

(19)



(11)

**EP 1 498 513 B9**

(12)

**CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:

**Corrected version no 1 (W1 B1)**  
**Corrections, see**  
**Description Paragraph(s) 205**

(51) Int Cl.:

**H01G 9/045<sup>(2006.01)</sup> C22F 1/04<sup>(2006.01)</sup>**

(86) International application number:

**PCT/JP2003/005384**

(48) Corrigendum issued on:

**31.08.2011 Bulletin 2011/35**

(87) International publication number:

**WO 2003/091482 (06.11.2003 Gazette 2003/45)**

(45) Date of publication and mention of the grant of the patent:

**02.02.2011 Bulletin 2011/05**

(21) Application number: **03719219.2**

(22) Date of filing: **25.04.2003**

(54) **PROCESS FOR PRODUCING ALUMINUM MATERIAL FOR ELECTROLYTIC CAPACITOR ELECTRODE, ALUMINUM MATERIAL FOR ELECTROLYTIC CAPACITOR ELECTRODE AND PROCESS FOR PRODUCING ELECTRODE MATERIAL FOR ELECTROLYTIC CAPACITOR**

VERFAHREN ZUR HERSTELLUNG VON ALUMINIUMMATERIAL FÜR EINE ELEKTRODE EINES ELEKTROLYTISCHEN KONDENSATORS, ALUMINIUMMATERIAL FÜR EINE ELEKTRODE EINES ELEKTROLYTISCHEN KONDENSATORS UND VERFAHREN ZUR HERSTELLUNG VON ELEKTRODENMATERIAL FÜR EINEN ELEKTROLYTISCHEN KONDENSATOR

PROCEDE DE PRODUCTION D'UNE MATIERE A BASE D'ALUMINIUM POUR ELECTRODE DE CONDENSATEUR ELECTROLYTIQUE, MATIERE A BASE D'ALUMINIUM POUR ELECTRODE DE CONDENSATEUR ELECTROLYTIQUE ET PROCEDE DE PRODUCTION D'UNE MATIERE D'ELECTRODE POUR CONDENSATEUR ELECTROLYTIQUE

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT RO SE SI SK TR**

(73) Proprietor: **Showa Denko K.K.**

**Tokyo 105-8518 (JP)**

(30) Priority: **25.04.2002 JP 2002123666**

**05.07.2002 JP 2002196867**

**18.07.2002 JP 2002209455**

**18.07.2002 JP 2002209459**

**04.03.2003 JP 2003057737**

**06.03.2003 JP 2003060611**

**06.03.2003 JP 2003060614**

**16.04.2003 JP 2003111747**

(72) Inventors:

- **NISHIMORI, H.,**  
Sakai Reg. Off. **SHOWA DENKO K.K.**

- Sakai-shi,  
Osaka 590-0982 (JP)

- **YAMAGUCHI, T.,**  
Sakai Reg. Off. **Showa Denko K.K.**

- Sakai-shi,  
Osaka 590-0982 (JP)

- **KATO, Y.,**  
Sakai Reg. Off. **Showa Denko K.K.**

- Sakai-shi,  
Osaka 590-0982 (JP)

- **SAKAGUCHI, M.,**  
Sakai Reg. Off. **Showa Denko K.K.**

- Sakai-shi,  
Osaka 590-0982 (JP)

(43) Date of publication of application:

**19.01.2005 Bulletin 2005/03**

**EP 1 498 513 B9**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

- **KODAMA, K.,**  
Sakai Reg. Off. Showa Denko K.K.  
Sakai-shi,  
Osaka 590-0982 (JP)
- **HODZUMI, S.,**  
Sakai Reg. Off. Showa Denko K.K.  
Sakai-shi,  
Osaka 590-0982 (JP)

(74) Representative: **Viering, Jentschura & Partner**  
**Postfach 22 14 43**  
**80504 München (DE)**

(56) References cited:  
**JP-A- 2 008 354**            **JP-A- 3 257 147**  
**JP-A- 3 287 748**            **JP-A- 4 036 444**  
**JP-A- 5 335 188**            **JP-A- 11 087 189**  
**JP-A- 2001 006 985**

**Description**

**[0001]** Priority is claimed to Japanese Patent Application No. 2002-123666, filed on April 25, 2002, Japanese Patent Application No. 2002-196867, filed on July 5, 2002, Japanese Patent Application No. 2002-209455, filed on July 18, 2002, Japanese Patent Application No. 2002-209459, filed on July 18, 2002, Japanese Patent Application No. 2003-57737, filed on March 4, 2003, Japanese Patent Application No. 2003-60611, filed on March 6, 2003, Japanese Patent Application No. 2003-60614, filed on March 6, 2003 and Japanese Patent Application No. 2003-111747, filed on April 16, 2003.

**Technical Field**

**[0002]** The present invention relates to a method for manufacturing an aluminum material for electrolytic capacitors, an aluminum material for electrolytic capacitor electrodes, a method for manufacturing an electrode material for electrolytic capacitors, and an aluminum electrolytic capacitor.

**[0003]** In this specification, the wording of "aluminum" is used within the meaning including its aluminum alloy, and the wording of "aluminum material" is used within the meaning including a foil, a plate and a formed article using the same.

**Background Art**

**[0004]** Since an aluminum material generally used as an electrode material for aluminum electrolytic capacitors is required to have a larger surface area and a larger capacitance per unit area, such aluminum material is subjected to electrochemical or chemical etching to thereby enlarge the effective area thereof.

**[0005]** Furthermore, in order to increase the effective area thereof, various aspects of studies such as material compositions, manufacturing steps and etching methods have been conducted with respect to increasing the number of etching pits and enlarging each etching pit.

**[0006]** For example, in a method of manufacturing an aluminum material for electrolytic capacitors in which tunnel-like pits are formed by a direct-current electrolysis etching method, final annealing is generally performed in an inert atmosphere or in a vacuum at about 500°C to generate (100) face crystal orientation. The final annealing denotes a step to be carried out after finish cold rolling or after finish cold rolling and washing.

**[0007]** Some documents disclose that when crystalline oxide particles are generated on a surface of an aluminum material at the time of final annealing etch pits grow at around crystals at the time of electrolytic etching (e.g., The 95th Autumn Conference of Japan Institute of Light Metals Lecture Summary, page 265 (1998), Kiyoshi FUKUOKA, Nobuo OSAWA, Tetsuya MOTOI; Journal of The Surface Finishing Society of Japan 50 [7] page 643 (1999), Nobuo OSAWA, Kiyoshi FUKUOKA). It is believed that the generation of crystalline oxide grains on the surface of the aluminum material contributes to enhancement of capacitance.

**[0008]** As mentioned above, however, in an inert atmosphere or in a vacuum atmosphere which is a common atmosphere for final annealing, since the oxygen amount in such atmosphere is extremely small, final annealing hardly causes crystallization. To the contrary, when high temperature annealing is performed in an oxidation atmosphere, the oxide layer becomes thicker, resulting in deteriorated uniformity of etch pits.

**[0009]** As a method for yielding a larger amount of crystals on a surface of an aluminum material, Japanese Examined Laid-open Patent Publication No. S58-34926 discloses formation of hydration treated film by, for example, a method in which steam or damp air is blown against a surface of an aluminum material before final annealing, a method in which an aluminum material is heated in an atmosphere at about 200 °C, or the so-called Boehmite treatment method in which an aluminum material is immersed in heated water or amine aqueous solution.

**[0010]** Although a hydration treated film enhances the precipitation of crystalline oxide on a surface of an aluminum material by the subsequent final annealing, the hydration treated film contains a large amount of Al-OH group on the surface, which may cause adhesion of aluminum materials when batch annealing is performed in a state in which an aluminum material is coiled or aluminum plates are piled. Furthermore, in the method of heating an aluminum material in an atmosphere at about 200 °C, a precise atmospheric control such as a vapor amount control is required to obtain a reproducible intended oxide film. Therefore, there is a disadvantage that it takes a time for the surface of the aluminum foil to reach the predetermined temperature.

**[0011]** Furthermore, Japanese Unexamined Laid-open Patent Publication No. S63-116417 discloses the technique for yielding  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by continuous final annealing in an oxidizing atmosphere containing oxygen and/or moisture. However, since the final annealing time is short, the yielding of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may become insufficient.

**[0012]** Furthermore, Japanese Unexamined Laid-open Patent Publication No. H7-201673 discloses a method of manufacturing an aluminum material for electrolytic capacitor electrodes for obtaining high capacitance with improved etching characteristics. This method includes a step of eliminating a surface layer of an aluminum foil, a step of heating and oxidizing the aluminum foil from which the surface layer is eliminated in the above step under the conditions of temperature:

40 to 350 °C, dew point: 0 to 80 °C, and time: 30 to 1,800 seconds, and then a step of annealing the aluminum foil in a non-oxidizing atmosphere after the heating and oxidizing at the above step.

5 [0013] Furthermore, Japanese Unexamined Laid-open Patent Publication No. H5-279815 discloses a method of manufacturing an aluminum foil for electrolytic capacitor positive electrodes **characterized in that** a thickness of a barrier-type oxide film on the aluminum foil surface is controlled to be 2.5 angstrom or less at the washing treatment before the final annealing, and the aluminum foil is heat-treated in an oxidizing atmosphere at 150 to 400 °C after the washing treatment but before the finish annealing treatment to thereby grow the thickness of the barrier-type oxidizing film on the aluminum foil surface to 10 angstrom or less. It also describes that the preferable time for the heat-treatment is 5 minutes to 3 hours.

10 [0014] In the aforementioned methods disclosed in Japanese Unexamined Laid-open Patent Publication No. H7-201673 and Japanese Unexamined Laid-open Patent Publication No. H5-279815, a stable surface oxide film of the aluminum material can be obtained because the heating is performed after the washing. However, since the heating method is an atmospheric heating method, the oxide film to be generated by the heating is easily affected by the influence of the atmosphere, and therefore it takes a time for the heat treatment.

15 [0015] Furthermore, Japanese Unexamined Laid-open Patent Publication No. H5-200406 discloses that surface layer eliminating washing is performed before the finish rolling and a continuous low temperature heating is performed before the final annealing, to thereby increase the capacitance and eliminate the difference of capacitance in the width direction of the aluminum material coil.

20 [0016] However, in the method of Japanese Unexamined Laid-open Patent Publication No. H5-200406, since the atmospheric heating is performed before the final annealing, the oxide film of the aluminum surface layer becomes stable. However, there are disadvantages that a precise atmospheric control such as a vapor amount control is required to obtain a reproducible intended oxide film and it takes a time for the surface of the aluminum foil to reach the predetermined temperature.

25 [0017] Furthermore, Japanese Unexamined Laid-open Patent Publication No. H11-36053 discloses a method for increasing capacitance in which an aluminum material is heated in an atmosphere, in a vacuum or in an inert atmosphere after final annealing to generate defects which become origins of pits on the surface of the aluminum material to thereby prevent the dissolution of the surface other than the above portions. Also, Japanese Unexamined Laid-open Patent Publication No. H5-255821 discloses that an aluminum foil after final annealing (finish annealing) is washed with alkaline aqueous solution and then heated in an atmosphere at 150 to 400 °C to thereby increase the capacitance and eliminate uneven capacitance.

30 [0018] However, since the aforementioned conventional heat treatment after the final annealing is performed in an atmosphere, in vacuum or in inert gas, it is easily affected by the influences of oxygen and/or vapor, a precise atmospheric control such as a vapor amount control is required to obtain a reproducible intended oxide film. Therefore, there is a disadvantage that it takes a time for the surface of the aluminum foil to reach the predetermined temperature.

35 [0019] An object of the present invention is to provide an aluminum material for electrolytic capacitor electrodes capable of obtaining uniform etching characteristics and an enhanced surface increasing ratio by etching by short time treatment without requiring a precise atmospheric control and a method of manufacturing such aluminum material.

[0020] Another object of the present invention is to provide a method of manufacturing an electrolytic capacitor electrode material and an aluminum electrolytic capacitor using the aforementioned aluminum material.

#### 40 Disclosure of Invention

[0021] According to the present invention, a method of manufacturing an aluminum material for electrolytic capacitor electrodes is **characterized in that**, in manufacturing an aluminum material for electrolytic capacitor electrodes by  
45 subjecting an aluminum slab to hot rolling, cold rolling and final annealing, a step for heating the aluminum material by bringing into contact with a heating body is performed after the hot rolling.

[0022] The contact heating step of the aluminum material by bringing into contact with the heating body can be performed at any time provided that the contact heating step is performed after the hot rolling. Concretely, the contact heating step can be performed at least one time between the start of the cold rolling and the completion thereof.

50 [0023] Alternatively, the contact heating step of the aluminum material for bringing into contact with the heating body can be performed after the cold rolling, but before or after the final annealing.

[0024] The reasons for employing the contact heating as a heating method are that the heating control can be relatively easily performed because the surface temperature of the aluminum material can be reached a prescribed temperature uniformly and immediately and that the influence of the atmosphere can be minimized because the heating can be  
55 performed quickly and immediately.

[0025] Other objects and advantages of the present invention will be apparent from the following preferred embodiments.

**Best Mode for Carrying Out the Invention**

(First embodiment)

5 [0026] In this embodiment, the contact heating step for heating the aluminum material by bringing into contact with the heating body is performed at least one time at an intermediate step between the initiation of the cold rolling and the termination thereof.

[0027] That is, the inventors of the application revealed that heating the aluminum material by bringing it into contact with a heating body at least one time at an intermediate step between the initiation of cold rolling (including finish cold rolling) and the termination thereof to form close and uniform aluminum surface oxide film yields an aluminum material for electrolytic capacitor electrodes with uniform etching characteristics and high capacitance after the final annealing.

10 [0028] The reasons for employing the contact heating as a heating method are that the heating control can be performed relatively easily because the surface temperature of the aluminum material can be reached a prescribed temperature uniformly in a short time and that the atmospheric influence can be minimized because the heating can be performed in a short time.

[0029] The aluminum material heated by at least one time contact with the heating body during the cold rolling step is subjected to cold rolling, then washing if necessary, and thereafter final annealing.

[0030] Some documents disclose that, in cases where crystalline oxide particles are formed on the aluminum surface at the time of final annealing, etch pits will generate around crystals at the time of electrolytic etching (see, e.g., Journal of The Surface Finishing Society of Japan 50[7], p643 (1999), Nobuo OSAWA, Kiyoshi FUKUOKA). It is considered that yielding crystalline oxide particles on the aluminum surface contributes to increasing of capacitance.

20 [0031] In the aluminum material having a surface oxide film formed closely and uniformly by the contact heating, the subsequent cold rolling causes uniformly distributed defects on the entire surface of the aluminum material. When the cold rolled aluminum material is subjected to final annealing as it is or after washing with washing solution not capable of melting aluminum, an aluminum material for electrolytic capacitor electrodes in which substances such as fine crystalline oxides that will become nuclei of etch pits are uniformly dispersed on the surface of the aluminum material can be obtained.

[0032] The substances that can be nuclei of etch pits are not limited to crystalline oxides, but can be high density or thick non-crystalline substances or substances containing crystalline oxides or metal aluminum within noncrystalline. Examples of crystalline oxides include  $Al_2O_3$  such as  $\gamma-Al_2O_3$ ,  $AlOOH$  such as boehmite, and composite oxides included metal ingredients (such as Mg, Pb, Cu) other than aluminum. However, the crystalline oxides are not limited to metal oxides or metal hydroxides.

25 [0033] It is believed that substances different in property from another portion yielded in the oxide film of the aluminum material surface will become nuclei of etch pits at the time of etching. It is presumed that the quick heating of the aluminum material before the final annealing yields substances containing crystals, amorphous in the state before being transitioned to a crystal or a substance containing crystals or metal aluminum in amorphous and that these substances will become the nuclei of etch pits.

[0034] In cases where the aluminum material is subjected to washing with washing liquid which causes melting of aluminum before the final annealing, the oxides yielded on the surface of the aluminum material by the contact heating will be eliminated. However, the surface layer can be uniformly melted with the washing liquid as compared with the case in which no contact heating is performed, resulting in an aluminum material with uniformly distributed substances which will become nuclei of etch pits after the final annealing.

30 [0035] Furthermore, in this embodiment, in cases where intermediate annealing is performed during the cold rolling steps for the purpose of eliminating the crystal structure distortion of the aluminum alloy caused by the precedent rolling step, the contact heating of the aluminum alloy is performed before the intermediate annealing to obtain fine and uniform surface oxide film of the aluminum material. This prevents the growing of the oxide film at the time of the intermediate annealing, which in turn results in an aluminum surface oxide film homogeneous in the widthwise and longitudinal directions of the coiled aluminum material.

[0036] Hereinafter, a method of manufacturing an aluminum material for electrolytic capacitors will be explained.

35 [0037] The purity of the aluminum material is not specifically limited as long as it falls within a range capable of being used for electrolytic capacitors. The preferable purity is 99.9% or above, more preferably 99.95% or above. In the present invention, the purity of the aluminum material is defined by a value obtained by subtracting the total concentration (%) of Fe, Si, Cu, Mn, Cr, Zn, Ti and Ga from 100%.

40 [0038] Although the method of manufacturing the aluminum material is not limited, a melted component adjustment of aluminum materials slab casting, homogenization heat treatment, hot rolling, cold rolling including finish cold rolling (low reduction rolling) and final annealing will be performed in this order. At an intermediate step of the cold rolling between the initiation of the cold rolling and the termination thereof, the aluminum material is heated by bringing it into contact with a heating body at least one time. For example, the contact heating is performed during the primary cold

rolling before the finish cold rolling, or between the primary cold rolling and the finish cold rolling. The manufacturing step conditions of the aluminum material may be changed in accordance with the etching conditions of the aluminum material.

5 [0039] For the purpose of eliminating the distortion of the crystal structure of the aluminum material caused by the primary rolling, an intermediate annealing may be performed during the cold rolling steps. Furthermore, for the purpose of eliminating impurities and/or oils on the surface of the aluminum material, washing can be performed at a step before the intermediate annealing or a step after the cold rolling but before the final annealing.

10 [0040] The aforementioned contact heating of the aluminum material is performed to obtain an aluminum material for electrolytic capacitor electrodes with uniform etching characteristics and high capacitance after the final annealing by forming a fine and homogeneous surface oxide film of the aluminum material.

15 [0041] However, if the rolling reduction ratio after the contact heating is too large, the effect of equalizing etching characteristic by the contact heating deteriorates. Accordingly, the rolling reduction ratio after the contact heating is preferably 60% or less, more preferably 30% or less, wherein the rolling reduction ratio is defined by  $[(A-B)/A] \times 100\%$ , where "A" ( $\mu\text{m}$ ) is the thickness of the aluminum material after the last contact heating but before the resumption of cold rolling, and "B" ( $\mu\text{m}$ ) is the thickness of the aluminum material after the termination of the entire cold rolling.

20 [0042] The means for the contact heating can be any means capable of attaining the contact heating such as a heated roll, a heated belt or a heated plate to heat one side or both sides of the aluminum material. The heating surface material of the heating body can be an arbitrarily selected material such as stainless, plating, ceramic, Teflon (registered trademark) resin, and silicone resin. However, it is preferable to select a material which does not cause adhesion of the surface oxide film to the surface of the heating body.

25 [0043] The surface temperature of the heating body which comes into contact with an aluminum material is preferably 50 to 450 °C. If the surface temperature is below 50 °C, the heating becomes insufficient, which may result in insufficient generation of substances which will become nuclei of etch pits such as crystalline oxide particles at the time of final annealing. To the contrary, if the surface temperature exceeds 450°C, the oxide film becomes too thick, causing wrinkles at the time of cooling, which may cause operational problems. More preferably, the surface temperature of the heating body is 60 to 400°C. still more preferably 100 to 350°C. The optimal surface temperature of the heating body is 160 to 290°C.

30 [0044] The preferable contact time of the surface of the aluminum material and the surface of the heating body is 0.001 to 60 seconds. If the contact time is less than 0.001 second, heating the surface of the aluminum material becomes insufficient, which may cause uneven generation of substances which will become etch pits. To the contrary, even if the heating is performed 60 seconds or more, the homogenization effects of the oxide film may be saturated. It is more preferable that the contact time is 0.01 to 30 seconds. It is still more preferable that the contact time is 0.1 to 10 seconds.

35 [0045] The surface temperature of the heating body and the contact time can be determined arbitrarily considering the characteristics of the surface oxide film of the aluminum material before the contact heating. The contact heating atmosphere is not specifically limited, and the contact heating can be performed in the air without performing specific atmospheric control.

40 [0046] As an example of a heating apparatus using a heating roll as the heating body, a device provided with at least two heating rolls for performing the contact heating of the front and rear surfaces of the aluminum material can be exemplified. In cases where the aluminum material after the contact heating with heating rolls wrinkles at the time of rolling the aluminum material, the aluminum material can be rolled up after cooling the aluminum material by passing through one or a plurality of cooling bodies such as cooling rolls after the heating with heating rolls or the like. Especially, in cases where cooling rolls are used as cooling bodies, the cooling can be performed easily and continuously. Furthermore, before heating the aluminum material with heating rolls to the targeted contact heating temperature, the aluminum material can be pre-heated to a temperature lower than the targeted contact heating temperature by using other heating rolls.

45 [0047] The liquid for washing the aluminum material before an intermediate annealing, or after the cold rolling but before the final annealing, is not limited to a specific one, but can be organic solvent, alkaline aqueous solution, acid aqueous solution, amine aqueous solution, aqueous ammonia, or water containing surfactant.

50 [0048] As the aforementioned organic solvent, alcohol, diol, aromatic hydrocarbon such as toluene · xylene, alkane series hydrocarbon, cyclohexane, ketone, ether, ester and petrochemical products can be exemplified. However, the organic solvent is not limited to the above. Furthermore, a plurality of organic solvent can be mixed. In the case of organic solvent capable of being mixed with water, such organic solvent can be mixed with water as occasion demands.

55 [0049] As washing liquid for washing the aluminum material before an intermediate annealing, or after the cold rolling but before the final annealing, alkaline aqueous solution or acid aqueous solution can be used. Although alkaline contained in the alkali aqueous solution is not limited to a specific one, sodium hydroxide, potassium hydroxide, calcium hydroxide and sodium silicate can be exemplified. Aqueous solution containing at least one of the aforementioned acids can be used as washing liquid.

[0050] The method of contacting the aluminum material with washing liquid in the aforementioned washing is not

limited to a specific method. As such a method, immersing, contacting the aluminum material with the surface of the washing liquid and spraying can be exemplified.

5 **[0051]** After the final cold rolling, and further washing if necessary, for the primary purpose of the encourage of the production of substances which will become nuclei of etch pits and the enhancement of the etching characteristics by arranging the crystal orientation of the aluminum material into (100) orientation, final annealing is performed.

10 **[0052]** In the final annealing, it is preferable to perform the final annealing such that the total thickness of the oxide film after the final annealing becomes 2.5 to 5 nm which is a thickness according to the Hunter Fowle method (see M.S. Hunter and P. Fowle, J. electrochem. Soc. 101[9], 483(1954)) so as not to causes a deterioration of the etching characteristics due to the excessively increased thickness of the oxide film at the final annealing. It is preferable that the (100) area ratio of the aluminum material after the final annealing is 90% or above.

15 **[0053]** Although the atmosphere at the final annealing is not specifically limited, it is preferable to heat the aluminum material within an atmosphere containing a less amount of moisture and oxygen so as not to excessively increase the thickness of the oxide film. Concretely, it is preferable to perform the heating in inert gas such as argon or nitrogen or in a vacuum of 0.1Pa or below.

20 **[0054]** The final annealing method is not specifically limited. For example, batch annealing can be performed in a state in which the aluminum material is wound into a coil, a coiled aluminum material can be continuously annealed while unwinding and then wound into a coil, or at least one of batch annealing and continuous annealing can be performed plural times.

25 **[0055]** The temperature and the time of the final annealing is not specifically limited. For example, in the case where batch annealing is performed in a coiled state, it is preferable to perform the final annealing at the aluminum actual temperature of 450 to 600 °C, for 10 to 50 hours because of the following reasons. If the aluminum actual temperature is less than 450 °C and the time is less than 10 minutes, the generation of the substances which will become nuclei of etch pits in the oxide film becomes insufficient, causing a nondense status of the substances, which in turn results in an insufficient surface area increasing effect at the time of etching due to crystals as etching nuclei. This may also cause insufficient generation of (100) face crystal orientation. To the contrary, if the annealing is performed at the temperature of 600 °C or above, the aluminum material easily adheres with each other in the case where batch annealing is performed in the coiled manner. Even if the annealing is performed for more than 50 hours, the etching area increasing effect will be saturated, which merely results in an increased heat energy cost. It is more preferable that the aluminum actual temperature is 460 to 580°C and the time is 20 minutes to 40 hours.

30 **[0056]** The temperature rising rate/pattern is not specifically limited. The temperature can be raised at a constant rate, or the temperature can be raised or lowered stepwise while repeating temperature rising and holding. In any event, any temperature rising rate/patter can be accepted provided that the annealing is performed for a total of 10 minutes to 50 hours within the temperature zone in which the aluminum actual temperature is from 450 to 600 °C. The thickness of the aluminum material for electrolytic capacitor electrodes is not limited to a specific one.

35 **[0057]** The aluminum material to which the final annealing was executed is subjected to etching treatment to increase the surface area increasing ratio. Although the etching conditions are not specifically limited, it is preferable to employ a DC etching method. By employing a DC etching method, at the portions that will become nuclei of etch pits enhanced the generation thereof during the final annealing, the aluminum material is etched deeply to thereby generate a number of tunnel-like pits, resulting in high capacitance.

40 **[0058]** After the etching, it is preferable to subject the etched aluminum material to formation to obtain an anode material. Especially, it is preferable to use it as an electrode material for electrolytic capacitors formiddle voltage or high voltage. Needless to say, the aluminum material can also be used as a cathode material.

45 **[0059]** Aluminum electrolytic capacitors can be made by employing the aforementioned anode material and/or cathode material as an electrode material. In this electrolytic capacitor, since the area increased ratio of the electrode material is enhanced, the capacitor has large capacitance.

50 **[0060]** In this embodiment, since the final annealing is performed after the heating of the aluminum material by contacting it with a heating body during the cold rolling steps, an aluminum material for electrolytic capacitors with even etching characteristics can be manufactured. Especially, since the contact heating is employed as a heating method, the surface temperature of the aluminum foil can be reached a targeted temperature evenly in a short time. Thus, the temperature control can be performed with comparative easy. Furthermore, since the heating can be completed quickly in a short time, it becomes possible to lessen the atmospheric influence. Accordingly, by etching this aluminum material for electrolytic capacitors, etch pits generate homogeneously. As a result, etching can be performed effectively, which in turn increases the area enlarging rate. This results in an electrolytic capacitor electrode material with increased capacitance, enabling an aluminum electrolytic capacitor with larger capacitance.

55 **[0061]** The capacitance of the etched foil after the formation was subjected may be measured by a conventional method, e.g., using a platinum sheet as a counter electrode in 80g/l ammonium borate at the frequency of 120Hz and at the temperature of 30 °C.

**[0062]** The electrolytic capacitor of the present invention is not limited to the embodiment.

(Second embodiment)

**[0063]** In this embodiment, the contact heating step for heating the aluminum material by bringing it into contact with the heating body is performed after the cold rolling but before the final annealing.

**[0064]** That is, after the cold rolling, the aluminum material is heated by bringing the aluminum material into contact with a heating body to thereby yield substances which will become etch pit nuclei on the surface of the aluminum material by the subsequent annealing. The reasons for employing the contact heating as a heating method are that the heating control can be performed relatively easily because the surface temperature of the aluminum material can be reached a prescribed temperature uniformly in a short time and that the atmospheric influence can be minimized because the heating can be performed in a short time.

**[0065]** In manufacturing an aluminum material for electrolytic capacitors, conventionally, in order to generate (100) face crystal orientation, final annealing is performed in an inert gas atmosphere or in a vacuum at a temperature range of 450 to 600 °C. However, insufficient amount of substances which will become nuclei will be generated. Thus, the contact heating is performed before the final annealing to quickly heat the aluminum material to enhance the generation of the substances which will become nuclei of etch pits such as crystalline oxide particles at the time of the final annealing.

**[0066]** The substances that can be nuclei of etch pits are not limited to crystalline oxides, but can be high density or thick non-crystalline substances or substances containing crystalline oxides or metal aluminum within noncrystalline. Examples of crystalline oxides include  $Al_2O_3$  such as  $\gamma-Al_2O_3$ ,  $AlOOH$  such as boehmite, and composite oxides included metal ingredients (such as Mg, Pb, Cu) other than aluminum. However, the crystalline oxides are not limited to metal oxides or metal hydroxides.

**[0067]** It is believed that substances different in property from another portion yielded in the oxide film of the aluminum material surface will become nuclei of etch pits at the time of etching. It is presumed that the quick heating of the aluminum material before the final annealing yields substances containing crystals, amorphous in the state before being transitioned to a crystal or a substance containing crystals or metal aluminum in amorphous and that these substances will become the nuclei of etch pits.

**[0068]** The reasons for employing the contact heating using a heating body as a quick heating method are that the contact heating has such advantages that: the surface temperature of the aluminum material can be reached a targeted temperature in a short time and therefore the productivity is excellent; there is less atmospheric influence because of quick heating; and uniform oxide film can be formed in the width and longitudinal directions of the aluminum coil provided that the surface temperature of the heating body which comes into contact with the surface of the aluminum material is uniform.

**[0069]** Hereinafter, a method of manufacturing an aluminum material for electrolytic capacitors will be explained.

**[0070]** The purity of the aluminum material is not specifically limited as long as it falls within a range capable of being used for electrolytic capacitors. The preferable purity is 99.9% or above, more preferably 99.95% or above. The purity of the aluminum material is defined by a value obtained by subtracting the total concentration (%) of Fe, Si, Cu, Mn, Cr, Zn, Ti and Ga from 100%.

**[0071]** Although the method of manufacturing the aluminum material is not limited, a melted component adjustment of aluminum materials · slab casting, homogenization heat treatment, hot rolling, cold rolling including finish cold rolling (low reduction rolling) and final annealing will be performed in this order. It is preferable that (100) area ratio of the aluminum material is 90% or above, and the manufacturing conditions of the aluminum material can be arbitrarily changed in relation to the etching conditions of the aluminum material. For the purpose of eliminating the distortion of the crystal structure of the aluminum material caused by the prior rolling, annealing (hereinafter referred to as "intermediate annealing") may be performed during the cold rolling steps. Furthermore, for the purpose of eliminating impurities and/or oils on the surface of the aluminum material, washing can be performed at a step before the intermediate annealing.

**[0072]** The liquid used for washing a step before the intermediate annealing is not limited to a specific one, but can be alkaline aqueous solution, acid aqueous solution, or organic solvent.

**[0073]** The aluminum material obtained after the rolling steps has oil on the surface thereof. Therefore, if desired, it is preferable to perform washing of the aluminum material before the final annealing but at least before the contact heating, which will be explained later, or after the contact heating. The washing enhances the effects of the contact heating, resulting in large capacitance.

**[0074]** In cases where the contact heating is performed without performing the washing after the rolling and large abrasion particles, etc., are adhered to the surface of the aluminum material, it is preferable to eliminate the particles by washing.

**[0075]** The washing liquid to be used for washing before the contact heating or after the contact heating aims degreasing. Therefore, organic solvent or water containing surfactant can be used as the washing liquid.

**[0076]** As the aforementioned organic solvent, substance which does not cause melting of aluminum can be used. For example, alcohol, diol, aromatic hydrocarbon such as toluene-xylene, alkane series carbon hydride, cyclohexane, ketone, ether, ester and petrochemical products can be exemplified. However, the organic solvent is not limited to the

above.

**[0077]** As the aforementioned alcohol, methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), 1-propanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 2-propanol (CH<sub>3</sub>CH<sub>2</sub>OHCH<sub>3</sub>), 1-butanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 2-butanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(OH)CH<sub>3</sub>), and 1-pentanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 2-pentanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(OH)CH<sub>3</sub>) can be exemplified. The preferable alcohol is one represented by C<sub>n</sub>H<sub>2n+1</sub>OH (n=a natural number of 1 to 10). Alicyclic hydrocarbon derivative such as cyclohexanol can also be used.

**[0078]** As the aforementioned diol, 1,2-ethanediol (HOCH<sub>2</sub>CH<sub>2</sub>OH), 1,2-propanediol (CH<sub>3</sub>CH(OH)CH<sub>2</sub>OH), and 1,3-propanediol (HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH) can be exemplified.

**[0079]** As the aforementioned alkane series hydrocarbon, pentane (C<sub>5</sub>H<sub>12</sub>), hexane (C<sub>6</sub>H<sub>14</sub>), heptane (C<sub>7</sub>H<sub>16</sub>), octane (C<sub>8</sub>H<sub>18</sub>), nonane (C<sub>9</sub>H<sub>20</sub>) and decane (C<sub>10</sub>H<sub>22</sub>) can be exemplified. The preferable one is represented by C<sub>n</sub>H<sub>2n+2</sub> (n=a natural number of 5 to 15). Alicyclic hydrocarbon such as cyclohexane can also be used.

**[0080]** As the aforementioned ketone, acetone (CH<sub>3</sub>COCH<sub>3</sub>), 2-butanone (CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub>), 3-pentanone (CH<sub>3</sub>CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub>), 3-methyl-2-butanone (CH<sub>3</sub>COCH(CH<sub>3</sub>)<sub>2</sub>) can be exemplified. The preferable one is represented by R<sup>1</sup>COR<sup>2</sup> (R<sup>1</sup> and R<sup>2</sup>: aliphatic hydrocarbon group, the total carbon number of R<sup>1</sup> and R<sup>2</sup> is 8 or less). Cyclic keton such as cyclohexanone (C<sub>6</sub>H<sub>10</sub>O) can also be used.

**[0081]** As the aforementioned ether, glycol ether, such as a substance represented by R<sup>1</sup>-O-R<sup>2</sup> (R<sup>1</sup> and R<sup>2</sup>: aliphatic hydrocarbon group, the total carbon number of R<sup>1</sup> and R<sup>2</sup> is 8 or less), 2-methoxy ethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH), 2-etoxyethanol(CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH), 2-butoxyethanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH), or 2-(2-etoxy)etoxyethanol (CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH), can be exemplified.

**[0082]** As the aforementioned ester, acetic ester represented by CH<sub>3</sub>COOR (R: aliphatic hydrocarbon radical whose carbon number is 1 to 5).

**[0083]** As the aforementioned petrochemical product, industrial gasoline (JIS K 2201), motor gasoline (JIS K 2202), aviation gasoline (JIS K 2206), Toyu (kerosene) (JIS K 2203), light oil (JIS K 2204), aviation gasoline (JIS K 2206), petroleum ether (JIS K 8593), petroleum benzine (JIS K 8594), ligroin (JIS K 8937) and kerosene can be exemplified.

**[0084]** As the aforementioned organic solvent, a plurality of organic solvent can be mixed. In the case of organic solvent capable of being mixed with water, such organic solvent can be mixed with water as occasion demands.

**[0085]** As the surfactant contained in the washing liquid in which surfactant is added to water, anionic surfactant, cationic surfactant or nonionic surfactant can be used.

**[0086]** As the anionic surfactant, sulfuric ester salt or sulfonate can be exemplified.

**[0087]** As the sulfuric ester salt, R-OSO<sub>3</sub>N<sub>a</sub> (R=saturated hydrocarbon group whose carbon number is 8-18 or unsaturated hydrocarbon group having one double bond) can be utilized. Concretely, sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub>Na), hexadecyl sodium sulfate (C<sub>16</sub>H<sub>33</sub>OSO<sub>3</sub>Na), Stearyl sodium sulfate (C<sub>18</sub>H<sub>37</sub>OSO<sub>3</sub>Na) and oleyl sodium sulfate (C<sub>18</sub>H<sub>35</sub>OSO<sub>3</sub>Na) can be exemplified.

**[0088]** As the sulfonate, sulfonate represented by R-SO<sub>3</sub>Na (R=saturated hydrocarbon group whose carbon number is 8~18 or unsaturated hydrocarbon group having one double bond) or R-SO<sub>3</sub>N<sub>a</sub> (R=saturated hydrocarbon group whose alkyl radical has a carbon number of 8-14 or alkyl benzyl group which is unsaturated hydrocarbon group having one double bond) can be used.

**[0089]** As the cation surfactant, quaternary ammonium salt represented by R-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>·Cl<sup>-</sup> (R=saturated hydrocarbon group whose carbon number is 8-16) can be used.

**[0090]** As the nonionic surfactant, polyethyleneglycol type nonionic surfactant represented by R-O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H (R=saturated hydrocarbon group whose carbon number is 8~16 or unsaturated hydrocarbon group having one double bond, n=6~14) or R-O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H (R=saturated hydrocarbon group whose alkyl radical has a carbon number of 8-12 or alkylphenyl group which is unsaturated hydrocarbon group having one double bond, n=6~14) can be exemplified. Nonionic surfactant with "n" exceeding the aforementioned range can be contained in the nonionic surfactant at the molar ratio of 50% or less.

**[0091]** Water to which at least one of the aforementioned surfactants is added can be used as the washing liquid. Surfactant whose carbon number is smaller than the aforementioned range can be contained at the molar ratio of 50% or less. It is preferable to avoid mixing the anion surfactant and the cation surfactant since the mixing thereof in water causes precipitation.

**[0092]** Although the concentration of the surfactant is not specifically limited, it is preferable that the concentration is the critical micelle concentration or above to enhance the washing effects.

**[0093]** In the aforementioned washing step, the method of contacting the aluminum material with organic solvent or surfactant solution used as washing liquid is not limited to a specific method. As such a method, immersing, contacting the aluminum material with the surface of the washing liquid and spraying can be exemplified.

**[0094]** To eliminate oil and/or abrasion particles on the surface of the aluminum material, the aluminum material can be brought into contact with, or further rubbed with a brush or a sponge when the aluminum material is in contact with the washing liquid.

**[0095]** In the washing step, the contact time of the aluminum material with the washing liquid is not specifically limited.

However, it is preferable that the contact time is more than 0.5 second but less than 10 minutes. If the contact time of the aluminum material with the washing liquid is less than 0.5 second, the washing becomes insufficient. To the contrary, even if the contact time is longer than 10 minutes, the washing effect will be saturated. In cases where the washing liquid is organic solvent, the preferable liquid temperature of the washing liquid is 5 to 60 °C, and in cases where the washing liquid is water containing surfactant, the preferable liquid temperature of the washing liquid is 5 to 80 °C. If the liquid temperature is lower than the lower limit, the detergency will be insufficient. To the contrary, even if the liquid temperature is raised above the upper limit, the detergency will be saturated.

**[0096]** After washing the aluminum material, the aluminum material can be dried if necessary. The drying can be performed by, for example, heating in air, heating in an inert gases atmosphere, heating in a vacuum. In the case where the drying is performed in air, the preferable atmospheric temperature is 200 °C or below, and the drying time is 10 minutes or less because the drying temperature exceeding 200°C or the heating time exceeding 10 minutes causes a too-grown oxide film, resulting in deteriorated etching characteristics.

**[0097]** The aluminum material rolled or the aluminum material rolled and then washed will be subjected to contact heating to generate a larger number of nuclei of etch pits by the subsequent annealing. The means for the contact heating can be any means capable of attaining the contact heating such as a heated roll, a heated belt or a heated plate. To easily and continuously perform the contact heating, it is preferable to use the heated roll. Furthermore, the aluminum material can be heated both sides or either one side. The heating surface material of the heating body can be an arbitrarily selected material such as stainless, plating, ceramic, Teflon (registered trademark) resin, and silicone resin. However, it is preferable to select a material which does not cause adhesion of the surface oxide film of the aluminum material to the surface of the heating body.

**[0098]** The surface temperature of the heating body which comes into contact with the aluminum material is preferably 50 to 450 °C. If the surface temperature is below 50 °C, the heating becomes insufficient, which may result in insufficient generation of substances which will become nuclei of etch pits such as crystalline oxide particles at the time of final annealing which will be performed after the contact heating. To the contrary, if it exceeds 450°C, the oxide film becomes too thick, causing wrinkles at the time of the cooling, which may cause operational problems. More preferably, the surface temperature of the heating body is 80 to 400°C, still more preferably 100 to 350°C. The optimal surface temperature of the heating body is 160 to 290°C.

**[0099]** The preferable contact time of the surface of the aluminum material and the surface of the heating body is 0.001 to 60 seconds. If the contact time is less than 0.001 second, the heating of the surface of the aluminum material becomes insufficient, which may cause insufficient generation of substances which will become nuclei of etch pits. To the contrary, even if the heating is performed longer than 60 seconds, the oxide film becomes too thick, which may impede the generation of etch pits. The more preferable contact time is 0.001 to 30 seconds, still more preferably 0.01 to 10 seconds. The optimal contact time is 0.1 to 7 seconds.

**[0100]** The surface temperature of the heating body and the contact time can be determined arbitrarily considering the characteristics of the surface oxide film of the aluminum material before the contact heating. The contact heating atmosphere is not specifically limited, and the contact heating can be performed in the air without performing specific atmospheric control.

**[0101]** As an example of a heating apparatus using heating rolls as the heating body, a device provided with at least two heating rolls for performing the contact heating of the front and rear surfaces of the aluminum material can be exemplified. In cases where the aluminum material after the contact heating with heating rolls wrinkles at the time of rolling the aluminum material, the aluminum material can be rolled up after cooling the aluminum material bypassing through one or a plurality of cooling bodies such as cooling rolls after the heating with heating rolls or the like. Especially, in cases where cooling rolls are used as cooling bodies, the cooling can be performed easily and continuously. Furthermore, before heating the aluminum material with heating rolls to the targeted contact heating temperature, the aluminum material can be pre-heated to a temperature lower than the targeted contact heating temperature by the use of other heating rolls.

**[0102]** Subsequent to the contact heating, after the a forementioned washing if necessary, for the primary purpose of the encourage of the production of substances which will become nuclei of etch pits and the enhancement of the etching characteristics by arranging the crystal orientation of the aluminum material into (100) orientation, final annealing is performed.

**[0103]** Needless to say, after the final rolling but before the final annealing, another steps other than the aforementioned steps, such as slitting step for dividing the coiled aluminum material, can also be performed.

**[0104]** In the final annealing, it is preferable to perform the final annealing such that the total thickness of the oxide film after the final annealing becomes 2.5 to 5 nm which is a thickness according to the Hunter Fowle method (see M.S. Hunter and P. Fowle, J. electrochem. Soc. 101[9], 483(1954)) so as not to causes a deterioration of the etching characteristics due to the excessively increased thickness of the oxide film at the final annealing. It is preferable that the (100) area ratio of the aluminum material after the final annealing is 90% or above.

**[0105]** Although the atmosphere at the final annealing is not specifically limited, it is preferable to heat the aluminum

material within an atmosphere containing a less amount of moisture and oxygen so as not to excessively increase the thickness of the oxide film. Concretely, it is preferable to perform the heating in an inert gas such as argon or nitrogen or in a vacuum of 0.1Pa or below.

5 [0106] The final annealing method is not specifically limited. For example, batch annealing can be performed in a state in which the aluminum material is wound into a coil, a coiled aluminum material can be continuously annealed while unwinding and then wound into a coil, or either batch annealing or continuous annealing can be performed plural times.

10 [0107] The temperature and the time of the final annealing are not specifically limited. For example, in the case where batch annealing is performed in a coiled state, it is preferable to perform the final annealing at the aluminum actual temperature of 450 to 600 °C for 10 minutes to 50 hours because of the following reasons. If the aluminum actual temperature is less than 450 °C and the time is less than 10 minutes, the generation of the substances which will become nuclei of etch pits in the oxide film becomes insufficient, causing a nondense status of the substances, which in turn results in an insufficient surface area increasing effect at the time of etching due to crystals as etching nuclei. This may also cause insufficient generation of (100) face crystal orientation. To the contrary, if the annealing is performed at the temperature of 600 °C or above, the aluminum material easily adheres with each other in the case where batch annealing is performed in the coiled manner. Even if the annealing is performed for more than 50 hours, the etching area increasing effect will be saturated, which merely results in an increased heat energy cost. It is more preferable that the aluminum actual temperature is 460 to 600 °C, more preferably 500 to 580°C, and the time is 20 minutes to 40 hours.

15 [0108] The temperature rising rate/pattern is not specifically limited. The temperature can be raised at a constant rate, or the temperature can be raised or lowered stepwise while repeating temperature rising and holding. In any event, any temperature rising rate/patter can be accepted provided that the annealing is performed for a total of 10 minutes to 50 hours within the temperature zone in which the aluminum actual temperature is from 450 to 600 °C. The thickness of the aluminum material for electrolytic capacitor electrodes to be obtained after the final annealing is not limited to a specific one.

20 [0109] The aluminum material to which the final annealing was executed is subjected to etching treatment to increase the surface area increasing ratio. Although the etching conditions are not specifically limited, it is preferable to employ a DC etching method. By employing a DC etching method, at the portions that will become nuclei of etch pits enhanced the generation thereof during the final annealing, the aluminum material is etched deeply to thereby generate a number of tunnel-like pits, resulting in high capacitance.

25 [0110] After the etching, it is preferable to subject the etched aluminum material to a formation to obtain an anode material. Especially, it is preferable to use it as an electrode material for electrolytic capacitors for middle voltage or high voltage. Needless to say, the aluminum material can also be used as a cathode material.

30 [0111] Aluminum electrolytic capacitors can be made by employing the aforementioned anode material and/or cathode material as an electrode material. In this electrolytic capacitor, since the area increased ratio of the electrode material is enhanced, the capacitor has large capacitance.

35 [0112] In this embodiment, since the aluminum material is brought into contact with a heating body after the cold rolling and then subjected to the final annealing, an aluminum material for electrolytic capacitors with excellent etching characteristics because of a large number of yielded substances which will become etch pit nuclei on the surface of the aluminum material can be manufactured. Especially, since the contact heating is employed as a heating method, the surface temperature of the aluminum foil can be reached a targeted temperature evenly in a short time. Thus, the temperature control can be performed with comparative easy. Furthermore, since the heating can be completed quickly in a short time, it becomes possible to lessen the atmospheric influence. Accordingly, by etching this aluminum material for electrolytic capacitors, etch pits generate homogeneously. As a result, etching can be performed effectively, which in turn increases the area enlarging rate. This results in an electrolytic capacitor electrode material with increased capacitance, enabling an aluminum electrolytic capacitor with larger capacitance.

40 [0113] Furthermore, by performing the washing of the aluminum material after or before the contact heating with a heating body, capacitance increasing effect can be obtained.

45 The capacitance of the etched foil after the formation was subjected may be measured by a conventional method, e.g., using a platinum sheet as a counter electrode in 80g/l ammonium borate at the frequency of 120Hz and at the temperature of 30 °C.

50 [0114] The electrolytic capacitor of the present invention is not limited to the embodiment.

(Third embodiment)

55 [0115] In this embodiment, an aluminum material is washed with liquid capable of melting aluminum after the cold rolling, and then a contact heating step for heating the aluminum material by bringing it into contact with the heating body is performed after the final annealing.

[0116] The contact heating of the aluminum material by bringing it into contact with a heating body is excellent in that the surface temperature of the aluminum material can be reached the targeted temperature with the contacting surface

of the heating body in a short time, and has a merit that the temperature control can be performed easily.

[0117] The reason why the etching of the aluminum material obtained by the aforementioned manufacturing method causes an increased effective area thereof is that the contact heating performed before the annealing makes the oxide film of the aluminum material surface layer stable, which causes uniform generation of crystalline particles which will become etch pits on the surface of the aluminum material at the time of the final annealing.

[0118] Examples of the aforementioned crystalline oxide particles include  $Al_2O_3$  such as  $\gamma$ - $Al_2O_3$ ,  $AlOOH$  such as boehmite, oxide or hydroxide of metal ingredients (such as Mg, Pb, Cu) other than aluminum, or composite metal oxides or hydroxides included aluminum and metal ingredients (such as Mg, Pb, Cu) other than aluminum, but is not limited thereto. Furthermore, the crystalline oxide particle can be either monocrystal or polycrystal. Furthermore, the particle can be a particle in which one or plural crystals are covered with amorphous substances, or can be aggregated oxide crystals having amorphous oxides therebetween.

[0119] Hereinafter, a method of manufacturing an aluminum material for electrolytic capacitor electrodes will be explained.

[0120] The purity of the aluminum material is not specifically limited as long as it falls within a range capable of being used for electrolytic capacitor electrodes. The preferable purity is 99.9% or above, more preferably 99.95% or above. In the present invention, the purity of the aluminum material is defined by a value obtained by subtracting the total concentration (%) of Fe, Si, Cu, Mn, Cr, Zn, Ti and Ga from 100%.

[0121] The aluminum material to be subjected to washing with a liquid capable of melting aluminum is generally manufactured by the steps of: a melted component adjustment of aluminum materials · slab casting; homogenization heat treatment; hot rolling; cold rolling; intermediate annealing; and finish cold rolling (low reduction rolling). In these steps, a conventional method can be employed, and the method is not specifically limited. The manufacturing conditions of the aluminum material can be arbitrarily changed in relation to the etching conditions of the aluminum material.

[0122] For the purpose of eliminating the distortion of the crystal structure of the aluminum material caused by the prior rolling, annealing (intermediate annealing) may be performed during the cold rolling steps. Furthermore, for the purpose of eliminating impurities and/or oils on the surface of the aluminum material, washing using acid solution, alkaline solution, or organic solvent can be performed at a step before the intermediate annealing.

[0123] In order to yield a uniform and stable oxide film on the surface layer of the aluminum material to thereby disperse crystalline oxide particles which will become etch pit nuclei on the surface of the aluminum material at the time of the final annealing, the aluminum material is washed with a liquid capable of melting aluminum after the final rolling, and thereafter subjected to the contact heating.

[0124] As the liquid capable of dissolving aluminum, aqueous solution containing at least one element selected from the group consisting of acid, alkali, ammonia and amine. It is preferable to perform at least one of alkali washing and acid washing after the final rolling.

[0125] As the alkali of the alkali washing liquid for the alkali is not limited to a specific one, but sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium silicate, sodium tertiary phosphate, di-sodium hydrogen phosphate, and sodium hypochlorite can be exemplified. Aqueous solution containing at least one of the aforementioned alkalis can be used as washing liquid.

[0126] It is preferable that the alkali concentration in the alkali washing liquid is 0.005 to 50% (mass%, hereinafter simply referred to as "%"), the liquid temperature is 5 to 80 °C, and the washing time is 1 second to 10 minutes. If the alkali concentration is less than 0.005% or the liquid temperature is 5°C, there is a possibility that the surface homogenization effect by the washing cannot be obtained. If the alkali concentration exceeds 50%, it takes a lot of trouble to eliminate the alkali remaining on the surface of the aluminum material after the alkali washing. If the liquid temperature exceeds 80 °C, the aluminum material dissolves quickly, which makes it difficult to control the washing. If the alkali washing time is less than 1 second, the washing becomes insufficient. However, even if the washing time exceeds 10 minutes, the washing effect will be saturated, which may cause excessive dissolving of the aluminum material. More preferably, the alkali concentration in the alkali washing liquid is 0.05 to 10%, the liquid temperature is 10 to 70 °C, and the washing time is 2 seconds to 5 minutes.

[0127] After the alkali washing, it is preferable to perform water washing for the purpose of eliminating the residuals of the washing liquid compositions on the surface of the aluminum material.

[0128] On the other hand, although the acid of the acid washing liquid for the acid washing is not specifically limited, Lewis acid can be used. For example, inorganic acid such as hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, boric acid or hydrofluoric acid, and organic acid such as acetic acid, oxalic acid or citric acid can be exemplified, and aqueous solution containing at least one of these acids can be used as the washing liquid. Furthermore, in order to enhance the degreasing power, surfactant can be added to acid aqueous solution. It is preferable that the concentration of the acid is 0.05 to 50%, the liquid temperature is 5 to 80 °C, and the washing time is 0.5 second to 10 minutes. If the acid concentration at the time of the acid washing, the liquid temperature and the washing time are below the aforementioned lower limit, the washing may be insufficient. To the contrary, if the acid concentration, the liquid temperature and the washing time exceeds the aforementioned upper limit, the washing effect will be saturated, resulting in an increased

cost. More preferably, the acid concentration is 0.05 to 30%, the liquid temperature is 10 to 70 °C and the washing time is 1 second to 5 minutes.

**[0129]** After the acid washing, it is preferable to perform water washing for the purpose of eliminating the residuals of the acid washing liquid compositions on the surface of the aluminum material.

**[0130]** As the method of the alkali washing and the acid washing, an immersing method or a spraying method can be exemplified, but the washing method is not limited to a specific one.

**[0131]** It is enough to perform at least one of the alkali washing and the acid washing. However, both the washing can be performed at least one time. In the case of performing both washing, although the order is not specifically limited, it is preferable that the alkali washing is initially performed and the acid washing follows. In this case, after effectively removing the contaminated layer of the surface of the aluminum material by the alkali washing, the surface thereof is neutralized by performing the acid washing, resulting in a formation of homogeneous and stable oxide film.

**[0132]** The acid concentration in the case of performing the acid washing after the alkali washing can be lower than the aforementioned range of 0.05 to 50%, and the washing time can be shorter than the aforementioned range of 0.5 second to 10 minutes.

**[0133]** Before the alkali washing or acid washing, the aluminum material can be subjected to organic solvent washing for the purpose of decreasing. As the organic solvent, aromatic hydrocarbon such as alcohol or toluene xylene, pentane, hexane, aliphatic hydrocarbon, acetone, ketone, and ester can be exemplified.

**[0134]** Subsequently, the aluminum material subjected to the washing using a liquid capable of making aluminum dissolve is heated by bringing it into contact with a heating body.

**[0135]** The means for the contact heating can be anything capable of attaining the contact heating such as a heated roll, a heated belt or a heated plate, or a combination thereof. Furthermore, the aluminum material can be heated simultaneously from both sides, or heated one side then another side, or heated only either one side. The heating surface material of the heating body can be an arbitrarily selected material such as stainless, plating, ceramic, Teflon (registered trademark) resin, and silicone resin. However, it is preferable to select a material which does not cause adhesion of the surface oxide film of the aluminum material to the surface of the heating body.

**[0136]** The surface temperature of the heating body which is brought into contact with the aluminum material is preferably 50 to 450 °C. If the surface temperature is below 50 °C, the crystallization ratio of the surface layer oxide film after the annealing or the control of the crystalline oxide particles become insufficient. To the contrary, if it exceeds 450°C, the oxide film becomes too thick, causing wrinkles at the time of the cooling, which may cause operational problems. More preferably, the surface temperature of the heating body is 80 to 400°C, optimally 80 to 300°C.

**[0137]** The preferable contact time of the surface of the aluminum material and the surface of the heating body is 0.001 to 60 seconds. If the contact time is less than 0.001 second, the heating of the surface of the aluminum material becomes insufficient. If the heating time exceeds 60 seconds, the oxide film becomes too thick. In either case, the generation of etch pits may be impeded. The more preferable contact time is 0.001 to 30 seconds, still more preferably 0.01 to 20 seconds. The optimal contact time is 0.05 to 15 seconds.

**[0138]** The surface temperature of the heating body and the contact time can be determined arbitrarily considering the characteristics of the oxide film of the aluminum material surface before the contact heating. The contact heating atmosphere is not specifically limited, and the contact heating can be performed in the air without performing specific atmospheric control.

**[0139]** Subsequent to the contact heating, for the primary purpose of improving the etching characteristics by arranging the crystal orientation of the aluminum material into (100) orientation, final annealing is performed.

**[0140]** In the final annealing, it is preferable to perform the final annealing such that the total thickness of the oxide film after the final annealing becomes 2.5 to 5.0 nm which is a thickness according to the Hunter Fowle method (see M.S. Hunter and P. Fowle, J. electrochem. Soc. 101[9], 483(1954)) so as not to causes a deterioration of the etching characteristics due to the excessively increased thickness of the oxide film at the final annealing. It is preferable that the (100) area ratio of the aluminum material after the final annealing is 90% or above.

**[0141]** Although the atmosphere at the final annealing is not specifically limited, it is preferable to heat the aluminum material within an atmosphere containing a less amount of moisture and oxygen so as not to excessively increase the thickness of the oxide film. Concretely, it is preferable to perform the heating in an inert gas such as argon or nitrogen or in a vacuum of 0.1Pa or below.

**[0142]** The final annealing method is not specifically limited. For example, batch annealing can be performed in a state in which the aluminum material is wound into a coil, a coiled aluminum material can be continuously annealed while unwinding and then wound into a coil, or either batch annealing or continuous annealing can be performed plural times.

**[0143]** The holding temperature and the time of the final annealing is not specifically limited. For example, in the case of performing batch annealing in a coiled state, it is preferable to perform the final annealing at the aluminum actual temperature of 450 to 600 °C for 10 minutes to 50 hours because of the following reasons. If the aluminum actual temperature is less than 400 °C and the time is less than 10 minutes, the generation of the crystalline oxide particles which will become nuclei of etch pits in the oxide film becomes insufficient, causing a nondense status of the substances,

which in turn results in an insufficient surface area increasing effect at the time of etching in the presence of crystals as etching nuclei. This may also cause insufficient generation of (100) side crystal orientation. To the contrary, if the annealing is performed at the temperature of 600 °C or above, the aluminum material easily adheres with each other in the case of performing batch annealing in the coiled manner. Even if the annealing is performed for more than 50 hours, the etching area increasing effect will be saturated, which merely results in an increased heat energy cost. It is more preferable that the aluminum actual temperature is 460 to 560 °C and the time is 30 minutes to 40 hours.

**[0144]** The temperature rising rate/pattern is not specifically limited. The temperature can be raised at a constant rate, or the temperature can be raised or lowered stepwise while repeating temperature rising and holding. In any event, any temperature rising rate/patter can be accepted provided that the annealing is performed for a total of 10 minutes to 50 hours within the temperature zone in which the aluminum actual temperature is from 450 to 600 °C.

**[0145]** The thickness of the aluminum material for electrolytic capacitor electrodes to be obtained after the final annealing is not limited to a specific one.

**[0146]** The aluminum material to which the final annealing was executed is subjected to etching treatment to increase the surface area. Although the etching conditions are not specifically limited, it is preferable to employ a DC etching method. By employing a DC etching method, crystalline oxide particles existing on the surface of the aluminum material will become nuclei of etch pits to thereby generate a number of tunnel-like pits.

**[0147]** After the etching, it is preferable to subject the etched aluminum material to a formation to obtain an anode material. Especially, it is preferable to use it as an electrode material for electrolytic capacitors for middle voltage or high voltage. Needless to say, the aluminum material can also be used as a cathode material.

**[0148]** With this embodiment, the aluminum material after the washing with a solution capable of dissolving aluminum is subjected to contact heating to stabilize the surface layer oxide film of the aluminum material, and then annealed. Thus, an aluminum material for electrolytic capacitor electrodes excellent in etching characteristics and capable of obtaining high capacitance can be manufactured. Especially, since the contact heating is employed as a heating method, the surface temperature of the aluminum material can be reached a targeted temperature evenly in a short time. Thus, the temperature control can be performed with comparative easy. Furthermore, since the heating can be completed quickly in a short time, it becomes possible to lessen the atmospheric influence.

**[0149]** The capacitance of the etched foil after the formation was subjected may be measured by a conventional method, e.g., using a platinum sheet as a counter electrode in 80g/l ammonium borate at the frequency of 120Hz and at the temperature of 30 °C.

**[0150]** The electrolytic capacitor of the present invention is not limited to the embodiment.

(Fourth embodiment)

**[0151]** In this embodiment, the contact heating step for heating the aluminum material by bringing it into contact with the heating body is performed after the final annealing.

**[0152]** That is, by heating the aluminum material after the final annealing by bringing the aluminum material into contact with a heating body, the surface layer oxide film of the aluminum material can be formed homogeneously, resulting in an aluminum material for electrolytic capacitor electrodes excellent in etching characteristics. The reasons for employing the contact heating as a heating method are that the heating control has advantages: the surface temperature of the aluminum material can be reached a prescribed temperature uniformly in a short time with the heating body surface; the control is relatively easy; the productivity is high; the atmospheric influence can be minimized because of the quick heating; and uniform oxide film can be performed in the widthwise and longitudinal directions of the aluminum material.

**[0153]** Hereinafter, a method of manufacturing an aluminum material for electrolytic capacitors will be explained.

**[0154]** The purity of the aluminum material is not specifically limited as long as it falls within a range capable of being used for electrolytic capacitors. The preferable purity is 99.9% or above, more preferably 99.95% or above. The purity of the aluminum material is defined by a value obtained by subtracting the total concentration (%) of Fe, Si, Cu, Mn, Cr, Zn, Ti and Ga from 100%.

**[0155]** Although the method of manufacturing the aluminum material is not specifically limited, a melted component adjustment of aluminum materials · slab casting, homogenization heat treatment, hot rolling, cold rolling including finish cold rolling (low reduction rolling) and final annealing will be performed in this order. The manufacturing conditions of the aluminum material can be arbitrarily changed in relation to the etching conditions of the aluminum material. For the purpose of eliminating the distortion of the crystal structure of the aluminum material caused by the prior rolling, annealing ("intermediate annealing") may be performed during the rolling steps.

**[0156]** Furthermore, for the purpose of eliminating impurities and/or oils on the surface of the aluminum material, washing can be performed after the hot rolling, during the cold rolling, or after the finish cold rolling but before the final annealing. The washing solution to be used for the washing is not limited to a specific one, and alkaline aqueous solution, acid aqueous solution or organic solvent can be utilized for example.

**[0157]** The aluminum material subjected to the hot rolling can be treated in a coiled state until the contact heating

which will be performed after the final annealing. The aluminum material can be cut at the intermediate step to handle as cut samples. In the case of treating in a coiled state, a slit can be formed at any step before the final annealing, after the final annealing, or after the contact heating.

5 [0158] Subsequent to the final cold rolling, after the washing, etc. if required, for the primary purpose of improving the etching characteristics by arranging the crystal orientation of the aluminum material into (100) orientation, final annealing will be performed.

10 [0159] In the final annealing, it is preferable to perform the final annealing such that the total thickness of the oxide film after the final annealing becomes 2.5 to 5 nm which is a thickness according to the Hunter Fowle method (see M.S. Hunter and P. Fowle, J. electrochem. Soc. 101[9], 483(1954)) so as not to cause a deterioration of the etching characteristics due to the excessively increased thickness of the oxide film at the final annealing. It is preferable that the (100) area ratio of the aluminum material after the final annealing is 90% or above.

15 [0160] Although the atmosphere at the final annealing is not specifically limited, it is preferable to heat the aluminum material within an atmosphere containing a less amount of moisture and oxygen so as not to excessively increase the thickness of the oxide film. Concretely, it is preferable to perform the heating in an inert gas such as argon or nitrogen or in a vacuum of 0.1Pa or below.

[0161] The final annealing method is not specifically limited. For example, batch annealing can be performed in a state in which the aluminum material is wound into a coil, a coiled aluminum material can be continuously annealed while unwinding and then wound into a coil, or either batch annealing or continuous annealing can be performed plural times.

20 [0162] The temperature and the time of the final annealing are not specifically limited. For example, in the case of performing batch annealing in a coiled state, it is preferable to perform the final annealing at the aluminum actual temperature of 450 to 600 °C for 10 to 50 hours because of the following reasons. If the aluminum actual temperature is less than 450 °C and the time is less than 10 minutes, there is a possibility that the state of the aluminum surface layer does not become suitable for etching and the growth of (100) face crystal orientation becomes insufficient. To the contrary, if the annealing is performed at the temperature of 600 °C or above, the aluminum material easily adheres with each other in the case of performing batch annealing in the coiled manner. Even if the annealing is performed for more than 50 hours, the etching area increasing effect will be saturated, which merely results in an increased heat energy cost. It is more preferable that the aluminum actual temperature is 460 to 580 °C and the time is 20 minutes to 40 hours.

25 [0163] The temperature rising rate/pattern is not specifically limited. The temperature can be raised at a constant rate, or the temperature can be raised or lowered stepwise while repeating temperature rising and holding. In any event, any temperature rising rate/patter can be accepted provided that the annealing is performed for a total of 10 minutes to 50 hours within the temperature zone in which the aluminum actual temperature is from 450 to 600 °C.

30 [0164] After the final annealing, the aluminum material is subjected to, after the surface washing if necessary, the contact heating to obtain a homogeneous surface oxide film. The heating means can be anything provided that it is capable of attaining the contact heating such as a heated roll, a heated belt or a heated plate. Furthermore, the aluminum material can be heated one side then another side, or heated only either one side. The heating surface material of the heating body can be an arbitrarily selected material such as stainless, plating, ceramic, Teflon (registered trademark) resin, and silicone resin. However, it is preferable to select a material which does not cause adhesion of the surface oxide film of the aluminum material to the surface of the heating body.

35 [0165] The surface temperature of the heating body which will be brought into contact with the aluminum material is preferably 50 to 450 °C. If the surface temperature is below 50 °C, the heating may become insufficient, resulting in non-uniform etch pits by etching. To the contrary, if it exceeds 450°C, the oxide film becomes too thick, causing wrinkles at the time of the cooling, which may cause operational problems. More preferably, the surface temperature of the heating body is 80 to 400°C, still more preferably 100 to 350 °C. The optimal surface temperature of the heating body is 160 to 290 °C.

40 [0166] The preferable contact time of the surface of the aluminum material and the surface of the heating body is 0.001 to 60 seconds. If the contact time is less than 0.001 second, a homogeneous surface oxide layer of the aluminum material cannot be obtained, causing uneven generation of etch pits. To the contrary, if the heating time exceeds 60 seconds, the oxide film becomes too thick, which impedes the generation of the etch pits. The more preferable contact time is 0.01 to 30 seconds, still more preferably 0.05 to 10 seconds.

45 [0167] The surface temperature of the heating body and the contact time can be determined arbitrarily considering the characteristics of the oxide film of the aluminum material before the contact heating. The contact heating atmosphere is not specifically limited, and the contact heating can be performed in the air without performing specific atmospheric control.

50 [0168] As an example of a heating apparatus using heating rolls as the heating body, a device provided with at least two heating rolls for performing the contact heating of the front and rear surfaces of the aluminum material can be exemplified. In cases where the aluminum material after the contact heating with heating rolls wrinkles at the time of rolling the aluminum material, the aluminum material can be rolled up after cooling the aluminum material by passing through one or a plurality of cooling bodies such as cooling rolls after the heating with heating rolls or the like. Especially,

in cases where cooling rolls are used as cooling bodies, the cooling can be performed easily and continuously. Furthermore, before heating the aluminum material with heating rolls to the targeted contact heating temperature, the aluminum material can be pre-heated to a temperature lower than the targeted contact heating temperature by the use of another heating rolls.

5 **[0169]** The thickness of the aluminum material for electrolytic capacitor electrodes to be obtained after the final annealing is not limited to a specific one.

**[0170]** The aluminum material to which the contact heating was executed after the final annealing is subjected to etching treatment to increase the surface area. Although the etching conditions are not specifically limited, it is preferable to employ a DC etching method. By employing a DC etching method for aluminum with homogeneous surface layer oxide film, a number of tunnel-like pits are generated, which in turn realizes high capacitance.

10 **[0171]** After the etching, it is preferable to subject the etched aluminum material to a formation to obtain an anode material. Especially, it is preferable to use it as an electrode material for electrolytic capacitors for middle voltage or high voltage. Needless to say, the aluminum material can also be used as a cathode material.

15 **[0172]** Aluminum electrolytic capacitors can be made by employing the aforementioned anode material and/or cathode material as an electrode material. In this electrolytic capacitor, since the area increased ratio of the electrode material is enhanced, the capacitor has large capacitance.

**[0173]** With this embodiment, by heating the aluminum material by coming into contact with a heating body after the final annealing, the surface layer oxide film of the aluminum material can be homogenized. Thus, an aluminum material for electrolytic capacitor electrodes excellent in etching can be manufactured. Especially, since the contact heating is employed as a heating method, the surface temperature of the aluminum material can be reached a targeted temperature evenly in a short time. Thus, the temperature control can be performed with comparative easy. Furthermore, since the heating can be completed quickly in a short time, it becomes possible to lessen the atmospheric influence. Accordingly, by etching the aluminum material for electrolytic capacitors, the etch pits can be generated homogeneously, causing an enhanced surface area increasing ratio, which in turn results in an aluminum material for electrolytic capacitor electrodes with increased capacitance. As a result, an aluminum electrolytic capacitance having a larger capacitance can be obtained.

20 **[0174]** The capacitance of the etched foil after the formation was subjected may be measured by a conventional method, e.g., using a platinum sheet as a counter electrode in 80g/l ammonium borate at the frequency of 120Hz and at the temperature of 30 °C.

30 **[0175]** The electrolytic capacitor of the present invention is not limited to the embodiment.

#### EXAMPLE

[First examples]

35 **[0176]** These examples correspond to the first embodiment.

(Example 1)

40 **[0177]** A plate obtained by hot-rolling an aluminum slab was subjected to cold rolling to obtain an aluminum material coil 250  $\mu\text{m}$  in thick with a purity of 99.99%. This aluminum material coil was further subjected to cold rolling to obtain an material 140  $\mu\text{m}$  in thick, then brought into contact with a heating roll with a surface temperature of 200 °C for 2 seconds, and thereafter brought into contact with a cooling roll with a surface temperature of 30 °C. Subsequently, the coiled aluminum material was held in a nitrogen atmosphere at the actual temperature of 250 °C for 24 hours to execute the intermediate annealing, and then subjected to finish cold rolling.

45 **[0178]** The aluminum material after the finish cold rolling was washed with n-hexane. The actual temperature of the washed aluminum material was raised from the room temperature to 540°C in an argon atmosphere at the rate of 50 °C/h, then hold at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and taken out of the furnace to thereby obtain an aluminum material 500 mm in width and 1,000 m in length for electrolytic capacitor electrodes.

50 (Examples 2 to 16)

**[0179]** In the same manner as in Example 1, a plate obtained by hot-rolling an aluminum slab was subjected to cold rolling to obtain an aluminum material coil 250  $\mu\text{m}$  in thick with a purity of 99.99%. Then, the steps shown in Table 1 were performed sequentially to thereby obtain an aluminum material 500 mm in width and 1,000 m in length for electrolytic capacitor electrodes, respectively.

## EP 1 498 513 B9

(Comparative Example 1)

**[0180]** An aluminum material for electrolytic capacitor electrodes was obtained in the same manner except that the contact heating was not performed during the cold rolling.

5 **[0181]** Each of the aluminum materials obtained in the aforementioned Examples and Comparative Example was immersed in an aqueous solution having a liquid temperature of 75 °C, containing HCl 1.0 mol/l and H<sub>2</sub>SO<sub>4</sub> 3.5 mol/l, and then electrolyzed at the current density of 0.2 A/cm<sup>2</sup>. Each electrolyzed aluminum material was further immersed in a hydrochloric acid-sulfuric acid mixed aqueous solution having the aforementioned compositions at the temperature of 90 °C for 360 seconds to increase the pit diameter to thereby obtain an etched foil. The obtained etched foil was  
10 subjected to formation at the voltage of 270 V in accordance with EIAJ standard to obtain a capacitance measuring sample.

**[0182]** The capacitance of each aluminum material obtained in Examples and Comparative Example was measured at a total of 6 portions, i.e., three portions, a widthwise central portion and two inside portions of 100 mm from the right and left widthwise edges at the longitudinal portions of 100 m and 900 m from the longitudinal end portion of the coiled aluminum material.

15 **[0183]** The measured capacitance of each sample is shown in Table 1 as a relative value where Comparative Example is 100.

20

25

30

35

40

45

50

55

Table 1

Example No	Step ①	Step ②	Step ③	Step ④	Step ⑤	Step ⑥	Step ⑦	Step ⑧	Capacitance *2	Capacitance difference *3	Rolling rate after final contact rolling
1	-	Performed	200°C 1 sec. *1	Performed	-	Performed	Performed	540°C 24 hours	110	1	21
2	-	Performed	120°C 10 sec. *1	Performed	-	Performed	Performed	540°C 24 hours	105	2	21
3	-	Performed	100°C 5 sec. *1	Performed	-	Performed	Performed	540°C 24 hours	104	2	21
4	-	Performed	160°C 4 sec.	Performed	-	Performed	Performed	540°C 24 hours	106	1	21
5	-	Performed	280°C 2 sec.	Performed	-	Performed	Performed	540°C 24 hours	108	1	21
6	-	Performed	350°C 0.5 sec.	Performed	-	Performed	Performed	540°C 24 hours	107	1	21
7	-	Performed	400°C 0.005 sec.	Performed	-	Performed	Performed	540°C 24 hours	105	2	21
8	-	Performed	200°C 2 sec.	Performed	-	Performed	Performed	540°C 24 hours	111	1	21
9	-	Performed	200°C 2 sec.	Performed	-	Performed	Performed	470°C 24 hours	102	1	21
10	-	Performed	200°C 2 sec.	Performed	-	Performed	Performed	560°C 24 hours	106	1	21
11	200°C 2 sec.	Performed	200°C 2 sec.	Performed	-	Performed	Performed	540°C 24 hours	108	1	21
12	200°C 2 sec.	Performed	-	Performed	200°C 2 sec.	Performed	Performed	540°C 24 hours	107	2	21
13	-	Performed	200°C 2 sec. *1	Performed	-	Performed	Performed	540°C 24 hours	108	1	21
14	200°C 2 sec.	Performed	-	Performed	-	Performed	Performed	540°C 24 hours	102	2	56
15	-	Performed	90°C 30sec.	Performed	-	Performed	Performed	540°C 24 hours	104	2	21
16	-	Performed	60°C 60sec.	Performed	-	Performed	Performed	500°C 24 hours	103	2	21
Comparative Example 1	-	Performed	-	Performed	-	Performed	Performed	540°C 24 hours	100	3	-

[0184] In Table 1, the content of each step, \*1, \*2 and \*3 is shown as follows.

- Step ① contact heating: aluminum material 250 μm in thick is contact-heated in an air atmosphere  
 Step ② cold rolling: aluminum material 250 μm in thick is cold-rolled into a thickness of 140 μm  
 Step ③ contact heating: aluminum material 140 μm in thick is contact-heated in an air atmosphere  
 Step ④ intermediate annealing: annealing at 250 °C for 24 hours in a nitrogen atmosphere  
 Step ⑤ contact heating: aluminum material 140 μm in thick is contact-heated in an air atmosphere  
 Step ⑥ finish cold rolling: aluminum material 140 μm in thick is cold-rolled into a thickness of 110 μm  
 Step ⑦ washing: immersing the aluminum material into n-hexane

## EP 1 498 513 B9

Step © final annealing: the annealing temperature shown in Table denotes the aluminum material actual holding temperature. The raising rate from the room temperature to the holding temperature is 50 °C/h.

\*1: after the contact heating, cooling with cooling rolls (roll surface temperature: 30°C) is performed.

\*2: relative value of average capacitor of each sample, where the average value of capacitance at 6 positions of the aluminum material coil of Comparative Example 1 is 100.

\*3: capacitance difference

1: capacitance at all of 6 positions is an average value  $\pm 1.5\%$  or less

2: capacitance at all of 6 positions is an average value  $\pm 2\%$  or less, there exists a portion where the capacitance is higher than the average value by 1.5% or more or a portion where the capacitance is lower than an average value by 1.5% or more

3: there exists a portion where the capacitance is higher than the average by 2% or more or exists a portion where the capacitance is lower than the average by 2% or more

**[0185]** From the Examples and Comparative Example shown in Table 1, performing the contact eating during the cold rolling can make capacitance fluctuations smaller and increase the capacitance.

[Second Example]

**[0186]** This example corresponds to a second embodiment.

[Examples 101 to 112 and Comparative Examples 101 to 103]

(Example 101)

**[0187]** An aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 2 seconds by pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C. In a state in which the contact-heated aluminum materials are piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 102)

**[0188]** In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 2 seconds by pinched by and between two sheets of stainless heating plates having a surface temperature of 250 °C. In a state in which the contact-heated aluminum materials are piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 103)

**[0189]** In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 2 seconds by pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C. In a state in which the contact-heated aluminum materials are piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 560 °C at the rate of 50°C/h, and then held at 560 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 104)

5 [0190] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 1 second by pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C. In a state in which the contact-heated aluminum materials are piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 105)

15 [0191] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute. Then, two heating rolls (each having a hard chrome plated surface) whose surface temperature was set to be 200°C were prepared. The front surface of the aluminum material was contacted with the first heating roll for 1 second to thereby perform the contact heating. Subsequently, the rear surface of the aluminum material was contacted with the second heating roll for 1 second to thereby perform the contact heating. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

25 (Example 106)

30 [0192] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 1 second by pinched by and between two sheets of stainless heating plates having a surface temperature of 90 °C. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

35 (Example 107)

40 [0193] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute. Then, two heating rolls (each having a hard chrome plated surface) whose surface temperature was set to be 380 °C were prepared. The front surface of the aluminum material was contacted with the first heating roll for 0.1 second to thereby perform the contact heating. Subsequently, the rear surface of the aluminum material was contacted with the second heating roll for 0.1 second to thereby perform the contact heating. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

50 (Example 108)

55 [0194] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute. Then, two heating rolls (each having a hard chrome plated surface) whose surface temperature was set to be 250°C were prepared. The front surface of the aluminum material was contacted with the first heating roll for 0.005 second to thereby perform the contact heating. Subsequently, the rear surface of the aluminum material was contacted with the second heating roll for 0.005 second to thereby perform the contact heating. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours.

## EP 1 498 513 B9

Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 109)

5  
[0195] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 30 seconds by pinched by and between two sheets of stainless heating plates having a surface temperature of 150 °C. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

15 (Example 110)

[0196] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 2 seconds by pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 480 °C at the rate of 50°C/h, and then held at 480 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

25 (Example 111)

[0197] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute, and then contact-heated in the air for 2 seconds by pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C. In a state in which the contact-heated aluminum materials were piled up, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 580 °C at the rate of 50°C/h, and then held at 580 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 112)

[0198] In the same manner as in Example 101 except that the aluminum material was closely disposed between stainless plates having a surface temperature of 10 °C for 10 seconds, a high purity aluminum material for electrolytic capacitors was obtained.

(Comparative Example 101)

45 [0199] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute. Then, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Comparative Example 102)

55 [0200] In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute. Then, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 480 °C at the rate of 50°C/h, and then held at 480 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum

material for electrolytic capacitors was obtained.

(Comparative Example 103)

5 **[0201]** In the same manner as in Example 101, an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick was prepared. The obtained aluminum material was immersed in alkane series hydrocarbon for 2 seconds, dried in air at 90 °C for 1 minute. Then, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 580 °C at the rate of 50°C/h, and then held at 580 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

10 **[0202]** Each aluminum material obtained in the aforementioned Examples and Comparative Examples was immersed in acid, and then subjected to electrolytic etching in hydrochloric acid-sulfuric acid aqueous solution. Thereafter, the aluminum material was immersed in acid aqueous solution to increase the pitch diameter to thereby obtain an etched foil. The obtained etched foil was subjected to formation at the voltage of 270 V in accordance with EIAJ standard to obtain a capacitance measuring sample.

15 **[0203]** The contact heating conditions, the actual temperature of the aluminum material at the time of the annealing, and the capacitance evaluations in each Example and Comparative Example are shown in Table 2. The capacitance evaluation is a relative value when Comparative Example 101 is 100).

20 Table 2

	Contact heating conditions			Annealing actual temp. / °C	Capacitance evaluation (relative value when Comp. Example 1 is 100)
	Surface temp. of heating body / °C	Contact time /sec.	Heating body		
Example 101	200	2	Heating plate	540	104
Example 102	250	2	Heating plate	540	104
Example 103	200	2	Heating plate	560	106
Example 104	200	1	Heating plate	540	104
Example 105	200	1	Heating roll	540	104
Example 106	90	1	Heating plate	540	104
Example 107	380	0.1	Heating roll	540	105
Example 108	250	0.005	Heating roll	540	104
Example 109	150	30	Heating plate	540	104
Example 110	200	2	Heating plate	480	104
Example 111	200	2	Heating plate	580	105
Example 112	200	2 (Cooling after heating)	Heating plate	540	105
Comp. Ex. 101	No contact heating			540	100
Comp. Ex. 102	No contact heating			480	96
Comp. Ex. 103	No contact heating			580	100

50 **[0204]** As will be apparent from Table 2, in Examples, by performing the contact heating using heating plates or heating rolls before the annealing, the capacitance was increased as compared with Comparative Examples 101 to 103 in which no contact heating was performed.

55 [Examples 113 to 230 and Comparative Example 104]

**[0205]** Washing solution in which organic solvent shown in Tables 3 and 4 and surfactant shown in Table 5 were added to water was prepared.

EP 1 498 513 B9

Table 3

Washing liquid No.	Type	Liquid temp. (°C)
A1	methanol (CH <sub>3</sub> OH)	25
A2	ethanol (C <sub>2</sub> H <sub>5</sub> OH)	25
A3	1-propanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	25
A4	2-propanol (CH <sub>3</sub> CH <sub>2</sub> (OH)CH <sub>3</sub> )	25
A5	1-butanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	25
A6	2-butanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> (OH)CH <sub>3</sub> )	25
A7	1-pentanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	25
A8	1-decanol (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> OH)	25
A9	cyclohexanol (C <sub>6</sub> H <sub>11</sub> OH)	25
A10	1,2-ethanediol (HOCH <sub>2</sub> CH <sub>2</sub> OH)	25
A11	1,2-propanediol (CH <sub>3</sub> CH(OH)CH <sub>2</sub> OH)	25
A12	1,3-propanediol (HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	25
A13	pentane (C <sub>5</sub> H <sub>12</sub> )	25
A14	octane (C <sub>8</sub> H <sub>18</sub> )	25
A15	decane (C <sub>10</sub> H <sub>22</sub> )	25
A16	pentadecane (C <sub>15</sub> H <sub>32</sub> )	25
A17	cyclohexane (C <sub>6</sub> H <sub>12</sub> )	25
A18	acetone (CH <sub>3</sub> COCH <sub>3</sub> )	25
A19	2-butanone (CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> )	25
A20	3-pentanone (C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> )	25
A21	3-methyl-2 butanone (CH <sub>3</sub> COCH(CH <sub>3</sub> ) <sub>2</sub> )	25
A22	5-nonanone (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> )	25
A23	cyclohexanone (C <sub>6</sub> H <sub>10</sub> O)	25
A24	ethoxyethane (C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> )	25
A25	ethoxypropane (C <sub>2</sub> H <sub>5</sub> O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> )	25
A26	butoxibutane (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> )	25
A27	2-methoxyethanol (CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)	25
A28	2-ethoxyethanol (CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)	25
A29	2-butoxiethanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)	25
A30	2-(2-ethoxy) ethoxyethanol (CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)	25

Table 4

Washing liquid No.	Type	Liquid temp. (°C)
A31	methyl acetate (CH <sub>3</sub> COOCH <sub>3</sub> )	25
A32	ethyl acetate (CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> )	25
A33	propyl acetate (CH <sub>3</sub> COO(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> )	25
A34	butyl acetate (CH <sub>3</sub> COO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> )	25

EP 1 498 513 B9

(continued)

Washing liquid No.	Type	Liquid temp. (°C)
A35	pentyl acetate (CH <sub>3</sub> COO(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> )	25
A36	toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	25
A37	xylene (C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> )	25
A38	toluene: xylene=1:1 (Volume ratio)	25
A39	toluene: xylene: 2- butanone=1:1:1	25
A40	kerosene	25

Table 5

Mark	Surfactant	Concentration of the surfactant (mol/l)	Liquid temp. (°C)
B1	C <sub>8</sub> H <sub>17</sub> OSO <sub>3</sub> Na (Octyl sodium sulfate)	170 × 10 <sup>-3</sup>	25
B2	C <sub>10</sub> H <sub>21</sub> OSO <sub>3</sub> Na (decyl sodium sulfate)	50 × 10 <sup>-3</sup>	25
B3	C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> Na (dodecyl sodium sulfate)	10 × 10 <sup>-3</sup>	25
B4	C <sub>16</sub> H <sub>33</sub> OSO <sub>3</sub> Na (hexadecyl sodium sulfate)	0.8 × 10 <sup>-3</sup>	25
B5	C <sub>18</sub> H <sub>37</sub> OSO <sub>3</sub> Na (stearyl sodium sulfate)	0.25 × 10 <sup>-3</sup>	25
B6	C <sub>18</sub> H <sub>35</sub> OSO <sub>3</sub> Na (oleyl sodium sulfate)	0.4 × 10 <sup>-3</sup>	25
B7	C <sub>8</sub> H <sub>17</sub> SO <sub>3</sub> Na (octyl sulfonic acid sodium)	200 × 10 <sup>-3</sup>	25
B8	C <sub>10</sub> H <sub>21</sub> SO <sub>3</sub> Na (decyl sulfonic acid sodium)	60 × 10 <sup>-3</sup>	25
B9	C <sub>12</sub> H <sub>25</sub> SO <sub>3</sub> Na (dodecyl sulfonic acid sodium)	15 × 10 <sup>-3</sup>	25
B10	C <sub>16</sub> H <sub>33</sub> SO <sub>3</sub> Na (hexadecyl sulfonic acid sodium)	1.5 × 10 <sup>-3</sup>	25
B11	C <sub>18</sub> H <sub>37</sub> SO <sub>3</sub> Na (stearyl sulfonic acid sodium)	1.3 × 10 <sup>-3</sup>	25
B12	C <sub>18</sub> H <sub>35</sub> SO <sub>3</sub> Na (oleyl sulfonic acid sodium)	2 × 10 <sup>-3</sup>	25
B13	C <sub>8</sub> H <sub>17</sub> -C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> Na (octa benzene sulfonic acid sodium)	15 × 10 <sup>-3</sup>	25
B14	C <sub>10</sub> H <sub>21</sub> -C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> Na (decyl benzene sulfonic acid sodium)	5 × 10 <sup>-3</sup>	25
B15	C <sub>12</sub> H <sub>25</sub> -C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> Na (dodecyl benzene sulfonic acid sodium)	1.7 × 10 <sup>-3</sup>	25
B16	C <sub>14</sub> H <sub>29</sub> -C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> Na (tetradecyl benzene sulfonic acid sodium)	1 × 10 <sup>-3</sup>	25
B17	C <sub>10</sub> H <sub>21</sub> -N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ·Cl <sup>-</sup> (decyl trimethylammonium chloride)	200 × 10 <sup>-3</sup>	25
B18	C <sub>12</sub> H <sub>25</sub> -N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ·Cl <sup>-</sup> (dodecyltrimethylammonium chloride)	25 × 10 <sup>-3</sup>	25
B19	C <sub>16</sub> H <sub>33</sub> <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ·Cl <sup>-</sup> (hexadecyl trimethylammonium chloride)	2 × 10 <sup>-3</sup>	25
B20	octanol EO 6 mol affixture (C <sub>8</sub> H <sub>17</sub> O (CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> H)	150 × 10 <sup>-3</sup>	25
B21	dodecanol EO 6 mol affixture (C <sub>12</sub> H <sub>25</sub> O (CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> H)	12 × 10 <sup>-3</sup>	25

EP 1 498 513 B9

(continued)

Mark	Surfactant	Concentration of the surfactant (mol/l)	Liquid temp. (°C)
B22	hexadecanol EO 6 mol affixture (C <sub>16</sub> H <sub>33</sub> O (CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> H)	2 × 10 <sup>-3</sup>	25
B23	dodecanol EO 10 mol affixture (C <sub>12</sub> H <sub>25</sub> O (CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> H)	16 × 10 <sup>-3</sup>	25
B24	dodecanol EO 14 mol affixture (C <sub>12</sub> H <sub>25</sub> O (CH <sub>2</sub> CH <sub>2</sub> O) <sub>14</sub> H)	25 × 10 <sup>-3</sup>	25
B25	octyl phenol EO 10 mol affixture (C <sub>8</sub> H <sub>17</sub> -C <sub>6</sub> H <sub>4</sub> -O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> H)	12 × 10 <sup>-3</sup>	25
B26	nonyl phenol EO 10 mol affixture (C <sub>9</sub> H <sub>19</sub> -C <sub>6</sub> H <sub>4</sub> -O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> H)	8 × 10 <sup>-3</sup>	25
B27	dodecylphenol EO 10 mol affixture (C <sub>12</sub> -C <sub>25</sub> -C <sub>6</sub> H <sub>4</sub> -O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> H)	2 × 10 <sup>-3</sup>	25
B28	nonyl phenol EO 6 mol affixture (C <sub>9</sub> H <sub>19</sub> -C <sub>6</sub> H <sub>4</sub> -O (CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> H)	7 × 10 <sup>-3</sup>	25
B29	nonyl phenol EO 14 mol affixture (C <sub>9</sub> H <sub>19</sub> -C <sub>6</sub> H <sub>4</sub> -O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>14</sub> H)	15 × 10 <sup>-3</sup>	25

(Example 113)

**[0206]** An aluminum material with a purity of 99.99% rolled into 110 μ m in thick was immersed in the A1 solution shown Table 3 for 2 seconds, and dried in air at 90 °C for 60 seconds. Then, the aluminum material was pinched by two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds.

**[0207]** Subsequently, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Examples 114 to 188)

**[0208]** An aluminum material with a purity of 99.99% rolled into 110 μ m in thick, which was the same aluminum material as in Example 113, was washed and dried under the conditions of the steps shown in Tables 6 to 9. Then, the aluminum material was pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds. In Examples 253 to 282, the aluminum material was contacted by and rubbed with a brush when the aluminum material was immersed in the washing solution.

**[0209]** Subsequently, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Examples 189 to 196)

**[0210]** An aluminum material with a purity of 99.99% rolled into 110 μ m in thick, which was the same aluminum material as in Example 113, was pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds.

**[0211]** Subsequently, the aluminum material was washed and dried under the conditions of the step 3 shown in Table 8. The aluminum material was contacted by and rubbed with a brush when the aluminum material was immersed in the washing solution.

**[0212]** In the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

## EP 1 498 513 B9

(Examples 197 to 202)

5 **[0213]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick, which was the same aluminum material as in Example 113, was washed and dried under the conditions of the step 1 shown in Table 8. Then, the aluminum material was pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds. The contact heated aluminum material was washed and dried under the conditions of the Step 3 shown in Table 8.

10 **[0214]** Under the conditions in Step 3, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C /h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Examples 203 to 207)

15 **[0215]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick, which was the same aluminum material as in Example 113, was washed and dried under the conditions of the steps shown in Table 8. Then, the aluminum material was pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds.

20 **[0216]** In the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Examples 208 to 211)

25 **[0217]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick, which was the same aluminum material as in Example 113, was pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds. Subsequently, the aluminum material was washed and dried under the conditions of the step 3 shown in Tables 9 and 10. The aluminum material was contacted by and rubbed with a brush when the aluminum material was immersed in the washing solution.

30 **[0218]** In the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Examples 212 to 228)

35 **[0219]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick, which was the same aluminum material as in Example 113, was washed and dried under the conditions of the step 1 shown in Table 10, and was subjected to the contact heating under the conditions of Step 2 in Table 9.

40 **[0220]** Then, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 229)

45 **[0221]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick, which was the same aluminum material as in Example 113, was pinched by and between two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds. In the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

50 (Example 230)

55 **[0222]** In the same manner as in Example 224 except that the aluminum material was brought into contact with cooling rolls having a surface temperature of 25 °C after the contact heating with the heating rolls, a high purity aluminum material

for electrolytic capacitors was obtained.

(Comparative Example 104)

5 **[0223]** The actual temperature of an aluminum material with a purity of 99.99% rolled into 110  $\mu\text{m}$  in thick, which was the same aluminum material as in Example 113, was raised in an argon atmosphere from the room temperature to 540  $^{\circ}\text{C}$  at the rate of 50 $^{\circ}\text{C}/\text{h}$ , and then held at 540  $^{\circ}\text{C}$  for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

10 **[0224]** Each aluminum material obtained in the aforementioned Examples 113 to 230 and Comparative Example 104 was immersed in an aqueous solution containing HCl 1.0  $\text{mol}\cdot\text{dm}^{-3}$  and  $\text{H}_2\text{SO}_4$  3.5  $\text{mol}\cdot\text{dm}^{-3}$  and having a liquid temperature of 75  $^{\circ}\text{C}$ , then subjected to electrolytic etching at the current density of 0.2  $\text{A}/\text{cm}^2$ . The electrolytically etched aluminum material was further immersed in a hydrochloric acid-sulfuric acid aqueous solution having the same compositions as mentioned above at 90  $^{\circ}\text{C}$  for 360 seconds to increase the pit diameter to thereby obtain an etched foil. The obtained etched foil was subjected to formation at the voltage of 270 V in accordance with EIAJ standard to obtain a capacitance measuring sample. The measured capacitance of each sample is shown in Tables 6 to 10 as a relative value when Comparative Example 104 is 100.

15

20

25

30

35

40

45

50

55

Table 6

\* heating body 1: heating plate, 2: heating roll

	Step 1 washing/drying before contact heating						Step 2 Contact heating			Step 3 Washing/drying after contact heating						Step 4 Annealing Actual temp. / °C	Capacitance Evaluation (relative value when comp. Example 104 is 100)
	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.	Surface temp. of heating body / °C	Contact time / sec.	Heating body	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.		
Example 113	A1	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 114	A2	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 115	A3	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 116	A4	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 117	A5	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 118	A6	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 119	A7	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 120	A8	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 121	A9	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 122	A10	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 123	A11	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 124	A12	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 125	A13	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 126	A14	2	-	-	0	60	200	2	1	-	-	-	-	-	-	540	107
Example 127	A15	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 128	A16	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 129	A17	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 130	A18	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109
Example 131	A19	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 132	A20	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 133	A21	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 134	A22	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 135	A23	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 136	A24	2	-	-	90	60	200	2	1	-	-	-	-	-	-	540	109

Table 7 \* heating body 1: heating plate, 2: heating roll.

	Step 1 washing/drying before contact heating						Step 2 Contact heating			Step 3 Washing/drying after contact heating						Step 4 Annealing Actual temp. / °C	Capacitance Evaluation (relative value when Comp. Example 104 is 100)
	Washing liquid	Immersing time /sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.	Surface temp. of heating body / °C	Contact time / sec.	Heating body	Washing liquid	Immersing time /sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.		
Example 137	A25	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 138	A26	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 139	A27	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 140	A28	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 141	A29	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 142	A30	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 143	A31	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 144	A32	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	110
Example 145	A33	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 146	A34	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 147	A35	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 148	A36	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 149	A37	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 150	A38	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 151	A39	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 152	A40	2	.	.	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 153	B1	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 154	B2	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 155	B3	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 156	B4	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 157	B5	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 158	B6	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 159	B7	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 160	B8	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109

Table 8

\* heating body 1: heating plate, 2: heating roll

	Step 1 washing/drying before contact heating						Step 2 Contact heating			Step 3 Washing/drying after contact heating						Step 4 Annealing Actual temp. / °C	Capacitance Evaluation (relative value when Comp. Example 104 is 100)
	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.	Surface temp. of heating body / °C	Contact time / sec.	Heating body	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.		
Example 161	B9	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 162	B10	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 163	B11	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 164	B12	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 165	B13	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 166	B14	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 167	B15	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 168	B16	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 169	B17	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 170	B18	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 171	B19	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 172	B20	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 173	B21	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 174	B22	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 175	B23	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 176	B24	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 177	B25	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 178	B26	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 179	B27	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 180	B28	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 181	B29	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	108
Example 182	B30	2	Yes	Yes	90	60	200	2	1	.	.	.	.	.	.	540	109
Example 183	B3	60	.	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107
Example 184	B6	60	.	Yes	90	60	200	2	1	.	.	.	.	.	.	540	107

Table 9

\* heating body 1: heating plate, 2: heating roll

	Step 1 Washing/drying before contact heating						Step 2 Contact heating			Step 3 Washing/drying after contact heating						Step 4 Annealing Actual temp. / °C	Capacitance Evaluation (relative value when comp. Example 104 is 100)
	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.	Surface temp. of heating body / °C	Contact time / sec.	Heating body	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.		
Example 185	B9	60	-	Yes	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 186	B10	60	-	Yes	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 187	B11	60	-	Yes	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 188	B12	60	-	Yes	90	60	200	2	1	-	-	-	-	-	-	540	107
Example 189	-	-	-	-	-	-	200	2	1	A2	2	Yes	-	90	2	540	109
Example 190	-	-	-	-	-	-	200	2	1	A6	2	Yes	-	90	2	540	110
Example 191	-	-	-	-	-	-	200	2	1	A14	2	Yes	-	90	2	540	110
Example 192	-	-	-	-	-	-	200	2	1	A40	2	Yes	-	90	2	540	110
Example 193	-	-	-	-	-	-	200	2	1	B3	2	Yes	Yes	90	10	540	110
Example 194	-	-	-	-	-	-	200	2	1	B14	2	Yes	Yes	90	10	540	110
Example 195	-	-	-	-	-	-	200	2	1	B19	2	Yes	Yes	90	10	540	110
Example 196	-	-	-	-	-	-	200	2	1	B28	2	Yes	Yes	90	10	540	110
Example 197	A4	2	-	-	90	60	200	2	1	A4	2	Yes	-	90	60	540	110
Example 198	A6	2	-	-	90	60	200	2	1	A4	2	Yes	-	90	60	540	110
Example 199	A40	2	-	-	90	60	200	2	1	A4	2	Yes	-	90	60	540	110
Example 200	B3	2	Yes	Yes	90	60	200	2	1	A4	2	Yes	-	90	60	540	111
Example 201	B19	2	Yes	Yes	90	60	200	2	1	A4	2	Yes	-	90	60	540	111
Example 202	B28	2	Yes	Yes	90	60	200	2	1	A4	2	Yes	-	90	60	540	111
Example 203	B3	4	Yes	Yes	200	60	200	2	1	-	-	-	-	90	60	540	103
Example 204	B3	4	Yes	Yes	90	60	200	2	1	-	-	-	-	-	-	540	108
Example 205	B3	4	Yes	Yes	60	60	200	2	1	-	-	-	-	-	-	540	110
Example 206	B3	4	Yes	Yes	40	60	200	2	1	-	-	-	-	-	-	540	113
Example 207	B3	4	Yes	Yes	-	-	200	2	1	-	-	-	-	-	-	540	113
Example 208	-	-	-	-	-	-	200	2	1	A4	2	Yes	-	200	60	540	106

Table 10

\* heating body 1: heating plate, 2: heating roll

	Step 1 washing/drying heating						before contact		Step 2 Contact heating		Step 3 Washing/drying contact heating						after		Step 4 Annealing Actual temp. / °C	Capacitance Evaluation (relative value when Comp. Example 104 is 100)
	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.	Surface temp. of heating body / °C	Contact time / sec.	Heating body	Washing liquid	Immersing time / sec.	Brushing during the immersion	Washing with water	Drying temperature / °C	Drying time / sec.					
Example 209	-	-	-	-	-	-	200	2	1	A4	2	Yes	-	90	60	540	111			
Example 210	-	-	-	-	-	-	200	2	1	A4	2	Yes	-	60	60	540	113			
Example 211	-	-	-	-	-	-	200	2	1	A4	2	Yes	-	40	60	540	113			
Example 212	B3	3	Yes	Yes	60	20	100	0.5	2	-	-	-	-	-	-	540	106			
Example 213	B3	3	Yes	Yes	60	20	160	0.5	2	-	-	-	-	-	-	540	116			
Example 214	B3	3	Yes	Yes	60	20	220	0.5	2	-	-	-	-	-	-	540	118			
Example 215	B3	3	Yes	Yes	60	20	250	0.5	2	-	-	-	-	-	-	540	116			
Example 216	B3	3	Yes	Yes	60	20	290	0.5	2	-	-	-	-	-	-	540	114			
Example 217	B3	3	Yes	Yes	60	20	350	0.5	2	-	-	-	-	-	-	540	107			
Example 218	B3	3	Yes	Yes	60	20	380	0.5	2	-	-	-	-	-	-	540	105			
Example 219	B3	3	Yes	Yes	60	20	175	0.005	2	-	-	-	-	-	-	540	105			
Example 220	B3	3	Yes	Yes	60	20	175	0.01	2	-	-	-	-	-	-	540	107			
Example 221	B3	3	Yes	Yes	60	20	175	0.05	2	-	-	-	-	-	-	540	109			
Example 222	B3	3	Yes	Yes	60	20	175	0.1	2	-	-	-	-	-	-	540	113			
Example 223	B3	3	Yes	Yes	60	20	175	1	2	-	-	-	-	-	-	540	114			
Example 224	B3	3	Yes	Yes	60	20	175	3	2	-	-	-	-	-	-	540	114			
Example 225	B3	3	Yes	Yes	60	20	175	5	2	-	-	-	-	-	-	540	114			
Example 226	B3	3	Yes	Yes	60	20	175	7	2	-	-	-	-	-	-	540	112			
Example 227	B3	3	Yes	Yes	60	20	175	10	2	-	-	-	-	-	-	540	107			
Example 228	B3	3	Yes	Yes	60	20	175	20	2	-	-	-	-	-	-	540	105			
Example 229	-	-	-	-	-	-	200	2	1	-	-	-	-	-	-	540	105			
Example 230	B3	3	Yes	Yes	60	20	175	5	2	-	-	-	-	-	-	540	116			
Com. Example 104	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	540	100			

In Example 230, cooling with cooling rolls is performed after heat roll heating

[0225] From the comparison between Example 229 and Comparative Example 104 in Table 10, it is confirmed that performing the contact heating before the final annealing increases capacitance. Furthermore, from the comparison between Examples 113 to 211 and Example 229, it is confirmed that performing the washing either before or after the contact heating further increases the capacitance.

[0226] Furthermore, from Examples 203 to 211, when the drying temperature after the washing is 200 °C or below, capacitance increases, when it is below 90 °C, the capacitance further increases.

[Third Example]

[0227] This example corresponds to the third embodiment.

[0228] Organic solutions for organic solvent washing to be performed before alkali washing or acid washing of the aluminum material after the final rolling are shown in Table 11, the alkali washing solutions are shown in Table 12, and the acid washing solutions are shown in Table 13.

## EP 1 498 513 B9

Table 11 organic solvent washing liquid

Mark	organic solvent	Liquid temp. (°C)
A101	acetone	25
A102	n- hexane	25
A103	2- propanol	25

Table 12 Type of alkali washing liquid (aqueous solution)

Mark	Type of alkali	Concentration / mass%	Liquid temp.(°C)
B101	sodium hydroxide	0.1	35
B102	potassiumhydroxide	0.1	35
B103	calcium hydroxide	0.1	35
B104	sodium metasilicate	0.2	35
B105	sodium orthosilicate	0.2	35
B106	sodium orthosilicate	0.2	50
B107	sodium tertiary phosphate	0.2	50

Table 13 Type of acid washing liquid (aqueous solution)

Mark	Type of acid	Concentration / mass%	Liquid temp. (°C)
C101	hydrochloric acid	3	30
C102	sulfuric acid	3	30
C103	nitric acid	3	30
C104	phosphoric acid	3	30
C105	nitric acid	3	50

(Example 301)

**[0229]** An aluminum foil (aluminum material) with a purity of 99.99% rolled into 110 μm in thick was subjected to washing with A102 liquid in Table 11, drying, washing with B106 in Table 12 for 40 seconds, washing with water, drying,

**[0230]** Then, the aluminum material was pinched by two sheets of stainless heating plates having a surface temperature of 250 °C to perform the contact heating for 2 seconds.

**[0231]** Subsequently, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to 500 °C at the rate of 50°C/h, and then held at 500 °C for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Examples 302 to 349)

**[0232]** An aluminum foil with a purity of 99.99% rolled into 110 μm in thick, which was the same in Example 301, was subjected to washing and drying under the conditions in Table 14 or 15, and then subjected to the contact heating under the conditions of Table 4 or 5.

**[0233]** After the organic solvent washing, drying was performed. After the acid washing and alkali washing, washing with water was performed. Further, in Examples 341, 343 and 344, a heating roll having a chrome plated surface was used as a heating body.

**[0234]** Subsequently, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to the annealing actual temperature shown in Table 14 or 15 at the

rate of 50°C/h, and then held at the annealing actual temperature for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

5 (Comparative Example 301 to 304)

**[0235]** An aluminum foil with a purity of 99.99% rolled into 110 μm in thick, which was the same as in Example 301, was subjected to washing with A101 liquid in Table 11, drying, washing with B105 in Table 2 for 40 seconds, and drying in order under the conditions in Table 15.

10 **[0236]** Then, without performing the contact heating, in the piled state, the actual temperature of the contact heated aluminum material was raised in an argon atmosphere from the room temperature to the annealing actual temperature shown in Table 5 at the rate of 50°C/h, and then held at the annealing actual temperature for 24 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

15 **[0237]** Each aluminum foil obtained in the aforementioned Examples and Comparative Examples was immersed in an aqueous solution containing HCl 1.0 mol·dm<sup>-3</sup> and H<sub>2</sub>SO<sub>4</sub> 3.5 mol·dm<sup>-3</sup> and having a liquid temperature of 75 °C, then subjected to electrolytic etching at the current density of 0.2 A/cm<sup>2</sup>. The electrolytically etched aluminum foil was further immersed in a hydrochloric acid-sulfuric acid aqueous solution having the same compositions as mentioned above at 90 °C for 360 seconds to increase the pit diameter to thereby obtain an etched foil.

20 **[0238]** The obtained etched foil was subjected to formation at the formation voltage of 270 V in accordance with EIAJ standard to make an anodic material to thereby obtain a capacitance measuring sample. The measured capacitance of each sample is shown in Tables 14 and 15 as a relative value when Comparative Example 301 is 100.

25

30

35

40

45

50

55

Table 14

	Step 1 Organic solvent washing (immersion time 2 sec.)	Step 2 Alkali washing		Step 3 Acid washing		Step 4 Contact heating			Step 5 Annealing (Actual temp. °C)	Capacitance evaluation (relative value when comp. Example 301 is 100)
		Type	Immersion time (sec.)	type	Immersion time (sec.)	Heating body	Surface temp. of heating body(°C)	Contact time (sec.)		
Example 301	A102	B106	40	C101	60	Heating plate	250	2	500	117
Example 302	A102	B106	40	C101	60	Heating plate	250	2	540	116
Example 303	A102	B106	40	C102	60	Heating plate	250	2	540	115
Example 304	-	-	-	C105	60	Heating plate	250	2	500	112
Example 305	A102	B105	10	C102	10	Heating plate	200	2	500	115
Example 306	A102	B101	40	C103	30	Heating plate	200	2	500	116
Example 307	A103	B101	10	C103	2	Heating plate	200	2	500	117
Example 308	-	B101	10	C101	60	Heating plate	200	2	500	115
Example 309	-	B101	10	C102	60	Heating plate	200	2	500	115
Example 310	-	B101	10	C103	60	Heating plate	200	2	500	116
Example 311	-	B101	10	C104	60	Heating plate	200	2	500	118
Example 312	-	B102	10	C101	60	Heating plate	200	2	500	118
Example 313	-	B102	10	C102	60	Heating plate	200	2	500	117
Example 314	-	B102	10	C103	60	Heating plate	200	2	500	115
Example 315	-	B102	10	C104	60	Heating plate	200	2	500	118
Example 316	-	B103	10	C101	60	Heating plate	200	2	500	116
Example 317	-	B103	10	C102	60	Heating plate	200	2	500	117
Example 318	-	B103	10	C103	60	Heating plate	200	2	500	116
Example 319	-	B103	10	C104	60	Heating plate	200	2	500	116
Example 320	-	B104	400	C101	60	Heating plate	200	2	500	119
Example 321	-	B104	210	C102	60	Heating plate	200	2	500	121
Example 322	-	B104	210	C103	60	Heating plate	200	2	500	119
Example 323	-	B104	210	C104	60	Heating plate	200	2	500	119
Example 324	-	B105	210	C101	60	Heating plate	200	2	500	121
Example 325	-	B105	210	C102	60	Heating plate	200	2	500	119
Example 326	-	B105	210	C103	60	Heating plate	200	2	500	121
Example 327	-	B105	210	C104	60	Heating plate	200	2	500	119
Example 328	A101	-	-	C101	60	Heating plate	200	2	500	111
Example 329	A101	-	-	C102	60	Heating plate	200	2	500	112

Table 15

	Step 1 Organic solvent washing (immer- sion time 2 sec.)	Step 2 Alkali washing		Step 3 Acid washing		Step 4 Contact heating			Step 5 Annealing (Actual temp. °C)	Capacitance evaluation (relative value when comp. Example 301 is 100)
		type	Immersion time (sec.)	type	Immersion time (sec.)	Heating body	Surface temp. of heating body(°C)	Contact time (sec.)		
Example 330	A101	-	-	C103	60	Heating plate	200	2	500	113
Example 331	A101	-	-	C104	60	Heating plate	200	2	500	112
Example 332	-	B101	10	-	-	Heating plate	200	2	500	108
Example 333	-	B102	10	-	-	Heating plate	200	2	500	109
Example 334	-	B103	10	-	-	Heating plate	200	2	500	108
Example 335	-	B104	10	-	-	Heating plate	200	2	500	109
Example 336	A101	B105	40	-	-	Heating plate	200	2	500	107
Example 337	A101	B105	40	-	-	Heating plate	250	2	500	108
Example 338	A101	B105	40	-	-	Heating plate	200	2	540	108
Example 339	A101	B105	40	-	-	Heating plate	250	2	540	109
Example 340	A101	B105	40	-	-	Heating plate	200	1	500	108
Example 341	A101	B105	40	-	-	Heating roll	200	1	500	108
Example 342	A101	B105	40	-	-	Heating plate	90	2	500	106
Example 343	A101	B105	40	-	-	Heating roll	380	0.1	500	107
Example 344	A101	B105	40	-	-	Heating roll	250	0.005	500	106
Example 345	A101	B105	40	-	-	Heating plate	150	30	500	106
Example 346	A101	B105	40	-	-	Heating plate	250	2	460	106
Example 347	A101	B105	40	-	-	Heating plate	250	2	580	108
Example 348	A101	B107	10	-	-	Heating plate	200	2	500	111
Example 349	A101	B107	10	C103	60	Heating plate	200	2	500	117
Com. Example 301	A101	B105	40	-	-	No contact heating			540	100
Com. Example 302	A101	B105	40	-	-	No contact heating			560	100
Com. Example 303	A101	B105	40	-	-	No contact heating			460	98
Com. Example 304	A101	B105	40	-	-	No contact heating			580	100

[0239] As will be understood from the above Tables, according to the embodiments of the present invention, performing the contact heating after the alkali washing and/or the acid washing increases capacitance as compared with the case where no contact heating is performed.

[Fourth Embodiment]

[0240] This embodiment corresponds to the fourth embodiment.

(Example 401)

[0241] An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was pinched by two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 402)

[0242] In the same manner as in Example 401 except that the surface temperature of the heating plate is 80°C and the contact time to the heating body is 28 seconds, an aluminum material for electrolytic capacitor electrodes was obtained.

(Example 403)

**[0243]** In the same manner as in Example 401 except that the surface temperature of the heating plate is 100°C and the contact time to the heating body is 20 seconds, an aluminum material for electrolytic capacitor electrodes was obtained.

(Example 404)

**[0244]** In the same manner as in Example 401 except that the surface temperature of the heating plate is 160°C and the contact time to the heating body is 10 seconds, an aluminum material for electrolytic capacitor electrodes was obtained.

(Example 405)

**[0245]** In the same manner as in Example 401 except that the surface temperature of the heating plate is 290°C and the contact time to the heating body is 2 seconds, an aluminum material for electrolytic capacitor electrodes was obtained.

(Example 406)

**[0246]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 500 °C at the rate of 50°C/h, and then held at 500 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was pinched by two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 3 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 407)

**[0247]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 470 °C at the rate of 50°C/h, and then held at 470 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was pinched by two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 15 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 408)

**[0248]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 560 °C at the rate of 50°C/h, and then held at 560 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was pinched by two sheets of stainless heating plates having a surface temperature of 200 °C to perform the contact heating for 2 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 409)

**[0249]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 540 °C at the rate of 50°C/h, and then held at 540 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was brought into contact with a heating roll having a surface temperature of 350 °C to perform the contact heating for 0.01 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 410)

**[0250]** An aluminum material with a purity of 99.99% rolled into 110  $\mu$  m in thick was immersed in a 0.1 mass% sodium

## EP 1 498 513 B9

hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 500 °C at the rate of 50°C/h, and then held at 500 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was brought into contact with a heating roll having a surface temperature of 380 °C to perform the contact heating for 0.01 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 411)

**[0251]** In the same manner as in Example 410 except that the surface temperature of the heating roll is 200°C and the contact time to the heating roll is 0.05 seconds, an aluminum material for electrolytic capacitor electrodes was obtained.

(Example 412)

**[0252]** An aluminum material with a purity of 99.99% rolled into 110 μ m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 520 °C at the rate of 50°C/h, and then held at 520 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was brought into contact with a heating roll having a surface temperature of 200 °C to perform the contact heating for 0.1 seconds. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Example 413)

**[0253]** An aluminum material with a purity of 99.99% rolled into 110 μ m in thick was immersed in a 0.1 mass% sodium hydroxide aqueous solution having a temperature of 35 °C for 10 seconds, and then washed with water and dried. Subsequently, in the piled state, the actual temperature of the aluminum material was raised in an argon atmosphere from the room temperature to 500 °C at the rate of 50°C/h, and then held at 500 °C for 4 hours. Subsequently, the aluminum material was cooled and then brought out of the furnace. Then, the aluminum material was brought into contact with a heating roll having a surface temperature of 200 °C to perform the contact heating for 2 seconds and then brought into contact with a cooling roll having a surface temperature of 30 °C. Thus, a high purity aluminum material for electrolytic capacitors was obtained.

(Comparative Example 401)

**[0254]** In the same manner as in Example 410 except that the contact heating was not performed, an aluminum material for electrolytic capacitor electrodes was obtained.

**[0255]** Each aluminum foil obtained in the aforementioned Examples 401 to 413 and Comparative Example 401 was immersed in an aqueous solution containing HCl 1.0 mol/l and H<sub>2</sub>SO<sub>4</sub> 3.5 mol/l and having a liquid temperature of 75 °C, then subjected to electrolytic etching at the current density of 0.2 A/cm<sup>2</sup>. The electrolytically etched aluminum foil was further immersed in a hydrochloric acid-sulfuric acid aqueous solution having the same compositions as mentioned above at 90 °C for 360 seconds to increase the pit diameter to thereby obtain an etched foil.

**[0256]** The obtained etched foil was subjected to formation at the voltage of 270 V in accordance with EIAJ standard to make an anodic material to thereby obtain a capacitance measuring sample. The measured capacitance of each sample is shown in Table 16 as a relative value when Comparative Example 401 is 100.

Table 16

	Annealing actual temp. / °C	Contact heating conditions			Capacitance evaluation (relative value when comp. example 401 is 100)
		Surface temp. of heating body / °C	Contact time /sec.	Heating body	
Example 401	540	200	2	Heating plate	108
Example 402	540	80	28	Heating plate	103
Example 403	540	100	20	Heating plate	104

(continued)

	Annealing actual temp. / °C	Contact heating conditions			Capacitance evaluation (relative value when comp. example 401 is 100)	
		Surface temp. of heating body / °C	Contact time /sec.	Heating body		
5						
	Example 404	540	160	10	Heating plate	106
10	Example 405	540	290	2	Heating plate	107
	Example 406	500	200	3	Heating plate	106
	Example 407	470	200	15	Heating plate	102
15	Example 408	560	200	2	Heating plate	106
	Example 409	540	350	0.01	Heating roll	104
	Example 410	500	380	0.01	Heating roll	103
20	Example 411	500	200	0.05	Heating roll	106
	Example 412	520	200	0.1	Heating roll	107
	Example 413	500	200	2	Heating roll(*)	107
25	Com. Example 401	540	No contact heating			100
	* After heating with a heating roll, cooling rolls having a surface temperature of 30°C come into contact with the aluminum material.					

30 **[0257]** From the comparison between the aforementioned Examples and Comparative Examples, it is understood that performing the contact heating after the final annealing can increase capacitance.

### INDUSTRIAL APPLICABILITY

35 **[0258]** The present invention can be used as a method for manufacturing an aluminum material for electrolytic capacitors, an aluminum material for electrolytic capacitor electrodes, a method for manufacturing an electrode material for electrolytic capacitors, and an aluminum electrolytic capacitor.

### Claims

- 40
1. A method of manufacturing an aluminum material for electrolytic capacitor electrodes, the method comprising, in manufacturing an aluminum material for electrolytic capacitor electrodes by subjecting an aluminum slab to hot rolling, cold rolling and final annealing, a contact heating step for heating the aluminum material is performed by bringing the aluminum material into contact with a heating body after the hot rolling.
  - 45 2. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 1, wherein the contact heating step for heating the aluminum material with the heating body is performed at least once between a start of the cold rolling and a completion thereof.
  - 50 3. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 2, wherein a rolling reduction ratio of the aluminum material after the contact heating step is 60% or less, wherein the roll reduction ratio is represented by  $[(A-B)/A] \times 100(\%)$ , where "A" ( $\mu\text{m}$ ) is a thickness of the aluminum material after the last contact heating among the contact heating performed at least once during the cold rolling but before the resumption of the cold rolling, and "B" ( $\mu\text{m}$ ) is a thickness of the aluminum material after the entire cold rolling.
  - 55 4. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 3, wherein the roll reduction ratio after the contact heating is 30% or less.

5. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 1, wherein the contact heating step for heating the aluminum material with the heating body is performed after the cold rolling but before the final annealing.
- 5 6. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 5, further comprising a washing step for washing the aluminum material performed before or after the contact heating step.
7. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 5, wherein the aluminum material is washed before the contact with the heating body, then dried or not dried, and thereafter heated by bringing the aluminum material into contact with the heating body.
- 10 8. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 5, wherein the aluminum material is washed after the contact with the heating body, then dried or not dried, and thereafter annealed.
- 15 9. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 5 to 8, wherein washing liquid for washing the aluminum material is organic solvent.
- 20 10. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 9, wherein the organic solvent is one element or a mixture of two or more elements selected from the group consisting of alcohol represented by  $C_nH_{2n+1}OH$  ( $n$ (integer)=1-10), cyclohexanol ( $C_6H_{11}OH$ ), 1,2-ethanediol ( $HOCH_2CH_2OH$ ), 1,2-propanediol ( $CH_3CH(OH)CH_2H$ ), 1,3-propanediol ( $HOCH_2CH_2CH_2OH$ ), alkane series hydrocarbon represented by  $C_nH_{2n+2}$  ( $n$ (integer)=5-15), cyclohexane, ketone represented by  $R^1COR^2$  ( $R^1$  and  $R^2$ : aliphatic hydrocarbon radical, the total carbon number of  $R^1$  and  $R^2$  is 8 or less), cyclohexanone ( $C_6H_{10}O$ ), ether represented by  $R^1-O-R^2$  ( $R^1$  and  $R^2$ : aliphatic hydrocarbon group, the total carbon number of  $R^1$  and  $R^2$  is 8 or less), 2-methoxy ethanol ( $CH_3OCH_2CH_2OH$ ), 2-etoxyethanol ( $CH_3CH_2OCH_2CH_2OH$ ), 2-butoxyethanol ( $CH_3CH_2CH_2CH_2OCH_2CH_2OH$ ), 2-(2-etoxy)etoxyethanol ( $CH_3CH_2OCH_2CH_2OCH_2CH_2OH$ ), ethyl acetate represented by  $CH_3COOR$  ( $R$ : aliphatic hydrocarbon group, the carbon number is 1-5), and toluenexylene.
- 25 11. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 5 to 8, wherein washing liquid for washing the aluminum material is water to which surfactant is added.
- 30 12. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 11, wherein the surfactant is an anionic surfactant or a mixture of plural anionic surfactant selected from the group consisting of anionic surfactant (sulfate ester salt) represented by  $R-OSO_3Na$  ( $R$ =saturated hydrocarbon group whose carbon number is 8-18 or unsaturated hydrocarbon group having one double bond), anionic surfactant (sulfonic acid salt) represented by  $R-SO_3Na$  ( $R$ =saturated hydrocarbon radical whose carbon number is 8-18 or unsaturated hydrocarbon group having one double bond) or  $R-SO_3Na$  ( $R$ =saturated hydrocarbon radical whose alkyl radical has a carbon number of 8-14 or unsaturated hydrocarbon group having one double bond), cationic surfactant (quaternary ammonium salt) represented by  $R-N^+(CH_3)_3 \cdot Cl^-$  ( $R$ =saturated hydrocarbon group whose carbon number is 8~16), polyethyleneglycol type nonionic surfactant represented by  $R-O-(CH_2CH_2O)_nH$  ( $R$ =saturated hydrocarbon group whose carbon number is 8~16 or unsaturated hydrocarbon radical having one double bond,  $n=6\sim 14$ ) or  $R-O-(CH_2CH_2O)_nH$  ( $R$ =saturated hydrocarbon group whose alkyl radical has a carbon number of 8~12 or alkylphenyl radical which is unsaturated hydrocarbon group having one double bond,  $n=6\sim 14$ ), a mixture of plural cationic surfactant, a mixture of plural nonionic surfactant, a mixture of one or more anionic surfactant and one or more nonionic surfactant, or a mixture of one or more cationic surfactant and one or more nonionic surfactant.
- 35 13. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 7, wherein drying temperature after the washing is 200 °C or below.
- 40 14. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 7 or 8, wherein drying temperature after the washing is 90 °C or below.
- 45 15. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 1, wherein the aluminum material is washed with liquid capable of dissolving aluminum after the cold rolling, and then the contact heating step for heating the aluminum material with the heating body is performed after the final annealing.
- 50 16. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 15,
- 55

wherein the washing with the liquid capable of dissolving aluminum is alkali washing.

- 5
17. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 15, wherein the washing with the liquid capable of dissolving aluminum is acid washing.
18. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 15, wherein the washing with the liquid capable of dissolving aluminum is a sequence of alkali washing and acid washing.
- 10
19. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 15 to 18, wherein the aluminum material is subjected to organic solvent washing before the alkali washing or the acid washing.
- 15
20. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 16, 18 and 19, wherein alkali washing liquid for the alkali washing is solution containing one or more alkali selected from the group consisting of sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium orthosilicate, sodium metasilicate, and sodium tertiary phosphate.
- 20
21. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 17 to 19, wherein acid washing liquid for the acid washing is solution containing one or more acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid.
22. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 1, wherein the contact heating step for heating the aluminum material with the heating body is performed after the final annealing.
- 25
23. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 1 to 22, wherein a surface temperature of the heating body is 50 to 450 °C and a contact time of the aluminum member and the heating body is 0.001 to 60 seconds.
- 30
24. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 23, wherein the surface temperature of the heating body is 60 to 400 °C.
- 35
25. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 23, wherein the surface temperature of the heating body is 80 to 400 °C.
- 40
26. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 23 to 25, wherein the contact time of the aluminum member and the heating body is 0.001 to 60 seconds.
27. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 23 to 25, wherein the contact time of the aluminum member and the heating body is 0.001 to 30 seconds.
- 45
28. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 1 to 27, wherein an intermediate annealing is performed during the cold rolling.
29. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 1 to 28, wherein the final annealing is performed in an inert gas atmosphere at the aluminum actual temperature of 450 to 600 °C.
- 50
30. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 1 to 29, wherein the heating body is a heating roll.
- 55
31. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of claims 1 to 30, wherein the aluminum material is cooled after the contact with the heating body.
32. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in claim 31, wherein the cooling of the aluminum material is performed by bringing the aluminum material into contact with a cooling roll.
33. The method of manufacturing an aluminum material for electrolytic capacitor electrodes as recited in any one of

claims 1 to 32, wherein the aluminum purity of the aluminum material is 99.9% or more.

34. An aluminum material for electrolytic capacitors manufactured by a method as recited by any one of claims 1 to 33.

5 35. The aluminum material for electrolytic capacitors as recited in claim 34, the aluminum material is for middle voltage or high voltage.

10 36. A method of manufacturing an electrode material for electrolytic capacitors, wherein etching is subjected to the aluminum material manufactured by the method as recited in any one of claims 1 to 33.

37. The method of manufacturing an electrode material for electrolytic capacitors as recited in claim 36, wherein the etching is DC etching.

15 38. An aluminum electrolytic capacitor employing the aluminum electrode material manufactured by the method as recited in claim 36 or 37 as an electrode material.

### Patentansprüche

20 1. Ein Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden, wobei das Verfahren das Herstellen eines Aluminiummaterials für elektrolytische Kondensatorelektroden umfasst, indem eine Aluminiumplatte Warmwalzen, Kaltwalzen und Fertigglühen unterzogen wird, wobei ein Kontaktheizungs-Schritt für das Erwärmen des Aluminiummaterials durch In-Kontakt-bringen des Aluminiummaterials mit einem Heizkörper nach dem Warmwalzen durchgeführt wird.

25 2. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 1 beschrieben, wobei der Kontaktheizungs-Schritt für das Erwärmen des Aluminiummaterials mit dem Heizkörper mindestens einmal zwischen einem Start des Kaltwalzens und einer Beendigung davon durchgeführt wird.

30 3. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 2 beschrieben, wobei ein Walzreduktions-Verhältnis des Aluminiummaterials nach dem Kontaktheizungs-Schritt 60% oder weniger ist, wobei das Walzreduktions-Verhältnis durch  $[(A-B)/A] \times 100(\%)$  repräsentiert wird, wobei "A" ( $\mu\text{m}$ ) eine Dicke des Aluminiummaterials nach dem letzten Kontaktheizen unter dem Kontaktheizen, das mindestens einmal während des Kaltwalzens aber vor der Wiederaufnahme des Kaltwalzens durchgeführt wird, ist, und "B" ( $\mu\text{m}$ ) eine Dicke des Aluminiummaterials nach dem kompletten Kaltwalzen ist.

35 4. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 3 beschrieben, wobei das Walzreduktions-Verhältnis nach dem Kontaktheizen 30% oder weniger ist.

40 5. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 1 beschrieben, wobei der Kontaktheizungs-Schritt für das Erwärmen des Aluminiummaterials mit dem Heizkörper nach dem Kaltwalzen aber vor dem Fertigglühen durchgeführt wird.

45 6. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 5 beschrieben, dass weiter einen Wasch-Schritt für das Waschen des Aluminiummaterials umfasst, der vor oder nach dem Kontaktheizungs-Schritt durchgeführt wird.

50 7. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 5 beschrieben, wobei das Aluminiummaterial vor dem Kontakt mit dem Heizkörper gewaschen wird, dann getrocknet oder nicht getrocknet wird, und danach erwärmt wird, indem das Aluminiummaterial mit dem Heizkörper in Kontakt gebracht wird.

55 8. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 5 beschrieben, wobei das Aluminiummaterial nach dem Kontakt mit dem Heizkörper gewaschen wird, dann getrocknet oder nicht getrocknet wird und danach geglüht wird.

9. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 5 bis 8 beschrieben, wobei die Waschflüssigkeit zum Waschen des Aluminiummaterials ein organi-

sches Lösungsmittel ist.

- 5 10. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 9 beschrieben, wobei das organische Lösungsmittel ein Element oder eine Mischung von zwei oder mehr Elementen ist, die aus der Gruppe, die aus Alkohol, der durch  $C_nH_{2n+1}OH$  ( $n$  (ganze Zahl) = 1-10), Cyclohexanol ( $C_6H_{11}OH$ ), 1,2-Ethandiol ( $HOCH_2CH_2OH$ ), 1,2-Propandiol ( $CH_3CH(OH)CH_2OH$ ), 1,3-Propandiol ( $HOCH_2CH_2CH_2OH$ ) repräsentiert wird, Kohlenwasserstoff der Alkan-Reihe, der durch  $C_nH_{2n+2}$  ( $n$  (ganze Zahl) = 5-15), Cyclohexan repräsentiert wird, Keton, das durch  $R^1COR^2$  ( $R^1$  und  $R^2$ : aliphatischer Kohlenwasserstoffrest, wobei die Gesamtkohlenstoffanzahl von  $R^1$  und  $R^2$  ist 8 oder weniger ist), Cyclohexanon ( $C_6H_{10}O$ ) repräsentiert wird, Ether, der durch  $R^1-O-R^2$  ( $R^1$  und  $R^2$ : aliphatische Kohlenwasserstoff-Gruppe, wobei die Gesamtkohlenstoffanzahl von  $R^1$  und  $R^2$  8 oder weniger ist), 2-Methoxyethanol ( $CH_3OCH_2CH_2OH$ ), 2-Etoxyethanol ( $CH_3CH_2OCH_2CH_2OH$ ), 2-Butoxyethanol ( $CH_2CH_2CH_2CH_2OCH_2CH_2OH$ ), 2-(2-Ethoxy)ethoxyethanol ( $CH_3CH_2OCH_2CH_2OCH_2CH_2OH$ ) repräsentiert wird, Ethylacetat, das durch  $CH_3COOR$  ( $R$ : aliphatische Kohlenwasserstoff-Gruppe, wobei die Kohlenstoffanzahl 1-5 ist) und Toluolxylen repräsentiert wird, besteht, ausgewählt werden.
- 10 11. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 5 bis 8 beschrieben, wobei die Waschflüssigkeit zum Waschen des Aluminiummaterials Wasser ist, zu dem ein Tensid hinzugegeben wird.
- 15 12. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 11 beschrieben, wobei das Tensid ein anionisches Tensid oder eine Mischung aus mehreren anionischen Tensiden ist, die aus der Gruppe, die aus einem anionischen Tensid (Sulfatester-Salz), das durch  $R-OSO_3Na$  ( $R$  = gesättigte Kohlenwasserstoff-Gruppe, deren Kohlenstoffanzahl 8-18 ist oder ungesättigte Kohlenwasserstoff-Gruppe mit einer Doppelbindung) repräsentiert wird, einem anionischen Tensid (Sulfonsäure-Salz), das durch  $R-SO_3Na$  ( $R$  = gesättigter Kohlenwasserstoffrest, dessen Kohlenstoffanzahl 8-18 ist oder ungesättigte Kohlenwasserstoff-Gruppe mit einer Doppelbindung) oder  $R-SO_3Na$  ( $R$  = gesättigter Kohlenwasserstoffrest, dessen Alkylrest eine Kohlenstoffanzahl von 8-14 hat oder ungesättigte Kohlenwasserstoff-Gruppe mit einer Doppelbindung) repräsentiert wird, einem kationischen Tensid (quartäres Ammoniumsalz), das durch  $R-N^+(CH_3)_3 \cdot Cl^-$  ( $R$  = gesättigte Kohlenwasserstoff-Gruppe, deren Kohlenstoffanzahl 8-16 ist) repräsentiert wird, einem nicht-ionischen Tensid vom Polyethylenglykol-Typ, das durch  $R-O-(CH_2CH_2O)_nH$  ( $R$  = gesättigte Kohlenwasserstoff-Gruppe, deren Kohlenstoffanzahl 8-16 ist oder ungesättigter Kohlenwasserstoffrest mit einer Doppelbindung,  $n$  = 6-14) oder  $R-O-(CH_2CH_2O)_nH$  ( $R$  = gesättigte Kohlenwasserstoff-Gruppe, deren Alkylrest eine Kohlenstoffanzahl von 8-12 hat oder Alkylphenylrest, der eine ungesättigte Kohlenwasserstoff-Gruppe mit einer Doppelbindung ist,  $n$  = 6-14) repräsentiert wird, einer Mischung aus mehreren kationischen Tensiden, einer Mischung aus mehreren nicht-ionischen Tensiden, einer Mischung aus mehreren anionischen Tensiden und einem oder mehreren nicht-ionischen Tensiden, oder einer Mischung aus einem oder mehreren kationischen Tensiden und einem oder mehreren nicht-ionischen Tensiden besteht, ausgewählt wird.
- 20 25 30 35 40 13. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 7 beschrieben, wobei die Trockentemperatur nach dem Waschen 200 °C oder weniger ist.
14. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 7 oder 8 beschrieben, wobei die Trockentemperatur nach dem Waschen 90 °C oder weniger ist.
- 45 15. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 1 beschrieben, wobei das Aluminiummaterial mit einer Flüssigkeit gewaschen wird, die Aluminium nach dem Kaltwalzen lösen kann, und der Kontaktheizungs-Schritt zum Erwärmen des Aluminiummaterials mit dem Heizkörper nach dem Fertigglühen durchgeführt wird.
- 50 16. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 15 beschrieben, wobei das Waschen mit der Flüssigkeit, die Aluminium lösen kann, eine Basenwaschung ist.
17. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 15 beschrieben, wobei das Waschen mit der Flüssigkeit, die Aluminium lösen kann, eine Säurewaschung ist.
- 55 18. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 15 beschrieben, wobei das Waschen mit der Flüssigkeit, die Aluminium lösen kann, eine Aufeinanderfolge von Basenwaschung und Säurewaschung ist.

## EP 1 498 513 B9

19. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 15 bis 18 beschrieben, wobei das Aluminiummaterial einer Waschung mit einem organischen Lösungsmittel unterzogen wird, bevor der Basenwaschung oder der Säurewaschung.
- 5 20. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 16, 18 und 19 beschrieben, wobei eine Basenwaschflüssigkeit für die Basenwaschung eine Lösung ist, die eine oder mehrere Basen enthält, die aus der Gruppe, die aus Natriumhydroxid, Kaliumhydroxid, Calciumhydroxid, Natriumorthosilikat, Natriummetasilikat und tertiärem Natriumphosphat besteht, ausgewählt wird.
- 10 21. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 17 bis 19 beschrieben, wobei eine Säurewaschflüssigkeit für die Säurewaschung eine Lösung ist, die eine oder mehrere Säuren enthält, die aus der Gruppe, die aus Salzsäure, Schwefelsäure, Salpetersäure und Phosphorsäure besteht, ausgewählt wird.
- 15 22. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 1 beschrieben, wobei der Kontaktheizungs-Schritt für das Erwärmen des Aluminiummaterials mit dem Heizkörper nach dem Fertigglühen durchgeführt wird.
- 20 23. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 1 bis 22 beschrieben, wobei eine Oberflächentemperatur des Heizkörpers 50 bis 450 °C ist und eine Kontaktzeit des Aluminiumelements und des Heizkörpers 0.001 bis 60 Sekunden ist.
- 25 24. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 23 beschrieben, wobei die Oberflächentemperatur des Heizkörpers 60 bis 400 °C ist.
- 30 25. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 23 beschrieben, wobei die Oberflächentemperatur des Heizkörpers 80 bis 400 °C ist.
- 35 26. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 23 bis 25 beschrieben, wobei die Kontaktzeit des Aluminiumelements und des Heizkörpers 0.001 bis 60 Sekunden ist.
- 40 27. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 23 bis 25 beschrieben, wobei die Kontaktzeit des Aluminiumelements und des Heizkörpers 0.001 bis 30 Sekunden ist.
- 45 28. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 1 bis 27 beschrieben, wobei ein Zwischenglühen während des Kaltwalzens durchgeführt wird.
- 50 29. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 1 bis 28 beschrieben, wobei das Fertigglühen in einer Inertgas-Atmosphäre bei der tatsächlichen Aluminiumtemperatur von 450 bis 600 °C durchgeführt wird.
- 55 30. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 1 bis 29 beschrieben, wobei der Heizkörper eine Heizwalze ist.
31. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 1 bis 30 beschrieben, wobei das Aluminiummaterial nach dem Kontakt mit dem Heizkörper gekühlt wird.
32. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in Anspruch 31 beschrieben, wobei das Kühlen des Aluminiummaterials durch In-Kontakt-bringen des Aluminiummaterials mit einer Kühlwalze durchgeführt wird.
33. Das Verfahren zur Herstellung eines Aluminiummaterials für elektrolytische Kondensatorelektroden wie in einem der Ansprüche 1 bis 32 beschrieben, wobei die Aluminiumreinheit des Aluminiummaterials 99.9% oder mehr ist.
34. Ein Aluminiummaterial für elektrolytische Kondensatoren, das durch ein Verfahren wie in einem der Ansprüche 1

bis 33 beschrieben hergestellt wird.

35. Das Aluminiummaterial für elektrolytische Kondensatoren wie in Anspruch 34 beschrieben, wobei das Aluminiummaterial für Mittenspannung oder Hochspannung ist.

36. Ein Verfahren zur Herstellung eines Elektrodenmaterials für elektrolytische Kondensatoren, wobei das Aluminiummaterial, das durch das Verfahren wie in einem der Ansprüche 1 bis 33 beschrieben, Ätzen unterzogen wird.

37. Das Verfahren zur Herstellung eines Elektrodenmaterials für elektrolytische Kondensatoren wie in Anspruch 36 beschrieben, wobei das Ätzen DC-Ätzen ist.

38. Ein elektrolytischer Aluminiumkondensator, der das Aluminiumelektrodenmaterial, das durch das Verfahren wie in Anspruch 36 oder 37 beschrieben hergestellt wird, als ein Elektrodenmaterial verwendet.

## Revendications

1. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique, le procédé comportant, dans la fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique par soumission d'une brame d'aluminium à un laminage à chaud, un laminage à froid et un recuit final, d'effectuer une étape de chauffage par contact pour chauffer le matériau d'aluminium en amenant le matériau d'aluminium en contact avec un corps chauffant après laminage à chaud.

2. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 1, dans lequel l'étape de chauffage par contact pour chauffer le matériau d'aluminium avec le corps chauffant est effectuée au moins une fois entre un début du laminage à froid et son achèvement.

3. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 2, dans lequel un rapport de réduction du laminage du matériau d'aluminium après l'étape de chauffage par contact est de 60 % ou moins, où le rapport de réduction du laminage est représenté par  $[(A - B)/A] \times 100$  (%), où « A » ( $\mu\text{m}$ ) est une épaisseur du matériau d'aluminium après le dernier chauffage par contact parmi le chauffage par contact effectué au moins une fois pendant le laminage à froid mais avant la reprise du laminage à froid, et « B » ( $\mu\text{m}$ ) est une épaisseur du matériau d'aluminium après l'intégralité du laminage à froid.

4. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 3, dans lequel le rapport de réduction du laminage après chauffage par contact est de 30 % ou moins.

5. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 1, dans lequel l'étape de chauffage par contact pour chauffer le matériau d'aluminium avec le corps chauffant est effectuée après le laminage à froid mais avant le recuit final.

6. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 5, comprenant en outre une étape de lavage pour laver le matériau d'aluminium, effectuée avant ou après l'étape de chauffage par contact.

7. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 5, dans lequel le matériau d'aluminium est lavé avant le contact avec le corps chauffant, puis séché ou non séché, et ensuite chauffé en amenant le matériau d'aluminium en contact avec le corps chauffant.

8. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 5, dans lequel le matériau d'aluminium est lavé après le contact avec le corps chauffant, puis séché ou non séché, et ensuite recuit.

9. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 5 à 8, dans lequel le liquide de lavage servant à laver le matériau d'aluminium est un solvant organique.

10. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la

revendication 9, dans lequel le solvant organique est un élément ou un mélange de deux éléments ou plus choisis dans le groupe consistant en un alcool représenté par  $C_nH_{2n+1}OH$  ( $n$  (entier) = 1 à 10), le cyclohexanol ( $C_6H_{11}OH$ ), le 1,2-éthanediol ( $HOCH_2CH_2OH$ ), le 1,2-propanediol ( $CH_3CH(OH)CH_2OH$ ), le 1,3-propanediol ( $HOCH_2CH_2CH_2OH$ ), un hydrocarbure de la série des alcanes représentés par  $C_nH_{2n+2}$  ( $n$  (entier) = 5 à 15), le cyclohexane, une cétone représentée par  $R^1COR^2$  ( $R^1$  et  $R^2$  : radical hydrocarbure aliphatique, le nombre total d'atomes de carbone de  $R^1$  et  $R^2$  est de 8 ou moins), la cyclohexanone ( $C_6H_{10}O$ ), un éther représenté par  $R^1-O-R^2$  ( $R^1$  et  $R^2$ : groupe hydrocarbure aliphatique, le nombre total d'atomes de carbone de  $R^1$  et  $R^2$  est de 8 ou moins), le 2-méthoxy éthanol ( $CH_3OCH_2CH_2OH$ ), le 2-éthoxyéthanol ( $CH_3CH_2OCH_2CH_2OH$ ), le 2-butoxyéthanol ( $CH_3CH_2CH_2CH_2OCH_2CH_2OH$ ), le 2-(2-éthoxy)éthoxyéthanol ( $CH_3CH_2OCH_2CH_2OCH_2CH_2OH$ ), l'acétate d'éthyle représenté par  $CH_3COOR$  ( $R$  : groupe hydrocarbure aliphatique, le nombre d'atomes de carbone est de 1 à 5), et le toluènesylène.

11. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 5 à 8, dans lequel le liquide de lavage pour laver le matériau d'aluminium est de l'eau à laquelle est ajouté un tensioactif.
12. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 11, dans lequel le tensioactif est un tensioactif anionique ou un mélange de plusieurs agents tensioactifs anioniques choisis dans le groupe consistant en un tensioactif anionique (sel d'ester-sulfate) représenté par  $R-OSO_3Na$  ( $R$  = groupe hydrocarbure saturé dont le nombre d'atomes de carbone est de 8 à 18 ou groupe hydrocarbure insaturé comportant une double liaison), un tensioactif anionique (sel d'acide sulfonique) représenté par  $R-SO_3Na$  ( $R$  = radical hydrocarbure saturé dont le nombre d'atomes de carbone est de 8 à 18 ou groupe hydrocarbure insaturé comportant une double liaison) ou  $R-SO_3Na$  ( $R$  = radical hydrocarbure saturé dont le radical alkyle a un nombre d'atomes de carbone de 8 à 14 ou groupe hydrocarbure insaturé comportant une double liaison), un tensioactif cationique (sel d'ammonium quaternaire) représenté par  $R-N^+(CH_3)_3 \cdot Cl^-$  ( $R$  = groupe hydrocarbure saturé dont le nombre d'atomes de carbone est de 8 à 16), un tensioactif non ionique de type polyéthylèneglycol représenté par  $R-O-(CH_2CH_2O)_nH$  ( $R$  = groupe hydrocarbure saturé dont le nombre d'atomes de carbone est de 8 à 16 ou radical hydrocarbure insaturé comportant une double liaison,  $n$  = 6 à 14) ou  $R-O-(CH_2CH_2O)_nH$  ( $R$  = groupe hydrocarbure saturé dont le radical alkyle a un nombre d'atomes de carbone de 8 à 12 ou radical alkylphényle qui est un groupe hydrocarbure insaturé comportant une double liaison,  $n$  = 6 à 14), un mélange de plusieurs agents tensioactifs cationiques, un mélange de plusieurs agents tensioactifs non ioniques, un mélange d'un ou plusieurs agents tensioactifs anioniques et d'un ou plusieurs agents tensioactifs non ioniques ou un mélange d'un ou plusieurs agents tensioactifs cationiques et d'un ou plusieurs agents tensioactifs non ioniques.
13. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 7, dans lequel la température de séchage après le lavage est de 200 °C ou moins.
14. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 7 ou 8, dans lequel la température de séchage après le lavage est de 90°C ou moins.
15. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 1, dans lequel le matériau d'aluminium est lavé avec un liquide capable de dissoudre l'aluminium après le laminage à froid, puis l'étape de chauffage par contact pour chauffer le matériau d'aluminium avec un corps chauffant est effectuée après le recuit final.
16. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 15, dans lequel le lavage avec le liquide capable de dissoudre l'aluminium est un lavage alcalin.
17. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 15, dans lequel le lavage avec le liquide capable de dissoudre l'aluminium est un lavage à l'acide.
18. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 15, dans lequel le lavage avec le liquide capable de dissoudre l'aluminium est une séquence de lavage alcalin et de lavage à l'acide.
19. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 15 à 18, dans lequel le matériau d'aluminium est soumis à un lavage par solvant organique avant le lavage alcalin ou le lavage à l'acide.

## EP 1 498 513 B9

- 5  
20. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 16, 18 et 19, dans lequel le liquide de lavage alcalin pour le lavage alcalin est une solution contenant un ou plusieurs alcali choisis dans le groupe consistant en l'hydroxyde de sodium, l'hydroxyde de potassium, l'hydroxyde de calcium, l'orthosilicate de sodium, le métasilicate de sodium et le phosphate de sodium tertiaire.
- 10  
21. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 17 à 19, dans lequel le liquide de lavage à l'acide pour le lavage à l'acide est une solution contenant un ou plusieurs acides choisis dans le groupe consistant en l'acide chlorhydrique, l'acide sulfurique, l'acide nitrique et l'acide phosphorique.
- 15  
22. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 1, dans lequel l'étape de chauffage par contact pour chauffer le matériau d'aluminium avec le corps chauffant est effectuée après le recuit final.
- 20  
23. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 1 à 22, dans lequel une température de chauffage du corps chauffant est de 50 à 450 °C et un temps de contact de la pièce en aluminium et du corps chauffant est de 0,001 à 60 secondes.
- 25  
24. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 23, dans lequel la température de surface du corps chauffant est de 60 à 400°C.
- 25  
25. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 23, dans lequel la température de surface du corps chauffant est de 80 à 400°C.
- 30  
26. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 23 à 25, dans lequel le temps de contact de l'organe en aluminium et du corps chauffant est de 0,001 à 60 secondes.
- 30  
27. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 23 à 25, dans lequel le temps de contact de l'organe en aluminium et du corps chauffant est de 0,001 à 30 secondes.
- 35  
28. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 1 à 27, dans lequel un recuit intermédiaire est effectué pendant le laminage à froid.
- 40  
29. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 1 à 28, dans lequel le recuit final est effectué dans une atmosphère de gaz inerte à la température effective de l'aluminium de 450 à 600°C.
- 45  
30. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 1 à 29, dans lequel le corps chauffant est un rouleau chauffant.
- 50  
31. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 1 à 30, dans lequel le matériau d'aluminium est refroidi après le contact avec le corps chauffant.
- 55  
32. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon la revendication 31, dans lequel le refroidissement du matériau d'aluminium est effectué en amenant le matériau d'aluminium en contact avec un rouleau refroidissant.
33. Procédé de fabrication d'un matériau d'aluminium pour des électrodes de condensateur électrolytique selon l'une quelconque des revendications 1 à 32, dans lequel la pureté de l'aluminium du matériau d'aluminium est de 99,9 % ou plus.
34. Matériau d'aluminium pour des condensateurs électrolytiques fabriqué par un procédé tel que présenté dans l'une quelconque des revendications 1 à 33.

## EP 1 498 513 B9

35. Matériau d'aluminium pour des condensateurs électrolytiques selon la revendication 34, dans lequel le matériau d'aluminium est destiné à une moyenne tension ou à une haute tension.

5 36. Procédé de fabrication d'un matériau d'électrode pour des condensateurs électrolytiques, dans lequel le matériau d'aluminium fabriqué par le procédé tel que présenté dans l'une quelconque des revendications 1 à 33 est soumis à un gravage.

10 37. Procédé de fabrication d'un matériau d'électrode pour des condensateurs électrolytiques selon la revendication 36, dans lequel le gravage est un gravage à courant continu.

15 38. Condensateur électrolytique en aluminium employant le matériau d'électrode en aluminium fabriqué par le procédé tel que présenté dans la revendication 36 ou 37, en tant que matériau d'électrode.

20

25

30

35

40

45

50

55

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- JP 2002123666 A [0001]
- JP 2002196867 A [0001]
- JP 2002209455 A [0001]
- JP 2002209459 A [0001]
- JP 2003057737 A [0001]
- JP 2003060611 A [0001]
- JP 2003060614 A [0001]
- JP 2003111747 A [0001]
- JP S5834926 B [0009]
- JP S63116417 B [0011]
- JP H7201673 B [0012] [0014]
- JP H5279815 B [0013] [0014]
- JP H5200406 B [0015] [0016]
- JP H1136053 B [0017]
- JP H5255821 B [0017]

**Non-patent literature cited in the description**

- **Kiyoshi FUKUOKA ; Nobuo OSAWA ; Tetsuya MOTOI.** *The 95th Autumn Conference of Japan Institute of Light Metals Lecture Summary*, 1998, 265 [0007]
- *Journal of The Surface Finishing Society of Japan*, 1999, vol. 50 (7), 643 [0007]
- **Nobuo OSAWA ; Kiyoshi FUKUOKA.** *Journal of The Surface Finishing Society of Japan*, 1999, vol. 50 (7), 643 [0030]
- **M.S. Hunter ; P. Fowle.** *J. electrochem. Soc.*, 1954, vol. 101 (9), 483 [0052] [0104] [0140] [0159]