of aluminum material may be inadequate. If the surface layer is removed by 500 nm or more, etch pit nucleation on the surface layer of aluminum material will

be suppressed, thus even degrading etching characteristic and reducing capacitance. Preferably, the removal amount of the surface layer by washing would be not less than 1.5 nm and not more than 200 nm, more preferably, not less than 5 nm and not more than 200 nm, and most preferably, not less than 10 nm and not more than 150 nm.

Although density of the oxide film on the surface layer of aluminum material differs from that of aluminum, which is metal, the removal amount of surface layer of aluminum material, D (nm), in this application shall be defined as $D(\text{nm}) = E \times 10^7 / 2.7$, using E (g/cm^2), decrease in mass per unit surface area by washing and density of aluminum, $2.7\text{g}/\text{cm}^3$. Although a method of bringing cleaning liquid with aluminum material is not specifically defined, immersion, contact of aluminum material with surface of cleaning liquid, spraying, etc, may be possible.

Any process or process condition other than those defined in this invention shall not be specifically defined, and common procedure may be just followed. In addition, a method of manufacturing aluminum material may be changed, as appropriate, depending on a relationship with etching conditions of the aluminum material.

Further, degreasing may also be carried out after cold rolling and before removal of a surface layer of aluminum material by washing. Although a method of degreasing is not specifically defined, degreasing may be possible by bringing the aluminum material into contact with a solution prepared by adding a

surfactant to water, or organic solvent. Although a method of bringing aluminum material into contact with a solution prepared by adding a surfactant to water, or organic solvent is not specifically defined, immersion, contact of aluminum material onto surface of cleaning liquid, spraying, etc. may be possible.

Unless otherwise defined, the organic solvent may be, for instance, alcohol, diol, aromatic hydrocarbons such as toluene and xylene, etc., alkane series of hydrocarbons, cyclohexane, ketone, ether, ester, petrochemical products, etc.

Examples of alcohol mentioned above include methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$), 2-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2(\text{OH})\text{CH}_3$), 1-butanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2-butanol ($\text{CH}_3\text{CH}_2\text{CH}_2(\text{OH})\text{CH}_3$), 1-pentanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2-pentanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2(\text{OH})\text{CH}_3$), etc., and those that can be expressed by $\text{C}_n\text{H}_{2n+1}$ (n =a natural number of 1 to 10) are preferable. In addition, alicyclic hydrocarbons such as cyclohexanol, etc. can also be used.

As examples of diol mentioned above, 1,2-ethanediol ($\text{HOCH}_2\text{CH}_2\text{OH}$), 1,2-propanediol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$), 1,3-propanediol ($\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$), etc., may be exemplified.

Examples of alkane series of hydrocarbons mentioned above include pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}), decane ($\text{C}_{10}\text{H}_{22}$), etc., and what is expressed by $\text{C}_n\text{H}_{2n+2}$ (n =a natural number of 5 to 15) is preferable. In addition, any alicyclic hydrocarbon such as cyclohexane, etc. may be applicable.

As examples of ketone mentioned above, acetone (CH_3COCH_3),

2-butanone ($\text{CH}_3\text{COC}_2\text{H}_5$), 3-pentanone ($\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$), 3-methyl-2-butanone ($\text{CH}_3\text{COCH}(\text{CH}_3)_2$), etc. may be exemplified, and those that can be expressed by R_1COR_2 (R_1 and R_2 : being an aliphatic hydrocarbon group, and a total carbon number of R_1 and R_2 is not more than 8) are preferable. In addition, any cyclic ketone such as cyclohexanone ($\text{C}_6\text{H}_{10}\text{O}$), etc., may be used.

Examples of ether mentioned above include any substance expressed by $\text{R}_1\text{-O-R}_2$ (R_1 and R_2 : being an aliphatic hydrocarbon group, and a total carbon number of R_1 and R_2 is not more than 8), and glycolether such as 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$), 2-ethoxyethanol ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$), 2-butoxyethanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$), 2-(2-ethoxy)-ethoxyethanol ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$), etc.

As examples of ester mentioned above, acetic ester expressed by CH_3COOR (R : an aliphatic hydrocarbon group with a carbon number being 1 to 5) may be exemplified.

Examples of petrochemical products mentioned above include industrial-gasoline (JIS K 2201), motor gasoline (JIS K 2202), aviation gasoline (JIS K 2206), lamp oil (JIS K 2203), light oil (JIS K 2204), petroleum ether (JIS K 8593), petroleum benzine (JIS K 8594), ligroin (JIS K 8937), kerosene, etc.

Unless otherwise defined, as a surfactant contained in a solution to be used for degreasing that is prepared by adding the surfactant to water, anionic surfactant, cationic surfactant, and nonionic surfactant may be used.

As anionic surfactant, sulfate ester salt and sulfonate may

be used.

As sulfate ester salt mentioned above, R-OSO₃Na (R=a saturated hydrocarbon group having carbon number of 8 to 18 or unsaturated hydrocarbon group having one double bond) may be used, and specifically, sodium dodecyl sulfate (C₁₂H₂₅OSO₃Na), sodium hexadecyl sulfate (C₁₆H₃₃OSO₃Na), sodium stearyl sulfate (C₁₈H₃₇OSO₃Na), sodium oleyl sulfate (C₁₈H₃₅OSO₃Na), etc. may be exemplified.

As sulfonate mentioned above, those expressed by R-SO₃Na (R= a saturated hydrocarbon group having carbon number of 8 to 18 or unsaturated hydrocarbon group having one double bond) or R-SO₃Na (R: a saturated hydrocarbon group with alkyl group having carbon number 8 to 14, or unsaturated hydrocarbon group having one double bond) such as sodium dodecylbenzene sulfonate (C₁₂H₂₅-C₆H₄-SO₃Na), etc. may be used.

As cationic surfactant, quaternary ammonium salt expressed by R-N(CH₃)₃ · Cl (R= an unsaturated hydrocarbon group with a carbon number of 8 to 16) may be used.

As nonionic surfactant, nonionic surfactant of polyethyleneglycol type expressed by R-O-(-CH₂CH₂O)_nH (R= a saturated hydrocarbon group with a carbon number of 8 to 16 or unsaturated hydrocarbon group having one double bond, n=6 to 14) or R-O-(-CH₂CH₂O)_nH (R=a saturated hydrocarbon group with alkyl group having a carbon number of 8 to 12, or alkyl phenyl radical that is an unsaturated hydrocarbon group having one double bond, n=6 to 14) may be exemplified. In addition, any surfactant with

n exceeding the above limits may be contained in nonionic surfactant, with molar ratio of 50% or less.

At least one kind of the above surfactants may be added to water and used as a cleaning liquid. Any surfactant with a carbon number of the surfactant below the above range may be used with the molar ratio of 50% or less. Since mixing of anion surfactant and cationic surfactant in water generates precipitates, it would be preferable to avoid the mixing.

Unless otherwise defined, preferably, adding concentration of the surfactants would be above critical micelle concentration so as to fulfill the degreasing effect.

Unless otherwise defined, for processing atmosphere in final annealing of aluminum material, in order to avoid increasing thickness of oxide coating, heating in an atmosphere with less water and oxygen is preferable. To be specific, heating in inert gases such as argon, nitrogen, etc. or in vacuum of 0.1Pa or less is preferable. In addition, hydrogen gas could be preferably used as an atmosphere for final annealing.

Preferably, area fraction of cube orientation of aluminum material after final annealing is not less than 90%.

Although a final annealing method is not specifically defined, it may be batch annealing with aluminum material wound around a coil or the material may be wound around the coil, after the coil is rewound and it is continuously annealed. At least either of batch annealing or continuous annealing may be carried out once or more.

Although the annealing temperature and annealing time are not specifically defined, if batch annealing is to be done on coiled material, it would be preferably annealed at 450 to 600°C for a time of 10 min to 50 hr. This is because it might not be possible to obtain a surface on which etch pit could be generated uniformly, if the temperature is less than 450°C and the time is less than 10 min. On the contrary, if annealing takes place above 600°C, aluminum material tends to stick together in the case of batch annealing on coiled material. In addition, even though it is annealed more than 50 hr, the surface expansion effect by etching becomes saturated, even leading to increased thermal energy cost. Preferably, the annealing temperature is 450 to 590°C, in particular, and more preferably 460 to 580°C. Preferably, the annealing time is 20 min to 40 hr.

In addition, temperature rising rate/pattern is not specifically defined. Temperature rising at a certain rate is also applicable, or step-by-step temperature rising/cooling is applicable by repeating cycles of temperature rising and temperature maintenance. In the annealing process, annealing in the temperature zone from 450 to 600°C for a total of 10 min to 50 hr will be applicable.

[Manufacturing process according on a Second Embodiment (till end of final annealing)]

In this embodiment, manufacture of aluminum material, although it is not defined, takes place in the order of adjustment of soluble

components/slab casting, hot rolling, cold rolling, intermediate annealing in the oxidative atmosphere, finish cold rolling (rolling with low reduction in thickness), and final annealing, and removal of a surface layer of aluminum material by washing takes place in a process after intermediate annealing in the oxidative atmosphere and before final annealing.

The intermediate annealing in the oxidative atmosphere is conducted by atmosphere heating, rather than by contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark. Hence, this invention has adopted intermediate annealing by atmosphere heating.

As a method of heating during intermediate annealing in the oxidative atmosphere, ventilation heating, radiation heating, etc. can be exemplified. In addition, although temperature rising speed/pattern is not specifically defined, it should be conducted under the conditions that increase area fraction of cube orientation after final annealing. In addition, the form of aluminum material to be heated is not specifically defined. The aluminum material may be batch annealed with it wound around a coil or the material may be wound around the coil, after the coil is rewound and it is continuously annealed.

Preferably, the oxygen concentration in the oxidative atmosphere during intermediate annealing would be not less than 0.1 volume %. If the oxygen concentration is less than 0.1 volume %,

the aluminum material surface may not be oxidized adequately when it is heated. Preferably, the oxygen concentration would be not less than 1 volume %, more preferably not less than 5 volume %, in particular, and air could be preferably utilized as the oxidative atmosphere. If air is used as oxidative atmosphere, there is no need to control the oxygen concentration, thereby being able to plan cost reduction of the intermediate annealing process.

Preferably, the intermediate annealing temperature in the oxidative atmosphere would be not less than 200°C and not more than 320°C. Intermediate annealing falling within the temperature range could oxidize the aluminum material and achieve uniform solubility of the surface layer thereof. If the intermediate annealing temperature is less than 200°C, a sufficient texture that allows recrystallized grain with the cube orientation during final annealing to grow preferentially cannot be obtained. If it exceeds 320°C, recrystallized grains that will block preferential growth of the cube orientation grain during final annealing will grow. The intermediate annealing temperature and duration that allow acquisition of the favorable area fraction of cube orientation depend on composition of the aluminum material, and the condition that allows acquisition of a high area fraction of cube orientation after final annealing should be selected.

Finish cold rolling is a process that is conducted to control cube orientation in combination with intermediate annealing, for which a publicly known method may be used.

Preferably, the rolling reduction in finish cold rolling would be not less than 10% and not more than 25%. If the rolling reduction is less than 10%, strain by working for preferentially growing crystal grains with cube orientation is not adequate. If the rolling reduction exceeds 25%, in final annealing non-cube orientation grains grow due to introduced strain by working, which will inhibit preferential growth of crystal grains with cube orientation.

In a process following intermediate annealing and preceding final annealing, removal of the surface layer of aluminum material is carried out.

Although the cleaning liquid is not specifically defined, alkaline aqueous solution or acid aqueous solution may be used. Removal of the surface layer may be done with either alkaline aqueous solution or acid aqueous solution, or the surface layer may be removed with alkaline solution and then washed with acid aqueous solution.

As alkali, sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate may be exemplified, and one or more alkali selected from the above alkalis may be used as cleaning liquid by being dissolved in water.

As acid, one or more acid selected from hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorus element shall be used. As acids including phosphorus element, orthophosphoric acid (hereafter referred to as phosphoric acid),

pyrophoric acid, metaphosphoric acid, and polyphosphoric acid may be exemplified. In addition, as acid to be used in removing the surface layer of aluminum material, perchloric acid and hypochlorous acid may be used.

The removal amount of the surface layer of aluminum material may be adjusted by keeping at an appropriate level concentration of alkalis or acids, temperature of alkaline or acid aqueous solution, and contact time of the aluminum material with alkaline or acid aqueous solution.

In addition, in order to enhance cleaning effect of the surface layer of aluminum material, a surfactant or chelating agent may be added to the cleaning liquid.

The removal amount of the surface layer of aluminum material by washing is a mean value, and shall be preferably not less than 1 mm and not more than 500nm per side of the aluminum material. If the removal amount of the surface layer is less than 1 mm, removal of the oxide film on the surface layer of aluminum material may not be adequate. If the surface layer is removed by 500 nm or more, etch pit nucleation on the surface layer of aluminum material will be suppressed, thus even degrading etching characteristic and reducing capacitance. When washing is done after cold rolling ends, preferably, the removal amount of the surface layer by washing would be not less than 1.5 nm and not more than 200 nm.

Although density of the oxide film on the surface layer of aluminum material differs from that of aluminum, which is metal, the removal amount of surface layer of aluminum material, D (nm),

in this application, it shall be defined as $D(\text{nm}) = E \times 10^7 / 2.7$, using $E (\text{g/cm}^2)$, decrease in mass per unit surface area by washing and density of aluminum, 2.7g/cm^3 .

Washing should be carried out by bringing the aluminum material into contact with the cleaning liquid. Although a method of contact is not specifically defined, immersion, contact of the aluminum material with surface of the cleaning liquid, spraying, etc, may be possible.

The removal of the surface layer of aluminum material by washing may take place following finish cold rolling and preceding final annealing, or following intermediate annealing and preceding finish cold rolling.

In addition, in a process after hot rolling and before intermediate annealing, the surface layer of aluminum material may be removed by washing with said cleaning liquid. Although the cleaning liquid to be used in cleaning in a process after hot rolling and before intermediate annealing may be selected in accordance with the intended use, and shall not be specifically defined, the same cleaning liquid as that to be used in washing after the intermediate annealing may be used.

Degreasing may take place in a process after cold rolling prior to intermediate annealing and before final annealing. The same method of degreasing as that described in the manufacturing process on the first embodiment may be used, description of which is thus omitted here.

The process atmosphere during final annealing of aluminum

material, area fraction of cube orientation of the aluminum material after final annealing, a method of final annealing, and temperature, time, temperature rising rate/pattern during annealing are same as those described in the manufacturing process on the first embodiment.

[Manufacturing process according on a Third Embodiment (till end of final annealing)]

In this embodiment, manufacture of aluminum material, although it is not defined, takes place in the order of adjustment of soluble components/slab casting, hot rolling, cold rolling, intermediate annealing in the oxidative atmosphere, finish cold rolling (rolling with reduction in thickness), heating in the oxidative atmosphere, removal of a surface layer of aluminum material by washing, and final annealing.

Heating in the oxidative atmosphere to be conducted after finish cold rolling and before final annealing, and subsequent removal of the surface layer of aluminum material by washing may be carried out once, respectively, or heating in the oxidative atmosphere and subsequent removal of the surface layer of aluminum material by washing may be alternately carried out several times.

The intermediate annealing in the oxidative atmosphere is conducted by atmosphere heating rather than contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark.

Hence, this invention implements intermediate annealing with atmosphere heating.

As a method of heating during intermediate annealing in oxidative atmosphere, ventilation heating, radiation heating, etc. can be exemplified. In addition, although temperature rising speed/pattern in heating the aluminum material in the oxidative atmosphere is not specifically defined, heating should be conducted under the conditions that increase area fraction of cube orientation after final annealing. In addition, the form of aluminum material to be heated is not specifically defined. The aluminum material may be batch annealed with it wound around a coil, or the material may be wound around the coil, after the coil is rewound and it is continuously annealed.

Preferably, the intermediate annealing temperature in the oxidative atmosphere would be not less than 200°C and not more than 320°C. If the intermediate annealing temperature is less than 200°C, sufficient texture that allows recrystallized grain having the cube orientation during final annealing to grow preferentially cannot be obtained. If it exceeds 320°C, recrystallized grains that will block preferential growth of the cube orientation grain during final annealing will grow. The intermediate annealing temperature and duration that allow acquisition of the favorable area fraction of cube orientation depend on composition of the aluminum material, and the condition that allows acquisition of a high area fraction of cube orientation after final annealing should be selected.

Intermediate annealing falling within the said temperature range could oxidize the aluminum material and achieve uniform solubility of the surface layer thereof.

Finish cold rolling is a process that is conducted to control a cube orientation in combination with intermediate annealing, for which a publicly known method may be used.

Preferably, the rolling reduction in finish cold rolling would be not less than 10% and not more than 25%. If the rolling reduction is less than 10%, strain by working for preferentially growing crystal grains having cube orientation is not adequate. If the rolling reduction exceeds 25%, in final annealing non-cube orientation grains grow due to introduced strain by working, which will inhibit preferential growth of crystal grains with cube orientation.

Heating in oxidative atmosphere in a process following finish cold rolling is conducted by atmosphere heating rather than contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark. Hence, this invention has adopted atmosphere heating.

As a method of heating in the oxidative atmosphere to be conducted in a process following finish cold rolling, ventilation heating, radiation heating, etc. can be exemplified. Heat of the aluminum material following cold rolling may be used for heating in the oxidative atmosphere. Temperature rising rate/pattern in

heating the aluminum material in the oxidative atmosphere is not specifically defined, and temperature rising at a certain temperature is also applicable, or step-by-step temperature rising/cooling is applicable by repeating cycles of temperature rising and temperature maintenance.

In addition, the form of aluminum material to be heated is not specifically defined. The aluminum material may be batch annealed with it wound around a coil or the material may be wound around the coil, after the coil is rewound and it is continuously annealed.

Preferably, the heating temperature of the aluminum material in the oxidative atmosphere to be conducted in a process following finish cold rolling would be 50 to 400° C.

If the heating temperature is less than 50° C, the surface layer of aluminum material may not be oxidized adequately and the aluminum material may not dissolve uniformly when the surface layer thereof is removed. When the heating temperature exceeds 400° C, the oxide film on the surface layer of aluminum material thickens, thereby deteriorating solubility of the aluminum material and making it difficult to dissolve the aluminum material uniformly. Preferably, the heating temperature of the aluminum material would be 70 to 350° C, and 70 to 240° C, in particular.

Preferably, the heating time in the oxidative atmosphere to be conducted in a process after finish cold rolling would be not less than 3 seconds and not more than 72 hr.

If heating time is less than 3 seconds, the surface layer

of aluminum material may not be oxidized adequately and the aluminum material may not melt uniformly when the surface layer thereof is removed. When the heating time exceeds 72 hr, dissolving uniformity during removal of the surface layer of aluminum material becomes almost flat, and thus cost will be higher due to energy consumption during heating. Preferable heating time, in particular, is not less than 10 seconds and not more than 48 hr, and particularly, not less than 70 seconds and not more than 48 hr.

Preferably, the oxygen concentration in the oxidative atmosphere during intermediate annealing in the oxidative atmosphere and during heating of the aluminum material in the oxidative atmosphere to be conducted in a process following finish cold rolling would be not less than 0.1 volume %. If the oxygen concentration is less than 0.1 volume %, the surface of aluminum material may not be adequately oxidized when it is heated. Preferably, the oxygen concentration would be not less than 1 volume %, in particular. More preferably, it would be not less than 5 volume %, in particular, and air can be preferably used as the oxidative atmosphere.

Although a cleaning liquid to be used for removal of the surface layer of aluminum material by washing is not specifically defined, alkaline solution or acid aqueous solution may be used. Removal of the surface layer may be done with either alkaline solution or acid aqueous solution, or the surface layer may be removed with alkaline solution and then washed with acid aqueous

solution.

As alkali, sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate may be exemplified, and one or more alkali selected from the above alkalis may be used as cleaning liquid by being dissolved in water.

As acid, one or more acid selected from those including hydrochloric acid, sulfuric acid, nitric acid, and acids including phosphorus element shall be used. As acids including phosphorus element, orthophosphoric acid (hereafter referred to as phosphoric acid), pyrophoric acid, metaphosphoric acid, and polyphosphoric acid may be exemplified. In addition, as acid to be used in removing the surface layer of aluminum material, perchloric acid and hypochlorous acid may be used.

The removal amount of the surface layer of aluminum material may be adjusted by keeping at an appropriate level concentration of alkalis or acids, temperature of alkaline or acid aqueous solution, and contact time of the aluminum material with alkaline or acid aqueous solution. In addition, in order to enhance cleaning effect of the surface layer of aluminum material, a surfactant or chelating agent may be added to the cleaning liquid.

Preferably, the amount of aluminum surface to be removed by washing after heating in the oxidative atmosphere to be conducted in a process following finish cold rolling is a mean value, and would be preferably not less than 1 mm and not more than 500nm per side of the aluminum material. If the removal

amount of the surface layer is less than 1 mm, removal of the oxide film on the surface layer of aluminum material may be inadequate. If the surface layer is removed by 500 nm or more, etch pit nucleation on the surface layer of aluminum material will be suppressed, thus even degrading etching characteristic and reducing capacitance. Preferably, the removal amount of the surface layer would be not less than 1.5 nm and not more than 200 nm.

Although density of the oxide film on the surface layer of aluminum material differs from that of aluminum, which is metal, the removal amount of surface layer of aluminum material, D (nm), in this application shall be defined as $D(\text{nm}) = E \times 10^7 / 2.7$, using E (g/cm^2), decrease in mass per unit surface area by washing and density of aluminum, $2.7\text{g}/\text{cm}^3$.

Although a method of bringing cleaning liquid with aluminum material is not specifically defined, immersion, contact of aluminum material with surface of cleaning liquid, spraying, etc, may be possible.

In addition to washing after heating in the oxidative atmosphere to be conducted in a process following finish cold rolling, removal of the surface layer of aluminum material by washing may be done in a process after intermediate annealing and before finish cold rolling. The conditions of washing may be implemented to the extent of the conditions of washing after said heating in the oxidative atmosphere.

In addition, in a process following hot rolling and preceding

intermediate annealing, the surface layer of aluminum material may be removed by washing with the said cleaning liquid. Although the cleaning liquid to be used in a process after hot rolling and before intermediate annealing may be selected in accordance with the intended use, and shall not be specifically defined, it may be same as the cleaning liquid to be used in washing after said heating in the oxidative atmosphere.

Degreasing may take place in a process after last cold rolling prior to intermediate annealing and before removal of the surface layer of aluminum material by washing to be carried out at last. The same method of degreasing as that described in the manufacturing process on the said first embodiment may be used, description of which is thus omitted here.

The process atmosphere during final annealing of aluminum material, area fraction of cube orientation of the aluminum material after final annealing, a method of final annealing, and temperature, time, temperature rising rate/pattern during annealing are same as those described in the manufacturing process on the first embodiment.

[Manufacturing process according on a Fourth Embodiment (till end of final annealing)]

In this embodiment, manufacture of aluminum material, although it is not defined, takes place in the order of adjustment of soluble components/slab casting, hot rolling, cold rolling, intermediate annealing, addition of tensile strain, heating in

the oxidative atmosphere, removal of a surface layer of aluminum material by washing, and final annealing.

Heating in the oxidative atmosphere to be conducted after application of tensile strain and before final annealing, and subsequent removal of the surface layer of aluminum material by washing may be implemented once, respectively, or heating in the oxidative atmosphere and subsequent removal of the surface layer of aluminum material by washing may be alternately carried out several times.

Application of tensile strain is the process that is conducted to control a cube orientation in combination with intermediate annealing. Unlike finish cold rolling, since application of tensile strain is free from the problem that much lubricant attaches to the surface of aluminum material, the surface of aluminum material is easy to oxidize by subsequent heating in the oxidative atmosphere. Addition of tensile strain also has the feature that during final annealing, coarsening of aluminum crystal grains is less likely to occur even though it has thicker foil than that of finish cold rolling, thus making it easier to manufacture thick aluminum material. Although a method of tensile strain application is not specifically defined, a method described in WO 2004/003248 A1 may be applied.

Preferably, tensile strain to be applied after intermediate annealing would be not less than 1% and not more than 15%. When the tensile strain is less than 1%, strain by working for preferentially growing crystal grains with a cube orientation is

inadequate. When it exceeds 15%, the aluminum material may break while being drawn. To apply tensile strain, one-axis tension wherein tension strain is given to only one direction relative to the aluminum material, namely, longitudinally, or two-axis tension wherein tensile strain is given to 2 directions, namely, in lengthwise direction and width direction may be applied.

Heating in the oxidative atmosphere in a process following addition of tensile strain is conducted by atmosphere heating rather than contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark. Hence, this invention has adopted atmosphere heating.

As a method of heating in the oxidative atmosphere, ventilation heating, radiation heating, etc. can be exemplified. In addition, shape of aluminum material to be heated is not specifically defined. The aluminum material wound around the coil may be batch heated or it may be wound around the coil, after the coil is rewound and it is continuously heated.

Preferably, heating temperature of the aluminum material in the oxidative atmosphere to be conducted in a process following addition of tensile strain would be 50 to 400°C.

When the heating temperature is less than 50°C, oxidation of the surface layer of aluminum material may not be adequate and the aluminum material may not melt uniformly when the surface layer thereof is removed. When the heating temperature exceeds 400°C,

oxide film of the surface layer of aluminum material will be thick, which deteriorates solubility of the aluminum material and makes it difficult to melt the aluminum material in uniform manner. Particularly preferable heating temperature would be 70 to 350° C, and 70 to 240° C, in particular.

Preferably, the duration of heating in the oxidative atmosphere to be conducted in a process following addition of tensile strain would be not less than 3 seconds and not more than 72 hr. If the heating time is less than 3 seconds, the surface layer of aluminum material may not be oxidized adequately and the aluminum material may not dissolve uniformly when the surface layer is removed. When the heating time exceeds 72 hr, melting uniformity during removal of the surface layer of aluminum material becomes almost flat, and thus cost will be higher due to energy consumption during heating. Preferable heating time, in particular, would be not less than 10 seconds and not more than 48 hr, and particularly, not less than 70 seconds and not more than 48 hr.

Preferably, oxygen concentration in the oxidative atmosphere during heating of aluminum material in the oxidative atmosphere to be conducted in a process following addition of tensile strain would be not less than 0.1 volume %. If the oxygen concentration is less than 0.1 volume %, the surface of aluminum material may not be adequately oxidized when it is heated. Preferably, the oxygen concentration would be not less than 1 volume %, in particular. More preferably, it would be not less

than 5 volume %, in particular, and air can be preferably used as the oxidative atmosphere.

Although a cleaning liquid to be used in removing the surface layer of aluminum material by washing is not specifically defined, alkaline solution or acid aqueous solution may be used. Removal of the surface layer may be done with either alkaline solution or acid aqueous solution, or the surface layer may be removed with alkaline solution and then washed with acid aqueous solution.

As alkali, sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate may be exemplified, and one or more alkali selected from the above alkalis may be used as cleaning liquid by being dissolved in water.

As acid, one or more acid selected from hydrochloric acid, sulfuric acid, nitric acid, and acids containing elemental phosphorus shall be used. As acids including phosphorus element, orthophosphoric acid (hereafter referred to as phosphoric acid), pyrophoric acid, metaphosphoric acid, and polyphosphoric acid may be exemplified. In addition, as acid to be used in removing the surface layer of aluminum material, perchloric acid and hypochlorous acid may be used.

The removal amount of the surface layer of aluminum material may be adjusted by keeping at an appropriate level concentration of alkalis or acids, temperature of alkaline or acid aqueous solution, and contact time of the aluminum material with alkaline or acid aqueous solution.

In addition, in order to enhance cleaning effect of the surface layer of aluminum material, a surfactant or chelating agent may be added to the cleaning liquid.

The removal amount of the surface layer of aluminum material by washing after heating in the oxidative atmosphere is a mean value, and would be preferably not less than 1 nm and not more than 500nm per side of the aluminum material. If the removal amount of the surface layer is less than 1 nm, removal of the oxide film on the surface layer of aluminum material may be inadequate. If the surface layer is removed by 500 nm or more, etch pit nucleation on the surface layer of aluminum material will be suppressed, thus even degrading etching characteristic and reducing capacitance. Preferably, the removal amount of the surface layer would be not less than 1.5 nm and not more than 200 nm.

Although density of the oxide film on the surface layer of aluminum material differs from that of aluminum, which is metal, the removal amount of surface layer of aluminum material, D (nm), in this application shall be defined as $D(\text{nm}) = E \times 10^7 / 2.7$, by E (g/cm^2), decrease in mass per unit surface area by washing and density of aluminum, $2.7\text{g}/\text{cm}^3$.

Although a method of bringing cleaning liquid with aluminum material is not specifically defined, immersion, contact of aluminum material with surface of cleaning liquid, spraying, etc, may be possible.

Removal of the surface layer of aluminum material by washing

may take place in a process after intermediate annealing and before heating in the oxidative atmosphere to be conducted after final cold rolling or application of tensile strain. The conditions of washing may be implemented to the extent of the conditions of washing after said heating in the oxidative atmosphere.

In addition, the surface layer of aluminum material may be removed by washing in a process after hot rolling and before intermediate annealing. Although the cleaning liquid to be used in a process after hot rolling and before intermediate annealing may be selected in accordance with the intended use, and shall not be specifically defined, it may be same as the cleaning liquid to be used in washing after said heating in the oxidative atmosphere.

The process atmosphere during final annealing of aluminum material, area fraction of cube orientation of the aluminum material after final annealing, a method of final annealing, and temperature, time, temperature rising speed/pattern during annealing are same as those described in the manufacturing process on the said first embodiment.

[Manufacturing process on a Fifth Embodiment (Till end of final annealing)]

Manufacture of aluminum material, although it is not limited, takes place in the order of adjustment of soluble components of aluminum material/slab casting, hot rolling, cold rolling, intermediate annealing in the oxidative atmosphere, tensile

strain application, and final annealing. Prior to the final annealing, after the intermediate annealing, aluminum material has its surface layer removed by washing. The removal of surface layer of aluminum material by washing may be carried out at least once. For instance, aluminum material may be washed before the tensile strain application after the intermediate annealing in the oxidative atmosphere, and then, aluminum material may be washed before the final annealing after the tensile strain application.

In addition to the above manufacturing process, it is more preferable that aluminum material is heated in oxidative atmosphere before final annealing after tensile strain application. When aluminum material is heated in oxidative atmosphere before final annealing after tensile strain application, removal of surface layer of aluminum material by washing is carried out before final annealing after heating in the oxidative atmosphere. The surface of aluminum material may be removed before heating in oxidative atmosphere after intermediate annealing in oxidative atmosphere, and before final annealing after heating in oxidative atmosphere, respectively.

The heating in the oxidative atmosphere before final annealing after tensile strain application, and the subsequent removal of surface layer of aluminum material by washing may be carried out once, respectively. The heating in the oxidative atmosphere and the subsequent removal of surface layer of aluminum material by washing may be alternately carried out several times.

The intermediate annealing in the oxidative atmosphere is

conducted by atmosphere heating rather than contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark. Hence, in this invention, the intermediate annealing is conducted by atmosphere heating.

As a method of heating during the intermediate annealing in the oxidative atmosphere, ventilation heating, radiation heating, etc. can be exemplified. In addition, although temperature rising rate/pattern at the time of heating aluminum material in the oxidative atmosphere is not specifically limited, it should be conducted under the conditions that increase area fraction of cube orientation after the final annealing. In addition, shape of aluminum material to be heated is not specifically limited. Aluminum material wound around the coil may be batch annealed or it may be wound around the coil, after the coil is rewound and it is continuously annealed.

Preferably, oxygen concentration in the oxidative atmosphere in the intermediate annealing would be not less than 0.1 volume %. If the oxygen concentration is less than 0.1 volume %, the surface of aluminum material may not be adequately oxidized when it is heated.

Preferably, the oxygen concentration would be not less than 1 volume %, in particular, and more preferably, not less than 5 volume %, and air can be preferably used as an oxidative atmosphere. If air is used as the oxidative atmosphere, there is no need to

control the oxygen concentration, thereby being able to plan cost reduction of the intermediate annealing process.

Preferably, the intermediate annealing temperature in the oxidative atmosphere would be not less than 200°C and not more than 320°C. The intermediate annealing falling within the said temperature range could oxidize aluminum material and achieve uniform solubility of the surface layer thereof. If the intermediate annealing temperature is less than 200°C, a sufficient organization that allows recrystallized grain with the cube orientation during final annealing to grow preferentially cannot be obtained. If it exceeds 300°C, recrystallized grains that will block preferential growth of the cube orientation grain during final annealing will grow. The intermediate annealing temperature and time that allow acquisition of the favorable area fraction of cube orientation to be obtained depend on composition of aluminum material, and the condition that allows acquisition of a high area fraction of cube orientation after final annealing should be selected.

The tensile strain application is a process that is used to control a cube orientation in combination with intermediate annealing. Since the tensile strain application does not have a problem that a lot of lubricating oil adheres to the surface of aluminum material during the finish cold-rolling, the surface of aluminum material is easily oxidized when aluminum material is then heated in the oxidative atmosphere. The tensile strain application has a feature that aluminum crystal grains hardly

become coarse during the final annealing compared with the finish cold-rolling even if a foil has a large thickness, and thick aluminum material is easily manufactured. Although a method for tensile strain application is not particularly limited, the method described in the patent document 2 is applicable.

The tensile strain is preferably not less than 1 % and not more than 15 %. When the tensile strain is less than 1 %, sufficient stress by working that allows crystallized grain having a cube orientation during final annealing to grow preferentially cannot be obtained. When the tensile strain exceeds 15 %, aluminum material may be ruptured in a tensile process. The tensile strain may given by uniaxial tensile for giving the tensile strain in one direction to aluminum material, for instance, only in a length direction, and by biaxial tensile for giving the tensile strain in different two directions, for instance, in the length direction and a width direction. Aluminum material may be bent and deformed to generate tensile strain.

The said heating in the oxidative atmosphere conducted after the tensile strain application is conducted by atmosphere heating rather than contact with a heating body. In atmosphere heating, as aluminum material does not come in contact with the heating body, unlike heating by coming in contact with a heating body, heating leaves no wrinkle or mark. Hence, this invention has adopted atmosphere heating.

As a method of heating in the oxidative atmosphere after the tensile strain application, ventilation heating, radiation

heating, etc. can be exemplified. In addition, shape of aluminum material to be heated is not specifically limited. Aluminum material wound around the coil may be batch heated or it may be wound around the coil, after the coil is rewound and it is continuously heated.

Preferably, heating temperature of aluminum material in the oxidative atmosphere after the tensile strain application would be 50 to 400°C.

When the heating temperature is less than 50°C, oxidation of the surface layer of aluminum material may not be adequate and aluminum material may not melt uniformly when the surface layer thereof is removed. When the heating temperature exceeds 400°C, oxide film of the surface layer of aluminum material will be thick, which deteriorates solubility of aluminum material and makes it difficult to melt aluminum material in uniform manner. Particularly preferable heating temperature is 70 to 350°C, and 70 to 240°C most preferably.

Preferably, heating time in the oxidative atmosphere after the tensile strain application is not less than 3 sec and not more than 72 hr. If heating time is less than 3 sec, the surface layer of aluminum material may not be oxidized adequately and aluminum material may not melt uniformly when the surface layer thereof is removed. When the heating time exceeds 72 hr, melting uniformity during removal of the surface layer of aluminum material becomes almost flat, and thus cost will be higher due to energy consumption during heating. Preferable heating time, in

particular, is not less than 10 sec and not more than 48 hr, and most preferably, not less than 70 sec and not more than 48 hr.

For the heating temperature and time in the oxidative atmosphere, appropriate conditions should be selected, depending on a heating method. For instance, when aluminum material is heated with it wound around a coil, it would be preferably heated at 50 to 240°C for 30 min to 72 hr, and more preferably at 70 to 240°C for 1 to 48 hr.

For the heating temperature and time in the oxidative atmosphere, appropriate conditions should be selected, depending on a heating method. For instance, when aluminum material is heated with it wound around a coil, it would be preferably heated at 50 to 240°C for 30 min to 72 hr, and more preferably at 70 to 240°C for 1 to 48 hr. In addition, when aluminum material unwound from a coil or sheet-cut aluminum material is heated, the heating time t (hour) would be preferably $10/(1.44 \times x^{1.5}) \leq t \leq 72$, where x is the heating temperature (°C). It would be more preferably $10/(1.44 \times x^{1.5}) \leq t \leq 48$.

Preferably, oxygen concentration in the oxidative atmosphere during heating of aluminum material in the oxidative atmosphere after the tensile strain application would be not less than 0.1 volume %. If the oxygen concentration is less than 0.1 volume %, the surface of aluminum material may not be adequately oxidized when it is heated. Preferably, the oxygen concentration would be not less than 1 volume %, in particular, and more

preferably, not less than 5 volume %, and air can be preferably used as the oxidative atmosphere.

Although cleaning fluid to be used in removing a surface layer of aluminum material by washing before the tensile strain application after intermediate annealing in oxidative atmosphere is not specifically limited, alkaline solution or acid solution may be used. The surface layer may be removed by using either alkaline solution or acid solution, or it may be washed with acid solution after being removed with alkaline solution.

As alkali, sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate, and sodium carbonate may be exemplified, and one or more alkali selected from the above alkalis may be used as cleaning fluid by being dissolved in water.

As acid, one or more acid selected from those including hydrochloric acid, sulfuric acid, nitric acid, and elemental phosphorus shall be used. As acids containing elemental phosphorus, orthophosphoric acid (hereafter referred to as phosphoric acid), pyrophoric acid, metaphosphoric acid, and polyphosphoric acid may be exemplified.

In addition, as acid to be used in removing the surface layer of aluminum material, perchloric acid and hypochlorous acid may be used. The removal amount of the surface layer of aluminum material may be adjusted by keeping at an appropriate level concentration of alkalis or acids, temperature of alkaline or acid aqueous solution, and contact time of aluminum material with

alkaline or acid aqueous solution.

In addition, in order to enhance cleaning effect of the surface layer of aluminum material, a surface active agent or chelating agent may be added to the cleaning fluid.

The said removal amount of the surface layer of aluminum material by washing after heating in oxidative atmosphere is a mean value, and shall be preferably not less than 1 nm and not more than 500 nm per side of aluminum material. If the removal amount of the surface layer is less than 1 nm, removal of the oxide film on the surface layer of aluminum material may be inadequate. If the surface layer is removed by 500 nm or more, etch pit nucleation on the surface layer of aluminum material will be suppressed, thus even degrading etching characteristic and reducing capacitance. Preferably, the removal amount of the surface layer by washing would be not less than 1.5 nm and not more than 200 nm.

Although density of the oxide film on the surface layer of aluminum material differs from that of aluminum, which is metal, the removal amount of surface layer of aluminum material, D (nm), in this application, it shall be defined as $D \text{ (nm)} = E \times 10^7 / 2.7$, using $E \text{ (g/cm}^2\text{)}$, decrease in mass per unit surface area by washing and density of aluminum, 2.7 g/cm^3 .

Although a method of bringing cleaning fluid with aluminum material is not specifically limited, immersion, contact of aluminum material with surface of cleaning fluid, spraying, etc, may be possible.

The removal of the surface layer of aluminum material by washing may be conducted before heating in oxidative atmosphere after the tensile strain application after intermediate annealing, and washing conditions may be conducted in the range of the washing conditions after oxidative atmosphere heating.

In addition, the surface layer of aluminum material may be removed by washing with said cleaning fluid before the intermediate annealing after the hot rolling. Although the cleaning fluid to be used in cleaning in a process before the intermediate annealing after the hot rolling may be selected in accordance with the intended use, and shall not be specifically limited, the same cleaning fluid as that to be used in washing after the said intermediate annealing may be used.

The process atmosphere during final annealing of aluminum material, area fraction of cube orientation of aluminum material after the final annealing, a method of the final annealing, and temperature, time, temperature rising rate/pattern during annealing are same as those described in the manufacturing process on the said first embodiment.

[Process after Final Annealing]

The thickness of aluminum material for electrolytic capacitor electrodes obtained after final annealing is not particularly specified. One having a thickness of 200 μ m or less and one having a thickness of 200 μ m or more such a foil are also contained in the invention.

Aluminum material subjected to the final annealing is etched

for enhancing the enlarged area rate. Although etching process conditions are not limited particularly, it is preferable to employ a direct-current etching method. The direct-current etching method etches deeply and thickly at the core of an etch pit whose the generation is promoted during the annealing, generates many tunnel-like pits, and realizes large capacitance.

Aluminum material is preferably used as an anode material by performing chemical forming after the etching process, and particularly, aluminum material is preferably used as an electrolytic capacitor electrode material for middle and high voltages. However, the use of aluminum material as a cathode material is not interfered. The electrolytic capacitor using the electrode material can realize large capacitance.

Processes and process conditions other than the processes specified in the invention are not limited, and are performed according to an ordinary method. The manufacturing process of aluminum material is preferably changed with relation to the etching conditions of aluminum material.

The capacitance is preferably measured according to an ordinary method, and for instance, a method can be exemplified, wherein an etched foil subjected to the formation of dielectric by anodizing is measured at 120 Hz by using a stainless plate as a counter electrode in 80 g/L of an ammonium borate solution of 30 °C.

Examples

Examples and Comparative Examples of the present invention will, hereinafter, be shown.

1. First Example (corresponding to a manufacturing process related to first embodiment)

[Example using a sheet shaped aluminum material]

An aluminum slab was hot-rolled, an obtained sheet was then cold-rolled, and processed by an intermediate annealing, and then was further cold-rolled for finishing to obtain an aluminum material having a thickness of 110 μm , and a purity of 99.99 mass %. And the aluminum material was cut to obtain a sheet. Table 1-1 shows types of the processes performed after cold rolling (process 1-1 to process 5-1), Table 2-1 shows conditions of the heating in the oxidative atmosphere (process 2-1) in Table 1-1, and Table 3-1 and Table 4-1 show removing conditions of the surface layer of aluminum material (process 4-1) by washing in Table 1-1. An amount of the surface layer removing of aluminum material was controlled by an immersion period to a washing liquid.

An amount of the surface layer removing of aluminum material was controlled by an immersion period to a washing liquid, and when an acid washing is carried out after an alkali washing, an amount of removing was controlled by adjusting the immersion period to the alkali washing liquid.

Example 1-1

A hot-rolling, a cold-rolling, an intermediate annealing,

and a finish cold-rolling were given sequentially to an aluminum slab. As Table 5-1 shows, the sheet-shaped aluminum material obtained having a thickness of 110 μm and a purity of 99.99% was degreased using n-hexane (process 1-1). After heating for 24 hr (process 2-1) at 150 °C in air, an average of 10 nm of a surface layer of the aluminum material was removed (process 4-1) by immersing into a sulfuric acid solution of 20 mass % at 80 °C. Then, final annealing was given to the material at 540 °C in argon atmosphere for 4 hr (process 5-1) to obtain an aluminum material for electrolytic capacitor electrodes.

Example 2-1 to Example 49-1, Comparative Example 1-1 to-
Comparative Example 3-1

Under conditions shown in Table 5-1 to 7-1, aluminum materials for electrolytic capacitor electrodes were obtained.

The aluminum materials obtained in each of the Examples and the Comparative Examples were immersed in an aqueous solution including 1.0 mol/L of HCl and 3.5 mol/L of H_2SO_4 at 75 °C of solution temperature. A direct-current electrolytic etching was given to the materials with a current density of 0.2 A/ cm^2 using a solution having the same composition at the same temperature.

The aluminum materials after electrolytic treatment were further immersed in the hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90 °C, and then etched foils having a thicker diameter of a pit were obtained. Formation of dielectric by anodizing was given to the obtained etched foils at a forming voltage of 270 V, according

to an EIAJ standard and samples for capacitance measurement were obtained.

Table 5-1 to 7-1 show relative electric capacities when capacitance of Comparative Example 3-1 is set as 100.

[Table 1-1]

Process

		Method
Process 1-1	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 2-1	Heating in an oxidative atmosphere	Operate on the conditions in Table 2-1 in an atmosphere containing oxygen
Process 3-1	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 4-1	Washing	Remove the surface layer of an aluminum material on the conditions in Table 3-1, rinse with water and dry in air
Process 5-1	Final annealing	Operate in an argon atmosphere

[Table 2-1]

Conditions in Process 2-1 (Heating in an oxidative atmosphere)

Atmosphere	Heating temperature (°C)	Heating time	Heating condition
Air	50	72 hr	Condition A-1
	70	48 hr	Condition B-1
	100	24 hr	Condition C-1
	150	24 hr	Condition D-1
	200	30 min	Condition E-1
	350	10 sec	Condition F-1
	380	5 sec	Condition G-1
	100	30 min	Condition H-1
Oxygen: 5 volume %, Nitrogen: 95 volume %	100	24 hr	Condition I-1
Oxygen: 1 volume %, Nitrogen: 99 volume %	100	24 hr	Condition J-1
Oxygen: 0.1 volume %, Nitrogen: 99.9 volume %	100	24 hr	Condition K-1
Air	330	70 sec	Condition L-1

[Table 3-1]

Conditions in Process 4-1 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	7 nm	Condition 1-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	10 nm	Condition 2-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 3-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	150 nm	Condition 4-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	180 nm	Condition 5-1
Immerse in a calcium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 6-1
Immerse in a potassium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 7-1
Immerse in a sodium orthosilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 8-1
Immerse in a sodium metasilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 9-1
Immerse in a trisodium phosphate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 10-1
Immerse in a sodium carbonate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 11-1
Immerse in a (sodium hydroxide of 0.2 mass %+calcium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 12-1
Immerse in a (sodium hydroxide of 0.2 mass %+potassium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 13-1
Immerse in a (sodium hydroxide of 0.2 mass %+sodium orthosilicate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 14-1
Immerse in a (sodium hydroxide of 0.2 mass %+trisodium phosphate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 15-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	490 nm	Condition 16-1

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 4-1]

Conditions in Process 4-1 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 17-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 18-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 19-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in an orthophosphoric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 20-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an sulfuric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 21-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +a nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 22-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 23-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +a nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 24-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 25-1
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 26-1
Immerse in a hydrochloric acid aqueous solution of 8 mass % at 80°C (*1)→Rinse with water→Dry	1.3 nm	Condition 27-1
Immerse in a sulfuric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 28-1
Immerse in a nitric acid aqueous solution of 4.5 mass % at 80°C (*1)→Rinse with water→Dry	1.7 nm	Condition 29-1
Immerse in a phosphoric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 30-1

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time to solutions.

[Table 5-1]

	Process 1-1 Degreasing	Process 2-1 Heat treatment	Process 3-1 Degreasing	Process 4-1 Washing	Process 5-1 Final annealing	Relative capacitance %
Example 1-1	Method 1	Condition D-1	—	Condition 28-1	540°C, 4 hr	118
Example 2-1	Method 1	Condition D-1	—	Condition 30-1	540°C, 4 hr	117
Example 3-1	—	Condition D-1	—	Condition 28-1	540°C, 4 hr	117
Example 4-1	—	Condition D-1	—	Condition 17-1	540°C, 4 hr	112
Example 5-1	—	Condition D-1	—	Condition 18-1	540°C, 4 hr	112
Example 6-1	—	Condition D-1	—	Condition 19-1	540°C, 4 hr	112
Example 7-1	—	Condition D-1	—	Condition 20-1	540°C, 4 hr	111
Example 8-1	—	Condition D-1	—	Condition 21-1	540°C, 4 hr	112
Example 9-1	—	Condition D-1	—	Condition 22-1	540°C, 4 hr	112
Example 10-1	—	Condition D-1	—	Condition 23-1	540°C, 4 hr	111
Example 11-1	—	Condition D-1	—	Condition 24-1	540°C, 4 hr	111
Example 12-1	—	Condition D-1	—	Condition 25-1	540°C, 4 hr	111
Example 13-1	—	Condition D-1	—	Condition 26-1	540°C, 4 hr	112
Example 14-1	—	Condition D-1	—	Condition 29-1	540°C, 4 hr	115
Example 15-1	—	Condition D-5	—	Condition 27-1	540°C, 4 hr	110

[Table 6-1]

	Process 1-1 Degreasing	Process 2-1 Heat treatment	Process 3-1 Degreasing	Process 4-1 Washing	Process 5-1 Final annealing	Relative capacitance %
Example 16-1	Method 1	Condition C-1	—	Condition 3-1	540°C, 4 hr	115
Example 17-1	Method 1	Condition C-1	—	Condition 6-1	540°C, 4 hr	113
Example 18-1	Method 1	Condition C-1	—	Condition 7-1	540°C, 4 hr	114
Example 19-1	Method 1	Condition C-1	—	Condition 8-1	540°C, 4 hr	114
Example 20-1	Method 1	Condition C-1	—	Condition 9-1	540°C, 4 hr	114
Example 21-1	Method 1	Condition C-1	—	Condition 10-1	540°C, 4 hr	113
Example 22-1	Method 1	Condition C-1	—	Condition 11-1	540°C, 4 hr	113
Example 23-1	Method 1	Condition C-1	—	Condition 2-1	540°C, 4 hr	114
Example 24-1	Method 1	Condition C-1	—	Condition 4-1	540°C, 4 hr	112
Example 25-1	Method 1	Condition C-1	—	Condition 1-1	540°C, 4 hr	107
Example 26-1	Method 1	Condition C-1	—	Condition 5-1	540°C, 4 hr	110
Example 27-1	Method 1	Condition D-1	—	Condition 3-1	540°C, 4 hr	114
Example 28-1	Method 1	Condition E-1	—	Condition 3-1	540°C, 4 hr	114
Example 29-1	Method 1	Condition F-1	—	Condition 3-1	540°C, 4 hr	106
Example 30-1	Method 1	Condition G-1	—	Condition 3-1	540°C, 4 hr	105
Example 31-1	Method 1	Condition B-1	—	Condition 3-1	540°C, 4 hr	110
Example 32-1	Method 1	Condition A-1	—	Condition 3-1	540°C, 4 hr	106
Example 33-1	Method 1	Condition I-1	—	Condition 3-1	540°C, 4 hr	114
Example 34-1	Method 1	Condition J-1	—	Condition 3-1	540°C, 4 hr	110
Example 35-1	Method 1	Condition K-1	—	Condition 3-1	540°C, 4 hr	106
Example 36-1	Method 1	Condition H-1	—	Condition 12-1	540°C, 4 hr	112
Example 37-1	Method 1	Condition H-1	—	Condition 13-1	540°C, 4 hr	113
Example 38-1	Method 1	Condition H-1	—	Condition 14-1	540°C, 4 hr	113
Example 39-1	Method 1	Condition H-1	—	Condition 15-1	540°C, 4 hr	111
Example 40-1	—	Condition C-1	Method 1	Condition 3-1	540°C, 4 hr	114
Example 41-1	Method 2	Condition C-1	—	Condition 3-1	540°C, 4 hr	115
Example 42-1	—	Condition C-1	Method 2	Condition 3-1	540°C, 4 hr	114

[Table 7-1]

	Process 1-1	Process 2-1	Process 3-1	Process 4-1	Process 5-1	Relative capacitance %
	Degreasing	Heat treatment	Degreasing	Washing	Final annealing	
Example 43-1	—	Condition C-1	—	Condition 3-1	540°C, 4 hr	113
Example 44-1	Method 1	Condition C-1	—	Condition 3-1	570°C, 4 hr	115
Example 45-1	Method 1	Condition C-1	—	Condition 3-1	580°C, 4 hr	111
Example 46-1	Method 1	Condition C-1	—	Condition 3-1	470°C, 4 hr	104
Example 47-1	Method 1	Condition C-1	—	Condition 3-1	460°C, 24 hr	103
Example 48-1	—	Condition H-1	—	Condition 4-1	540°C, 24 hr	109
Example 49-1	Method 1	Condition L-1	—	Condition 3-1	540°C, 4 hr	107
Comparative Example 1-1	—	—	—	Condition 4-1	540°C, 4 hr	98
Comparative Example 2-1	—	Condition H-1	—	—	540°C, 4 hr	98
Comparative Example 3-1	—	Operate Condition 4-1 of Process 4-1 and Condition H-1 of Process 2-1 sequentially			540°C, 4 hr	100

As is understood from results of the Tables, removing by washing of the surface layer of aluminum material, after heated in the oxidative atmosphere, after the end of cold-rolling and, before final annealing can give an aluminum material for electrolytic capacitor electrodes having outstanding etching characteristics.

On one hand, since solubility of the aluminum materials at the time of washing was uneven, Comparative Example 1-1 annealed after the surface layer removing of the aluminum material by washing without the heating in the oxidative atmosphere gave low capacitance. On the other hand, since much pollution layers and oils by the roll coating at the time rolling remain, Comparative Example 2-1 annealed without removing of the surface layer of aluminum material by the washing after the heating in the oxidative atmosphere gave a low capacitance.

Although Comparative Example 3-1 heated in the oxidative atmosphere after the removing by washing of an aluminum material surface layer has a higher capacitance as compared with those in Comparative Example 1-1 and Comparative Example 2-1. It is because the surface layer of aluminum material unevenly dissolved at the time of washing was not enough equalized by heating in the oxidative atmosphere, capacitance lower than the capacitance in the Example was shown.

[Example using a coiled aluminum material]

A hot-rolling and a cold rolling were given to the aluminum slab of composition 102 shown in Table 8-1, and an aluminum material

coil with a width of 500 mm was obtained.

And after an intermediate annealing, this aluminum material coil was cold-rolled with a 20% of rolling reduction, and an aluminum material having a thickness of 110 μm and a length of 2000 m was obtained.

Subsequently, in Examples 201 to 204, the surface layer was removed by washing, after a heating in the oxidative atmosphere. In Comparative Example 201, a surface layer was removed by washing without a heating in the oxidative atmosphere.

Then, to the aluminum material, a final annealing for 4 hr was given at 540 °C in an argon atmosphere, and an aluminum material for electrolytic capacitor electrodes was obtained.

Table 9-1 shows conditions of heating in the oxidative atmosphere, and Table 10-1 shows conditions of the surface layer of aluminum material removing by washing. An amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

The aluminum material coils obtained in each Example and each Comparative Example were uncoiled and immersed into an aqueous solution with a liquid temperature of 75 °C including HCl of 1.0 mol/L, and H₂SO₄ of 3.5 mol/L, and subsequently, a direct current electrolytic etching was given in the aqueous solution having a same composition at a same temperature using a condition of current

density 0.2 A/cm².

The aluminum materials after electrolytic treatment were further immersed in the hydrochloric acid-sulfuric acid mixed aqueous solution having the above-mentioned composition for 360 sec at 90 °C, and etched foil with a thicker pit diameter was obtained. The obtained etched foil was chemically converted with a chemical conversion voltage of 270 V according to EIAJ standards to obtain a sample for capacitance measurement.

Table 11-1 shows relative electrostatic capacities when the capacitance of Comparative Example 201 is set as 100.

[Table 8-1]

Si, Fe, Cu and Pb concentration of Aluminum Slab

	Concentration/mass %			
	Fe	Si	Cu	Pb
Composition 101	0.0030	0.0038	0.0020	0.00014
Composition 102	0.0015	0.0022	0.0055	0.00006
Composition 103	0.0008	0.0008	0.0060	0.00004

[Table 9-1]

Conditions of heating in an oxidative atmosphere after finish cold rolling or tensile strain giving

Atmosphere	Heating temperature °C	Heating time	Heating system	Heating condition
Air	150	24 hr	Heating in the state where a coil is rolled	Condition H101
	350	10 sec	Heating in the state where a coil is unrolled	Condition H102

[Table 10-1]

Conditions in washing

Unroll a coil after washing the coil, remove the surface layer of the coil, dry and roll up the coil	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*101)→Rinse with water→Dry	100 nm	Condition 101
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*101)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 102
Immerse in a sulfuric acid aqueous solution of 20 mass % at 80 °C (*101)→Rinse with water→Dry	10 nm	Condition 103

*101: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time to solutions.

[Table 11-1]

	Composition	Intermediate annealing	Finish cold rolling	Heating in an oxidative atmosphere	Surface layer removing	Final annealing	Relative capacitance %
Example 201	Composition 102	Operation	Rolling reduction: 20%	Condition H101	Condition 103	540°C, 4 hr	116
Example 202	Composition 102	Operation	Rolling reduction: 20%	Condition H102	Condition 103	540°C, 4 hr	116
Example 203	Composition 102	Operation	Rolling reduction: 20%	Condition H101	Condition 102	540°C, 4 hr	113
Example 204	Composition 102	Operation	Rolling reduction: 20%	Condition H101	Condition 101	540°C, 4 hr	110
Comparative Example 201	Composition 102	Operation	Rolling reduction: 20%	—	Condition 101	540°C, 4 hr	100

As is understood from results of the Tables, in Examples 201 to 204, since, before the final annealing after termination of a cold rolling, the surface layer of aluminum material was removed by washing after performing heating in an oxidizing atmosphere, aluminum material was dissolved homogenously at the time of surface layer removing, and outstanding etching characteristics and high capacitance were obtained.

On the other hand, in Comparative Example 201, since heating in an oxidizing atmosphere was not performed, ununiform solubility of the aluminum material at the time of the surface layer of aluminum material removing by washing was given to show a low capacitance.

2. Second Example (corresponding to a manufacturing process concerning a second embodiment)

[Example using a sheet shaped aluminum material]

As shown in Table 1-2, aluminum ingots with different composition were prepared. Table 1-2 shows concentrations of Fe, Si, and Cu included in the ingots. Plates obtained by hot-rolling of these aluminum ingots were cold-rolled, and sheet shaped aluminum materials of 130 μm in thickness were prepared. Table 2-2 shows the process after degreasing, Table 3-2 shows the conditions of the process 2-2 (intermediate annealing) in Table 2-2, and Table 4-2 and 5-2 show the conditions of the process 4-2, and the process 7-2 (aluminum material surface layer removing by washing) in Table 2-2.

In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

[Table 1-2]

Si, Fe, and Cu concentration of an aluminum ingot

	Concentration/mass %		
	Fe	Si	Cu
Composition 1-2	0.0050	0.0050	0.0040
Composition 2-2	0.0030	0.0038	0.0020
Composition 3-2	0.0015	0.0022	0.0055
Composition 4-2	0.0008	0.0008	0.0060

[Table 2-2]

Process

Process 1-2	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 2-2	Intermediate annealing	Operate on the conditions in Table 3-2.
Process 3-2	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 4-2	Washing	Remove the surface layer of an aluminum material on the conditions in Table 4-2 or Table 5-2, rinse with water and dry in air
Process 5-2	Finish cold rolling	Operate at a draft of 20%
Process 6-2	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 7-2	Washing	Remove the surface layer of an aluminum material on the conditions in Table 4-2 or Table 5-2, rinse with water and dry in air
Process 8-2	Final annealing	Operate in an argon atmosphere.

[Table 3-2]

Conditions in Process 2-2 (Intermediate annealing)

Atmosphere	Heating temperature °C	Heating time	Heating condition
Air	210	12 hr	Condition A-2
	210	30 hr	Condition B-2
	230	1 hr	Condition C-2
	260	18 hr	Condition D-2
	275	1 hr	Condition E-2
	275	7 hr	Condition F-2
	310	1 hr	Condition G-2
Oxygen: 5 volume %, Nitrogen: 95 volume %	260	18 hr	Condition H-2
Oxygen: 1 volume %, Nitrogen: 99 volume %	260	18 hr	Condition I-2
Oxygen: 0.1 volume %, Nitrogen: 99.9 volume %	260	18 hr	Condition J-2
Nitrogen: 99.99 volume % or more	260	18 hr	Condition K-2 (condition for Comparative Examples)

[Table 4-2]

Conditions in Process 4-2 and Process 7-2 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	7 nm	Condition 1-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	10 nm	Condition 2-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 3-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	190 nm	Condition 4-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	490 nm	Condition 5-2
Immerse in a calcium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 6-2
Immerse in a potassium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 7-2
Immerse in a sodium orthosilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 8-2
Immerse in a sodium metasilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 9-2
Immerse in a trisodium phosphate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 10-2
Immerse in a sodium carbonate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 11-2
Immerse in a (sodium hydroxide of 0.2 mass %+calcium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 12-2
Immerse in a (sodium hydroxide of 0.2 mass %+potassium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 13-2
Immerse in a (sodium hydroxide of 0.2 mass %+sodium orthosilicate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 14-2
Immerse in a (sodium hydroxide of 0.2 mass %+trisodium phosphate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	80 nm	Condition 15-2

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 5-2]

Conditions in Process 4-2 and Process 7-2 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 16-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 17-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 18-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in an orthophosphoric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 19-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an sulfuric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 20-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +a nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 21-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 22-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 23-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 24-2
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	80 nm	Condition 25-2
Immerse in a hydrochloric acid aqueous solution of 8 mass % at 80°C (*1)→Rinse with water→Dry	1.2 nm	Condition 26-2
Immerse in a nitric acid aqueous solution of 4.5 mass % at 80°C (*1)→Rinse with water→Dry	1.7 nm	Condition 27-2
Immerse in a sulfuric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	8 nm	Condition 28-2
Immerse in a phosphoric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	12 nm	Condition 29-2

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

Example 1-2

The aluminum ingot having Fe 0.0015 mass %, Si 0.0022 mass %, and Cu 0.0055 mass % (composition 3-2) in Table 1-2 was hot-rolled. The aluminum material with a thickness of 130 micrometer obtained by the cold rolling of the obtained plate was processed under the conditions shown in Table 6-2. That is, intermediate annealing for 18 hr was given at 260 °C in air (process 2-2). Then, finish cold rolling with a 20% of rolling reduction was given (process 5-2). After a degreasing with n-hexane of the aluminum material after the finish cold rolling (process 6-2), a 4 nm of aluminum material surface layer was removed by immersion into an 80°C 20 mass % sulfuric acid aqueous solution (process 7-2). Then, a final annealing of the aluminum material was carried out at 530 °C in argon atmosphere for 6 hr (process 8-2) to obtain an aluminum material for electrolytic capacitor electrodes.

Example 2-2 to Example 51-2 and Comparative Example 1-2 to Comparative Example 4-2

The aluminum ingots including Fe, Si, and Cu in Table 1-2 was hot-rolled, and the aluminum materials with a thickness of 130 µm obtained by a cold rolling of the obtained plates were processed under conditions of Table 6-2 to 9-2 to obtain aluminum materials for electrolytic capacitor electrodes.

In Tables 6-2 to 9-2, processes 1-2 to 8-2 are corresponding to processes 1-2 to 8-2 in Table 2-2, and detailed conditions of each process are described in Tables 2-2 to 5-2, and 6-2 to 9-2.

After immersion of the aluminum materials obtained in each

of the Examples and Comparative Examples into a 2 mol/L H_2SO_4 aqueous solution at 80 °C of liquid temperature, they were washed with water. Next, a direct current electrolytic etching was given with a current density 0.2 A/cm² in an aqueous solution at 80 °C of liquid temperatures including 1.0 mol/L of HCl and 3.5 mol/L of H_2SO_4 . The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution with the composition for 360 sec at 90 °C, and etched foils with a thicker pit diameter were obtained. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement.

Table 6-2 to Table 9-2 show relative electrostatic capacities when the capacitance of Comparative Example 1-2 is set as 100.

[Table 6-2]

	Ingot composition	Process 1-2	Process 2-2	Process 3-2	Process 4-2	Process 5-2	Process 6-2	Process 7-2	Process 8-2	Relative capacitance %
		Degreasing	Intermediate annealing	Degreasing	Washing	Finish cold rolling	Degreasing	Washing	Final annealing	
Example 1-2	Composition 3-2	—	Condition D-2	—	—	Operation	Method 1	Condition 29-2	530°C, 6 hr	117
Example 2-2	Composition 3-2	—	Condition D-2	—	—	Operation	Method 2	Condition 29-2	530°C, 6 hr	117
Example 3-2	Composition 3-2	Method 2	Condition D-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	117
Example 4-2	Composition 3-2	Method 1	Condition D-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	117
Example 5-2	Composition 3-2	—	Condition D-2	Method 1	—	Operation	—	Condition 29-2	530°C, 6 hr	116
Example 6-2	Composition 3-2	—	Condition D-2	Method 2	—	Operation	—	Condition 29-2	530°C, 6 hr	116
Example 7-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	115
Example 8-2	Composition 4-2	—	Condition A-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	112
Example 9-2	Composition 4-2	—	Condition B-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	113
Example 10-2	Composition 4-2	—	Condition C-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	112
Example 11-2	Composition 2-2	—	Condition E-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	113
Example 12-2	Composition 2-2	—	Condition F-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	113
Example 13-2	Composition 1-2	—	Condition G-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	111
Example 14-2	Composition 3-2	—	Condition H-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	114
Example 15-2	Composition 3-2	—	Condition I-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	113

[Table 7-2]

	Ingot composition	Process 1-2 Degreasing	Process 2-2 Intermediate annealing	Process 3-2 Degreasing	Process 4-2 Washing	Process 5-2 Finish cold rolling	Process 6-2 Degreasing	Process 7-2 Washing	Process 8-2 Final annealing	Relative capacitance %
Example 16-2	Composition 3-2	—	Condition J-2	—	—	Operation	—	Condition 29-2	530°C, 6 hr	111
Example 17-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 1-2	530°C, 6 hr	106
Example 18-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 2-2	530°C, 6 hr	108
Example 19-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 3-2	530°C, 6 hr	111
Example 20-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 4-2	530°C, 6 hr	110
Example 21-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 5-2	530°C, 6 hr	108
Example 22-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 6-2	530°C, 6 hr	111
Example 23-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 7-2	530°C, 6 hr	112
Example 24-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 8-2	530°C, 6 hr	111
Example 25-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 9-2	530°C, 6 hr	111
Example 26-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 10-2	530°C, 6 hr	112
Example 27-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 11-2	530°C, 6 hr	112
Example 28-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 12-2	530°C, 6 hr	111
Example 29-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 13-2	530°C, 6 hr	111
Example 30-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 14-2	530°C, 6 hr	112

[Table 8-2]

	Ingot composition	Process 1-2 Degreasing	Process 2-2 Intermediate annealing	Process 3-2 Degreasing	Process 4-2 Washing	Process 5-2 Finish cold rolling	Process 6-2 Degreasing	Process 7-2 Washing	Process 8-2 Final annealing	Relative capacitance %
Example 31-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 15-2	530°C, 6 hr	110
Example 32-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 16-2	530°C, 6 hr	111
Example 33-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 17-2	530°C, 6 hr	111
Example 34-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 18-2	530°C, 6 hr	111
Example 35-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 19-2	530°C, 6 hr	110
Example 36-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 20-2	530°C, 6 hr	111
Example 37-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 21-2	530°C, 6 hr	111
Example 38-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 22-2	530°C, 6 hr	110
Example 39-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 23-2	530°C, 6 hr	110
Example 40-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 24-2	530°C, 6 hr	110
Example 41-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 25-2	530°C, 6 hr	111
Example 42-2	Composition 3-2	—	Condition J-2	—	—	Operation	Method 1	Condition 26-2	530°C, 6 hr	109
Example 43-2	Composition 3-2	—	Condition J-2	—	—	Operation	Method 1	Condition 27-2	530°C, 6 hr	111
Example 44-2	Composition 3-2	—	Condition J-2	—	—	Operation	—	Condition 28-2	530°C, 6 hr	114
Example 45-2	Composition 3-2	—	Condition D-2	—	Condition 29-2	Operation	Method 1	—	530°C, 6 hr	110

[Table 9-2]

	Ingot composition	Process 1-2 Degreasing	Process 2-2 Intermediate annealing	Process 3-2 Degreasing	Process 4-2 Washing	Process 5-2 Finish cold rolling	Process 6-2 Degreasing	Process 7-2 Washing	Process 8-2 Final annealing	Relative capacitance %
Example 46-2	Composition 3-2	—	Condition D-2	—	Condition 29-2	Operation	Method 1	Condition 27-2	530°C, 6 hr	112
Example 47-2	Composition 3-2	—	Condition D-2	—	Condition 29-2	Operation	—	Condition 28-2	530°C, 6 hr	114
Example 48-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 3-2	570°C, 5 hr	108
Example 49-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 3-2	580°C, 5 hr	107
Example 50-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 3-2	470°C, 24 hr	106
Example 51-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	Condition 3-2	460°C, 24 hr	104
Comparative Example 1-2	Composition 3-2	—	Condition K-2	—	—	Operation	—	Condition 4-2	530°C, 6 hr	100
Comparative Example 2-2	Composition 3-2	—	Condition K-2	—	—	Operation	Method 1	—	530°C, 6 hr	100
Comparative Example 3-2	Composition 3-2	—	Condition D-2	—	—	Operation	—	—	530°C, 6 hr	95
Comparative Example 4-2	Composition 3-2	—	Condition D-2	—	—	Operation	Method 1	—	530°C, 6 hr	96

As described above, an intermediate annealing of an aluminum material carries out in the oxidative atmosphere, and dissolution by washing of the surface layer of aluminum material in a process before a final annealing and after the intermediate annealing, and the subsequent final annealing, may provide an aluminum material for electrolytic capacitor electrodes with outstanding etching characteristics.

On the other hand, in Comparative Example 1-2, an intermediate annealing in a 100% nitrogen atmosphere was performed, and after the finish cold rolling, the surface layer of aluminum material was removed by a washing and then a final annealing was given. In this Comparative Example 1-2, uneven solubility of the aluminum material at the time of washing, and a low capacitance was shown.

Comparative Example 2-2, in which the finish cold rolling and the degreasing were carried out after the intermediate annealing in the oxidative atmosphere and then final annealing was subsequently given, showed capacitance less than that of the Example due to remaining uneven surface layer formed by the rolling process.

Although an intermediate annealing was performed in the oxidative atmosphere in Comparative Example 3-2 and Comparative Example 4-2, the annealing was performed after the intermediate annealing. Therefore, since the surface layer removing by washing was not performed in a process before the final annealing, the oxide film of the surface of the aluminum materials after final

annealing was thicker, and thereby excellent etching characteristics were not acquired.

[Example using a coiled aluminum material]

A hot-rolling and a cold rolling were given to an aluminum slab having a composition in Table 11-2 to obtain an aluminum material coil with a width of 500 mm. The contents of each composition are same as shown in Table 8-1.

And each process of an intermediate annealing, a finish cold rolling, and a surface layer removing was sequentially given to the aluminum material coil under conditions in Table 11-2 to obtain an aluminum material with a thickness of 110 μm and a length of 2000 m.

Subsequently, a final annealing for 4 hr was carried out at 540 °C in an argon atmosphere, and an aluminum material for electrolytic capacitor electrodes was obtained.

Table 10-2 shows conditions of the intermediate annealing, and conditions of the surface layer of aluminum material removing are same as the conditions shown in Table 10-1. In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkaline cleaning liquid.

The aluminum material coils obtained in each the Example and Comparative Example were uncoiled and immersed in a 2 mol/L of H_2SO_4 aqueous solution at 80 °C of liquid temperature, then

washed with water. Subsequently, a direct current electrolytic etching was given to the coils with a current density of 0.2 A/cm^2 in an aqueous solution including HCl of 1.0 mol/L, and H_2SO_4 of 3.5 mol/L at a liquid temperature 80°C . The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90°C to obtain etched foils with a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement.

Table 11-2 shows relative capacitance when the capacitance of Comparative Example 401 is set as 100.

[Table 10-2]

Intermediate Annealing Atmosphere, Temperature and Time			Intermediate annealing in the state where a coil is rolled	
Atmosphere	Heating temperature °C	Heating time	Heating condition	
Air	230	20 hr	Condition A2	
	230	13 hr	Condition B2	
	260	18 hr	Condition C2	
	260	13 hr	Condition D2	
	275	7 hr	Condition E2	
	275	5 hr	Condition F2	
	290	1 hr	Condition G2	
Nitrogen: 99.99 volume % or more	260	20 hr	Condition H2 (condition for Comparative Examples)	
Nitrogen: 99.99 volume % or more	260	13 hr	Condition I2 (condition for Comparative Examples)	

[Table 11-2]

	Composition	Intermediate annealing	Finish cold rolling	Washing	Final annealing	Relative capacitance %
Example 401	Composition 103	Condition A2	Rolling reduction: 20%	Condition 103	550°C, 4 hr	117
Example 402	Composition 102	Condition C2	Rolling reduction: 20%	Condition 103	550°C, 4 hr	115
Example 403	Composition 101	Condition E2	Rolling reduction: 20%	Condition 103	550°C, 4 hr	110
Example 404	Composition 102	Condition C2	Rolling reduction: 20%	Condition 102	550°C, 4 hr	112
Example 405	Composition 102	Condition C2	Rolling reduction: 20%	Condition 101	550°C, 4 hr	109
Comparative Example 401	Composition 102	Condition H2	Rolling reduction: 20%	Condition 101	550°C, 4 hr	100

As is understood from results of the Tables, in Examples 401 to 405, the intermediate annealing in the oxidative atmosphere was carried out, and the surface layer of the aluminum material was removed by washing before final annealing. Therefore, the aluminum material was dissolved homogenously at the time of a surface layer removing, and these Examples have outstanding etching characteristics and high electrostatic capacities.

On the contrary, in Comparative Example 401, the intermediate annealing was carried out in a not less than 99.99 volume % of nitrogen atmosphere, and, subsequently the surface layer of aluminum material removing was carried out before the final annealing. Therefore, the aluminum material was not dissolved homogenously at the time of the surface layer of aluminum material removing by washing, therefore Comparative Example 401 shows a low capacitance.

3. Third Example (corresponding to Manufacturing Process Concerning third Embodiment)

[Example using a sheet shaped aluminum material]

As shown in Table 1-3, aluminum ingots with different composition were prepared. Table 1-3 shows concentrations of Fe, Si, and Cu included in the ingots. Plates obtained by hot-rolling these aluminum ingots were cold-rolled, and sheet shaped aluminum materials with a thickness of 130 μm were prepared. Table 2-3 shows conditions of a process after degreasing performed before an intermediate annealing, Table 3-3 shows conditions of a process

2-3 (intermediate annealing) in Table 2-3, Tables 4-3 and 5-3 shows conditions of a process 4-3 and a process 9-3 (aluminum material surface layer removing by washing) in Table 2-3, and Table 6-3 shows conditions of a process 7-3 and a process 10-3 (heating in the oxidative atmosphere) in Table 2-3.

In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

[Table 1-3]

Si, Fe, and Cu concentration of an aluminum ingot

	Concentration/mass %		
	Fe	Si	Cu
Composition 1-3	0.0050	0.0050	0.0020
Composition 2-3	0.0030	0.0038	0.0020
Composition 3-3	0.0015	0.0022	0.0055
Composition 4-3	0.0008	0.0008	0.0060

[Table 2-3]

Process

Process 1-3	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 2-3	Intermediate annealing	Operate on the conditions in Table 2-3.
Process 3-3	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 4-3	Washing	Operate on the conditions in Table 3-3.
Process 5-3	Finish cold rolling	Operate at a draft of 20%
Process 6-3	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 7-3	Heating	Operate on the conditions in Table 4-3 in an atmosphere containing oxygen
Process 8-3	Degreasing	Operate either the following method 1 or method 2 Method 1: Dry in air after immersing in n-hexane Method 2: Immersing in water containing sodium dodecyl sulfate of 0.2 mass %, rinse with water and dry in air
Process 9-3	Washing	Remove the surface layer of an aluminum material on the conditions in Table 3-3, rinse with water and dry in air
Process 10-3	Heating (Process for Comparative Examples)	Operate on the conditions in Table 4-3 in an atmosphere containing oxygen
Process 11-3	Final annealing	Operate in an argon atmosphere.

[Table 3-3]

Conditions in Process 2-3 (Intermediate annealing)

Atmosphere	Heating temperature °C	Heating time	Heating condition
Air	210	12 hr	Condition A-3
	210	30 hr	Condition B-3
	230	1 hr	Condition C-3
	260	18 hr	Condition D-3
	275	1 hr	Condition E-3
	275	7 hr	Condition F-3
	310	1 hr	Condition G-3
Oxygen: 5 volume %, Nitrogen: 95 volume %	260	18 hr	Condition H-3
Oxygen: 1 volume %, Nitrogen: 99 volume %	260	18 hr	Condition I-3
Oxygen: 0.1 volume %, Nitrogen: 99.9 volume %	260	18 hr	Condition J-3
Nitrogen: 99.99 volume % or more	260	18 hr	Condition K-3 (condition for Comparative Examples)

[Table 4-3]

Conditions in Process 4-3 and Process 9-2 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	7 nm	Condition 1-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	10 nm	Condition 2-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 3-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	190 nm	Condition 4-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	490 nm	Condition 5-3
Immerse in a calcium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 6-3
Immerse in a potassium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 7-3
Immerse in a sodium orthosilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 8-3
Immerse in a sodium metasilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 9-3
Immerse in a trisodium phosphate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 10-3
Immerse in a sodium carbonate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 11-3
Immerse in a (sodium hydroxide of 0.2 mass % + calcium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 12-3
Immerse in a (sodium hydroxide of 0.2 mass % + potassium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 13-3
Immerse in a (sodium hydroxide of 0.2 mass % + sodium orthosilicate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 14-3
Immerse in a (sodium hydroxide of 0.2 mass % + trisodium phosphate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 15-3

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 5-3]

Conditions in Process 4-3 and Process 9-3 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 16-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 17-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 18-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in an orthophosphoric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 19-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an sulfuric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 20-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +a nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 21-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 22-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 23-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 24-3
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 25-3
Immerse in a hydrochloric acid aqueous solution of 8 mass % at 80°C (*1)→Rinse with water→Dry	1.3 nm	Condition 26-3
Immerse in a sulfuric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 27-3
Immerse in a nitric acid aqueous solution of 4.5 mass % at 80°C (*1)→Rinse with water→Dry	1.7nm	Condition 28-3
Immerse in a phosphoric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10nm	Condition 29-3

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 6-3]

Conditions of Process 7-3 and Process 10-3 (Heating in an oxidative atmosphere)

Atmosphere	Heating temperature (°C)	Heating time	Heating condition
Air	50	72 hr	Condition H1-3
	70	48 hr	Condition H2-3
	100	24 hr	Condition H3-3
	150	24 hr	Condition H4-3
	200	30 min	Condition H5-3
	350	10 sec	Condition H6-3
	380	4 sec	Condition H7-3
	330	70 sec	Condition H8-3
	100	30 min	Condition H9-3
Oxygen: 5 volume %, Nitrogen: 95 volume %	100	24 hr	Condition H10-3
Oxygen: 1 volume %, Nitrogen: 99 volume %	100	24 hr	Condition H11-3
Oxygen: 0.1 volume %, Nitrogen: 99.9 volume %	100	24 hr	Condition H12-3

Example 1 - 3

The aluminum ingot having Fe 0.0015 mass %, Si 0.0022 mass %, and Cu 0.0055 mass % (composition 3) of Table 1-3 was hot-rolled, and an aluminum material having a thickness of 130 μm obtained by cold-rolling of the obtained plate was processed under the conditions shown in Table 7-3. That is, the aluminum material was degreased with n-hexane (process 1-3), and an intermediate annealing for 18 hr was given at 260 °C in air (process 2-3). Subsequently, a finish cold rolling with a 20% of rolling reduction was carried out (process 5-3). After degreasing with n-hexane of the aluminum material after the finish cold rolling (process 6-3), a heating at 150 °C for 24 hr in air was carried out (process 7-3). Furthermore, 10 nm of a surface layer of the aluminum material was removed by immersion into at 80 °C 20 mass % sulfuric acid aqueous solution (process 8-3). Subsequently, a final annealing was performed at 540 °C in argon atmosphere for 5 hr (process 11-3), and an aluminum material for electrolytic capacitor electrodes was obtained.

Example 2-3 to Example 72-3, Comparative Example 1-3 to Comparative Example 3-3

An aluminum ingot including Fe, Si, and Cu of Table 1-3 was hot-rolled, and an aluminum material with a thickness of 130 μm obtained by a cold rolling of the obtained plate, were processed under conditions shown in Table 7-3 to 11-3 to obtain an aluminum materials for electrolytic capacitor electrodes.

In Tables 7-3 to 11-3, a process 1-3 to a process 11-3

correspond to a process 1-3 to a process 11-3 in Table 2-3. Detailed conditions of each process are conditions described in Table 2-3, and Table 3-3 to Table 6-3.

The aluminum materials obtained in each of the Examples and Comparative Examples were immersed in an aqueous solution including 1.0 mol/L of HCl, and 3.5 mol/L of H₂SO₄ at 75 °C of liquid temperature, and subsequently, a direct current electrolytic etching was given with a current density of 0.2 A/cm². The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90 °C to obtain etched foils having a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement. Table 7-3 to Table 11-3 show relative electrostatic capacities when the capacitance of Comparative Example 3-3 is set as 100.

[Table 7-3]

	Ingot composition	Process 1-3 Degreasing	Process 2-3 Intermediate annealing	Process 3-3 Degreasing	Process 4-3 Washing	Process 5-3 Finish cold rolling	Process 6-3 Degreasing	Process 7-3 Heating	Process 8-3 Degreasing	Process 9-3 Washing	Process 10-3 Heating	Process 11-3 Final annealing	Relative capacitance %
Example 1-3	Composition 3-3	Method 1	Condition D-3	—	—	Operation	Method 1	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	120
Example 2-3	Composition 3-3	Method 2	Condition D-3	—	—	Operation	Method 2	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	120
Example 3-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	117
Example 4-3	Composition 3-3	—	Condition D-3	—	—	Operation	Method 2	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	119
Example 5-3	Composition 3-3	Method 2	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	118
Example 6-3	Composition 3-3	—	Condition D-3	—	—	Operation	Method 1	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	119
Example 7-3	Composition 3-3	Method 1	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	119
Example 8-3	Composition 3-3	Method 2	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	119
Example 9-3	Composition 3-3	—	Condition D-3	Method 1	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	118
Example 10-3	Composition 3-3	—	Condition D-3	Method 2	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	118
Example 11-3	Composition 3-3	—	Condition D-3	Method 1	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	118
Example 12-3	Composition 3-3	—	Condition D-3	Method 2	—	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	118
Example 13-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	Method 1	Condition 27-3	—	540°C, 5 hr	119
Example 14-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	Method 2	Condition 27-3	—	540°C, 5 hr	119
Example 15-3	Composition 3-3	—	Condition D-3	—	—	Operation	Method 1	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	119

[Table 8-3]

	Ingot composition	Process 1-3 Degreasing	Process 2-3 Intermediate annealing	Process 3-3 Degreasing	Process 4-3 Washing	Process 5-3 Finish cold rolling	Process 6-3 Degreasing	Process 7-3 Heating	Process 8-3 Degreasing	Process 9-3 Washing	Process 10-3 Heating	Process 11-3 Final annealing	Relative capacitance %
Example 16-3	Composition 3-3	—	Condition D-3	—	—	Operation	Method 2	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	118
Example 17-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	Method 1	Condition 20-3	—	540°C, 5 hr	118
Example 18-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	Method 2	Condition 20-3	—	540°C, 5 hr	118
Example 19-3	Composition 4-3	—	Condition A-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	111
Example 20-3	Composition 4-3	—	Condition B-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	115
Example 21-3	Composition 4-3	—	Condition C-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	110
Example 22-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	119
Example 23-3	Composition 2-3	—	Condition E-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	110
Example 24-3	Composition 2-3	—	Condition F-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	114
Example 25-3	Composition 1-3	—	Condition G-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	109
Example 26-3	Composition 3-3	—	Condition H-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	118
Example 27-3	Composition 3-3	—	Condition I-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	117
Example 28-3	Composition 3-3	—	Condition J-3	—	—	Operation	—	Condition H4-3	—	Condition 29-3	—	540°C, 5 hr	116
Example 29-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 1-3	—	540°C, 5 hr	107
Example 30-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 2-3	—	540°C, 5 hr	114

[Table 9-3]

	Ingot composition	Process 1-3	Process 2-3	Process 3-3	Process 4-3	Process 5-3	Process 6-3	Process 7-3	Process 8-3	Process 9-3	Process 10-3	Process 11-3	Relative capacitance %
		Degreasing	Intermediate annealing	Degreasing	Washing	Finish cold rolling	Degreasing	Heating	Degreasing	Washing	Heating	Final annealing	
Example 31-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 3-3	—	540°C, 5 hr	114
Example 32-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 4-3	—	540°C, 5 hr	112
Example 33-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 5-3	—	540°C, 5 hr	109
Example 34-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 6-3	—	540°C, 5 hr	111
Example 35-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 7-3	—	540°C, 5 hr	112
Example 36-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 8-3	—	540°C, 5 hr	112
Example 37-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 9-3	—	540°C, 5 hr	113
Example 38-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 10-3	—	540°C, 5 hr	111
Example 39-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 11-3	—	540°C, 5 hr	112
Example 40-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 12-3	—	540°C, 5 hr	111
Example 41-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 13-3	—	540°C, 5 hr	112
Example 42-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 14-3	—	540°C, 5 hr	113
Example 43-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 15-3	—	540°C, 5 hr	112
Example 44-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 16-3	—	540°C, 5 hr	115
Example 45-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 17-3	—	540°C, 5 hr	116

[Table 10-3]

	Ingot composition	Process 1-3 Degreasing	Process 2-3 Intermediate annealing	Process 3-3 Degreasing	Process 4-3 Washing	Process 5-3 Finish cold rolling	Process 6-3 Degreasing	Process 7-3 Heating	Process 8-3 Degreasing	Process 9-3 Washing	Process 10-3 Heating	Process 11-3 Final annealing	Relative capacitance %
Example 46-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 18-3	—	540°C, 5 hr	118
Example 47-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 19-3	—	540°C, 5 hr	116
Example 48-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 20-3	—	540°C, 5 hr	117
Example 49-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 21-3	—	540°C, 5 hr	117
Example 50-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 22-3	—	540°C, 5 hr	117
Example 51-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 23-3	—	540°C, 5 hr	116
Example 52-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 24-3	—	540°C, 5 hr	117
Example 53-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 25-3	—	540°C, 5 hr	117
Example 54-3	Composition 3-3	—	Condition J-3	—	—	Operation	Method 1	Condition H9-3	—	Condition 26-3	—	540°C, 5 hr	110
Example 55-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H1-3	—	Condition 2-3	—	540°C, 5 hr	106
Example 56-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H2-3	—	Condition 2-3	—	540°C, 5 hr	110
Example 57-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H3-3	—	Condition 2-3	—	540°C, 5 hr	115
Example 58-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 2-3	—	540°C, 5 hr	114
Example 59-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H5-3	—	Condition 2-3	—	540°C, 5 hr	113
Example 60-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H6-3	—	Condition 2-3	—	540°C, 5 hr	106

[Table 11-3]

	Ingot composition	Process 1-3	Process 2-3	Process 3-3	Process 4-3	Process 5-3	Process 6-3	Process 7-3	Process 8-3	Process 9-3	Process 10-3	Process 11-3	Relative capacitance %
		Degreasing	Intermediate annealing	Degreasing	Washing	Finish cold rolling	Degreasing	Heating	Degreasing	Washing	Heating	Final annealing	
Example 61-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H7-3	—	Condition 2-3	—	540°C, 5 hr	105
Example 62-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H8-3	—	Condition 2-3	—	540°C, 5 hr	106
Example 63-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H9-3	—	Condition 2-3	—	540°C, 5 hr	111
Example 64-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H10-3	—	Condition 2-3	—	540°C, 5 hr	114
Example 65-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H11-3	—	Condition 2-3	—	540°C, 5 hr	110
Example 66-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H12-3	—	Condition 2-3	—	540°C, 5 hr	105
Example 67-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 3-3	—	570°C, 5 hr	105
Example 68-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 3-3	—	580°C, 5 hr	111
Example 69-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 3-3	—	470°C, 24 hr	104
Example 70-3	Composition 3-3	—	Condition D-3	—	—	Operation	—	Condition H4-3	—	Condition 3-3	—	460°C, 24 hr	103
Example 71-3	Composition 3-3	—	Condition D-3	—	Condition 28-3	Operation	—	Condition H4-3	—	Condition 27-3	—	540°C, 5 hr	116
Example 72-3	Composition 3-3	—	Condition D-3	—	Condition 2-3	Operation	Method 1	Condition H9-3	—	Condition 28-3	—	500°C, 10 hr	110
Example 73-3	Composition 3-3	—	Condition D-3	—	Condition 17-3	Operation	Method 1	Condition H9-3	—	Condition 28-3	—	520°C, 4 hr	109
Comparative Example 1-3	Composition 3-3	—	Condition K-3	—	—	Operation	—	—	—	Condition 4-3	—	540°C, 5 hr	98
Comparative Example 2-3	Composition 3-3	—	Condition K-3	—	—	Operation	—	Condition H4-3	—	—	—	540°C, 5 hr	98
Comparative Example 3-3	Composition 3-3	—	Condition K-3	—	—	Operation	—	—	—	Condition 4-3	Condition H4-3	540°C, 5 hr	100

As described above, the intermediate annealing of the aluminum materials was carried out in the oxidative atmosphere, and after termination of a cold rolling, they were heated in the oxidative atmosphere. Subsequently, a surface layer of the aluminum materials was dissolved by washing, and then a final annealing was performed, and thus aluminum materials for electrolytic capacitor electrodes having outstanding etching characteristics might be obtained.

On the other hand, in Comparative Example 1-3, the intermediate annealing was performed in a 100% nitrogen atmosphere, the surface layer of the aluminum material was removed without heating in the oxidative atmosphere by washing after the finishing rolling, and subsequently final annealing was performed. Therefore Comparative Example 1-3 shows uneven solubility of the aluminum material at the time of washing, and has a low capacitance.

In Comparative Example 2-3, the intermediate annealing in 100% nitrogen, the finish cold rolling, and the heating in the oxidative atmosphere were carried sequentially, and subsequently, the final annealing was performed, without performing the surface layer removing of the aluminum material. Therefore, since much contamination layers and oils at the time of rolling remain, Comparative Example 2-3 shows a low capacitance.

In Comparative Example 3-3, the intermediate annealing in 100% nitrogen, the finish cold rolling, and the surface layer removing of the aluminum material by washing were carried out sequentially, and, subsequently the heating was performed in the

oxidative atmosphere. Therefore, the Comparative Example 3-3 has a higher capacitance as compared with Comparative Example 1-3 and Comparative Example 2-3. However, since the surface layer of the aluminum material unevenly dissolved at the time of washing was not enough equalized by heating in the oxidative atmosphere, a capacitance of the Comparative Example concerned is less than the capacitance in the Example.

[Example using a coiled aluminum material]

A hot-rolling and a cold rolling were given to an aluminum slab having a composition in Table 12-3 to obtain an aluminum material coil having a width of 500 mm. The contents of each composition are same as shown in Table 8-1.

And processes of an intermediate annealing, a finish cold rolling, a heating in the oxidative atmosphere, and a surface layer removing were given sequentially to this aluminum material coil under conditions as shown in Table 12-3 to obtain an aluminum material having a thickness of 110 μm and a length of 2000 m. A surface layer was removed by washing in Comparative Example 301, without performing a heating in the oxidative atmosphere.

Subsequently, a final annealing was performed at 540 °C in argon atmosphere for 4 hr, and an aluminum material for electrolytic capacitor electrodes was obtained.

The conditions of the intermediate annealing, the heating conditions in the oxidative atmosphere, and the conditions of the surface layer of aluminum material removing are same as the conditions shown in Table 10-2, Table 9-1, and Table 10-1.

respectively. In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkaline cleaning liquid.

The aluminum material coils obtained in each of the Example and the Comparative Example were uncoiled and immersed in an aqueous solution including 1.0 mol/L of HCl, and 3.5 mol/L of H₂SO₄ at 75 °C of liquid temperature, and subsequently, a direct current electrolytic etching was given with a current density 0.2 A/cm². The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90 °C to obtain etched foils having a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement.

Table 12-3 shows relative electrostatic capacities when the electrostatic capacitance of Comparative Example 301 is set as 100.

[Table 12-3]

	Composition	Intermediate annealing	Finish cold rolling	Heat in an oxidative atmosphere	Surface layer removing	Final annealing	Relative capacitance %
Example 301	Composition 103	Condition A2	Rolling reduction: 20%	Condition H101	Condition 103	530°C, 4 hr	120
Example 302	Composition 102	Condition C2	Rolling reduction: 20%	Condition H101	Condition 103	530°C, 4 hr	118
Example 303	Composition 101	Condition E2	Rolling reduction: 20%	Condition H101	Condition 103	530°C, 4 hr	113
Example 304	Composition 102	Condition C2	Rolling reduction: 20%	Condition H102	Condition 103	530°C, 4 hr	118
Example 305	Composition 102	Condition C2	Rolling reduction: 20%	Condition H101	Condition 102	530°C, 4 hr	115
Example 306	Composition 102	Condition C2	Rolling reduction: 20%	Condition H101	Condition 101	530°C, 4 hr	112
Comparative Example 301	Composition 102	Condition H2	Rolling reduction: 20%	—	Condition 101	530°C, 4 hr	100

As is understood from results of the Tables, in Examples 301 to 306, the intermediate annealing in the oxidative atmosphere was carried out, after termination of the cold rolling, the heating in the oxidative atmosphere was performed before final annealing, and subsequently, the surface layer of aluminum material was removed by washing. And therefore uniform solubility of the aluminum materials at the time of a surface layer removing was acquired, and Examples 301 to 306 have outstanding etching characteristics and high capacitance.

On the other hand, in Comparative Example 301, after the intermediate annealing was carried out in a not less than 99.99 volume % of nitrogen atmosphere, the surface layer of aluminum material was removed by washing without the heating in the oxidative atmosphere before the final annealing and after termination of the cold rolling. And therefore, a solubility of the aluminum material at the time of the surface layer of aluminum material removing by washing is uneven, and thus Comparative Example 301 has a low capacitance.

4. Fourth Example (corresponding to manufacturing process concerning fourth embodiment)

[Example using a sheet shaped aluminum material]

A plate obtained by a hot-rolling of an aluminum slab was cold-rolled, and, subsequently an intermediate annealing was given to prepare a sheet shaped aluminum material with a purity of 99.99 mass %. Table 1-4 shows processes carried out after the

intermediate annealing, Table 2-4 shows conditions of a process 3-4 (heating) in Table 1-4, and Table 3-4 and 4-4 show conditions of a process 4-4 (aluminum material surface layer removing by washing) in Table 1-4. All the thicknesses of the aluminum materials obtained after the final annealing were adjusted as 110 μm by regulation of the rolling reduction of the cold rolling performed before the intermediate annealing.

In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

[Table 1-4]

Process

Process 1-4	Tensile strain applying	Apply tensile strain of 7% by the one-axis tension of a rolling direction
Process 2-4	Finish cold rolling (Process for Comparative Examples)	Operate at a rolling reduction of 20%
Process 3-4	Heating	Operate on the conditions in Table 2-4 in an atmosphere containing oxygen
Process 4-4	Washing	Remove the surface layer of an aluminum material on the conditions in Table 3-4 and Table 4-4, rinse with water and dry in an air
Process 5-4	Heating (Process for Comparative Examples)	Operate on the conditions in Table 2-4 in an atmosphere containing oxygen.
Process 6-4	Final annealing	Operate in an argon atmosphere

* The thickness of an aluminum material obtained after final annealing was entirely set to 110 μm by adjusting the reduction of cold rolling before intermediate annealing.

[Table 2-4]

Conditions in Process 3-4 and Process 5-4 (Heating in an oxidative atmosphere)

Atmosphere	Heating temperature ($^{\circ}\text{C}$)	Heating time	Heating condition
Air	50	72 hr	Condition H1-4
	70	48 hr	Condition H2-4
	100	24 hr	Condition H3-4
	150	24 hr	Condition H4-4
	200	30 min	Condition H5-4
	350	10 sec	Condition H6-4
	380	5 sec	Condition H7-4
	330	70 sec	Condition H8-4
	100	30 min	Condition H9-4
Oxygen: 5 volume %, Nitrogen: 95 volume %	100	24 hr	Condition H10-4
Oxygen: 1 volume %, Nitrogen: 99 volume %	100	24 hr	Condition H11-4
Oxygen: 0.1 volume %, Nitrogen: 99.9 volume %	100	24 hr	Condition H12-4

[Table 3-4]

Conditions in Process 4-4 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	7 nm	Condition 1-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	10 nm	Condition 2-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 3-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	190 nm	Condition 4-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	490 nm	Condition 5-4
Immerse in a calcium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 6-4
Immerse in a potassium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 7-4
Immerse in a sodium orthosilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 8-4
Immerse in a sodium metasilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 9-4
Immerse in a trisodium phosphate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 10-4
Immerse in a sodium carbonate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 11-4
Immerse in a (sodium hydroxide of 0.2 mass %+calcium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 12-4
Immerse in a (sodium hydroxide of 0.2 mass %+potassium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 13-4
Immerse in a (sodium hydroxide of 0.2 mass %+sodium orthosilicate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 14-4
Immerse in a (sodium hydroxide of 0.2 mass %+trisodium phosphate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 15-4

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 4-4]

Conditions in Process 4-4 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 16-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 17-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 18-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in an orthophosphoric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 19-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an sulfuric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 20-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +a nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 21-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 22-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 23-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 24-4
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 25-4
Immerse in a hydrochloric acid aqueous solution of 8 mass % at 80°C (*1)→Rinse with water→Dry	1.3 nm	Condition 26-4
Immerse in a sulfuric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 27-4
Immerse in a nitric acid aqueous solution of 4.5 mass % at 80°C (*1)→Rinse with water→Dry	1.7 nm	Condition 28-4
Immerse in a phosphoric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 29-4

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

A plate obtained by a hot-rolling of an aluminum slab was cold-rolled, and then an intermediate annealing was further given to obtain an aluminum material with a purity 99.99 mass %. A tensile strain was given to this aluminum material as in a description in Table 5-4 (process 1-4), and then a heating for 24 hr was performed at 150 °C in air (process 3-4). Subsequently, this aluminum material was washed by immersion into 80 °C 20 mass % sulfuric acid aqueous solution to remove 10 nm of a surface layer (process 4-4). A final annealing was given to the aluminum material after washing at 550 °C in argon atmosphere for 4 hr (process 6-4), and an aluminum material for electrolytic capacitor electrodes was obtained.

Example 2-4 to Example 45-4, Comparative Example 1-4 to Comparative Example 4-4

Aluminum materials for electrolytic capacitor electrodes were obtained under conditions shown in Table 5-4 and 6-4.

After the aluminum materials obtained in each of the Examples and Comparative Examples were immersed in an aqueous solution including 1.0 mol/L of HCl, and 3.5 mol/L of H₂SO₄ at 75 °C of liquid temperature, a direct current electrolytic etching was given with a current density 0.2 A/cm². The aluminum materials after electrolytic treatment were further immersed in the hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90 °C to obtain etched foils having a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to

obtain samples for capacitance measurement.

Table 5-4 to 6-4 show relative electrostatic capacities when the capacitance of Comparative Example 4-4 is set as 100.

[Table 5-4]

	Process 1-4	Process 2-4	Process 3-4	Process 4-4	Process 5-4	Process 6-4	Relative capacitance %
Example 1-4	Operation	—	Condition H4-4	Condition 27-4	—	550°C, 4 hr	119
Example 2-4	Operation	—	Condition H4-4	Condition 29-4	—	550°C, 4 hr	119
Example 3-4	Operation	—	Condition H4-4	Condition 1-4	—	550°C, 4 hr	106
Example 4-4	Operation	—	Condition H4-4	Condition 2-4	—	550°C, 4 hr	113
Example 5-4	Operation	—	Condition H4-4	Condition 3-4	—	550°C, 4 hr	113
Example 6-4	Operation	—	Condition H4-4	Condition 4-4	—	550°C, 4 hr	111
Example 7-4	Operation	—	Condition H4-4	Condition 5-4	—	550°C, 4 hr	108
Example 8-4	Operation	—	Condition H4-4	Condition 6-4	—	550°C, 4 hr	110
Example 9-4	Operation	—	Condition H4-4	Condition 7-4	—	550°C, 4 hr	111
Example 10-4	Operation	—	Condition H4-4	Condition 8-4	—	550°C, 4 hr	111
Example 11-4	Operation	—	Condition H4-4	Condition 9-4	—	550°C, 4 hr	112
Example 12-4	Operation	—	Condition H4-4	Condition 10-4	—	550°C, 4 hr	110
Example 13-4	Operation	—	Condition H4-4	Condition 11-4	—	550°C, 4 hr	111
Example 14-4	Operation	—	Condition H4-4	Condition 12-4	—	550°C, 4 hr	110
Example 15-4	Operation	—	Condition H4-4	Condition 13-4	—	550°C, 4 hr	111
Example 16-4	Operation	—	Condition H4-4	Condition 14-4	—	550°C, 4 hr	112
Example 17-4	Operation	—	Condition H4-4	Condition 15-4	—	550°C, 4 hr	111
Example 18-4	Operation	—	Condition H4-4	Condition 16-4	—	550°C, 4 hr	114
Example 19-4	Operation	—	Condition H4-4	Condition 17-4	—	550°C, 4 hr	115
Example 20-4	Operation	—	Condition H4-4	Condition 18-4	—	550°C, 4 hr	117
Example 21-4	Operation	—	Condition H4-4	Condition 19-4	—	550°C, 4 hr	115
Example 22-4	Operation	—	Condition H4-4	Condition 20-4	—	550°C, 4 hr	116
Example 23-4	Operation	—	Condition H4-4	Condition 21-4	—	550°C, 4 hr	116
Example 24-4	Operation	—	Condition H4-4	Condition 22-4	—	550°C, 4 hr	116
Example 25-4	Operation	—	Condition H4-4	Condition 23-4	—	550°C, 4 hr	115
Example 26-4	Operation	—	Condition H4-4	Condition 24-4	—	550°C, 4 hr	116
Example 27-4	Operation	—	Condition H4-4	Condition 25-4	—	550°C, 4 hr	116
Example 28-4	Operation	—	Condition H1-4	Condition 2-4	—	550°C, 4 hr	105
Example 29-4	Operation	—	Condition H2-4	Condition 2-4	—	550°C, 4 hr	109

[Table 6-4]

	Process 1-4	Process 2-4	Process 3-4	Process 4-4	Process 5-4	Process 6-4	Relative capacitance %
Example 30-4	Operation	—	Condition H3-4	Condition 2-4	—	550°C, 4 hr	114
Example 31-4	Operation	—	Condition H4-4	Condition 2-4	—	550°C, 4 hr	113
Example 32-4	Operation	—	Condition H5-4	Condition 2-4	—	550°C, 4 hr	112
Example 33-4	Operation	—	Condition H6-4	Condition 2-4	—	550°C, 4 hr	105
Example 34-4	Operation	—	Condition H7-4	Condition 2-4	—	550°C, 4 hr	104
Example 35-4	Operation	—	Condition H8-4	Condition 2-4	—	550°C, 4 hr	105
Example 36-4	Operation	—	Condition H9-4	Condition 2-4	—	550°C, 4 hr	110
Example 37-4	Operation	—	Condition H10-4	Condition 2-4	—	550°C, 4 hr	113
Example 38-4	Operation	—	Condition H11-4	Condition 2-4	—	550°C, 4 hr	109
Example 39-4	Operation	—	Condition H12-4	Condition 2-4	—	550°C, 4 hr	104
Example 40-4	Operation	—	Condition H9-4	Condition 26-4	—	550°C, 4 hr	110
Example 41-4	Operation	—	Condition H9-4	Condition 28-4	—	550°C, 4 hr	111
Example 42-4	Operation	—	Condition H4-4	Condition 27-4	—	570°C, 4 hr	117
Example 43-4	Operation	—	Condition H4-4	Condition 27-4	—	580°C, 4 hr	116
Example 44-4	Operation	—	Condition H4-4	Condition 27-4	—	470°C, 4 hr	109
Example 45-4	Operation	—	Condition H4-4	Condition 27-4	—	460°C, 4 hr	108
Comparative Example 1-4	Operation	—	—	—	—	550°C, 4 hr	98
Comparative Example 2-4	—	Operation	—	Condition 4-4	—	550°C, 4 hr	98
Comparative Example 3-4	—	Operation	Condition H4-4	—	—	550°C, 4 hr	98
Comparative Example 4-4	—	Operation	—	Condition 4-4	Condition H4-4	550°C, 4 hr	100

In Example 1-4 to 45-4 in the Table, a tensile strain was given to the aluminum materials obtained by a hot-rolling, a cold rolling, and an intermediate annealing carried out sequentially, the aluminum materials are heated in the oxidative atmosphere after application of the tensile strain, and subsequently, the surface layer of aluminum material was dissolved by washing, and a final annealing was further given. Thereby aluminum materials for electrolytic capacitor electrodes having outstanding etching characteristics may be obtained.

On the other hand, in Comparative Example 1-4, the final annealing was performed, without the heating in the oxidative atmosphere, and the surface layer removing of the aluminum materials was performed by washing after application of tensile strain. Therefore, Comparative Example 1-4 has uneven solubility in the aluminum material surface at the time of etching, and capacitance lower than in the Example. In Comparative Example 2-4, the surface layer of aluminum material was removed without heating in the oxidative atmosphere by washing after the finish cold rolling, and then the annealing was performed, and therefore the Comparative Example has uneven solubility of the aluminum material at the time of washing. In Comparative Example 3-4, the finish cold rolling and the heating in the oxidative atmosphere were carried out sequentially, and subsequently the annealing was performed, without performing the surface layer removing of the aluminum material and therefore the Comparative Example has much

contamination layers and oils at the time of rolling remained. For these reasons, each of these Comparative Examples has a low capacitance. In Comparative Example 4-4, the finish cold rolling and the surface layer removing of the aluminum material by washing were carried out sequentially, and, subsequently the heating was given in the oxidative atmosphere. The Comparative Example 4-4 thus has a higher capacitance as compared with Comparative Example 1-4 to Comparative Example 3-4. However, since the surface layer of the aluminum material dissolved unevenly at the time of washing may not be enough equalized by the heating in the oxidative atmosphere, the capacitance is less than the capacitance in the Example.

[Example using a coiled aluminum material]

A hot-rolling and a cold rolling were given to the aluminum slab having the composition shown in Table 7-4 to obtain an aluminum material coil with a width of 500 mm. The contents of each composition are same as shown in Table 8-1.

And after the intermediate annealing was given to this aluminum material coil, under conditions as shown in Table 7-4, each process of the tensile strain application, the heating in the oxidative atmosphere, and the surface layer removing was carried sequentially to obtain an aluminum material having a thickness of 110 μm and a length of 2000 m. In Comparative Example 501, the heating in the oxidative atmosphere and the surface layer removing were not performed.

Subsequently, the final annealing for 5 hr was carried out

at 520 °C in argon atmosphere to obtain an aluminum material for electrolytic capacitor electrodes.

Table 7-4 shows the conditions of tensile strain application. Each condition of the heating in the oxidative atmosphere and the surface layer removing are same as conditions shown in Table 9-1 and Table 10-1, respectively. In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

Aluminum material coils obtained in each of the Examples and Comparative Examples were uncoiled and immersed in an aqueous solution including 1.0 mol/L of HCl, and 3.5 mol/L of H₂SO₄ at 75 °C of liquid temperature, and subsequently, a direct current electrolytic etching was given with a current density 0.2 A/cm². The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90 °C to obtain etched foils having a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement.

Table 7-4 shows relative electrostatic capacities when the capacitance of Comparative Example 501 is set as 100.

[Table 7-4]

	Composition	Tensile strain applying	Heating in an oxidative atmosphere	Washing	Final annealing	Relative capacitance %
Example 501	Composition 102	Tensile strain: 6%	Condition H101	Condition 103	520°C, 5 hr	121
Example 502	Composition 102	Tensile strain: 6%	Condition H102	Condition 103	520°C, 5 hr	121
Example 503	Composition 102	Tensile strain: 6%	Condition H101	Condition 102	520°C, 5 hr	117
Example 504	Composition 102	Tensile strain: 6%	Condition H101	Condition 101	520°C, 5 hr	115
Comparative Example 501	Composition 102	Tensile strain: 6%	—	—	520°C, 5 hr	100

As is understood from results of the Tables, in Examples 501 to 504, after tensile strain application, the heating in oxidative atmosphere was performed before the final annealing, and subsequently the surface layer of the aluminum materials was removed by washing. For this reason, the solubility of the aluminum materials at the time of surface layer removing became uniform, and thus the Examples have outstanding etching characteristics and a high capacitance.

On the other hand, in Comparative Example 501, since the heating in the oxidative atmosphere and the surface layer removing of the aluminum material by washing were not performed, the solubility of the aluminum material at the time of etching became uneven, and low capacitance is shown.

5. Fifth Example (corresponding to manufacturing process concerning Fifth embodiment)

[Example using sheet shaped aluminum material]

Aluminum ingots with different composition were prepared. Table 1-5 shows concentrations of Fe and Si, and Cu included in the ingots. Plates obtained by hot-rolling of these aluminum ingots were cold-rolled, and sheet shaped aluminum materials were prepared. Table 2-5 shows processes from an intermediate annealing to a final annealing, Table 3-5 shows conditions of a process 1-5 (intermediate annealing) in Table 2-5, Table 4-5 and 5-5 show conditions of a process 2-5 and a process 6-5 (aluminum material surface layer removing by washing) in Table 2-5, and Table

6-5 shows conditions of a process 5-5 and a process 7-5 (heating in oxidative atmosphere) in Table 2-5. By adjusting a rolling reduction in the cold rolling performed before the intermediate annealing, all thicknesses of aluminum materials obtained after the final annealing were set as 110 μm .

In addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

[Table 1-5]

Si and Fe and Cu concentration of an aluminum ingot

	Concentration/mass %		
	Fe	Si	Cu
Composition 1-5	0.0030	0.0030	0.0045
Composition 2-5	0.0024	0.0024	0.0040
Composition 3-5	0.0015	0.0022	0.0055
Composition 4-5	0.0008	0.0008	0.0060

[Table 2-5]

Process

Process 1-5	Intermediate annealing	Operate on the conditions in Table 3-5.
Process 2-5	Washing	Remove the surface layer of an aluminum material on the conditions in Table 4-5 and Table 5-5, rinse with water and dry in an air
Process 3-5	Tensile strain giving	Give tensile strain of 6 % by the one-axis tension of a rolling direction
Process 4-5	Finish cold rolling (Process for Comparative Examples)	Operate at a rolling reduction of 20 %
Process 5-5	Heat in an oxidative atmosphere	Operate on the conditions in Table 6-5 in an atmosphere containing oxygen
Process 6-5	Washing	Remove the surface layer of an aluminum material on the conditions in Table 4-5 and Table 5-5, rinse with water and dry in an air
Process 7-5	Heat in an oxidative atmosphere (Process for Comparative Examples)	Operate on the conditions in Table 6-5 in an atmosphere containing oxygen
Process 8-5	Final annealing	Operate in an argon atmosphere

[Table 3-5]

Conditions of Process 1-5 (intermediate annealing)

Atmosphere	Heating temperature °C	Heating time	Heating condition
Air	210	12 hr	Condition A-5
	210	30 hr	Condition B-5
	230	1 hr	Condition C-5
	260	12 hr	Condition D-5
	275	1 hr	Condition E-5
	275	7 hr	Condition F-5
	290	1 hr	Condition G-5
Oxygen: 5 volume %, nitrogen: 95 volume %	260	12 hr	Condition H-5
Oxygen: 1 volume %, nitrogen: 99 volume %	260	12 hr	Condition I-5
Oxygen: 0.1 volume %, nitrogen: 99.9 volume %	260	12 hr	Condition J-5
Nitrogen: 99.99 volume % or more	260	12 hr	Condition K-5 (condition for Comparative Examples)

[Table 4-5]

Conditions in Process 2-5 and Process 6-5 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	7 nm	Condition 1-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	10 nm	Condition 2-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 3-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	190 nm	Condition 4-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	490 nm	Condition 5-5
Immerse in a calcium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 6-5
Immerse in a potassium hydrate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 7-5
Immerse in a sodium orthosilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 8-5
Immerse in a sodium metasilicate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 9-5
Immerse in a trisodium phosphate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 10-5
Immerse in a sodium carbonate aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 11-5
Immerse in a (sodium hydroxide of 0.2 mass %+calcium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 12-5
Immerse in a (sodium hydroxide of 0.2 mass %+potassium hydroxide of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 13-5
Immerse in a (sodium hydroxide of 0.2 mass %+sodium orthosilicate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 14-5
Immerse in a (sodium hydroxide of 0.2 mass %+trisodium phosphate of 0.2 mass %) aqueous solution at 40°C (*1)→Rinse with water→Dry	100 nm	Condition 15-5

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 5-5]

Conditions in Process 2-5 and Process 6-5 (Removal of the surface layer of an aluminum material by washing)

Washing method	Quantity of removal of the surface layer of an aluminum material	Condition number
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 16-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 17-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 18-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in an orthophosphoric acid aqueous solution of 5 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 19-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an sulfuric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 20-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +a nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 21-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a hydrochloric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 22-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an nitric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 23-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a sulfuric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 24-5
Immerse in a sodium hydroxide aqueous solution of 0.2 mass % at 40°C (*1)→Rinse with water→Immerse in a nitric acid aqueous solution of 3 mass % +an orthophosphoric acid aqueous solution of 3 mass % at 40°C for 1 minute→Rinse with water→Dry	100 nm	Condition 25-5
Immerse in a hydrochloric acid aqueous solution of 8 mass % at 80°C (*1)→Rinse with water→Dry	1.3 nm	Condition 26-5
Immerse in a sulfuric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 27-5
Immerse in a nitric acid aqueous solution of 4.5 mass % at 80°C (*1)→Rinse with water→Dry	1.7 nm	Condition 28-5
Immerse in a phosphoric acid aqueous solution of 20 mass % at 80°C (*1)→Rinse with water→Dry	10 nm	Condition 29-5

*1: The quantity of removal of the surface layer of an aluminum material was controlled by changing immersion time in solutions.

[Table 6-5]

Conditions in Process 5-5 and Process 7-5 (Heating in an oxidative atmosphere)

Atmosphere	Heating temperature °C	Heating time	Heating condition
Air	50	72 hr	Condition H1-5
	70	48 hr	Condition H2-5
	100	24 hr	Condition H3-5
	150	24 hr	Condition H4-5
	200	30 minutes	Condition H5-5
	350	10 seconds	Condition H6-5
	380	4 seconds	Condition H7-5
	330	70 seconds	Condition H8-5
	100	30 minutes	Condition H9-5
Oxygen: 5 volume %, Nitrogen: 95 volume %	100	24 hr	Condition H10-5
Oxygen: 1 volume %, Nitrogen: 99 volume %	100	24 hr	Condition H11-5
Oxygen: 0.1 volume %, Nitrogen: 99.9 volume %	100	24 hr	Condition H12-5

Example 1-5

A plate obtained by the hot-rolling of the aluminum ingot in Table 1-5 having Fe 0.0015 mass %, Si 0.0022 mass %, and Cu 0.0055 mass % (composition 3 - 5) was cold-rolled to obtain an aluminum material. As described in Table 7-5 the aluminum material was given the intermediate annealing for 12 hr at 260 °C in air (process 1-5, condition D-5), and subsequently, a 6% of tensile strain was given (process 3-5). A heating was carried out to the aluminum material in air at 150 °C for 24 hr after a tensile strain application (process 5-5 and condition H4-5), and furthermore, 10 nm of surface layer of the aluminum material was removed by immersion into a 80 °C 20 mass % sulfuric acid aqueous solution (process 6-5, conditions 27-5). Subsequently, the final annealing for 5 hr was given to the aluminum material at 550 °C in argon atmosphere (process 8-5) to obtain an aluminum material for electrolytic capacitor electrodes.

Example 2-5 to Example 139-5, Comparative Example 1-5 to Comparative Example 5-5

A plate obtained by hot-rolling of an ingot having a composition shown in Table 1-5 was cold-rolled to obtain an aluminum material. The aluminum material was processed under conditions shown in Table 7-5 to 16-5, and aluminum materials for electrolytic capacitor electrodes were obtained.

The aluminum materials obtained in each of the Examples and Comparative Examples were immersed in an aqueous solution including 1.0 mol/L of HCl, and 3.5 mol/L of H₂SO₄ at 75 °C of liquid

temperature, and subsequently, a direct current electrolytic etching was given to the aluminum materials with a current density 0.2 A/cm^2 in the aqueous solution having a same composition at a same temperature. The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90°C to obtain etched foils having a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement.

Table 7-5 to Table 16-5 show relative electrostatic capacities when the capacitance of Comparative Example 4-5 is set as 100.

[Table 7-5]

	Ingot composition	Process 1-5		Process 2-5		Process 3-5		Process 4-5		Process 5-5		Process 6-5		Process 7-5		Process 8-5		Relative capacitance %
		Intermediate annealing	Condition	Washing	Tensile strain applying	Finish cold rolling	Heating	Washing	Heating	Washing	Heating	Washing	Heating	Final annealing				
Example 1-5	Composition 3-5	Condition D-5	—	—	Operation	—	Condition H4-5	Condition 27-5	—	Condition H4-5	Condition 27-5	—	550°C, 5 hr	122				
Example 2-5	Composition 3-5	Condition D-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	122				
Example 3-5	Composition 4-5	Condition A-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	112				
Example 4-5	Composition 4-5	Condition B-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	117				
Example 5-5	Composition 4-5	Condition C-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	112				
Example 6-5	Composition 3-5	Condition D-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	122				
Example 7-5	Composition 2-5	Condition E-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	112				
Example 8-5	Composition 2-5	Condition F-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	116				
Example 9-5	Composition 1-5	Condition G-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	111				
Example 10-5	Composition 3-5	Condition H-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	120				
Example 11-5	Composition 3-5	Condition I-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	120				
Example 12-5	Composition 3-5	Condition J-5	—	—	Operation	—	Condition H4-5	Condition 29-5	—	Condition H4-5	Condition 29-5	—	550°C, 5 hr	118				
Example 13-5	Composition 3-5	Condition D-5	—	—	Operation	—	Condition H4-5	Condition 1-5	—	Condition H4-5	Condition 1-5	—	550°C, 5 hr	109				
Example 14-5	Composition 3-5	Condition D-5	—	—	Operation	—	Condition H4-5	Condition 2-5	—	Condition H4-5	Condition 2-5	—	550°C, 5 hr	116				
Example 15-5	Composition 3-5	Condition D-5	—	—	Operation	—	Condition H4-5	Condition 3-5	—	Condition H4-5	Condition 3-5	—	550°C, 5 hr	116				

[Table 8-5]

	Ingot composition	Process 1-5		Process 2-5		Process 3-5		Process 4-5		Process 5-5		Process 6-5		Process 7-5		Process 8-5		Relative capacitance %
		Intermediate annealing	Washing	Tensile strain applying	Finish cold rolling	Heating	Washing	Heating	Final annealing									
Example 16-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 4-5	—	—	550°C, 5 hr	114							
Example 17-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 5-5	—	—	550°C, 5 hr	111							
Example 18-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 6-5	—	—	550°C, 5 hr	113							
Example 19-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 7-5	—	—	550°C, 5 hr	113							
Example 20-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 8-5	—	—	550°C, 5 hr	114							
Example 21-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 9-5	—	—	550°C, 5 hr	113							
Example 22-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 10-5	—	—	550°C, 5 hr	112							
Example 23-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 11-5	—	—	550°C, 5 hr	113							
Example 24-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 12-5	—	—	550°C, 5 hr	113							
Example 25-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 13-5	—	—	550°C, 5 hr	113							
Example 26-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 14-5	—	—	550°C, 5 hr	114							
Example 27-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 15-5	—	—	550°C, 5 hr	114							
Example 28-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 16-5	—	—	550°C, 5 hr	117							
Example 29-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 17-5	—	—	550°C, 5 hr	118							
Example 30-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 18-5	—	—	550°C, 5 hr	120							

[Table 9-5]

	Ingot composition	Process 1-5	Process 2-5	Process 3-5	Process 4-5	Process 5-5	Process 6-5	Process 7-5	Process 8-5	Relative capacitance %
		Intermediate annealing	Washing	Tensile strain applying	Finish cold rolling	Heating	Washing	Heating	Final annealing	
Example 31	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 19-5	—	550°C, 5 hr	119
Example 32	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 20-5	—	550°C, 5 hr	119
Example 33	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 21-5	—	550°C, 5 hr	119
Example 34	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 22-5	—	550°C, 5 hr	119
Example 35	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 23-5	—	550°C, 5 hr	118
Example 36	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 24-5	—	550°C, 5 hr	119
Example 37	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 25-5	—	550°C, 5 hr	119
Example 38	Composition 3-5	Condition J-5	—	Operation	—	Condition H9-5	Condition 26-5	—	550°C, 5 hr	112
Example 39	Composition 3-5	Condition D-5	—	Operation	—	Condition H1-5	Condition 2-5	—	550°C, 5 hr	107
Example 40	Composition 3-5	Condition D-5	—	Operation	—	Condition H2-5	Condition 2-5	—	550°C, 5 hr	112
Example 41	Composition 3-5	Condition D-5	—	Operation	—	Condition H3-5	Condition 2-5	—	550°C, 5 hr	116
Example 42	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 2-5	—	550°C, 5 hr	115
Example 43	Composition 3-5	Condition D-5	—	Operation	—	Condition H5-5	Condition 2-5	—	550°C, 5 hr	114
Example 44	Composition 3-5	Condition D-5	—	Operation	—	Condition H6-5	Condition 2-5	—	550°C, 5 hr	108
Example 45	Composition 3-5	Condition D-5	—	Operation	—	Condition H7-5	Condition 2-5	—	550°C, 5 hr	107

[Table 10-5]

	Ingot composition	Process 1-5 Intermediate annealing	Process 2-5 Washing	Process 3-5 Tensile strain applying	Process 4-5 Finish cold rolling	Process 5-5 Heating	Process 6-5 Washing	Process 7-5 Heating	Process 8-5 Final annealing	Relative capacitance %
Example 46-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H8-5	Condition 2-5	—	550°C, 5 hr	108
Example 47-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H9-5	Condition 2-5	—	550°C, 5 hr	113
Example 48-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H10-5	Condition 2-5	—	550°C, 5 hr	115
Example 49-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H11-5	Condition 2-5	—	550°C, 5 hr	112
Example 50-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H12-5	Condition 2-5	—	550°C, 5 hr	106
Example 51-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 3-5	—	570°C, 5 hr	112
Example 52-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 3-5	—	580°C, 5 hr	107
Example 53-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 3-5	—	470°C, 24 hr	106
Example 54-5	Composition 3-5	Condition D-5	—	Operation	—	Condition H4-5	Condition 3-5	—	460°C, 24 hr	105
Example 55-5	Composition 3-5	Condition D-5	Condition 28-5	Operation	—	Condition H4-5	Condition 27-5	—	550°C, 5 hr	118
Example 56-5	Composition 3-5	Condition D-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	117
Example 57-5	Composition 3-5	Condition D-5	Condition 29-5	Operation	—	—	—	—	550°C, 5 hr	117
Example 58-5	Composition 4-5	Condition A-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	112
Example 59-5	Composition 4-5	Condition B-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	113
Example 60-5	Composition 4-5	Condition C-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	112

[Table 11-5]

	Ingot composition	Process 1-5 Intermediate annealing	Process 2-5 Washing	Process 3-5 Tensile strain applying	Process 4-5 Finish cold rolling	Process 5-5 Heating	Process 6-5 Washing	Process 7-5 Heating	Process 8-5 Final annealing	Relative capacitance %
Example 61-5	Composition 2-5	Condition E-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	113
Example 62-5	Composition 2-5	Condition F-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	113
Example 63-5	Composition 1-5	Condition G-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	113
Example 64-5	Composition 3-5	Condition H-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	114
Example 65-5	Composition 3-5	Condition I-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	113
Example 66-5	Composition 3-5	Condition J-5	Condition 27-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 67-5	Composition 3-5	Condition D-5	Condition 1-5	Operation	—	—	—	—	550°C, 5 hr	106
Example 68-5	Composition 3-5	Condition D-5	Condition 2-5	Operation	—	—	—	—	550°C, 5 hr	108
Example 69-5	Composition 3-5	Condition D-5	Condition 3-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 70-5	Composition 3-5	Condition D-5	Condition 4-5	Operation	—	—	—	—	550°C, 5 hr	110
Example 71-5	Composition 3-5	Condition D-5	Condition 5-5	Operation	—	—	—	—	550°C, 5 hr	108
Example 72-5	Composition 3-5	Condition D-5	Condition 6-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 73-5	Composition 3-5	Condition D-5	Condition 7-5	Operation	—	—	—	—	550°C, 5 hr	112
Example 74-5	Composition 3-5	Condition D-5	Condition 8-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 75-5	Composition 3-5	Condition D-5	Condition 9-5	Operation	—	—	—	—	550°C, 5 hr	111

[Table 12-5]

	Ingot composition	Process 1-5	Process 2-5	Process 3-5	Process 4-5	Process 5-5	Process 6-5	Process 7-5	Process 8-5	Relative capacitance %
		Intermediate annealing	Washing	Tensile strain applying	Finish cold rolling	Heating	Washing	Heating	Final annealing	
Example 76-5	Composition 3-5	Condition D-5	Condition 10-5	Operation	—	—	—	—	550°C, 5 hr	112
Example 77-5	Composition 3-5	Condition D-5	Condition 11-5	Operation	—	—	—	—	550°C, 5 hr	112
Example 78-5	Composition 3-5	Condition D-5	Condition 12-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 79-5	Composition 3-5	Condition D-5	Condition 13-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 80-5	Composition 3-5	Condition D-5	Condition 14-5	Operation	—	—	—	—	550°C, 5 hr	112
Example 81-5	Composition 3-5	Condition D-5	Condition 15-5	Operation	—	—	—	—	550°C, 5 hr	110
Example 82-5	Composition 3-5	Condition D-5	Condition 16-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 83-5	Composition 3-5	Condition D-5	Condition 17-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 84-5	Composition 3-5	Condition D-5	Condition 18-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 85-5	Composition 3-5	Condition D-5	Condition 19-5	Operation	—	—	—	—	550°C, 5 hr	110
Example 86-5	Composition 3-5	Condition D-5	Condition 20-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 87-5	Composition 3-5	Condition D-5	Condition 21-5	Operation	—	—	—	—	550°C, 5 hr	111
Example 88-5	Composition 3-5	Condition D-5	Condition 22-5	Operation	—	—	—	—	550°C, 5 hr	110
Example 89-5	Composition 3-5	Condition D-5	Condition 23-5	Operation	—	—	—	—	550°C, 5 hr	110
Example 90-5	Composition 3-5	Condition D-5	Condition 24-5	Operation	—	—	—	—	550°C, 5 hr	110

[Table 13-5]

	Ingot composition	Process 1-5		Process 2-5		Process 3-5		Process 4-5		Process 5-5		Process 6-5		Process 7-5		Process 8-5		Relative capacitance %
		Intermediate annealing	Condition	Washing	Condition	Tensile strain applying	Operation	Finish cold rolling	Condition	Heating	Condition	Washing	Condition	Heating	Condition	Final annealing	Condition	
Example 91-5	Composition 3-5	Condition D-5	Condition	Condition 25-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	550°C, 5 hr	—	111
Example 92-5	Composition 3-5	Condition J-5	Condition	Condition 26-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	550°C, 5 hr	—	109
Example 93-5	Composition 3-5	Condition D-5	Condition	Condition 28-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	550°C, 5 hr	—	114
Example 94-5	Composition 3-5	Condition D-5	Condition	Condition 3-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	570°C, 5 hr	—	108
Example 95-5	Composition 3-5	Condition D-5	Condition	Condition 3-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	580°C, 5 hr	—	107
Example 96-5	Composition 3-5	Condition D-5	Condition	Condition 3-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	470°C, 24 hr	—	106
Example 97-5	Composition 3-5	Condition D-5	Condition	Condition 3-5	Condition	Operation	Operation	—	—	—	—	—	—	—	—	460°C, 24 hr	—	104
Example 98-5	Composition 3-5	Condition D-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition 27-5	Condition	—	—	550°C, 5 hr	—	117
Example 99-5	Composition 3-5	Condition D-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition 29-5	Condition	—	—	550°C, 5 hr	—	117
Example 100-5	Composition 4-5	Condition A-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition	Condition	—	—	550°C, 5 hr	—	112
Example 101-5	Composition 4-5	Condition B-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition	Condition	—	—	550°C, 5 hr	—	113
Example 102-5	Composition 4-5	Condition C-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition	Condition	—	—	550°C, 5 hr	—	112
Example 103-5	Composition 2-5	Condition E-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition	Condition	—	—	550°C, 5 hr	—	113
Example 104-5	Composition 2-5	Condition F-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition	Condition	—	—	550°C, 5 hr	—	113
Example 105-5	Composition 1-5	Condition G-5	Condition	—	—	Operation	Operation	—	—	—	—	Condition	Condition	—	—	550°C, 5 hr	—	113

[Table 14-5]

	Ingot composition	Process 1-5		Process 2-5		Process 3-5		Process 4-5		Process 5-5		Process 6-5		Process 7-5		Process 8-5		Relative capacitance %
		Intermediate annealing		Washing	Tensile strain applying	Finish cold rolling	Heating	Washing	Heating	Final annealing								
Example 106-5	Composition 3-5	Condition H-5	—	Operation	—	—	Condition 27-5	—	—	550°C, 5 hr	114							
Example 107-5	Composition 3-5	Condition I-5	—	Operation	—	—	Condition 27-5	—	—	550°C, 5 hr	113							
Example 108-5	Composition 3-5	Condition J-5	—	Operation	—	—	Condition 27-5	—	—	550°C, 5 hr	111							
Example 109-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 1-5	—	—	550°C, 5 hr	106							
Example 110-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 2-5	—	—	550°C, 5 hr	108							
Example 111-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 3-5	—	—	550°C, 5 hr	111							
Example 112-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 4-5	—	—	550°C, 5 hr	110							
Example 113-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 5-5	—	—	550°C, 5 hr	108							
Example 114-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 6-5	—	—	550°C, 5 hr	111							
Example 115-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 7-5	—	—	550°C, 5 hr	112							
Example 116-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 8-5	—	—	550°C, 5 hr	111							
Example 117-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 9-5	—	—	550°C, 5 hr	111							
Example 118-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 10-5	—	—	550°C, 5 hr	112							
Example 119-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 11-5	—	—	550°C, 5 hr	112							
Example 120-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 12-5	—	—	550°C, 5 hr	111							

[Table 15-5]

	Ingot composition	Process 1-5	Process 2-5	Process 3-5	Process 4-5	Process 5-5	Process 6-5	Process 7-5	Process 8-5	Relative capacitance %
		Intermediate annealing	Washing	Tensile strain applying	Finish cold rolling	Heating	Washing	Heating	Final annealing	
Example 121-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 13-5	—	550°C, 5 hr	111
Example 122-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 14-5	—	550°C, 5 hr	112
Example 123-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 15-5	—	550°C, 5 hr	110
Example 124-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 16-5	—	550°C, 5 hr	111
Example 125-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 17-5	—	550°C, 5 hr	111
Example 126-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 18-5	—	550°C, 5 hr	111
Example 127-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 19-5	—	550°C, 5 hr	110
Example 128-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 20-5	—	550°C, 5 hr	111
Example 129-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 21-5	—	550°C, 5 hr	110
Example 130-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 22-5	—	550°C, 5 hr	110
Example 131-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 23-5	—	550°C, 5 hr	110
Example 132-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 24-5	—	550°C, 5 hr	110
Example 133-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 25-5	—	550°C, 5 hr	111
Example 134-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 26-5	—	550°C, 5 hr	109
Example 135-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 28-5	—	550°C, 5 hr	114

[Table 16-5]

	Ingot composition	Process 1-5 Intermediate annealing	Process 2-5 Washing	Process 3-5 Tensile strain applying	Process 4-5 Finish cold rolling	Process 5-5 Heating	Process 6-5 Washing	Process 7-5 Heating	Process 8-5	
									Final annealing	Relative capacitance %
Example 136-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 3-5	—	570°C, 5 hr	108
Example 137-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 3-5	—	580°C, 5 hr	107
Example 138-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 3-5	—	470°C, 24 hr	106
Example 139-5	Composition 3-5	Condition D-5	—	Operation	—	—	Condition 3-5	—	460°C, 24 hr	104
Comparative Example 1-5	Composition 3-5	Condition K-5	—	Operation	—	—	—	—	550°C, 5 hr	98
Comparative Example 2-5	Composition 3-5	Condition K-5	—	—	Operation	—	Condition 4-5	—	550°C, 5 hr	98
Comparative Example 3-5	Composition 3-5	Condition K-5	—	—	Operation	Condition H4-5	—	—	550°C, 5 hr	98
Comparative Example 4-5	Composition 3-5	Condition K-5	—	—	Operation	—	Condition 4-5	Condition H4-5	550°C, 5 hr	100
Comparative Example 5-5	Composition 3-5	Condition D-5	—	—	Operation	—	—	—	550°C, 5 hr	95

As described above, when an aluminum material for electrolytic capacitor electrodes is manufactured in a manner wherein the hot-rolling and the cold rolling are performed, subsequently the intermediate annealing is given, tensile strain is given in a step before the start of the final annealing and after the intermediate annealing, and then the final annealing is given, the intermediate annealing is performed in the oxidative atmosphere, and a surface layer of the aluminum material is removed by washing in a process before the final annealing and after the intermediate annealing. The above-mentioned process enables realization of an aluminum material having outstanding etching characteristics.

Furthermore, an aluminum material for electrolytic capacitor electrodes having more excellent etching characteristics may be obtained by sequential implementation of the heating in the oxidative atmosphere, the surface layer removing of the aluminum material by washing, and the final annealing, after the intermediate annealing in the oxidative atmosphere, and the tensile strain application.

On the other hand, in Comparative Example 1-5, the intermediate annealing in a not less than 99.99 volume % of nitrogen atmosphere, and the tensile strain application were carried out sequentially, and then the final annealing was given without the surface layer of aluminum material removing by washing. Therefore, the Comparative Example 1-5 has uneven solubility in the aluminum material surface at the time of etching, and capacitance lower

than in the Example. In Comparative Example 2-5, the intermediate annealing in a not less than 99.99 volume % of nitrogen atmosphere, the finish cold rolling, and the surface layer removing of the aluminum material by washing were carried out sequentially, and subsequently, the final annealing was given. In the Comparative Example 2-5, the solubility of the aluminum material at the time of washing is uneven. In Comparative Example 3-5, the intermediate annealing in a not less than 99.99 volume % of nitrogen atmosphere, the finish cold rolling, and the heating in the oxidative atmosphere were sequentially carried out, and subsequently, the final annealing was performed, without the surface layer removing of the aluminum material. Therefore, since much contamination layers and oils at the time of rolling remain in the Comparative Example 3-5, all the materials show low electrostatic capacities.

In Comparative Example 4-5, the finish cold rolling, the surface layer removing of the aluminum material by washing, and the final annealing were sequentially carried out, after the intermediate annealing in a not less than 99.99 volume % of nitrogen atmosphere. Although the Comparative Example 4-5 has a higher capacitance as compared with the electrostatic capacities of Comparative Example 1-5 to Comparative Example 3-5, the value is less than that in the Example, because the surface layer of the aluminum material dissolved unevenly at the time of washing is not enough equalized by the heating in the oxidative atmosphere.

In Comparative Example 5-5, after the intermediate annealing

in the oxidative atmosphere, the finish cold rolling was performed and then the final annealing was performed.

Since the surface layer of aluminum material removing by washing is not performed, the Comparative Example 5-5 has a thicker aluminum material surface oxide film and a low capacitance.

[Example using coiled aluminum material]

A hot-rolling and a cold rolling were given to an aluminum slab having a composition shown in Table 17-5 to obtain an aluminum material coil having a width of 500 mm. The contents of each composition are same as shown in Table 8-1.

And to this aluminum material coil, each process of the intermediate annealing, the tensile strain application, the heating in the oxidative atmosphere, and the surface layer removing was sequentially carried out under conditions as shown in Table 17-5 to obtain an aluminum material having a thickness of 110 μm and a length of 2000 m. In addition, the heating in the oxidative atmosphere was not performed in Example 607 and Comparative Example 601, and furthermore in Comparative Example 601, the surface layer removing was not carried out.

Subsequently, the final annealing for 4 hr was carried out at 540 °C in argon atmosphere to obtain an aluminum material for electrolytic capacitor electrodes.

The conditions of the intermediate annealing, the tensile strain application, the heating in the oxidative atmosphere, and the surface layer removing are same as conditions shown in Table 10-2, Table 17-5, Table 9-1, and Table 10-1, respectively. In

addition, an amount of the surface layer removing of the aluminum materials was controlled by an immersion period into a washing liquid, and in case of an acid cleaning after an alkali cleaning performed, the amount of removing was controlled by regulation of the immersion period into an alkali cleaning liquid.

The aluminum material coils obtained in the Examples and Comparative Examples were uncoiled and immersed respectively in an aqueous solution including 1.0 mol/L of HCl and 3.5mol/L of H₂SO₄ at 75 °C of liquid temperature, and subsequently, a direct current electrolytic etching was given to the aluminum materials with a current density 0.2 A/cm² in the aqueous solution having a same composition at a same temperature. The aluminum materials after electrolytic treatment were further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having a same composition for 360 sec at 90 °C to obtain etched foils having a thicker pit diameter. The obtained etched foils were anodized with a forming voltage of 270 V according to EIAJ standards to obtain samples for capacitance measurement.

Table 17-5 shows relative electrostatic capacities when the capacitance of Comparative Example 601 is set as 100.

[Table 17-5]

	Composition	Intermediate annealing	Tensile strain applying	Heating in an oxidative atmosphere	Washing	Final annealing	Relative capacitance %
Example 601	Composition 103	Condition B2	Tensile strain: 6%	Condition H101	Condition 103	540°C, 5 hr	125
Example 602	Composition 102	Condition D2	Tensile strain: 6%	Condition H101	Condition 103	540°C, 5 hr	124
Example 603	Composition 101	Condition F2	Tensile strain: 6%	Condition H101	Condition 103	540°C, 5 hr	119
Example 604	Composition 102	Condition D2	Tensile strain: 6%	Condition H102	Condition 103	540°C, 5 hr	124
Example 605	Composition 102	Condition D2	Tensile strain: 6%	Condition H101	Condition 102	540°C, 5 hr	121
Example 606	Composition 102	Condition D2	Tensile strain: 6%	Condition H101	Condition 101	540°C, 5 hr	118
Example 607	Composition 102	Condition D2	Tensile strain: 6%	—	Condition 103	540°C, 5 hr	116
Comparative Example 601	Composition 102	Condition I2	Tensile strain: 6%	—	—	540°C, 5 hr	100

As is understood from results of the Tables, In Example 607, the intermediate annealing in the oxidative atmosphere was carried out, and the surface layer of aluminum material was removed by washing before the final annealing. Therefore, the solubility of the aluminum material at the time of surface layer removing becomes uniform, and the Example 607 has outstanding etching characteristics and a high capacitance.

In Examples 601 to 606, the tensile strain application, the heating in the oxidative atmosphere, the surface layer removing of the aluminum materials by washing, and the final annealing were sequentially carried out after the intermediate annealing in the oxidative atmosphere. In Examples 601 to 606, the solubility of the aluminum materials at the time of the surface layer removing became more uniform, further excellent etching characteristics, and high electrostatic capacities were realized.

On the contrary, in Comparative Example 601, the tensile strain application and the final annealing were sequentially carried out after the intermediate annealing in a not less than 99.99 volume % of nitrogen atmosphere. In the Comparative Example 601, the solubility of the aluminum material at the time of the surface layer of aluminum material removing during etching was uneven, and a low capacitance was shown.

Terms and descriptions as used herein are intended to describe embodiments concerning the present invention, and the invention is not intended to be limited to these terms and descriptions. The invention permits any designing modification,

unless deviated from spirits of the invention, as long as it is within the limits of Claims.

Industrial Applicability

The manufacturing method of an aluminum material for electrolytic capacitor electrodes of the invention may be used for manufacturing electrode materials of aluminum electrolytic capacitors used as electrical components and electronic parts.

CLAIMS

1. A method for manufacturing an aluminum material for electrolytic capacitor electrodes including the steps of hot-rolling, cold-rolling and final annealing, comprising the steps of:

heating an aluminum material in oxidative atmosphere after the hot-rolling and before commencing final annealing;

removing the surface layer of the aluminum material by washing after the heating; and,

subjecting the washed aluminum material to the final annealing.

2. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1, wherein heating of the aluminum material in oxidative atmosphere and removing of the surface layer by washing are conducted after finishing the cold-rolling.

3. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1 or 2, wherein a cleaning liquid used for washing is an alkaline aqueous solution.

4. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1 or 2,

wherein the cleaning liquid used for washing is an acid aqueous solution.

5. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1 or 2, wherein the aluminum material is sequentially washed by the alkaline aqueous solution and by the acid aqueous solution.

6. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claims 3 or 5, wherein an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

7. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 4 or 5, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and phosphorus-containing acid.

8. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 7, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere is not less than 1 nm, and not more

than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal D (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3),$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

9. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 8, wherein the heating temperature in the oxidative atmosphere is within the range of 50 to 400 °C.

10. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 9, wherein the heating time in the oxidative atmosphere is not less than 3 sec, and not more than 72 hr.

11. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 10, wherein the oxygen concentration in the oxidative atmosphere during heating is 0.1 volume % or more.

12. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 11, further comprising the step of degreasing the aluminum material before heating the aluminum material in the oxidative

atmosphere, or after heating the aluminum material in the oxidative atmosphere before washing the surface layer of the aluminum material.

13. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 12, wherein the aluminum material is degreased by using an organic solvent.

14. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 12, wherein the aluminum material is degreased by using water added with a surfactant.

15. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1, wherein the aluminum material is subjected to intermediate annealing during the cold-rolling and subjected to finish cold-rolling after intermediate annealing;

wherein the intermediate annealing is conducted in oxidative atmosphere, and the removing of the surface layer of the aluminum material by washing is conducted after the intermediate annealing.

16. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 15, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the finish cold-rolling before the

final annealing.

17. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 15, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the intermediate annealing before the finish cold-rolling.

18. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 15 to 17, wherein the oxygen concentration in the oxidative atmosphere during the intermediate annealing is 0.1 volume % or more.

19. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 15 to 18, wherein the aluminum material is subjected to the intermediate annealing in the oxidative atmosphere at a temperature not less than 200 °C, and not more than 320 °C.

20. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 15 to 19, wherein the cleaning liquid used for washing is the alkaline aqueous solution.

21. The method for manufacturing an aluminum material for

electrolytic capacitor electrodes according to any one of claims 15 to 19, wherein the cleaning liquid used for washing is the acid aqueous solution.

22. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 15 to 19, wherein the aluminum material is sequentially washed by the alkaline aqueous solution and the acid aqueous solution.

23. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 20 to 22, wherein an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

24. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 21 or 22, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and phosphorus-containing acid.

25. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 15 to 24, wherein the average quantity of removal of the surface

layer of the aluminum material obtained by washing is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal D (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3),$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

26. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 15 to 25, further comprising the step of degreasing the aluminum material after the cold-rolling before the intermediate annealing, before the final annealing.

27. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 26, wherein the aluminum material is degreased by using an organic solvent.

28. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 26, wherein the aluminum material is degreased by using water added with a surfactant.

29. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1, wherein

the aluminum material is subjected to an intermediate annealing during the cold-rolling and subjected to a finish cold-rolling after the intermediate annealing;

wherein the intermediate annealing is conducted in an oxidative atmosphere, and the heating of the aluminum material in the oxidative atmosphere and the removing of the surface layer by washing are conducted after the finish cold-rolling.

30. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 29, comprising the step of removing the surface of the aluminum material by washing the aluminum material after the intermediate annealing and before the finish cold-rolling.

31. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 29 or 30, wherein the cleaning liquid used for washing is the alkaline aqueous solution.

32. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 29 or 30, wherein the cleaning liquid used for washing is the acid aqueous solution.

33. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 29 or 30,

wherein the aluminum material is sequentially washed by the alkaline aqueous solution and the acid aqueous solution.

34. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 31 to 33, wherein an alkali in alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

35. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 32 or 33, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and a phosphorus-containing acid.

36. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 29 to 35, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere after the finish cold-rolling is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal } D \text{ (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 \text{ (g/cm}^3),$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

37. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 29 to 36, wherein the heating temperature in the oxidative atmosphere after the finish cold-rolling is within the range of 50 to 400 °C.

38. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 37, wherein the heating time in the oxidative atmosphere after the finish cold-rolling is not less than 3 sec, and not more than 72 hr.

39. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 29 to 38, wherein aluminum material is subjected to the intermediate annealing in the oxidative atmosphere at a temperature not less than 200 °C, and not more than 320 °C.

40. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 29 to 39, wherein the oxygen concentration in the oxidative atmosphere during heating after the finish cold-rolling is 0.1 volume % or more.

41. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 29 to 40, wherein the oxygen concentration in the oxidative atmosphere during the intermediate annealing is 0.1 volume % or more.

42. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 29 to 41, further comprising the step of degreasing the aluminum material before the intermediate annealing after the cold-rolling, before finally removing the surface layer of the aluminum material by washing the aluminum material.

43. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 42, wherein the aluminum material is degreased by using an organic solvent.

44. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 42, wherein the aluminum material is degreased by using water containing a surfactant.

45. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1, wherein the aluminum material is subjected to an intermediate annealing

after the cold-rolling and tensile-strained after the intermediate annealing and before commencing the final annealing; and the heating of the aluminum material in the oxidative atmosphere and the removing of the surface layer of the aluminum material by washing are conducted after giving the tensile strain.

46. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 45, wherein the cleaning liquid used for washing is the alkaline aqueous solution.

47. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 45, wherein the cleaning liquid used for washing is the acid aqueous solution.

48. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 45, wherein the aluminum material is sequentially washed by the alkaline aqueous solution and the acid aqueous solution.

49. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 46 to 48, wherein an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and

sodium carbonate.

50. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 47 or 48, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and a phosphorus-containing acid.

51. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 45 to 50, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal D (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 (\text{g/cm}^3),$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

52. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 45 to 51, wherein the heating temperature in the oxidative atmosphere is within the range of 50 to 400 °C.

53. The method for manufacturing an aluminum material for

electrolytic capacitor electrodes according to claim 52, wherein the heating time in the oxidative atmosphere is not less than 3 sec, and not more than 72 hr.

54. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 45 to 53, wherein the oxygen concentration in the oxidative atmosphere during heating is 0.1 volume % or more.

55. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 1, wherein the aluminum material is subjected to intermediate annealing in oxidative atmosphere after cold-rolling and tensile strain application after the intermediate annealing and before commencing the final annealing; and the removing of the surface layer of the aluminum material by washing is conducted at least one time after the intermediate annealing.

56. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 55, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the tensile strain application before the final annealing.

57. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 55, wherein

the surface layer of the aluminum material is removed by washing the aluminum material after the intermediate annealing before the tensile strain application.

58. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 57, wherein the surface layer of the aluminum material is removed by washing the aluminum material after the tensile strain application before the final annealing, after heating the aluminum material in the oxidative atmosphere.

59. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 58, wherein the cleaning liquid used for washing is the alkaline aqueous solution.

60. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 58, wherein the cleaning liquid used for washing is the acid aqueous solution.

61. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 58, wherein the aluminum material is sequentially washed by the alkaline aqueous solution and the acid aqueous solution.

62. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 59 to 61, wherein an alkali in the alkaline aqueous solution is one or more alkali selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium o-silicate, sodium m-silicate, sodium tertiary phosphate and sodium carbonate.

63. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 60 or 61, wherein an acid in the acid aqueous solution is one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid and a phosphor element.

64. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 63, wherein the average quantity of removal of the surface layer of the aluminum material obtained by washing after heating in the oxidative atmosphere after intermediate annealing is not less than 1 nm, and not more than 500 nm per the single-side of the aluminum material in the quantity of removal D (nm) specified below:

$$\text{quantity of removal } D \text{ (nm)} = E(\text{g/cm}^2) \times 10^7 / 2.7 \text{ (g/cm}^3\text{)},$$

where E is the decrease of mass per unit surface area by washing, and

2.7 g/cm³ is the density of aluminum.

65. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 57 to 64, wherein the heating temperature in the oxidative atmosphere after the tensile strain application is within the range of 50 to 400 °C.

66. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to claim 65, wherein the heating time in the oxidative atmosphere after the tensile strain application is not less than 3 sec, and not more than 72 hr.

67. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 66, wherein the intermediate annealing in the oxidative atmosphere is performed at a temperature not less than 200 °C, and not more than 300 °C.

68. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 55 to 67, wherein the oxygen concentration in the oxidative atmosphere during heating after the tensile strain application is 0.1 volume % or more.

69. The method for manufacturing an aluminum material for

electrolytic capacitor electrodes according to any one of claims 55 to 67, wherein the oxygen concentration in the oxidative atmosphere during the intermediate annealing is 0.1 volume % or more.

70. The method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 69, wherein the aluminum material is subjected to the final annealing in inert gas atmosphere.

71. A method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 70, wherein the aluminum material is subjected to the final annealing at a temperature not less than 450 °C, and not more than 600 °C.

72. A method for manufacturing an aluminum material for electrolytic capacitor electrodes according to any one of claims 1 to 71, wherein the aluminum purity of the aluminum material is 99.9 mass % or more.

73. The aluminum material for electrolytic capacitor electrodes manufactured by the method according to any one of claims 1 to 72.

74. The aluminum material for electrolytic capacitor

electrodes according to claim 73, wherein the aluminum material is an anode material for middle or high voltages

75. The method for manufacturing an electrode material for electrolytic capacitors, comprising the step of etching the aluminum material manufactured by any one of claims 1 to 72.

76. The method for manufacturing an electrode material for electrolytic capacitors according to claim 75, further comprising the step of performing formation of dielectric by anodizing after etching.

77. The method for manufacturing an electrode material for electrolytic capacitors according to claim 75 or 76, wherein at least a part of the etching is DC electrolytic etching.

78. The anode material for aluminum electrolytic capacitors manufactured by the method according to any one of claims 75 to 77.

79. The aluminum electrolytic capacitor comprising the aluminum electrode material manufactured by the method according to any one of claims 75 to 77 as electrode materials.

INTERNATIONALSEARCHREPORT

International application No.

PCT/JP2005/002968

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁷ H01G9/055, C22F1/04, C23G1/22, C23F1/20, C23F1/36, C25D11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ H01G9/055, C22F1/04, C23G1/22, C23F1/20, C23F1/36, C25D11/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2005
 Registered utility model specifications of Japan 1996-2005
 Published registered utility model applications of Japan 1994-2005

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIDS (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2003-15112 A1 (SHOWA DENKO K.K.) 2003.02.20 Full text & EP 1422732 A1 & CN 1533578 A & KR 2004030908 A & AU 2002323792 A1	1-79
Y	JP 7-180006 A1 (KOBE STEEL LTD.) 1995.07.18 Table 7; Par. Nos. [0020]-[0023] (Family: none)	1-79
Y	WO 2004-3248 A1 (SHOWA DENKO K.K.) 2004.01.08 Full text & EP 1541704 A1 & AU 2003280408 A1	45-69
A	JP 9-20970 A1 (KOBE STEEL LTD.) 1997.01.21 Full text (Family: none)	1-79

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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22.06.2005

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INTERNATIONALSEARCHREPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-311550 A1 (SHOWA ALUMINUM CORP.) 1992.11.04 Full text (Family: none)	1-79
A	JP 5-279815 A1 (NIPPON SEIHAKU K.K.) 1993.10.26 Full text (Family: none)	1-79
A	JP 6-188155 A1 (SHOWA ALUMINUM CORP.) 1994.07.08 Full text (Family: none)	1-79
A	JP 10-81945 A1 (SUMITOMO LIGHT METAL IND. CO.) 1998.03.31 Full text (Family: none)	1-79