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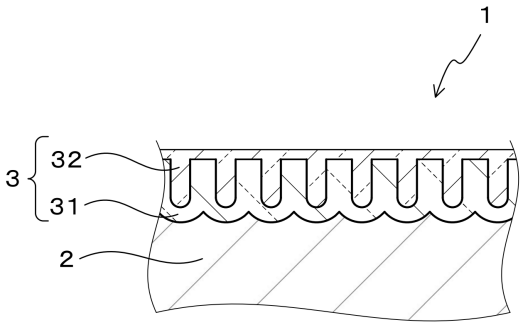
(54) SURFACE-TREATED ALUMINUM MATERIAL, METHOD FOR PRODUCING SAME, METAL HOUSING, AND KITCHEN DEVICE

(57) A surface-treated aluminum material (1) comprises: a 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 covers the oxide layer (31). The hydrated oxide layer (32) contains a hydrated oxide or hydrated oxides of aluminum and an oxide or oxides and/or a hydroxide or hydroxides of a prescribed metal element or metal elements. In the situation in which cathodic polarization measurements have been performed, using a prescribed measurement solution, on the base material (2) and on the surface-treated aluminum material (1) after it had been heated for 4 hours at a temperature of 200°C, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material (1) to the current density J2 of the base material (2) at a prescribed potential is 90×10^{-5} or less.

FIG. 1



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Description

[TECHNICAL FIELD]

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

[BACKGROUND ART]

[0002] Aluminum materials composed of aluminum or an aluminum alloy are utilized in various applications. An anodic oxide film can be provided on the surface(s) of these aluminum materials for purposes such as surface protection. In addition, a sealing treatment is sometimes performed for the purpose of closing up the pores formed in the anodic oxide film and increasing the corrosion resistance of the aluminum material.

[0003] For example, a method of surface-treating aluminum or an aluminum alloy is described in Patent Document 1, characterized by having: a step of forming an anodic oxide film on a surface of aluminum or an aluminum alloy; a first sealing treatment step of immersion in an aqueous solution, which contains nickel fluoride, at 20-35°C; and a second sealing treatment step of immersion in an aqueous solution, which contains nickel acetate, at 80-93°C.

[PRIOR ART LITERATURE]

[Patent Documents]

[0004] [Patent Document 1]
Japanese Laid-open Patent Publication 2021-70847

[SUMMARY OF THE INVENTION]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

[0005] However, with regard to aluminum materials obtained by the manufacturing method of Patent Document 1, cracks are more likely to form in the anodic oxide film when the temperature has risen, and there is a risk that debris composed of small pieces of the anodic oxide film might be formed. To curtail the formation of such debris, there is a demand to further increase the heat resistance of aluminum materials having anodic oxide films on their surfaces.

[0006] The present invention was conceived in view of this background, and it is an object to provide: a surface-treated aluminum material that is capable of curtailing the formation of cracks even when the temperature has risen; a method of manufacturing the same; a metal casing; and a kitchen appliance.

[MEANS FOR SOLVING THE PROBLEMS]

[0007] One aspect of the present invention is a surface-treated aluminum material comprising: 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 is composed of an oxide or oxides of aluminum, and has:

an oxide layer, which covers the base material; and
a hydrated oxide layer, which covers the oxide layer;

the hydrated oxide layer contains:

a hydrated oxide or hydrated oxides of aluminum; and
a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing one or two or more metal elements selected from the group consisting of Ni (nickel), Cr (chromium), Zr (zirconium), Si (silicon), Ti (titanium), Au (gold), Ag (solver), Co (cobalt), Mo (molybdenum), Mn (manganese), Nb (niobium), Ta (tantalum), W (tungsten), Zn (zinc), Fe (iron), Ir (iridium), and Sc (scandium); and

in the situation in which cathode polarization measurements are performed-using a measurement solution obtained by mixing a solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% such that the volumetric ratio of the NaCl solution to the acetic acid = 1000:1-on the base material and on the surface-treated

aluminum material after it had been heated for 4 hours at a temperature of 200°C, and the current density at the electric potential at the center of an electric-potential region of the base material that exhibits the diffusion-limited current of hydrogen ions was measured, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material to the current density J2 of the base material is 90×10^{-5} or less.

[0008] A second 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 is composed of an oxide or oxides of aluminum, and has:

an oxide layer, which covers the base material; and
a hydrated oxide layer, which covers the oxide layer;

the hydrated oxide layer contains:

a hydrated oxide or hydrated oxides of aluminum; and
a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing 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; and

a sample having the protective film on one surface of the base material was prepared from the surface-treated aluminum material and measured in a state in which a strain gauge is mounted on the sample on a rear surface of the surface having the protective film, the difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of the sample at a temperature of 200°C and the amount $\varepsilon 2$ of strain of the base material at a temperature of 200°C is 100×10^{-6} or less.

[0009] A third aspect of the present invention is a metal casing composed of the surface-treated aluminum material according to the above-mentioned aspects.

[0010] A fourth aspect of the present invention is a kitchen appliance comprising the metal casing.

[0011] A fifth aspect of the present invention is a method of manufacturing the surface-treated aluminum material according to the aforementioned aspects, 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 200°C or higher and 400°C or lower; and
thereafter, contacting the oxide layer with a sealing agent that contains the metal element(s), thereby forming the hydrated oxide layer on the oxide layer and sealing the pores.

[EFFECTS OF THE INVENTION]

[0012] A surface-treated aluminum material (referred to as "aluminum material" below) according to the first aspect has a protective film having the oxide layer and the hydrated oxide layer on a surface or surfaces of the base material. In addition, in the situation in which cathodic polarization measurements have been performed according to the above-mentioned specific method on the base material and on the surface-treated aluminum material after it was heated for 4 hours at a temperature of 200°C, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material to the current density J2 of the base material is 90×10^{-5} or less. Aluminum materials having such a characteristic excel in heat resistance, and can curtail the formation of cracks even in situations in which the temperature has risen.

[0013] A surface-treated aluminum material according to the second aspect has a protective film, which comprises the oxide layer and the hydrated oxide layer on a surface of the base material. In addition, the difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of the sample at a temperature of 200°C and the amount $\varepsilon 2$ of strain of the base material at a temperature of 200°C, measured using the above-mentioned specific method, is 100×10^{-6} or less. Aluminum materials having such a characteristic excel in heat resistance, and can curtail the formation of cracks even in situations in which the temperature has risen.

[0014] Because the metal casing according to the third aspect is constituted from the above-mentioned aluminum material, it excels in heat resistance and can curtail the formation of cracks even in situations in which the temperature has risen.

[0015] The metal casing on the kitchen appliance according to the fourth aspect is constituted from the above-mentioned aluminum material. As described above, because the above-mentioned aluminum material excels in heat resistance, it can curtail the formation of cracks in a metal casing on a kitchen appliance, even in situations in which the

temperature has risen.

[0016] In addition, in the method of manufacturing the aluminum material according to the fifth aspect, after an anodizing treatment has been performed on the base material, the oxide layer, which had formed owing to 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 internal stresses in the oxide layer have been relaxed, by contacting the oxide layer with a sealing agent and forming the hydrated oxide layer on the oxide layer while sealing the pores, heat resistance increases, and the formation of cracks can be curtailed even in situations in which the temperature has risen.

[0017] As described above, according to the above-mentioned aspects, a surface-treated aluminum material that excels in heat resistance and is capable of curtailing the formation of cracks even in situations in which the temperature has risen, a method of manufacturing the same, a metal casing, and a kitchen appliance can be provided.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0018]

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

[FIG. 2] FIG. 2 is a cross-sectional view of a base material on which an oxide layer is formed during a process of manufacturing the surface-treated aluminum material of Working Example 1.

[FIG. 3] FIG. 3 is an explanatory graph showing a cathodic polarization curve of the base material of Working Example 1.

[FIG. 4] FIG. 4 is an enlarged view of a step portion in the cathodic polarization curve of the base material.

[FIG. 5] FIG. 5 is an explanatory diagram for describing a method of measuring the amount of strain in the surface-treated aluminum material according to a reference example.

[FIG. 6] FIG. 6 is an explanatory graph showing results of measuring the amount of strain in the surface-treated aluminum material according to the reference example.

[MODES FOR CARRYING OUT THE INVENTION]

(Aluminum Material)

[0019] 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 may be used in accordance with the application of the aluminum material. In addition, the material of the base material can be selected, as appropriate, from the group consisting of aluminum and aluminum alloys in accordance with the application of the aluminum material. More specifically, for example, a 1000-series aluminum can be used as the aluminum constituting 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 constituting the base material.

[0020] A protective film that contains an oxide layer, which is composed of an oxide or oxides of aluminum and has been laminated on the base material, and a hydrated oxide layer, which has been laminated on the oxide layer, is provided on the base material. The hydrated oxide layer contains a hydrated oxide or hydrated oxides of aluminum, and one or more metal compounds selected from the group consisting of a metal oxide or metal oxides and a metal hydroxide or metal hydroxides, which contain(s) the metal element(s). 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 with respect to corrosive gas. For this reason, the corrosion resistance of the aluminum material can be increased by forming the protective film on the base material.

[0021] The thickness of the protective film preferably is 2 μm or more. Thereby, the corrosion resistance of the aluminum material can be further increased. From the viewpoint of corrosion resistance, the upper limit of the thickness of the protective film is not particularly limited; the thicker the protective film is made, the more the corrosion resistance of the aluminum material can be increased. From this viewpoint, the thickness of the protective film is more preferably 5 μm or more and yet more preferably 10 μm or more. It is noted that, from the viewpoint of manufacturing, the upper limit of the thickness of the protective film is, for example, 200 μm. From the viewpoint of reducing manufacturing time, the thickness of the protective film preferably is 100 μm or less.

[0022] A ratio A_M/A_H of the integrated value A_M of light-emission intensities of the metal element(s) to the integrated value A_H of the light-emission intensities of hydrogen measured in a range from the surface of the aluminum material to a depth of 500 nm by glow-discharge optical emission spectroscopy (referred to below as "GDOES") is preferably 0.1 or

more and 5.0 or less. The light-emission intensities of elements measured by GDOES indicate the content of said element(s), and a higher light-emission intensity signifies that a larger amount of said element(s) is included. In addition, a majority of the hydrated oxide layer is constituted by a hydroxide or hydroxides of aluminum. Accordingly, the value of the ratio A_M/A_H indicates the content of the metal element(s), which has been normalized in accordance with the amount of the hydroxide(s) of aluminum. Furthermore, by making the value of the ratio A_M/A_H for the aluminum material to be within the above-mentioned specific range, the effect of improving the corrosion resistance can be more reliably obtained.

[0023] The value of the ratio A_M/A_H can be calculated by the following method. First, using a depth-direction profile of the light-emission intensities acquired by GDOES for hydrogen in the aluminum material, the light-emission intensities of hydrogen at each measurement point present within a range from the surface of the aluminum material to a depth of 500 nm are added together, and this value is taken as the integrated value A_H of the light-emission intensities of hydrogen. Similarly, using a depth-direction profile of the light-emission intensities of the metal element(s) in the aluminum material, the light-emission intensity of the metal element(s) at each of the measurement points present within the range from the surface to the depth of 500 nm are added together, and this value is taken as the integrated value A_M of the light-emission intensities of the metal element(s). By dividing the integrated value A_M of the light-emission intensities of the metal element(s) by the integrated value A_H of the light-emission intensities of the hydrogen obtained in this manner, the value of the ratio A_M/A_H can be obtained.

[0024] In a situation in which a sealing test has been performed according to the method stipulated in JIS H8683-2:2013, the mass loss per unit of area of the aluminum material is preferably 0.3 g/dm^2 or less. In such an aluminum material, the pores in the oxide layer are sufficiently sealed by the hydrated oxide layer. Consequently, by making the mass loss per unit of area of the aluminum material to be within the above-mentioned specific range, the corrosion resistance of the aluminum material can be more reliably increased.

[0025] It is noted that a specific method of 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 a 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 min $\pm$5 s in the test solution, which is held at a temperature of 38°C $\pm$1°C.

[0026] 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.

[0027] The surface area S (unit: dm^2) of the protective film of the test piece obtained as described above, the mass m_1 (unit: g) of the test piece before immersion in the test solution, and the mass m_2 (unit: g) of the test piece after immersion in the test solution can be used to calculate the mass loss δ_S per unit of area (unit: g/dm^2) based on Equation (1) below.

$$\delta_S = (m_1 - m_2)/S \qquad (1)$$

[0028] Surface-treated aluminum materials according to the first aspect have the characteristic that, in the situation in which cathodic polarization measurements are performed-using a measurement solution obtained by mixing a solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% such that the volumetric ratio of NaCl solution:acetic acid = 1000:1-on the base material and on the surface-treated aluminum material after it had been heated at a temperature of 200°C for 4 hours, and the current density at the electric potential at the center of an electric-potential region of the base material that exhibits the diffusion-limited current of hydrogen ions was measured, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material to the current density J2 of the base material is 90 $\times$ 10^{-5} or less. Aluminum materials having a ratio J1/J2 of the current density J1 within the above-mentioned specific range have the characteristic that cracks form less readily when the temperature has risen and they excel in heat resistance.

[0029] From the same viewpoint of further improving the heat resistance of aluminum materials, the current-density ratio J1/J2 is preferably 70 $\times$ 10^{-5} or less, more preferably 50 $\times$ 10^{-5} or less, and yet more preferably 30$\times$ 10^{-5} or less. From the viewpoint of increasing the heat resistance of the aluminum material, there is no lower limit for the current-density ratio J1/J2; thus, given that definition, the current-density ratio J1/J2 is definitely a value greater than 0.

[0030] In addition, surface-treated aluminum materials according to the second aspect have the characteristic that the difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of a sample, which has the protective film on one surface of the base material and was prepared from the surface-treated aluminum material and measured in a state in which a strain gauge is mounted on the sample on a rear surface of the protective film-at a temperature of 200°C and the amount $\varepsilon 2$ of strain of the base material at a temperature of 200°C is 100 $\times$ 10^{-6} or less. Aluminum materials, in which the difference $\varepsilon 1 - \varepsilon 2$ of the amounts of strain is within the above-mentioned specific range, have the characteristic that cracks form less readily when the temperature has risen and they excel in heat resistance. It is noted that the lower limit of the difference $\varepsilon 1 - \varepsilon 2$ in the amounts of strain of the sample, which was prepared from the aluminum material, usually becomes -100 $\times$ 10^{-6} or more.

[0031] The method of preparing the sample from the surface-treated aluminum material is not particularly limited, and

various methods can be employed as long as the method chosen does not affect the amount of strain in the sample. In the situation in which the surface-treated aluminum material is, for example, a sheet having the protective film on only one surface of the base material, a small piece of the surface-treated aluminum material that is cut to an appropriate size can be used as the sample. In addition, in the situation in which the surface-treated aluminum material is, for example, a sheet having the protective film on both surfaces of the base material, the sample can be obtained by cutting the surface-treated aluminum material to an appropriate size to prepare a small piece and then removing one of the two protective films from the small piece. A method of, for example, dissolving the protective film using an acid or an alkali, or the like can be employed as a method of removing the protective film.

[0032] As described above, the aluminum materials can curtail the formation of cracks in the protective film even in the situation in which the temperature has risen. For this reason, the aluminum materials are suitable for applications such as a casing for an appliance that becomes a high temperature while in use, such as a kitchen appliance, or the like. More specifically, the aluminum materials are suited for use, for example, as a metal casing, such as for a kitchen appliance. For example, heating and cooking equipment, such as an oven, a microwave oven, a gas range, or a fryer, and a hot food showcase can be given as examples of kitchen appliances.

(Method of Manufacturing the Aluminum Material)

[0033] 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. 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 an 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 employed 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/cm^2 or more and 100 mA/cm^2 or less, as appropriate. In addition, the temperature of the electrolyte solution in the anodizing treatment can be set, for example, in a 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 method of manufacturing, after the anodizing treatment has been performed, the base material and the oxide layer are heated at a temperature of 200°C or higher and 400°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 heat resistance of the aluminum material can be improved.

[0038] In the situation in which the heating temperature of the oxide layer is too low, 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 layer more readily when the temperature of the aluminum material has risen. From the viewpoint of easily avoiding such a problem, the heating temperature of the oxide layer is set to 200°C or more. On the other hand, in the situation in which the heating temperature of the oxide layer is too high, 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 easily avoiding such a problem, the heating temperature of the oxide layer is set to 400°C or less.

[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 heat resistance of the aluminum material, the heating time from when heating

of the oxide layer is started to when heating is ended is preferably 1 min or more and less than 12 hours.

[0040] 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 in the oxide layer are sealed by the hydrated oxide layer. For example, an aqueous solution containing 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 can be used as the sealing agent. When an aqueous solution containing the above-mentioned metal element(s) is used as the sealing agent and is contacted with the oxide layer, the hydration reaction of the oxide or oxides of aluminum and the precipitation reaction of the metal element(s) progress in parallel. As a result, a hydrated oxide layer containing a hydrated oxide or hydrated oxides of aluminum, and an oxide or oxides and/or a hydrated oxide or hydrated oxides of the above-mentioned metal element(s) can be formed on the oxide layer.

[0041] The sealing agent is preferably an aqueous solution that contains ions of the metal element(s). By using such a sealing agent, the hydrated oxide layer can be more reliably formed. The metal element(s) in the sealing agent may be present as metal ions or may be present as complex ions. For example, an aqueous solution of a metal salt or metal salts that contains the above-mentioned metal element(s), such as aqueous nickel acetate, aqueous cobalt acetate, aqueous chromate, and aqueous silicate, can be used as the sealing agent.

[Working Examples]

(Working Example 1)

[0042] Working examples of a surface-treated aluminum material and a method of manufacturing the same will be described with reference to FIG. 1 to FIG. 2. As shown in FIG. 1, the surface-treated aluminum material 1 of the present example comprises: a 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 covers the oxide layer 31. The hydrated oxide layer 32 contains a hydrated oxide or hydrated oxides of aluminum, and a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing 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. In the situation in which cathodic polarization measurements are performed-using a measurement solution obtained by mixing a solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% such that the volumetric ratio of the NaCl solution:acetic acid = 1000:1-on the base material 2 and on the surface-treated aluminum material 1 after it had been heated for 4 hours at a temperature of 200°C, and the current density at the electric potential at the center of an electric-potential region of the base material 2 that exhibits the diffusion-limited current of hydrogen ions was measured, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material 1 to the current density J2 of the base material 2 is 90×10^{-5} or less.

[0043] 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 200°C or higher and 400°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.

[0044] Specific examples of the aluminum material 1 (Test Materials A1-A12) are shown in Table 1. The method of manufacturing Test Materials A1-A12 is, for example, as follows. First, aluminum sheets having the chemical compositions indicated by each of the alloy numbers listed in Table 1 and having a thickness of 1.1 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%.

[0045] 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/cm^2, and the treatment time is 60 min. 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 19 μm.

[0046] After having performed the anodizing treatment, the base material 2 is heated inside a heating furnace and the internal stresses in the oxide layer 31 are relaxed. The set temperature of the heating furnace is the value shown in the "Heating Temperature" column in Table 1, 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.

[0047] Thereafter, by immersing the base material 2, which has the oxide layer 31, in the sealing agent for 60 min, 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. The sealing agent used in the present example is, specifically, either of an aqueous solution, in which "Top Seal (registered trademark) H-298" manufactured by Okuno Chemical Industries Co., Ltd. has been diluted with water to a concentration of 40 mL/L, or an aqueous solution, in which "Top Seal L-100" manufactured by Okuno Chemical Industries Co., Ltd. has been dissolved in water at a concentration of 5 g/L. It is noted that "Top Seal H-298" is an aqueous solution in which nickel acetate serves as the main component. In addition, "Top Seal L-100" is a solid in which nickel fluoride serves as the main component. In Table 1, "Top Seal H-298" is recorded as "H-298" and "Top Seal L-100" is recorded as "L-100."

[0048] Test Materials A1-A12 shown in Table 1 could thereby be obtained based on the above. It is noted that Test Materials B1-B7 shown in Table 1 are test materials for comparison with Test Materials A1-A12. The method of manufacturing Test Materials B1-B2, B5-B7 was 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 was brought into contact with a sealing agent without being heated. In addition, the method of manufacturing Test Materials B3-B4 is the same as the method of manufacturing Test Material A1 except that the heating conditions in the heating furnace were modified as shown in Table 1.

[0049] Next, the method of measuring the cathodic polarization of Test Materials A1-A12 and Test Materials B1-B7 will be explained.

(Cathodic Polarization Measurement)

[0050] Using the following method, cathodic polarization measurements are performed on the base material and on the test material that had been heated for 4 hours at a temperature of 200°C; based on the resulting cathodic polarization curves, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material to the current density J2 of the base material is calculated. First, the test material is heated for 4 hours in an oven set to a temperature of 200°C. After removing the test material from the oven and cooling to room temperature, an evaluation region is established on the protective film, and portions other than the evaluation region on the surface of the test material are covered with silicone resin.

[0051] Next, an aqueous solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% are prepared, and a measurement solution is prepared by adding the acetic acid to the aqueous solution of NaCl such that the volumetric ratio of aqueous solution of NaCl to the acetic acid is an aqueous solution of NaCl:acetic acid = 1000:1. A test piece, a counter electrode, and a reference electrode, which are electrically connected to a potentiostat, are immersed in this measurement solution and left standing for 30 min to stabilize the electric potential of the measurement area. It is noted that degassing of the measurement solution is not performed. In addition, for example, an Ag/AgCl electrode can be used as the reference electrode.

[0052] After the electric potential of the measurement area had stabilized, a voltage is applied between the test piece and the counter electrode using the potentiostat, and the electric potentials of the measurement area are swept at a sweep rate of 20 mV/min until the electric potentials of the measurement area reached -2,000 mV relative to the reference electrode. A cathodic polarization curve for the post-heated test material is obtained by measuring the current density flowing in the measurement area at this time. In addition, a cathodic polarization curve for the base material is obtained by performing a similar measurement using the base material after the pretreatment of the anodizing treatment had been performed using the method described above. It is noted that the cathodic polarization measurements of both the test materials and the base materials are performed in the state in which the temperature of the measurement solution was maintained at 25°C in ambient atmosphere. In addition, the cathodic polarization measurements of the test materials and the base materials are performed in the state in which the measurement solution was not agitated and the measurement solution was substantially not flowing.

[0053] One example of the cathodic polarization curve of the base material is shown in FIG. 3. It is noted that, in FIG. 3, the ordinate is the electric potential of the measurement area (unit: V), and the abscissa is the current density (unit: $\mu A/cm^2$). In addition, the scale of the abscissa in FIG. 3 is a logarithmic scale. As shown in FIG. 3, the cathodic polarization curve of the base material has a step shape. During the cathodic polarization measurements, the change in the electric current becomes smaller relative to the change in the electric potential of the measurement areas as the electric current approaches the state in which it becomes rate limited owing to the diffusion of hydrogen ions. Accordingly, as shown in FIG. 3, in the cathodic polarization curve in which the electric potential is represented by the ordinate and the current density is represented by the abscissa, the electric-potential region that exhibits the diffusion-limited current of the hydrogen ions contains a portion in which the slope of the curve is steep at a step portion of the cathodic polarization curve.

[0054] An enlarged view of the step portion in the cathodic polarization curve in FIG. 3 is shown in FIG. 4. The following is the method of determining the electric-potential region that exhibited the diffusion-limited current of the hydrogen ions in the cathodic polarization curve of the base material. First, a tangent L is drawn at the step portion of the cathodic polarization curve at which the absolute value of the slope is the largest as shown in FIG. 4. Then, region R where this

tangent L and the cathodic polarization curve overlap is taken as the electric-potential region that represents the diffusion-limited current of the hydrogen ions. Current density J2 is calculated at the electric potential at the center of region R determined in this manner. In addition, in the cathodic polarization curve of the post-heated test material, current density J1 is calculated at the electric potential the same as the electric potential at the center of the electric-potential region in the cathodic polarization curve of the base material as described above.

[0055] Current density J1 calculated based on the cathodic polarization curve of the post-heated test material can be used as an indicator of the contact-surface area between the base material of the post-heated test material and the measurement solution; the higher the current density value, the greater the contact-surface area between the base material and the measurement solution. Accordingly, the ratio J1/J2 of the current density J1, calculated using the post-heated test piece, to the current density J2, calculated using the base material, can be used as an indicator of the percentage of increase in the surface area of the base material that was exposed by heating. More specifically, in the situation in which, for example, defects, such as cracks, are formed in the protective film of the post-heated test material, then the base material is sometimes exposed by the cracks. Accordingly, the current-density ratio J1/J2 becomes large in this situation. In Table 1, the current-density ratio J1/J2 for each test material is shown.

[Table 1]

[0056]

(Table 1)

	Base Material	Sealing Agent	Heating of Oxide Layer		Current-Density Ratio J1/J2
			Heating Temperature (°C)	Heating Time (Minutes)	
Test Material A1	AA6016	H-298	250	30	1×10^{-5}
Test Material A2	AA6016	H-298	250	3	3×10^{-5}
Test Material A3	AA6016	H-298	250	5	5×10^{-5}
Test Material A4	AA6016	H-298	250	10	6×10^{-5}
Test Material A5	AA6016	H-298	250	120	6×10^{-5}
Test Material A6	AA6016	H-298	300	10	2×10^{-5}
Test Material A7	AA6016	H-298	350	10	9×10^{-5}
Test Material A8	AA6016	H-298	400	10	12×10^{-5}
Test Material A9	AA6016	L-100	250	30	20×10^{-5}
Test Material A10	AA1050	H-298	250	30	4×10^{-5}
Test Material A11	AA3003	H-298	250	30	2×10^{-5}
Test Material A12	AA5052	H-298	250	30	3×10^{-5}
Test Material B1	AA6016	H-298	No heating		308×10^{-5}
Test Material B2	AA6016	L-100	No heating		734×10^{-5}
Test Material B3	AA6016	H-298	150	10	333×10^{-5}
Test Material B4	AA6016	H-298	500	10	322×10^{-5}
Test Material B5	AA1050	H-298	No heating		120×10^{-5}
Test Material B6	AA3003	H-298	No heating		91×10^{-5}
Test Material B7	AA5052	H-298	No heating		396×10^{-5}

[0057] As shown in Table 1, when Test Materials A1-A12 are being manufactured, after the oxide layer had formed 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. Consequently, the current-density ratio J1/J2 of each of these test materials is in the above-mentioned specific range, and the formation of cracks in the protective film could be curtailed even in the situation in which the temperature had risen. In addition, these test materials excelled in corrosion resistance because the oxide layer of the protective film was sealed by the hydrated oxide layer.

[0058] In contrast, when Test Materials B1-B2, B5-B7 are being manufactured, after the oxide layer had formed on the base material, the pores are sealed without heating the oxide layer. Consequently, the current-density ratio J1/J2 of each of these test materials is higher than the above-mentioned specific range, and therefore cracks tend to form in the situation in which the temperature has risen.

[0059] When Test Material B3 was being manufactured, the heating temperature when the oxide layer was heated was too low. Consequently, the current-density ratio J1/J2 of Test Material B3 is higher than the above-mentioned specific range, and cracks tend to form in the situation in which the temperature has risen.

[0060] When Test Material B4 was being manufactured, the heating temperature when the oxide layer was heated was too high. Consequently, the current-density ratio J1/J2 of Test Material B4 is higher than the above-mentioned specific range, and cracks tend to form in the situation in which the temperature has risen.

[0061] The mass loss per unit of area obtained by the sealing test stipulated in JIS H8683-2:2013 and the values of the ratio A_{Ni}/A_H of the integrated value A_{Ni} of the light-emission intensities of Ni to the integrated value A_H of the light-emission intensities of hydrogen obtained by glow-discharge optical emission spectroscopy for Test Material A1 and Test Material A10, from among Test Materials A1-A12 of the present example, are shown in Table 2. The specific method of the sealing test is as described above.

[0062] The measurement apparatus used for the glow-discharge optical emission spectroscopy is the "GDA750" manufactured by SPECTRUMA GmbH. Argon gas is used in the sputtering during GDOES, and, with regard to the sputtering conditions, the anode diameter is set to 2.5 mm, the output is set to 25 W, and the gas pressure is set to 350 Pa. The sputtering speed of the test materials during such conditions is approximately 40 nm/s. In addition, during GDOES, the depth-direction profile of the light-emission intensities of each of the elements is created by acquiring the light-emission intensities of hydrogen and Ni at 0.005-second intervals during the sputtering.

[0063] Then, using the depth-direction profile of the light-emission intensities for hydrogen, the light-emission intensities of hydrogen at each measurement point present within the range from the surface to the depth of 500 nm are added together, and this value is taken as the integrated value A_H of the light-emission intensities of hydrogen. Similarly, using a depth-direction profile of the light-emission intensities of nickel, the light-emission intensities of nickel at each of the measurement points present within the range from the surface to the depth of 500 nm are added together, and this value is taken as the integrated value A_{Ni} of the light-emission intensities of nickel. By dividing the integrated value A_{Ni} of the light-emission intensities of the above-mentioned metal elements by the integrated value A_H of the light-emission intensities of the hydrogen obtained in this manner, the value of the ratio A_{Ni}/A_H can be obtained.

[0064] It is noted that Test Materials C1-C2 in Table 2 are test materials for comparison with Test Material A1 and Test Material A10. The method of manufacturing Test Material C1 is the same as the method of manufacturing Test Material A1 except for the point that no sealing agent is used. The method of manufacturing Test Material C2 is the same as the method of manufacturing Test Material A1 except for the point that boiling water is used as the sealing agent.

[Table 2]

[0065]

(Table 2)

	Base Material	Sealing Agent	Heating of Oxide Layer		Integrated Value of Light-Emission Intensities			Sealing Test
			Heating Temperature (°C)	Heating Time (Minutes)	A_{Ni}	A_H	A_{Ni}/A_H	Mass-Loss Amount (g/dm^2)
Test Material A1	AA6016	H-298	250	30	420	870	0.5	0.0031
Test Material A10	AA6016	L-100	250	30	660	597	1.1	0.0124
Test Material C1	AA6016	None	250	30	-	-	-	0.3819
Test Material C2	AA6016	Boiling water	250	30	0	1505	0.0	-

[0066] As shown in Table 2, in the situation in which the sealing test was performed, the mass loss per unit of area of Test Material A1 and Test Material A10 is 0.3 g/dm^2 or less. In contrast, the mass loss per unit of area of Test Material C1, for

which no sealing treatment is performed, is greater than 0.3 g/dm^2. Accordingly, it can be understood from comparing Test Material A1 and Test Material A10 with Test Material C1 that the pores in the oxide layer of Test Material A1 and Test Material A10 are sufficiently closed up. In addition, because the sealing treatment is performed for Test Materials A2-A9, A11-A12 under the same conditions as those of Test Material A1 and Test Material A10, it can be presumed that the pores in the oxide layer of these test materials as well are also sufficiently closed up.

[0067] In addition, the values of ratio A_{Ni}/A_H in Test Material A1 and Test Material A10 are within the range of 0.1 or more and 5.0 or less. In contrast, the value of ratio A_{Ni}/A_H for Test Material C2, which uses a sealing agent that does not contain nickel, is 0. Accordingly, it can be understood from comparing Test Material A1 and Test Material A10 with Test Material C2 that the protective film, which includes the above-mentioned metal element, can be formed by contacting the oxide layer with the sealing agent, which includes the above-mentioned metal element.

(Working Example 2)

[0068] In the present example, an example is explained in which heat resistance was evaluated for the situation in which heating was performed at temperatures higher than those in Working Example 1. In the present example, Test Materials A1-A2 and Test Materials B1-B2 are prepared by the same method as that in Working Example 1, and these test materials are heated for 4 hours in an oven set to a temperature of 250°C. Thereafter, the cathodic polarization measurements are performed using the same method as that in Working Example 1, and the current-density ratios J1/J2 are computed. In Table 3, current-density ratios J1/J2 of Test Materials A1-A2 and Test Materials B1-B2 are shown.

[Table 3]

[0069]

(Table 3)

	Base Material	Sealing Agent	Heating of Oxide Layer		Current-Density Ratio J1/J2
			Heating Temperature (°C)	Heating Time (Minutes)	
Test Material A1	AA6016	H-298	250	30	53×10^{-5}
Test Material A2	AA6016	H-298	250	3	79×10^{-5}
Test Material B1	AA6016	H-298	No heating		280×10^{-5}
Test Material B2	AA6016	L-100	No heating		1162×10^{-5}

[0070] As shown in Table 3, current-density ratios J1/J2 of Test Materials A1-A2, in which the sealing treatment is performed after the oxide layer has been heated, become lower than current-density ratios J1/J2 of Test Materials B1-B2, in which heating of the oxide layer is not performed, even in the situation in which heating is performed at a temperature of 250°C. Accordingly, from these results as well, it can be understood that the heat resistance of the above-mentioned aluminum material can be increased by performing the sealing treatment after heating of the oxide layer has been performed.

(Reference Example)

[0071] In the present example, measurements of the amounts of strain in aluminum materials having the protective film on the base material will be explained. It is noted that, among the symbols used in the present example, unless particularly explained, the symbols that are the same as the symbols used in previously discussed examples indicate structural elements, etc. the same as structural elements, etc. in the previously discussed examples.

[0072] The method of manufacturing the test materials in the present example is as follows. First, an aluminum sheet having the chemical composition indicated by the alloy number AA6016 and having a thickness of 1.1 mm is prepared as the base material 2. Pretreatments of the anodizing treatment are performed on this base material 2 using methods similar to those in the working example, and next the anodizing treatment is performed. After having performed the anodizing treatment, the base material 2 is heated inside a heating furnace and the internal stresses in the oxide layer 31 are relaxed. The set temperature of the heating furnace is the value shown in the "Heating Temperature" column in Table 4, 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 4.

[0073] Thereafter, by immersing the base material 2, which has the oxide layer 31, in boiling water as the sealing agent

for 60 min, the hydrated oxide layer 32 forms on the oxide layer 31, and the pores 311 in the oxide layer 31 are sealed by the hydrated oxide layer 32. Based on the above, Test Material D1 shown in Table 1 could be obtained.

[0074] It is noted that Test Material E1 shown in Table 4 is a test material for comparison with Test Material D1, The method of manufacturing Test Material E1 is the same as the method of manufacturing Test Materials D1 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. In addition, the base materials shown in Table 4 are obtained by performing pretreatments of the anodizing treatment, using the methods described above, on a sheet material composed of an aluminum alloy having the chemical composition indicated by the alloy number AA6016.

[0075] To measure the amount of strain in the aluminum materials 1 that comprise Test Material D1 and Test Material E1, the base material 2 of the aluminum material 1 is exposed on the rear surface of the surface having the protective film 3, as shown in FIG. 5. Then, a strain gauge 4 is mounted on the exposed base material 2. The strain during heating of the base material 2 and the protective film 3 can be measured by heating the aluminum material 1 on which the strain gauge 4 was mounted in the aforementioned manner. It is noted that the structure of the protective film 3 is simplified in FIG. 5 for the sake of convenience of explanation.

[0076] Although not shown in the drawing, to measure the amount of strain in the base material 2, after the strain gauge has been mounted on one of the surfaces in the thickness direction of the base material 2, the base material 2 should be heated.

[0077] In FIG. 6, changes in the amounts of strain are shown in the situation in which Test Material D1, Test Material E1, and the base material were heated for 30 min using the heating furnace, which was set to a temperature of 200°C. In FIG. 6, the ordinate is the amount of strain and the abscissa is the time elapsed since the start of heating. Because the test materials immediately after the start of heating underwent thermal expansion commensurate with the temperature rise, as shown in FIG. 6, the respective amounts of strain increased sharply from the point in time when the test started up until several minutes elapsed thereafter. Thereafter, when the temperatures of the test material and the base material reached a roughly constant temperature, the respective amounts of strain of the test material and the base material became roughly constant values.

[0078] In Table 4, the maximum value of the amounts of strain while the test materials and the base material were being heated is shown. In addition, value $\varepsilon 1 - \varepsilon 2$ resulting from subtracting the maximum value $\varepsilon 2$ of the amount of strain of the base material from the maximum value $\varepsilon 1$ of the amount of strain of the corresponding test material is shown in Table 4. The difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of the corresponding test material and the amount $\varepsilon 2$ of strain of the base material indicates the magnitude of the internal stresses in the protective film released by the heating during the test; this means that the smaller the difference $\varepsilon 1 - \varepsilon 2$ of the amounts of strain, the smaller the internal stresses in the protective film.

[Table 4]

[0079]

(Table 4)

	Base Material	Sealing Agent	Protective Film	Heating of Oxide Layer		Maximum Value of Strain Amount	Difference Between Strain Amounts $\varepsilon 1-\varepsilon 2$
				Heating Temperature (°C)	Heating Time (Minutes)		
Test Material D1	A6016	Boiling water	Present	250	60	2298×10^{-6}	-11×10^{-6}
Test Material E1	A6016	Boiling water	Present	No heating		2461×10^{-6}	152×10^{-6}
Base Material	A6016	None	Not present	No heating		2309×10^{-6}	-

[0080] As shown in Table 4, the amount of strain of Test Material D1, on which the hydrated oxide layer is formed after the oxide layer is heated during the process of manufacturing the test material, is smaller than the amount of strain of Test Material E1, on which the hydrated oxide layer is formed without heating the oxide layer. It is conceivable that this is because the internal stresses of the oxide layer were relaxed by the heating of the oxide layer. In addition, it is conceivable that the internal stresses of the protective film are substantially unchanged during the sealing treatment performed after the heating of the oxide layer. Accordingly, from these results, it is presumed that, even for Test Materials A1-A12 of Working Example 1, the difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of each of the test materials and the amount $\varepsilon 2$ of strain of

the base material will become within the above-mentioned specific range, and the internal stresses of the protective film will be relaxed.

[0081] 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; 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.

[0082] For example, the surface-treated aluminum material according to the present invention can obtain the aspects according to [1]-[4] below.

[1] A surface-treated aluminum material comprising: 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 is composed of an oxide or oxides of aluminum, and has:

an oxide layer, which covers the base material; and
a hydrated oxide layer, which covers the oxide layer;

the hydrated oxide layer contains:

a hydrated oxide or hydrated oxides of aluminum; and
a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing 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; and

in the situation in which cathode polarization measurements are performed-using a measurement solution obtained by mixing a solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% such that the volumetric ratio of the NaCl solution to the acetic acid = 1000:1-on the base material and on the surface-treated aluminum material after it had been heated for 4 hours at a temperature of 200°C, and the current density at the electric potential at the center of an electric-potential region of the base material that exhibits the diffusion-limited current of hydrogen ions was measured, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material to the current density J2 of the base material is 90×10^{-5} or less.

[2] A surface-treated aluminum material comprising: 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 is composed of an oxide or oxides of aluminum, and has:

an oxide layer, which covers the base material; and
a hydrated oxide layer, which covers the oxide layer;

the hydrated oxide layer contains:

a hydrated oxide or hydrated oxides of aluminum; and
a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing 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; and

a sample having the protective film on one surface of the base material was prepared from the surface-treated aluminum material and measured in a state in which a strain gauge is mounted on the sample on a rear surface having the protective film, the difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of the sample at a temperature of 200°C and the amount $\varepsilon 2$ of strain of the base material at a temperature of 200°C is 100×10^{-6} or less.

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

[4] The surface-treated aluminum material according to any one of [1] to [3], wherein a ratio A_M/A_H of the integrated value A_M of light-emission intensities of the metal element(s) to the integrated value A_H of the light-emission intensities

of hydrogen measured in a range from a surface of the aluminum material to a depth of 500 nm by glow-discharge optical emission spectroscopy is 0.1 or more and 5.0 or less.

A metal casing according to the present invention may take the form according to [5] below.

[5] A metal casing composed of the surface-treated aluminum material according to any one of [1] to [4].

A kitchen appliance according to the present invention may take the form according to [6] below.

[6] A kitchen appliance comprising the metal casing according to [5].

A method of manufacturing the surface-treated aluminum material according to the present invention can obtain the aspects according to [7]-[10] below.

[7] A method of manufacturing the surface-treated aluminum material according to any one of [1]-[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 200°C or higher and 400°C or lower; and
thereafter, contacting the oxide layer with a sealing agent that contains the metal element(s), thereby forming the hydrated oxide layer on the oxide layer and sealing the pores.

[8] The method of manufacturing the surface-treated aluminum material according to [7], wherein, during the heating, the heating time from the start of heating the oxide layer to the end of heating is 1 min or more and less than 12 hours.

[9] The method of manufacturing the surface-treated aluminum material according to [7] or [8], 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.

[10] The method of manufacturing the surface-treated aluminum material according to any one of [7] to [9], wherein the sealing agent is an aqueous solution that contains ions of the metal element(s).

Claims

1. A surface-treated aluminum material comprising: 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 is composed of an oxide or oxides of aluminum, and has:

an oxide layer, which covers the base material; and
a hydrated oxide layer, which covers the oxide layer;

the hydrated oxide layer contains:

a hydrated oxide or hydrated oxides of aluminum; and
a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing 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; and

in the situation in which cathodic polarization measurements are performed-using a measurement solution obtained by mixing a solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% such that the volumetric ratio of the NaCl solution:acetic acid = 1000:1-on the base material and on the surface-treated aluminum material after it had been heated for 4 hours at a temperature of 200°C, and the current density at the electric potential at the center of an electric-potential region of the base material that exhibits the diffusion-limited current of hydrogen ions was measured, the ratio J1/J2 of the current density J1 of the surface-treated aluminum material to the current density J2 of the base material is 90×10^{-5} or less.

2. A surface-treated aluminum material comprising: 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 is composed of an oxide or oxides of aluminum, and has:

an oxide layer, which covers the base material; and
a hydrated oxide layer, which covers the oxide layer;

the hydrated oxide layer contains:

a hydrated oxide or hydrated oxides of aluminum; and
a metal oxide or metal oxides and/or a metal hydroxide or metal hydroxides containing 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; and

a sample having the protective film on one surface of the base material was prepared from the surface-treated aluminum material and measured in a state in which a strain gauge has been mounted on the sample on a rear surface of the protective film, the difference $\varepsilon 1 - \varepsilon 2$ between the amount $\varepsilon 1$ of strain of the sample at a temperature of 200°C and the amount $\varepsilon 2$ of strain of the base material at a temperature of 200°C is 100×10^{-6} or less.

3. The surface-treated aluminum material according to claim 1 or 2, wherein a mass loss per unit of area is 0.3 g/dm^2 or less in the situation in which a sealing test has been performed using a method stipulated in JIS H8683-2:2013.

4. The surface-treated aluminum material according to any one of claims 1-3, wherein a ratio A_M/A_H of the integrated value A_M of light-emission intensities of the metal element(s) to the integrated value A_H of the light-emission intensities of hydrogen measured in a range from a surface of the aluminum material to a depth of 500 nm by glow-discharge optical emission spectroscopy is 0.1 or more and 5.0 or less.

5. A metal casing composed of the surface-treated aluminum material according to any one of claims 1-4.

6. A kitchen appliance comprising the metal casing according to claim 5.

7. A method of manufacturing the surface-treated aluminum material according to any one of claims 1-4, 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 200°C or higher and 400°C or lower; and
thereafter, contacting the oxide layer with a sealing agent that contains the metal element(s), thereby forming the hydrated oxide layer on the oxide layer and sealing the pores.

8. The method of manufacturing the surface-treated aluminum material according to claim 7, wherein, during the heating, the heating time from the start of heating the oxide layer up until the end of the heating is 3 minutes or more and less than 12 hours.

9. The method of manufacturing the surface-treated aluminum material according to claim 7 or 8, 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.

10. The method of manufacturing the surface-treated aluminum material according to any one of claims 7-9, wherein the sealing agent is an aqueous solution that contains ions of the metal element(s).

FIG. 1

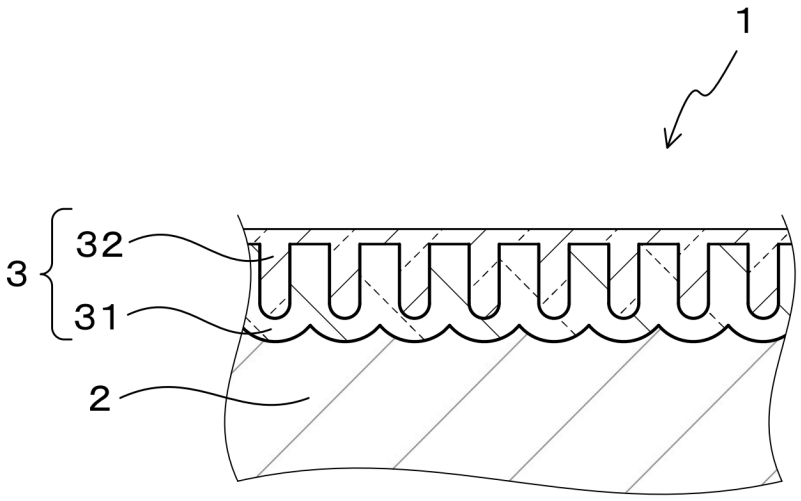


FIG. 2

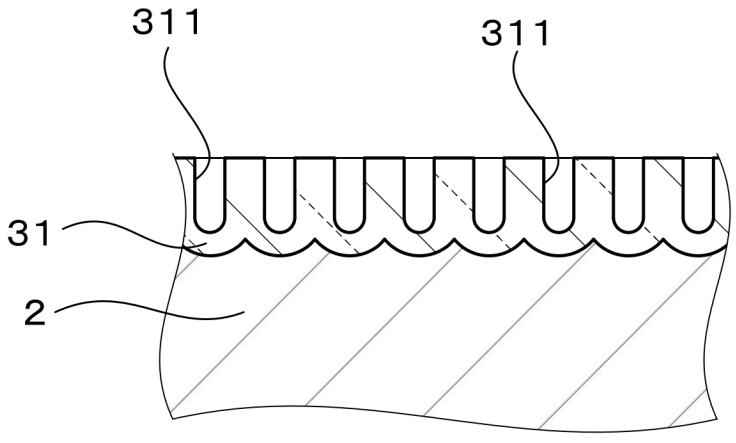


FIG. 3

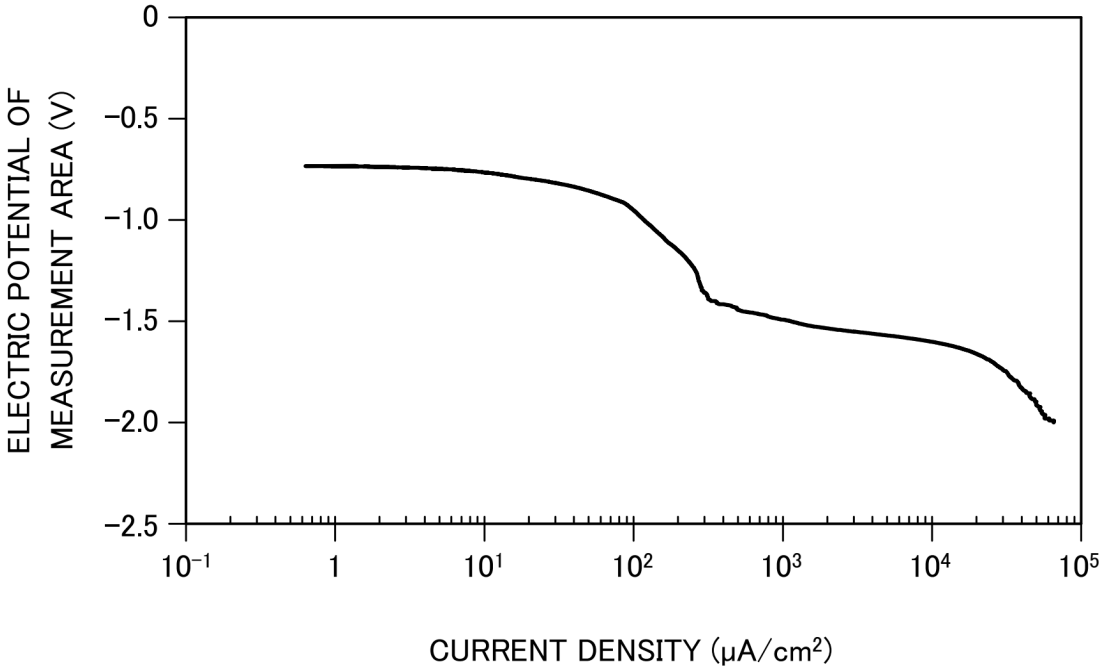

0
−0.5
−1.0
−1.5
−2.0
−2.5
ELECTRIC POTENTIAL OF MEASUREMENT AREA (V)
10−1
1
101
102
103
104
105
CURRENT DENSITY (μA/cm2)

FIG. 4

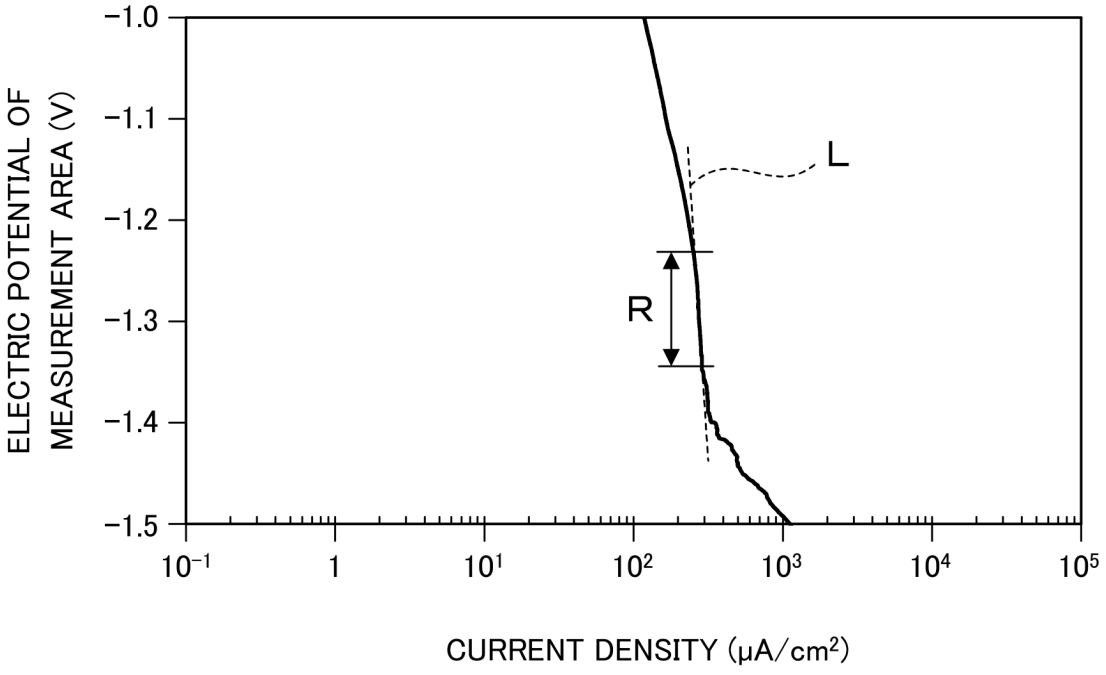

−1.0
−1.1
−1.2
−1.3
−1.4
−1.5
ELECTRIC POTENTIAL OF MEASUREMENT AREA (V)
L
R
10−1
1
101
102
103
104
105
CURRENT DENSITY (μA/cm2)

FIG. 5

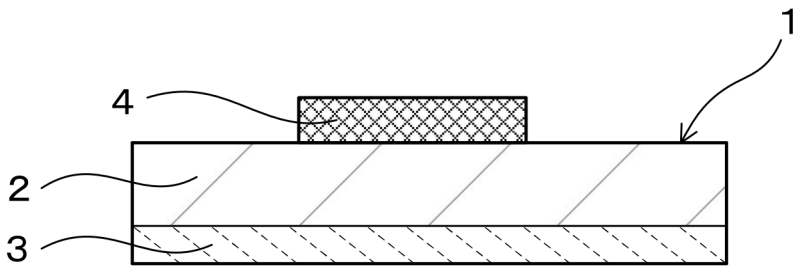
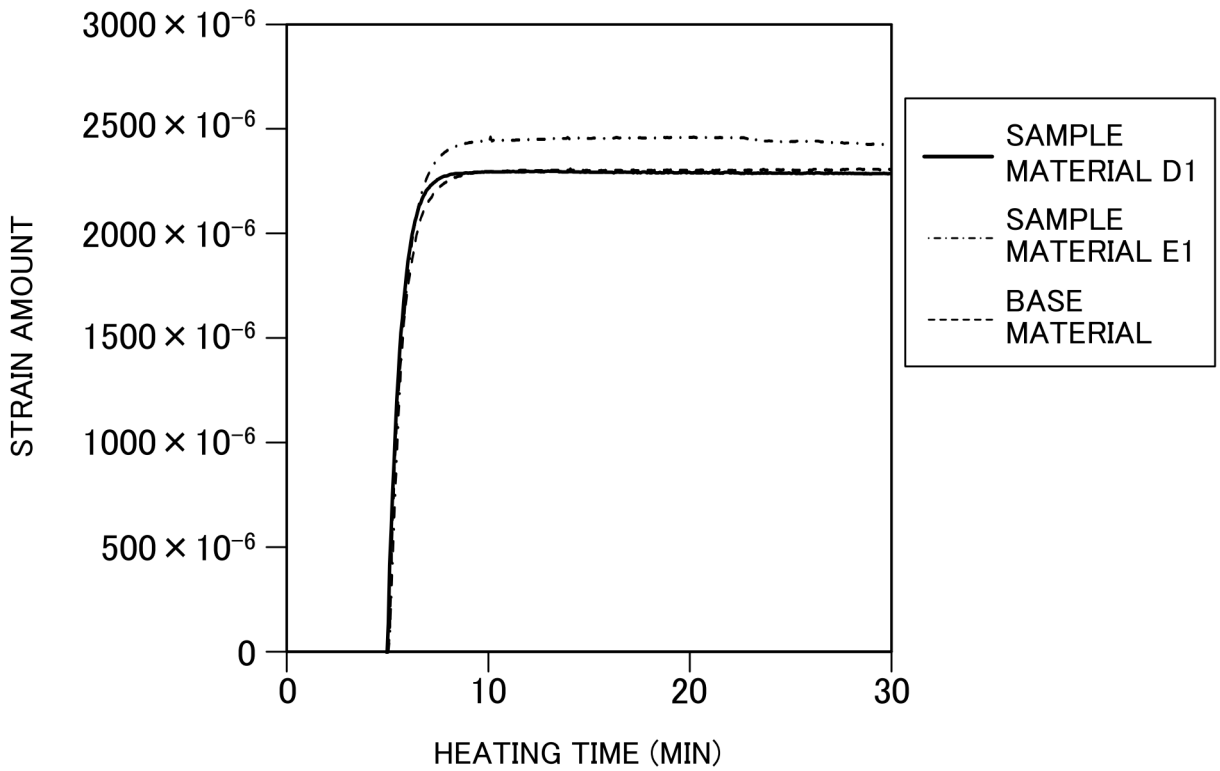

1
4
2
3

FIG. 6


3000 × 10⁻⁶
2500 × 10⁻⁶
2000 × 10⁻⁶
1500 × 10⁻⁶
1000 × 10⁻⁶
500 × 10⁻⁶
0
STRAIN AMOUNT
0
10
20
30
HEATING TIME (MIN)
SAMPLE MATERIAL D1
SAMPLE MATERIAL E1
BASE MATERIAL

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2024/027164

A. CLASSIFICATION OF SUBJECT MATTER

C25D 11/18(2006.01)i; ***C25D 11/04***(2006.01)i; ***C25D 11/06***(2006.01)i; ***C25D 11/08***(2006.01)i; ***C25D 11/16***(2006.01)i; ***C25F 3/04***(2006.01)i; ***C25F 3/20***(2006.01)i
FI: C25D11/18 301E; C25D11/04 308; C25D11/06 B; C25D11/08; C25D11/16; C25D11/18 301C; C25D11/18 313; C25F3/04 A; C25F3/20

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D11/18; C25D11/04; C25D11/06; C25D11/08; C25D11/16; C25F3/04; C25F3/20

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2024
Registered utility model specifications of Japan 1996-2024
Published registered utility model applications of Japan 1994-2024

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 10-18085 A (NIPPON LIGHT METAL COMPANY, LTD.) 20 January 1998 (1998-01-20) entire text	1-10
A	JP 57-57892 A (FUJIKURA ELECTRIC WIRE CORPORATION) 07 April 1982 (1982-04-07) entire text	1-10
A	CN 112708915 A (HAO, Yunxia) 27 April 2021 (2021-04-27) entire text	1-10

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 September 2024	**08 October 2024**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/027164

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 10-18085 A	20 January 1998	US 5892278 A entire text KR 10-1997-0077574 A	
JP 57-57892 A	07 April 1982	(Family: none)	
CN 112708915 A	27 April 2021	(Family: none)	

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2021070847 A **[0004]**