

[Document Name] SPECIFICATION

[Title of the Invention] SURFACE-TREATED ALUMINUM MATERIAL AND METHOD OF MANUFACTURING THE SAME

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[TECHNICAL FIELD]

[0001] The present invention relates to a surface-treated aluminum material and a method of manufacturing the same.

10 [BACKGROUND ART]

[0002] Aluminum materials composed of aluminum or aluminum alloys are used in various applications. An anodic oxide film can be provided on the surface(s) of these aluminum materials in order to achieve various purposes, such as increased corrosion resistance, improved scratch resistance, and improved design properties. Since there are various functions that can be imparted to the aluminum material by anodic oxide films, the field of applications for aluminum materials having anodic oxide films is increasingly expanding.

[0003] As an example of an aluminum material having an anodic oxide film, a component for a substrate processing apparatus that performs a plasma treatment on a substrate is disclosed in Patent Document 1, characterized by having a film that has been formed on a surface of the component by an anodizing treatment, in which the component is connected to the anode of a DC power source and immersed in a solution that contains an organic acid as a main component, wherein a semi-sealing treatment using boiling water is performed on the film, and discloses a method for forming the film.

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[PRIOR ART LITERATURE]

[Patent Document]

[0004] [Patent Document 1] Japanese Laid-open Patent Publication 2008-81815

30 [SUMMARY OF THE INVENTION]

[PROBLEM TO BE SOLVED BY THE INVENTION]

[0005] However, pores in the anodic oxide film formed by the film forming method of Patent Document 1 are not completely closed. Therefore, there is a problem that the corrosion resistance of components that have been treated by the film forming method of Patent

Document 1 is low.

5 [0006] Meanwhile, in order to increase the corrosion resistance of components that have been treated according to the film forming method of Patent Document 1, a method of performing a sealing treatment and completely closing up the pores in the anodic oxide film is conceivable. However, in this situation, cracks are more likely to form in the anodic oxide film when the temperature of the component has risen during use, and thus there is a risk of this actually leading to a decrease in corrosion resistance. Therefore, with regard to the components that have been treated according to the film forming method of Patent Document 1, there has been
10 a limit on increasing the maximum service temperature, i.e. the maximum temperature expected in environments in which the components are used, while maintaining high corrosion resistance.

[0007] The present invention was conceived in view of this background, and it is an object is
15 to provide a surface-treated aluminum material and a method of manufacturing the same, with which the maximum service temperature can easily be increased while maintaining high corrosion resistance.

[MEANS FOR SOLVING THE PROBLEMS]

20 [0008] One aspect of the present invention is a surface-treated aluminum material having: a base material, which is composed of aluminum or an aluminum alloy, and a protective film, which is formed on the base material, wherein:

the protective film has an oxide layer, which is composed of an oxide or oxides of aluminum and covers the base material; and

25 a hydrated oxide layer, which contains a hydrated oxide or hydrated oxides of aluminum and covers the oxide layer; and

in a situation in which a SWAAT test according to a method stipulated in ASTM-G85-A3 has been performed on the surface-treated aluminum material after it had been heated at a temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base
30 material, which occur on the surface of the surface-treated aluminum material when 48 hours have elapsed since the start of the test, is 1.0 sites/cm² or fewer.

[0009] Another aspect of the present invention is a method of manufacturing the surface-treated aluminum material according to the above-mentioned aspect, comprising:

forming the oxide layer, which has pores, on the base material by performing an anodizing treatment on the base material,

thereafter, heating the base material and the oxide layer at a temperature of 100°C or higher and 350°C or lower, and

5 thereafter, contacting the oxide layer with a sealing agent, and forming the hydrated oxide layer on the oxide layer while sealing the pores.

[EFFECTS OF THE INVENTION]

10 **[0010]** The surface-treated aluminum material (hereinafter referred to as the "aluminum material") has a protective film having the oxide layer and the hydrated oxide layer on the surface of a base material. In addition, in the situation in which a SWAAT test according to a method stipulated in ASTM-G85-A3 has been performed on the surface-treated aluminum material after it had been heated at a temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base material, which occur on the surface of the surface-treated
15 aluminum material when 48 hours have elapsed since the start of the test, is 1.0 sites/cm² or fewer. An aluminum material having such a characteristic can curtail the occurrence of cracks even when the temperature has risen. For this reason, the maximum service temperature of the aluminum material can easily be increased while maintaining high corrosion resistance.

20 **[0011]** In addition, in the above-mentioned method of manufacturing the aluminum material, after having performed an anodizing treatment on the base material, the oxide layer, which had been formed owing the anodizing treatment, is heated at a temperature within the above-mentioned specific range. Thus, by heating the oxide layer before sealing the pores in the oxide layer, internal stresses created when the oxide layer was formed can be relaxed. Then, after the
25 internal stresses in the oxide layer have been relaxed, by contacting the oxide layer with the sealing agent and forming the hydrated oxide layer on the oxide layer and sealing the pores, the occurrence of cracks is curtailed, even when the temperature of the aluminum material has risen, such that high corrosion resistance can be maintained in high-temperature environments.

30 **[0012]** Thus, according to the aspects described above, a surface-treated aluminum material and a method of manufacturing the same can be provided, with which the maximum service temperature can easily be increased while maintaining high corrosion resistance.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0013] [FIG. 1] FIG. 1 is a cross-sectional view of a surface-treated aluminum material according to a Working Example.

[FIG. 2] FIG. 2 is a cross-sectional view of a base material on which an oxide layer has been formed in the manufacturing process of the surface-treated aluminum material of the Working Example.

[MODES FOR CARRYING OUT THE INVENTION]

[0014] (Aluminum Material)

The base material of the aluminum material is constituted from aluminum or an aluminum alloy. The shape of the base material is not particularly limited, and various shapes can be used in accordance with the application of the aluminum material. For example, the base material may be an elongated material such as a rolled sheet or an extruded material, or may be a cast material or a forged material. In the situation in which the shape of the base material is a sheet shape, the thickness of the base material is not particularly limited. More specifically, the base material may be, for example, a cold-rolled sheet having a thickness of approximately 1 mm, or may be a hot-rolled sheet having a thickness of approximately 50 mm.

[0015] In addition, the material of the base material can be selected as appropriate, in accordance with the application of the aluminum material, from the group consisting of aluminum and aluminum alloys. More specifically, for example, a 1000-series aluminum can be used as the aluminum that constitutes the base material. In addition, for example, a 2000-series aluminum alloy, a 3000-series aluminum alloy, a 4000-series aluminum alloy, a 5000-series aluminum alloy, a 6000-series aluminum alloy, a 7000-series aluminum alloy, and an 8000-series aluminum alloy can be used as the aluminum alloy that constitutes the base material. In addition, the base material may be a clad material, in which two or more layers having mutually different chemical compositions have been laminated.

[0016] A protective film, which contains an oxide layer that is composed of an oxide or oxides of aluminum and has been laminated on the base material, and a hydrated oxide layer that contains a hydrated oxide or hydrated oxides of aluminum and has been laminated on the oxide layer, is provided on the base material. More specifically, the hydrated oxide layer may be constituted by the hydrated oxide(s) of aluminum. In addition, the hydrated oxide layer may contain a hydrated oxide or hydrated oxides and a metal salt or metal salts and/or a metal oxide or metal oxides. After having formed the oxide layer, which has numerous pores, on the surface

of the base material by performing an anodizing treatment on the base material, the protective film can be obtained, for example, by performing a sealing treatment and thereby closing up the pores in the oxide layer with the hydrated oxide layer. Such a protective film excels in corrosion resistance because the pores are sealed. For this reason, the corrosion resistance of the aluminum material can be increased by forming the protective film on the base material.

[0017] The thickness of the protective film is preferably 5 μm or more, more preferably 7 μm or more, and further preferably 10 μm or more. In this situation, the corrosion resistance of the aluminum material can be further increased. From the viewpoint of corrosion resistance, although the upper limit for the thickness of the protective film is not particularly limited, the upper limit of the manufacturability of the thickness of the protective film is, for example, 200 μm . From the viewpoint of further increasing the productivity of the aluminum material, the thickness of the protective film is preferably 60 μm or less.

[0018] In the situation in which a SWAAT test according to a method stipulated in ASTM-G85-A3 has been performed on the aluminum material after it had been heated at a temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base material, which occur on the surface of the aluminum material when 48 hours have elapsed since the start of the test, is 1.0 sites/cm² or fewer. Aluminum materials having such a characteristic can curtail the occurrence of cracks, even when used at high temperatures, and can increase corrosion resistance at high temperatures. Accordingly, the maximum service temperature of the aluminum material can easily be increased while maintaining high corrosion resistance.

[0019] From the viewpoint of more easily increasing the maximum service temperature of the aluminum material, in the situation in which a SWAAT test has been performed, under the conditions specified above, on the surface-treated aluminum material, the number of corrosion sites that have reached the base material, which occur on the surface of the surface of the aluminum material when 48 hours have elapsed since the start of the test, is preferably 0.80 sites/cm² or fewer, more preferably 0.60 sites/cm² or fewer, further preferably 0.50 sites/cm² or fewer, particularly preferably 0.30 sites/cm² or fewer, and most preferably 0.10 sites/cm² or fewer.

[0020] It is noted that the specific test methods for the SWAAT test and the method of calculating the number of corrosion sites are as follows. First, a corrosion test surface on a

portion of the surface of the protective film on the aluminum material is determined, and the region(s) on the surface of the protective film other than the corrosion test surface is (are) covered with masking tape. Next, the aluminum material is disposed in a corrosion testing apparatus so that the corrosion test surface faces up. Subsequently, a test solution is continuously sprayed on the corrosion test surface for 0.5 hours while maintaining the temperature in the testing apparatus tank at $49 \pm 2^\circ\text{C}$. It is noted that an aqueous solution having a pH of 2.8 or higher and 3.0 or lower, which was prepared by adding acetic acid to an artificial seawater solution having a composition stipulated in ASTM D1141-98, is used as the test solution in the SWAAT test. In addition, the test solution spraying rate is within the range of 1.0 ml/80 cm²/h or more and 2.0 ml/80 cm²/h or less.

[0021] After the test solution has been continuously sprayed onto the corrosion test surface for 0.5 hours, spraying of the test solution is stopped, and the aluminum material is left to stand in the testing apparatus for 1.5 hours. The temperature in the testing apparatus tank at this time is $49 \pm 2^\circ\text{C}$, and the relative humidity in the tank is 98% RH or higher. Thereafter, the above-mentioned spraying of test solution and leaving of the aluminum material to stand are repeatedly performed, and the SWAAT test is ended when the time elapsed from the start of the test has reached 48 hours.

[0022] After the SWAAT test has ended, the aluminum material, which has been taken out from the testing apparatus, is rinsed with water and then dried. Thereafter, corrosion products generated by the SWAAT test are removed by immersing the aluminum material in concentrated nitric acid. Thereafter, all of the corrosion sites that have appeared on the corrosion test surface are observed using a microscope and it is determined whether or not the base material is exposed at the bottom of the corrosion sites. Then, the number of corrosion sites where the base material is exposed at the bottom are counted. The number of corrosion sites that have reached the base material (units: sites/cm²) after the SWAAT test can be calculated by dividing the number of corrosion sites where the base material is exposed (units: sites) by the area of the corrosion test surface (units: cm²), which have been obtained as described above.

[0023] In the situation in which a CASS test according to a method stipulated in JIS H 8502:1999 has been performed after the aluminum material had been heated at a temperature of 200°C for 1 hour, it is preferable that the number of corrosion sites that have reached the

base material, which occur on the surface of the aluminum material when 24 hours have elapsed since the start of the test, is 2.0 sites/cm² or fewer. Aluminum materials having such a characteristic can curtail the occurrence of cracks even when used at high temperatures and can further increase corrosion resistance at high temperatures. Accordingly, the maximum service temperature of the aluminum material having such a characteristic can easily be increased while maintaining high corrosion resistance.

[0024] From the viewpoint of more easily increasing the maximum service temperature of the aluminum material, in the situation in which a CASS test has been performed on the aluminum material under the conditions specified above, the number of corrosion sites that have reached the base material, which occur on the surface of the surface of the aluminum material when 24 hours have elapsed since the start of the test, is preferably 1.8 sites/cm² or fewer, more preferably 1.6 sites/cm² or fewer, further preferably 1.4 sites/cm² or fewer, particularly preferably 1.2 sites/cm² or fewer, and most preferably 1.0 sites/cm² or fewer.

[0025] It is noted that the specific test methods for the CASS test and the method of calculating the number of corrosion sites are as follows. First, a corrosion test surface on a portion of the surface of the protective film on the aluminum material is determined, and the region(s) on the surface of the protective film other than the corrosion test surface is (are) covered with masking tape. Next, the aluminum material is disposed in a corrosion testing apparatus so that the corrosion test surface faces up. Thereafter, the test solution is continuously sprayed on the corrosion test surface while maintaining the temperature in the tank of the testing apparatus at 50 ±2°C. Then, the CASS test is ended when the elapsed time from the start of the test has reached 24 hours. It is noted that an aqueous solution having a pH of 3.0, which was prepared by dissolving 50 ±5 g/L of sodium chloride and 0.26 ±0.02 g/L of copper (II) chloride dihydrate in pure water and then adding approximately 1 mL/L of acetic acid, is used as the test solution in the CASS test. In addition, the test solution spraying rate is within the range of 1.0 ml/80 cm²/h or more and 2.0 ml/80 cm²/h or less.

[0026] After the CASS test has ended, the aluminum material, which has been taken out from the testing apparatus, is rinsed with water and then dried. Subsequently, corrosion products generated by the CASS test are removed by immersing the aluminum material in concentrated nitric acid. Subsequently, all of the corrosion sites that have appeared on the corrosion test surface are observed using a microscope and it is determined whether or not the base material

is exposed at the bottom of the corrosion sites. Then, the number of corrosion sites where the base material is exposed at the bottom are counted. The number of corrosion sites that have reached the base material (units: sites/cm²) after the CASS test can be calculated by dividing the number of corrosion sites where the base material is exposed (units: sites) by the area of the corrosion test surface (units: cm²), which have been obtained as described above.

[0027] In a situation in which a sealing test has been performed according to a method stipulated in JIS H8683-2:2013, the mass loss per unit area of the aluminum material is preferably 0.3 g/dm² or less. Because the pores in the oxide layer are sufficiently sealed by the hydrated oxide layer, such an aluminum material can more reliably increase the corrosion resistance of the aluminum material.

[0028] It is noted that the specific method for the sealing test is as follows. First, 35 mL of phosphoric acid and 20 g of anhydrous chromic acid are dissolved in water to prepare 1 L of test solution. Next, a test piece, which includes the protective film, is extracted from the aluminum material, and the surface area of the protective film on the test piece is measured. After contamination on the surface of this test piece has been removed, the mass of the test piece is measured. Subsequently, the test piece is immersed for 15 minutes $\pm$ 5 seconds in the test solution, which is held at a temperature of 38°C $\pm$ 1°C.

[0029] After immersion of the test piece in the test solution has been completed, the test piece is rinsed with running water and then further rinsed with deionized water or distilled water. Following the rinsing and after the test piece has been thoroughly dried, the mass of the test piece is measured.

[0030] The surface area A (unit: dm²) of the protective film on the test piece obtained as described above, the mass m₁ (unit: g) of the test piece before immersion in the test solution, and the mass m₂ (unit: g) of the test piece after immersion in the test solution can be used to calculate the mass loss δ_A per unit area (unit: g/dm²) based on Equation (1) below.

$$\delta_A = (m_1 - m_2) / A \quad (1)$$

[0031] As described above, the maximum service temperature of the aluminum material can easily be increased while maintaining high corrosion resistance. Therefore, the aluminum material is suitable for use in materials that reach high temperatures during use, such as cover

materials provided around the fans of cooking appliances, metal housings of kitchen equipment, and materials for semiconductor manufacturing equipment. More specifically, materials for semiconductor manufacturing equipment include, for example, chambers in semiconductor manufacturing equipment, such as film-forming equipment and etching equipment, components arranged within the chambers, and the like. Examples of kitchen equipment include, for example, cooking appliances such as ovens, microwaves, gas stoves, and fryers, hot food showcases, and the like.

[0032] (Method of Manufacturing the Aluminum Material)

To manufacture the surface-treated aluminum material, first, a base material composed of aluminum or an aluminum alloy is prepared. The method of manufacturing the base material is not particularly limited, and known methods can be employed. The base material may be manufactured, for example, by a method in which casting, rolling and heat treatment(s) are combined as appropriate. Either DC casting or continuous casting may be employed as the method of casting the base material.

[0033] In addition, after the base material has been manufactured and before performing the anodizing treatment, pretreatments of the anodizing treatment, such as degreasing, acid cleaning, and grinding may be performed, as necessary. Next, the oxide layer, which has pores, is formed on the base material by performing the anodizing treatment on the base material. The oxide layer can be formed on the surface(s) of the base material during the anodizing treatment by flowing a direct current between the base material and a counter electrode in a state in which the base material and the counter electrode are immersed in the electrolyte solution. The oxide layer thus formed is constituted from an oxide or oxides of aluminum, such as alumina, and has numerous pores.

[0034] The electrolyte solution used in the anodizing treatment may be, for example, an acidic electrolyte solution containing an electrolyte, such as sulfuric acid, phosphoric acid, or the like, or may be an alkaline electrolyte solution containing an electrolyte, such as sodium metaborate. The electrolyte solution employed in the anodizing treatment preferably contains an inorganic electrolyte composed of an inorganic cation, such as a metal ion or an ammonium ion, and one or two or more anions selected from the group consisting of a sulfate ion, a phosphate ion, and a borate ion. An oxide layer having a desired structure can be more easily formed by performing the anodizing treatment using an electrolyte solution that contains an inorganic electrolyte.

[0035] The current density of the direct current in the anodizing treatment can be set, for example, in a range of 1 mA/cm² or more and 100 mA/cm² or less, as appropriate. In addition, the temperature of the electrolyte solution in the anodizing treatment can be set, for example, within the range of 0°C or higher and 40°C or lower, as appropriate.

[0036] The thickness of the oxide layer formed in the anodizing treatment is preferably 2 μm or more. By making the thickness of the oxide layer 2 μm or more, the thickness of the protective film obtained after sealing can be made sufficiently thick, and an aluminum material that excels in corrosion resistance and in heat resistance can be more easily obtained.

[0037] In the above-mentioned manufacturing method, after the anodizing treatment has been performed, the base material and the oxide layer are heated at a temperature of 100°C or higher and 350°C or lower. By heating the oxide layer at a temperature within the above-mentioned specific range after the anodizing treatment has been performed and before sealing the pores in the oxide layer, internal stresses in the oxide layer can be relaxed. Then, by sealing the pores after the internal stresses of the oxide layer were relaxed, the internal stresses in the protective film after sealing can be reduced. As a result, the formation of cracks in the protective film when heated can be curtailed, and the corrosion resistance of the aluminum material at high temperatures can be increased.

[0038] In the situation in which the heating temperature of the oxide layer is lower than 100°C, there is a risk that the relaxation of the internal stresses in the oxide layer might be insufficient, and cracks might form in the protective film more readily when the temperature of the aluminum material rises, which might lead to a taika [*sic*] of the corrosion resistance. On the other hand, in the situation in which the heating temperature of the oxide layer exceeds 350°C, there is a risk that the oxide layer might be unable to follow the thermal expansion of the base material, and cracks might form in the protective film. From the viewpoint of more easily increasing the maximum service temperature of the aluminum material, the heating temperature of the oxide layer is preferably 130°C or higher and 330°C or lower, more preferably 150°C or higher and 310°C or lower, further preferably 180°C or higher and 290°C or lower, and particularly preferably 200°C or higher and 280°C or lower.

[0039] When heating the oxide layer, the heating may be ended immediately after the

temperature of the oxide layer has reached a desired temperature or that temperature may be maintained for a certain extent of time after the desired temperature of the oxide layer has been reached. From the viewpoint of sufficiently relaxing the internal stresses in the oxide layer and more reliably increasing the corrosion resistance of the aluminum material at high temperatures, the heating time from when heating of the oxide layer is started to when heating is ended is preferably 3 minutes or more.

[0040] In addition, the heating temperature of the oxide layer is preferably higher than or equal to the maximum service temperature of the surface-treated aluminum material. In this situation, the formation of cracks in the surface-treated aluminum material can be more reliably curtailed, and the corrosion resistance at high temperatures can be more reliably increased.

[0041] Although it is not entirely clear why the effects described above can be obtained by setting the heating temperature of the oxide layer to be higher than the maximum service temperature of the surface-treated aluminum material, the following reasons are, for example, conceivable. That is, it is conceivable that, when the oxide layer is heated in the method of manufacturing the aluminum material, from among the strains present in the oxide layer, strains having an energy lower than or equal to the heating temperature of the oxide layer are released, such that internal stresses are relaxed. Therefore, it is conceivable that, in a situation in which the temperature of the surface-treated aluminum material obtained by the manufacturing method is a temperature no greater than the heating temperature of the oxide layer, it will be in a state in which strains that should be released within the oxide layer do not exist. Accordingly, it is conceivable that, by setting the heating temperature of the oxide layer to be higher than or equal to the maximum service temperature of the surface-treated aluminum material, the formation of cracks associated with the release of strains in the oxide layer can be curtailed.

[0042] After the oxide layer has been heated, the oxide layer is contacted with a sealing agent. Thereby, a hydrated oxide layer is formed on the oxide layer and the pores are sealed by the hydrated oxide layer. For example, a substance that can react with an oxide or oxides of aluminum to form a hydrated oxide or hydrated oxides, such as hot water at a temperature of 80°C or higher, steam, an aqueous solution containing ions of one or more metal elements selected from the group consisting of Ni (nickel), Cr (chromium), Zr (zirconium), Si (silicon), Ti (titanium), Au (gold), Ag (silver), Co (cobalt), Mo (molybdenum), Mn (manganese), Nb (niobium), Ta (tantalum), W (tungsten), Zn (zinc), Fe (iron), Ir (iridium), and Sc (scandium),

can be used as the sealing agent. In the situation in which the sealing treatment is performed using hot water or steam, a hydrated oxide layer composed of a hydrated oxide or hydrated oxides of aluminum can be formed on the oxide layer.

5 **[0043]** In addition, in the situation in which the sealing is performed using an aqueous solution containing ions of the metal element(s), a hydrated oxide layer containing a hydrated oxide or hydrated oxides of aluminum and a salt or salts and/or an oxide or oxides of the metal element(s) can be formed on the oxide layer. The metal element(s) may be present as metal ions or may be present as complex ions in the aqueous solution. More specifically, an aqueous
10 solution of a metal salt containing the metal element(s), such as aqueous nickel acetate, aqueous cobalt acetate, aqueous chromate, and aqueous silicate, can be used as the sealing agent.

[0044] From the viewpoint of more easily obtaining an aluminum material that excels in corrosion resistance and heat resistance, the sealing agent is preferably hot water at a
15 temperature of 80°C or higher. In addition, by sealing the pores in the oxide layer with hot water, a hydrated oxide layer that does not contain a metal salt can be formed on the oxide layer. In the situation in which, for example, the aluminum material is used as a material for a semiconductor-manufacturing apparatus, a metal salt in the hydrated oxide layer might become the cause for contamination of the interior of the apparatus. Accordingly, by using hot water as
20 the sealing agent and forming a hydrated oxide layer that does not contain a metal salt, an aluminum material that is suitable as a material for semiconductor manufacturing equipment can be easily obtained. In the situation in which hot water is used as the sealing agent, the pores in the oxide layer are more preferably sealed by contacting the oxide layer with hot water as the sealing agent at 80°C or higher for 10 minutes or more and less than 120 minutes.

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Working Examples

[0045] Working examples of a surface-treated aluminum material and the method of manufacturing the same will be described with reference to FIG. 1 and FIG. 2. As shown in FIG. 1, the surface-treated aluminum material 1 according to the present example comprises: a
30 base material 2, which is composed of aluminum or an aluminum alloy; and a protective film 3, which is formed on the base material. The protective film 3 comprises: an oxide layer 31, which is composed of an oxide or oxides of aluminum and covers the base material 2; and a hydrated oxide layer 32, which contains a hydrated oxide or hydrated oxides of aluminum and covers the oxide layer 31. In the situation in which a SWAAT test according to a method

stipulated in ASTM-G85-A3 has been performed on the surface-treated aluminum material 1 that has been heated at a temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base material 2, which occur on the surface of the surface-treated aluminum material 1 when 48 hours have elapsed since the start of the test, is 1.0 sites/cm² or fewer.

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[0046] To manufacture the aluminum material 1 of the present example, an oxide layer 31, which has pores 311, is first formed on the base material 2, as shown in FIG. 2, by performing an anodizing treatment on the base material 2. Thereafter, the base material 2 and the oxide layer 31 are heated at a temperature of 100°C or higher and 350°C or lower and internal stresses in the oxide layer 31 are relaxed. Thereafter, the aluminum material 1 can be obtained by contacting the oxide layer 31 with the sealing agent, and forming a hydrated oxide layer 32 on the oxide layer 31 while sealing the pores 311.

[0047] In Table 1, specific examples of the aluminum material 1 (Test Materials A1-A3) are shown. The method of manufacturing Test Materials A1-A3 is, for example, as follows. First, aluminum sheets having a chemical composition indicated by alloy number A6016 and a thickness of 1 mm are prepared as the base material 2. Pretreatments of the anodizing treatment are performed on these base materials 2. Specifically, as the pretreatments, an alkaline etching treatment is first performed in which the base material 2 is immersed in an aqueous solution of sodium hydroxide having a concentration of 5 mass% and a temperature of 55°C. Subsequently, a desmutting treatment is performed by immersing the base material 2 in nitric acid having a concentration of 30 mass%. Subsequently, a chemical polishing process is performed by immersing the base material 2 in a mixed solution in which phosphoric acid and sulfuric acid are mixed at a temperature of 85°C and a volumetric ratio of phosphoric acid:sulfuric acid = 7:3. After the chemical polishing treatment, a desmutting treatment is performed again under the same conditions described above.

[0048] After the pretreatments have been performed on the base material 2 as described above, an anodizing treatment is performed on the base material 2, and the oxide layer 31 forms on the surface of the base material 2. The electrolyte solution used in the anodizing treatment is an aqueous solution of sulfuric acid having a concentration of 15 mass%, and the temperature of the electrolyte solution is 5°C. In addition, the current density in the anodizing treatment is 10 mA/cm², and the treatment time is 60 minutes. The oxide layer 31 thus formed is a so-called porous-type alumite film and, as shown in FIG. 2, has numerous pores 311. It is noted that the

thickness of the oxide layer 31 formed by performing the anodizing treatment under the conditions described above is approximately 15 μm .

[0049] After having performed the anodizing treatment, the base material 2 is heated inside a heating furnace to relax the internal stresses in the oxide layer 31. The set temperature of the heating furnace is the value shown in the "Heating Temperature" column in Table 1, and the residence time of the base material inside the furnace, that is, the time from the start of heating to the end of heating, is the value shown in the "Heating Time" column in Table 1.

[0050] Thereafter, by immersing the base material 2, which has the oxide layer 31, in hot water as the sealing agent at a temperature of 100°C for 60 minutes, the hydrated oxide layer 32, which is composed of the hydrated oxide(s) of aluminum, forms on the oxide layer 31, and the pores 311 in the oxide layer 31 are sealed by the hydrated oxide layer 32. Test Materials A1-A3 shown in Table 1 could thereby be obtained based on the above. It is noted that, in the situation in which the pores 311 in the oxide layer 31 are sealed under such conditions, the mass loss per unit of area of the aluminum material 1 became 0.01 g/dm² or less in the situation in which a sealing test was performed using the method stipulated in JIS H8683-2:2013.

[0051] It is noted that Test Materials B1 and B2 shown in Table 1 are test materials for comparison with Test Materials A1-A3. The method of manufacturing Test Material B1 is the same as the method of manufacturing Test Material A1 except that, after the oxide layer 31 was formed on the base material 2, the oxide layer 31 is contacted with the sealing agent without being heated. The method of manufacturing Test Material B2 is the same as the method of manufacturing Test Material B1, except that the heating temperature and heating time of the oxide layer 31 were each modified as shown in Table 1.

[0052] In Table 1, the results of the SWAAT test and the CASS test using Test Materials A1-A3 and Test Materials B1 and B2 are shown. The detailed methods for the SWAAT test and the CASS test are as follows.

[0053] (SWAAT Test)

First, each test material is heated for 1 hour at a temperature of 200°C. A corrosion test surface having a rectangular shape of 5 cm in length and 10 cm in width is established on the surface of the protective film on the test material after heating, and the regions other than the

corrosion test surface on the surface of the protective film are covered with masking tape. Then, after having disposed the test material in the corrosion testing apparatus so that the corrosion test surface faces up, a SWAAT test is performed according to a method stipulated in ASTM-G85-A3. When 48 hours have elapsed since the start of the test, the test material is taken out from the corrosion testing apparatus. After this test material has been rinsed with pure water, it is completely dried using a dryer. Thereafter, the test material is immersed in concentrated nitric acid at a temperature of 25°C for 5 minutes and corrosion products that were generated on the corrosion test surface are removed.

[0054] Next, all of the corrosion sites that were generated on the corrosion test surface are observed using a microscope and it is determined whether or not the base material is exposed at the bottom of the corrosion sites. Then, the number of corrosion sites, in which the base material is exposed at the bottom, are counted. The number of corrosion sites that have reached the base material (units: sites/cm²) after the SWAAT test can be calculated by dividing the number of corrosion sites in which the base material is exposed (units: sites) by the area of the corrosion test surface (units: cm²), which were obtained as described above.

[0055] (CASS Test)

First, each test material is heated for 1 hour at a temperature of 200°C. A corrosion test surface having a rectangular shape of 5 cm in length and 10 cm in width is established on the surface of the protective film on the test material after heating, and the regions other than the corrosion test surface on the surface of the protective film are covered with masking tape. Then, after having disposed the test material in the corrosion testing apparatus so that the corrosion test surface faces up, a CASS test is performed according to a method stipulated in JIS H 8502:1999. When 24 hours have elapsed since the start of the test, the test material is taken out from the corrosion testing apparatus. After this test material has been rinsed with pure water, it is completely dried using a dryer. Thereafter, the test material is immersed in concentrated nitric acid at a temperature of 25°C for 5 minutes and corrosion products that were generated on the corrosion test surface are removed.

[0056] Next, all of the corrosion sites that were generated on the corrosion test surface are observed using a microscope and it is determined whether or not the base material is exposed at the bottom of the corrosion sites. Then, the number of corrosion sites, in which the base material is exposed at the bottom, are counted. The number of corrosion sites that have reached

the base material (units: sites/cm²) after the CASS test can be calculated by dividing the number of corrosion sites in which the base material is exposed (units: sites) by the area of the corrosion test surface (units: cm²), which were obtained as described above.

5 **[0057]**

[Table 1]

(Table 1)

	Heating of the Oxide Layer		Number of corrosion sites that have reached the base material (sites/cm ²)	
	Heating Temperature (°C)	Heating Time (min)	SWAAT Test	CASS Test
Test Material A1	250	30	0	0.24
Test Material A2	300	30	0	0.28
Test Material A3	350	30	0.04	0.3
Test Material B1	None		>1	>5
Test Material B2	250	1	>1	>5

10 **[0058]** As shown in Table 1, for Test Materials A1-A3, after having formed the oxide layer on the base material, the oxide layer is heated at a temperature within the above-mentioned specific range before sealing the pores in the oxide layer. Therefore, in the situation in which the SWAAT test according to the method stipulated in ASTM-G85-A3 has been performed after having heated these test materials at a temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base material, which occur on the surface of the surface-treated aluminum material when 48 hours have elapsed since the start of the test, is 1.0 sites/cm² or fewer. An aluminum material having such a characteristic can curtail the occurrence of cracks, even when the temperature has risen. For this reason, the maximum service temperature of the aluminum material can easily be increased while maintaining high corrosion resistance.

20 **[0059]** On the other hand, because the pores in Test Material B1 are sealed without the oxide layer being heated after having formed the oxide layer on the base material, in the situation in which the SWAAT test has been performed under the specific conditions described above, there are a greater number of corrosion sites that have reached the base material, which occur on the surface of the surface-treated aluminum material. It is therefore difficult to increase the

maximum service temperature of Test Material B1.

[0060] With regard to Test Material B2, because the heating time when heating the oxide layer is too short, in the situation in which the SWAAT test has been performed under the specific conditions described above, there are a greater number of corrosion sites that have reached the base material, which occur on the surface of the surface-treated aluminum material. It is therefore difficult to increase the maximum service temperature of Test Material B2.

[0061] Aspects of the surface-treated aluminum material and the method of manufacturing the same according to the present invention were described above based on the working examples above; however, the specific aspects of the surface-treated aluminum material and the method of manufacturing the same according to the present invention are not limited to the aspects in the working examples, and the constitutions thereof can be modified, as appropriate, within a scope that does not depart from the gist of the present invention.

[0062] For example, the surface-treated aluminum material according to the present invention can obtain the aspects according to [1]-[4] below.

[0063] [1] A surface-treated aluminum material having a base material, which is composed of aluminum or an aluminum alloy, and a protective film, which is formed on the base material, wherein:

the protective film has an oxide layer, which is composed of an oxide or oxides of aluminum and covers the base material; and

a hydrated oxide layer, which contains a hydrated oxide or hydrated oxides of aluminum and covers the oxide layer; and

in the situation in which a SWAAT test according to a method stipulated in ASTM-G85-A3 has been performed on the surface-treated aluminum material after it had been heated at a temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base material, which occur on the surface of the surface-treated aluminum material when 48 hours have elapsed since the start of the test, is 1.0 sites/cm² or fewer.

[0064] [2] The surface-treated aluminum material according to [1], wherein, in a situation in which a CASS test according to a method stipulated in JIS H 8502:1999 has been performed on the surface-treated aluminum material after it had been heated at a temperature of 200°C for

1 hour, the number of corrosion sites that have reached the base material, which occur on the surface of the surface-treated aluminum material when 24 hours have elapsed since the start of the test, is 2.0 sites/cm² or fewer.

[3] The surface-treated aluminum material according to [1] or [2], wherein the thickness
5 of the protective film is 5 μm or more and 60 μm or less.

[0065] [4] The surface-treated aluminum material according to any one of [1] to [3], wherein, in a situation in which a sealing test according to a method stipulated in JIS H8683-2:2013 has been performed, the amount of mass loss per unit area is 0.3 g/dm² or less.

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[0066] In addition, the method of manufacturing the surface-treated aluminum material according to the present invention can obtain the aspects according to [5] to [9] below.

[0067] [5] A method of manufacturing the surface-treated aluminum material according to
15 any one of [1] to [4], comprising:

forming the oxide layer, which has pores, on the base material by performing an anodizing treatment on the base material;

thereafter, heating the base material and the oxide layer at a temperature of 100°C or higher and 350°C or lower; and

20 subsequently, contacting the oxide layer with a sealing agent and forming the hydrated oxide layer on the oxide layer while sealing the pores.

[0068] [6] The method of manufacturing the surface-treated aluminum material according to [5], wherein, during the heating, the heating time from the start of heating the oxide layer to
25 the end of heating is 3 minutes or more.

[7] The method of manufacturing a surface-treated aluminum material according to [5] or [6], wherein the electrolyte solution employed in the anodizing treatment contains an inorganic electrolyte composed of an inorganic cation and one or two or more anions selected from the group consisting of a sulfate ion, a phosphate ion, and a borate ion.

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[0069] [8] The method of manufacturing a surface-treated aluminum material according to any one of [5] to [7], wherein the sealing agent is hot water at 80°C or higher, an aqueous solution containing ions of one or two or more metal elements selected from the group consisting of Ni, Cr, Zr, Si, Ti, Au, Ag, Co, Mo, Mn, Nb, Ta, W, Zn, Fe, Ir, and Sc, or steam.

[9] The method of manufacturing the surface-treated aluminum material according to [8], wherein, during the sealing, the oxide layer is contacted with hot water as the sealing agent that is 80°C or higher for 10 minutes or more and less than 120 minutes.

[Document Name] SCOPE OF CLAIMS

[Claim 1] A surface-treated aluminum material having: a base material, which is
5 composed of aluminum or an aluminum alloy, and a protective film, which is formed on the
base material, wherein:

the protective film has an oxide layer, which is composed of an oxide or oxides of
aluminum and covers the base material; and

10 a hydrated oxide layer, which contains a hydrated oxide or hydrated oxides of
aluminum and covers the oxide layer; and

in a situation in which a SWAAT test according to a method stipulated in ASTM-G85-
A3 has been performed on the surface-treated aluminum material after it had been heated at a
temperature of 200°C for 1 hour, the number of corrosion sites that have reached the base
material, which occur on the surface of the surface-treated aluminum material when 48 hours
15 have elapsed since the start of the test, is 1.0 sites/cm² or fewer.

[Claim 2] The surface-treated aluminum material according to claim 1, wherein, in a
situation in which a CASS test according to a method stipulated in JIS H 8502:1999 has been
performed on the surface-treated aluminum material after it had been heated at a temperature
20 of 200°C for 1 hour, the number of corrosion sites that have reached the base material, which
occur on the surface of the surface-treated aluminum material when 24 hours have elapsed
since the start of the test, is 2.0 sites/cm² or fewer.

[Claim 3] The surface-treated aluminum material according to claim 1 or 2, wherein the
25 thickness of the protective film is 5 μm or more and 60 μm or less.

[Claim 4] The surface-treated aluminum material according to any one of claims 1 to 3,
wherein, in a situation in which a sealing test according to a method stipulated in JIS H8683-
2:2013 has been performed, the amount of mass loss per unit area is 0.3 g/dm² or less.

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[Claim 5] A method of manufacturing the surface-treated aluminum material according to
any one of claims 1 to 4, comprising:

forming the oxide layer, which has pores, on the base material by performing an
anodizing treatment on the base material;

thereafter, heating the base material and the oxide layer at a temperature of 100°C or higher and 350°C or lower; and

thereafter, contacting the oxide layer with a sealing agent, and forming the hydrated oxide layer on the oxide layer while sealing the pores.

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[Claim 6] The method of manufacturing the surface-treated aluminum material according to claim 5, wherein, during the heating, the heating time from the start of heating the oxide layer to the end of heating is 3 minutes or more.

10 [Claim 7] The method of manufacturing a surface-treated aluminum material according to claim 5 or 6, wherein the electrolyte solution employed in the anodizing treatment contains an inorganic electrolyte composed of an inorganic cation and one or two or more anions selected from the group consisting of a sulfate ion, a phosphate ion, and a borate ion.

15 [Claim 8] The method of manufacturing a surface-treated aluminum material according to any one of claims 5 to 7, wherein the sealing agent is hot water that is at 80°C or higher, an aqueous solution containing ions of one or two or more metal elements selected from the group consisting of Ni, Cr, Zr, Si, Ti, Au, Ag, Co, Mo, Mn, Nb, Ta, W, Zn, Fe, Ir, and Sc, or steam.

20 [Claim 9] The method of manufacturing the surface-treated aluminum material according to claim 8, wherein, during the sealing, the oxide layer is contacted with hot water as the sealing agent that is at 80°C or higher for 10 minutes or more and less than 120 minutes.