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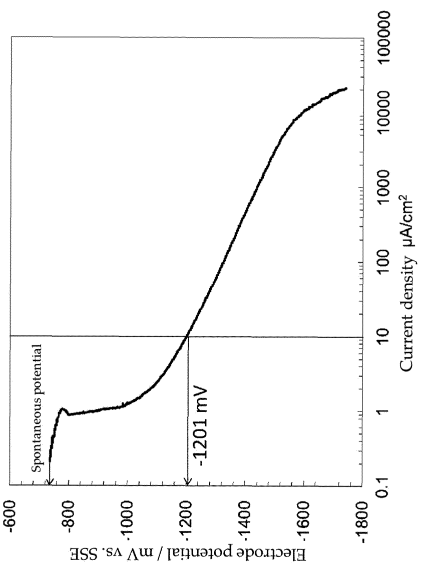
(54) ALUMINUM ALLOY MATERIAL AND METHOD FOR MANUFACTURING SAME

(57) An aluminum alloy material having a base material formed from an aluminum alloy, and a chemical treatment film on the surface of the base material, wherein, in a cathode polarization curve obtained by measuring the aluminum alloy material at a sweeping speed of 20 mV/min by using a saturated KCl silver-silver chloride electrode as a reference electrode in a 5 wt% NaCl static aqueous solution at a temperature of 25°C and a pH of 5.5, the electrode potential at which the absolute value of the current density reaches 10 μA/cm^2 is -1350 to -1150 mV.

[Fig. 2]



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Description

Technical Field

[0001] The present invention relates to an aluminum alloy material and a manufacturing method thereof.

Background Art

[0002] To improve surface properties of aluminum alloy materials, aluminum alloy materials subjected to various surface treatments have been conventionally proposed. Patent Literature 1 (Japanese Patent Application Publication No. 2014-62277) discloses an aluminum alloy plate, comprising: an aluminum alloy substrate; and an aluminum oxide film formed on a surface of the aluminum alloy substrate, wherein the aluminum oxide film contains at least one additive element having a P-B ratio (Pilling-Bedworth ratio) of 1.00 or more, 0.01 to 10 atom% of zirconium, and 0.1 atom% or more and less than 10 atom% of magnesium.

[0003] Patent Literature 2 (Japanese Patent Application Publication No. 2015-206117) discloses a surface-treated aluminum alloy plate to be subjected to chemical conversion treatment for use, comprising: an aluminum alloy plate containing magnesium; and an oxide film formed on a surface of the aluminum alloy plate, wherein the oxide film has a film thickness of 1 to 30 nm, a concentration of magnesium is 1 to 20 atom%, a concentration of zirconium is 0.2 to 10 atom%, and each of a concentration of a halogen and a concentration of phosphorus is less than 0.1 atom%.

Document List

[0004] Patent Literatures

Patent Literature 1: Japanese Patent Application Publication No. 2014-62277
Patent Literature 2: Japanese Patent Application Publication No. 2015-206117

Summary of Invention

Technical Problem

[0005] Aluminum alloy materials subjected to various surface treatments have been conventionally proposed, but an aluminum alloy material in which electrochemical activity of a surface is controlled has not been sufficiently investigated. The present inventors have made intensive investigation to solve the above problem, and as a result, have found that an aluminum alloy material having reduced electrochemical activity of a surface can be obtained by performing a specific surface treatment on the surface of a base material. The present inventors have found that deterioration of a boundary with another material is unlikely to occur in such an aluminum alloy material, and adhesion durability between the aluminum alloy material and the other material is improved to complete the present invention. That is, it is an object of the present invention to provide an aluminum alloy material having excellent adhesion durability to another material and a manufacturing method thereof.

Solution to Problem

[0006] To solve the above problem, the present invention has the following aspects.

[1] An aluminum alloy material, including: a base material made of an aluminum alloy; and a chemical conversion film on a surface of the base material, wherein
in a cathodic polarization curve measured on the aluminum alloy material in a 5 wt% NaCl static aqueous solution at 25°C having a pH of 5.5 with a saturated KCl silver-silver chloride electrode as a reference electrode at a sweep rate of 20 mV/min, an electrode potential at which an absolute value of a current density reaches 10 $\mu A/cm^2$ is -1350 mV to -1150 mV.
[2] The aluminum alloy material according to the above [1], wherein the base material is made of an aluminum alloy containing 0.3 to 5.0% by weight of Mg.
[3] The aluminum alloy material according to the above [1] or [2], wherein

the chemical conversion film contains a Ti compound and a Zr compound,
the Ti compound is at least one of Ti oxide and Ti hydroxide,
the Zr compound is at least one of Zr oxide and Zr hydroxide, and

a total amount of the Ti compound and the Zr compound in the chemical conversion film is 2 to 29 mg/m^2 in terms of metal element amount.

[4] A method of manufacturing an aluminum alloy material in which, in a cathodic polarization curve measured in a 5 wt% NaCl static aqueous solution at 25°C having a pH of 5.5 with a saturated KCl silver-silver chloride electrode as a reference electrode at a sweep rate of 20 mV/min, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is -1350 mV to -1150 mV, the method comprising:

performing acid etching on a base material made of an aluminum alloy containing Mg; and
applying chemical conversion treatment to a surface of the base material after the acid etching to form a chemical conversion film, wherein
an etching amount of the base material in performing acid etching [E: (mg/m^2)] with respect to a Mg amount in the base material [M (wt%)] satisfies a relationship of $10M \leq E \leq 200M$.

[5] The method of manufacturing an aluminum alloy material according to the above [4], wherein in forming a chemical conversion film, the chemical conversion treatment is applied by using a treatment liquid containing a fluorinated titanium compound and a fluorinated zirconium compound such that a total mass concentration of the fluorinated titanium compound and the fluorinated zirconium compound in the treatment liquid [C (ppm, in terms of metal element amount)] and a treating time [t (seconds)] satisfy $50 \leq C \times t \leq 1500$.

Effects of Invention

[0007] The present invention can provide an aluminum alloy material having excellent adhesion durability to another material and a manufacturing method thereof.

Brief Description of Drawings

[0008]

[Fig. 1] A diagram illustrating a plate-shaped aluminum alloy material provided for measurement of a cathodic polarization curve.
[Fig. 2] A graph indicating a cathodic polarization curve of an aluminum alloy material of Example 2.

Description of Embodiments

1. Aluminum Alloy Material

[0009] An aluminum alloy material of the present invention comprises: a base material made of an aluminum alloy; and a chemical conversion film on a surface of the base material. In a cathodic polarization curve measured on the aluminum alloy material in a 5 wt% NaCl static aqueous solution at 25°C having a pH of 5.5 with a saturated KCl silver-silver chloride electrode as a reference electrode at a sweep rate of 20 mV/min, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is -1350 mV to -1150 mV.

[0010] For example, in a case where a conventional aluminum alloy material is adhered to another member via an adhesive (another material), when a tensile stress is applied to a boundary between the aluminum alloy material and the adhesive with use, deterioration of the adhesion boundary between the aluminum alloy material and the adhesive (boundary deterioration) proceeds. A cause of the occurrence of the boundary deterioration is corrosion of the aluminum alloy material due to permeation of moisture or salinity from an end face of the adhesion, or growth of an oxide film on the surface due to a reaction between the permeated moisture and the aluminum alloy material. The permeation of moisture gradually occurs from the adhesion boundary, and also occurs by passing water vapor through the adhesive. In addition, in an environment of practical use of the adhesive, the adhered part is under a state where a tensile stress is persistently applied, and exposed to a corrosive environment at the same time. That is, both of mechanical deterioration of physically cleaving the adhesion boundary and chemical deterioration of permeating moisture and salinity into the adhesion boundary occur at the same time, and it is found to be a strict deteriorative environment exceeding a conventional presumption. As a result, with a conventional surface treatment method, the adhesion durability in such a strict environment is insufficient.

[0011] In contrast, by controlling electrochemical property on a surface within an appropriate range, the aluminum alloy material of the present invention can inhibit that the boundary between the aluminum alloy material and the adhesive is deteriorated due to application of the tensile stress and corrosion and deteriorated due to permeation of moisture, salinity, and the like. The electrochemical property on the surface of the aluminum alloy material can be measured by measurement of a polarization curve. In a cathodic polarization curve of the aluminum alloy material of the present invention, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is - 1350 mV to -1150 mV. Since the aluminum alloy material of the present invention has the characteristic of the cathodic polarization curve as above even when forming a boundary with a material other than the adhesive, the aluminum alloy material of the present invention can inhibit the boundary deterioration due to application of tensile stress, corrosion, or permeation of moisture, salinity, and the like.

[0012] A mechanism in which the electrochemical property on the surface of the aluminum alloy material affects the boundary deterioration is as follows. On the surface of the aluminum alloy, a dense natural oxide film generated by a reaction with the air and water and having a thickness of several nanometers is present. Since this natural oxide film is insulative and highly protective, corrosion resistance of the aluminum alloy is achieved. However, there are defect parts on the natural oxide film, and it is known that the defect parts become starting points of occurrence of corrosion. During occurrence of corrosion of the aluminum alloy, the following anode reaction and cathode reaction simultaneously proceed.

(Anode Reaction) $Al \rightarrow Al^{3+} + 3e^-$

(Cathode Reaction) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$2H^+ + 2e^- \rightarrow H_2$

[0013] This is because electrons generated by ionization (dissolution) of aluminum metal, which is the anode reaction, are required to be consumed by the cathode reaction (reduction reaction of dissolved oxygen or protons) to satisfy the electrically neutral condition. As described above, the defect parts present on the natural oxide film on the surface of the aluminum alloy act as active sites where these anode reaction and cathode reaction occur. However, among these defect parts on the film, defect parts which function as the site of the cathode reaction are limited to a precipitated product or the like that is present on the surface of the aluminum alloy and that has a high potential. That is, the corrosion of the aluminum alloy is rate-determined by a degree of activity of the cathode reaction (cathode activity) on the surface. A reaction between the surface of the aluminum alloy and moisture continues to grow the surface oxide film, and this is also the same mechanism as the above. Therefore, to effectively inhibit the deterioration of the adhesion boundary, it is effective to appropriately control the electrochemical property on the surface of the aluminum alloy, specifically the cathode activity.

[0014] When the cathode activity on the surface of the aluminum alloy is high, the corrosion reaction is likely to occur on the surface of the aluminum alloy, and enhances the deterioration of the adhesion boundary. Thus, by forming a chemical conversion film on the surface of the aluminum alloy with chemical conversion treatment, the cathode activity on the surface can be appropriately reduced, and the deterioration of the adhesion boundary can be inhibited. However, when an unnecessarily thick film is formed on the surface of the aluminum alloy due to an excessive chemical conversion treatment, the cathode activity on the surface is significantly reduced, but deterioration of the chemical conversion film itself and breakage or peeling in the chemical conversion film are likely to occur, leading to decrease in the adhesion durability. In the present invention, by preferably regulating the electrochemical characteristic on the surface of the aluminum alloy, the deterioration of the adhesion boundary and the decrease in the adhesion durability can be inhibited. Here, the electrochemical characteristic on the surface of the aluminum alloy can be evaluated by measurement of a polarization curve.

[0015] In a cathodic polarization curve of the aluminum alloy material of the present invention, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is -1350 mV to -1150 mV. In the cathodic polarization curve of the aluminum alloy material of the present invention, when the electrode potential at which the absolute value of the current density reaches 10 μA/cm^2 is higher than -1150 mV, the inhibition of the cathode activity on the surface of the aluminum alloy is insufficient, and the adhesion durability decreases. The electrode potential herein is, unless specifically described, a value measured with a saturated KCl silver-silver chloride electrode (SSE) at 25°C as a reference electrode. In addition, in the cathodic polarization curve of the aluminum alloy material of the present invention, when the electrode potential at which the absolute value of the current density reaches 10 μA/cm^2 is lower than -1350 mV, the formed chemical conversion film is unnecessarily thickened, leading to decrease in the adhesion durability. Therefore, it is preferable that the above electrode potential be -1330 mV to -1175 mV, and it is more preferable that the above electrode potential be -1310 mV to -1200 mV. In the cathodic polarization curve, the electrode potential at which the absolute value of the current density reaches 10 μA/cm^2 being within the above range allows the aluminum alloy material to have more excellent adhesion durability. In addition, by performing the appropriate surface treatment on the base material made of the aluminum alloy, the electrochemical characteristic on the surface can be controlled, and in the cathodic polarization curve, the electrode potential at which the absolute value of the current density reaches 10 μA/cm^2 can be controlled within the above range. Specifically, by appropriately controlling each condition of acid etching and chemical conversion treatment as the above surface treatment, and a treatment associated with these surface treatments, if necessary, the electrochemical characteristic on the surface of the aluminum alloy material can be optimized.

[0016] The cathodic polarization curve of the aluminum alloy material of the present invention is measured as follows. First, a container opened to the atmosphere at 25°C is prepared, 300 ml of a 5 mass% NaCl aqueous solution at 25°C having a pH of 5.5 is poured into the container, and left to stand. At this time, the pH of the NaCl aqueous solution can be adjusted to be a pH of 5.5 by using NaOH or HCl. The container used for the measurement is not particularly limited as long as it has a depth that can sufficiently immerse the material to be measured and it has no excessive aspect ratio (ratio between the diameter of the bottom face and the height of the container), and as an example, a beaker having a volume of 500 mL is appropriate. Fig. 1 is a diagram illustrating a plate-shaped aluminum alloy material provided for the measurement of the cathodic polarization curve. Fig. 1A illustrates a front face view, and Fig. 1B illustrates a rear face view. As illustrated in Fig. 1, the aluminum alloy provided for the measurement is cut to plate-shaped specimens with 5 cm × 2 cm by using shears. Among the specimens, a specimen without a scar nor a smear is selected. At a position distanced with approximately 5 mm from one end in the longitudinal direction of the plate-shaped specimen 10, a surface to be measured with 1 cm × 1 cm is exposed (the surface to be measured is provided at one position on only the front face of the specimen), and the remainder part is masked with a silicone resin to determine an evaluation area 11. At this time, on the opposite side to a part of the evaluation area 11, one end 12 in the longitudinal direction of the specimen is exposed with approximately 5 mm, and a terminal for the measurement is connected. Thereafter, the material to be measured and a counter electrode (platinum electrode) are immersed in the NaCl aqueous solution, and left to stand for 30 minutes. At this time, an approximately half in the longitudinal direction of the material to be measured is immersed under the solution level. At this time, the material to be measured is immersed so that a contacting part with the measurement terminal is not wet and so that the measurement surface is immersed under the solution level with 1 cm or longer. The platinum electrode is not particularly limited as long as it is used for a usual potentiodynamic polarization measurement, and as an example, a method in which a platinum wire with 0.7 mm in diameter and 120 mm in length is used and immersed under the solution level with 5 cm or longer in the measurement can be mentioned. During the measurement, degassing and stirring are not performed. As a reference electrode, a saturated KCl silver-silver chloride electrode (HS-205C, manufactured by DKK-TOA CORPORATION) at 25°C is used, and the polarization curve is measured with a three-electrode method. After 30 minutes from starting the immersion of the material to be measured, the potential is swept from a spontaneous potential of the material to be measured into the lower direction with a potentiostat (SDPS-511U, manufactured by Syrinx. Inc) to measure the cathodic polarization curve. At this time, the sweep rate of the potential is set to be 20 mV/min. Then, the electrode potential at which the absolute value of the current density has reached 10 $\mu A/cm^2$ is measured. Here, the absolute value of the current density being 10 $\mu A/cm^2$ means that the cathode current density becomes 10 $\mu A/cm^2$ with considering of removing the plus or minus sign from the measured current value. For example, with a measurement apparatus indicating a cathode current as minus, the measured value of the cathode current density is indicated as -10 $\mu A/cm^2$; thus, the minus sign is removed to be 10 $\mu A/cm^2$. The evaluation area 11 of the material to be measured is accurately measured, and the measured current is divided by the actual evaluation area 11 to calculate the current density. It is desired that the above measurement be performed on three different materials to be measured to determine an averaged value thereof. With determining the potential at which the current density has reached 10 $\mu A/cm^2$, a case where the current density instantaneously has reached 10 $\mu A/cm^2$ with noise or the like is ignored as an abnormal value. Thus, it is required that the polarization be performed until the potential at which the current density sufficiently exceeding 10 $\mu A/cm^2$ can be confirmed, and it is desired that the measurement be performed to -1600 mV or lower.

[0017] Hereinafter, each part forming the aluminum alloy material according to an embodiment will be described.

(Base material)

[0018] The base material is not particularly limited as long as it is made of an aluminum alloy, and can be a base material made of 1000-series aluminum alloy (pure aluminum alloy), 2000-series aluminum alloy (Al-Cu-Mg-based aluminum alloy), 3000-series aluminum alloy (Al-Mn-based aluminum alloy), 4000-series aluminum alloy (Al-Si-based aluminum alloy), 5000-series aluminum alloy (Al-Mg-based aluminum alloy), 6000-series aluminum alloy (Al-Mg-Si-based alloy), 7000-series aluminum alloy (Al-Zn-Mg-based aluminum alloy), and the like. From the viewpoints of strength and corrosion resistance of the base material made of the aluminum alloy, it is preferable that an aluminum alloy containing 0.3 to 5.0% by weight of Mg be used.

(Chemical Conversion Film)

[0019] The chemical conversion film is a film obtained by applying chemical conversion treatment, described later, to the surface of the base material. It is preferable that the chemical conversion film contain an inorganic compound, and it is more preferable that the chemical conversion film contain a Ti compound and a Zr compound. It is preferable that the Ti compound be at least one of Ti oxide and Ti hydroxide, and it is preferable that the Zr compound be at least one of Zr oxide and Zr hydroxide. When the chemical conversion film contains the Ti compound and the Zr compound, it is preferable that a total amount of the Ti compound and the Zr compound in the chemical conversion film be 2 to 29 mg/m^2, it is more preferable that it be 3 to 27 mg/m^2, and it is further preferable that it be 4 to 20 mg/m^2, in terms of metal element amount. The total amount of the Ti compound and the Zr compound being within the above range allows the aluminum alloy material to have excellent adhesion durability. It is preferable that each amount of the Ti compound and the Zr compound be at least 1 mg/m^2, and it is more preferable that it be at least 1.5 mg/m^2, in terms of metal element amount. The above "in terms of metal element amount" refers to amounts of Ti element and Zr element per m^2 of the chemical conversion film. It is preferable that a film thickness of the chemical conversion film be less than 50 nm, it is more preferable that it be less than 30 nm, and it is further preferable that it be 1 nm to 20 nm. The total amount of the Ti element and the Zr element per m^2 of the chemical conversion film can be measured by preparing a calibration curve based on a reference plate having a known amount of the film with an X-ray fluorescence spectrometer (XRF). The film thickness of the chemical conversion film can be measured with GD-OES (Glow Discharge Optical Emission Spectroscopy). When a value at which an emission intensity of aluminum has sufficiently reached a balk (base material) is set to a reference, the spattering depth at which the emission intensity reaches 50% of the reference value is specified as the film thickness.

2. Method of Manufacturing Aluminum Alloy Material

[0020] In a method of manufacturing the aluminum alloy material of the present invention, manufactured is an aluminum alloy material in which, in a cathodic polarization curve measured in a 5 wt% NaCl static aqueous solution at 25°C having a pH of 5.5 with a saturated KCl silver-silver chloride electrode as a reference electrode at a sweep rate of 20 mV/min, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is -1350 mV to -1150 mV. The manufacturing method includes: performing acid etching on a base material made of an aluminum alloy containing Mg; and applying chemical conversion treatment to a surface of the base material after the acid etching to form a chemical conversion film. The acid etching is performed so that an etching amount of the base material in performing acid etching [E: (mg/m^2)] with respect to a Mg amount in the base material [M (wt%)] satisfies a relationship of $10M \leq E \leq 200M$. In the aluminum alloy material manufactured with the method of manufacturing the aluminum alloy material of the present invention, in the cathodic polarization curve, the electrode potential at which the absolute value of the current density reaches 10 μA/cm^2 is -1350 mV to -1150 mV. Thus, it can be inhibited that the boundary between the aluminum alloy material and the adhesive deteriorates due to application of tensile stress and corrosion, and it can be inhibited that it deteriorates due to permeation of moisture, salinity, and the like. Since the aluminum alloy material of the present invention has the characteristic of the cathodic polarization curve as above even when forming a boundary with a material other than the adhesive, the aluminum alloy material of the present invention can inhibit the boundary deterioration due to application of tensile stress, corrosion, or permeation of moisture, salinity, and the like. In addition, The E being 10M or more allows the surface of the base material after the acid etching to be clean, and to form a chemical conversion film well adhered to the surface of the base material. In contrast, when the E exceeds 200M and becomes excessively large, a surface roughness generated by the etching and smut (a fine particle powder of an insoluble substance by an acid remained after the etching) affect the adhesion durability. This is presumably because the smut enters the inside of the surface roughness and becomes not easily removed to affect adhesiveness to the adhesive. Accordingly, the E being 200M or less can inhibit an unnecessary increase in the surface roughness and excessive generation of the smut, and can improve the adhesion durability between the aluminum alloy material and the other material. Hereinafter, each step of the method of manufacturing the aluminum alloy material of the present invention will be described in detail.

(Rolling and Heat Treatment)

[0021] As an example, after the aluminum alloy is formed to be an ingot according to a common method, a homogenizing treatment, a heat rolling, a cold rolling, an intermediate annealing, and a cold rolling, or a homogenizing treatment, a heat rolling, and a cold rolling are performed in this order, and an aluminum alloy plate that is rolled to have a final plate thickness is used as the base material. Thereafter, a heat treatment is performed on the aluminum alloy plate that is rolled to have the final plate thickness. At this time, when the heat treatment is performed in the atmosphere, magnesium, which is an easily oxidized element, in the aluminum alloy diffuses to the surface to be bonded to oxygen, and a layer containing a large amount of magnesium oxide is formed on the surface of the aluminum alloy plate.

(Degreasing Step)

[0022] Before performing acid etching, a degreasing step may be optionally performed. This is for a purpose of removing a rolling oil, a processing oil, a lubricant, and the like that adhere to the surface of the aluminum alloy plate in the step before acid washing. A solution used in this washing step is not particularly limited, and an alkaline washing agent, a surfactant, or a mixed liquid thereof, or an organic solvent is preferably used, and after that, a water washing step is performed. When an amount of oil that adheres to the surface of the aluminum alloy plate is small, the washing step may be omitted. When the degreasing step is performed and when an alkaline degreasing agent is used, dissolution of a certain amount of the aluminum alloy of the base material occurs. When the dissolution amount of the base material in the washing step is too large, a large amount of smut adheres to the plate surface, and may affect the following step. Thus, when the degreasing step is performed, it is preferable that the dissolution amount of the aluminum alloy be set to be 50 mg/m^2 or less, and it is more preferable that it be 40 mg/m^2 or less. Since an etching with an alkali cannot remove a substance having a low solubility in the alkali, such as magnesium oxide on the surface of the aluminum alloy plate, an alkali etching cannot be a replacement for the acid etching step.

(Performing Acid Etching)

[0023] In performing acid etching, the acid etching is performed on the base material made of the aluminum alloy containing Mg. The condition of performing acid etching is not particularly limited as long as it is a condition in that the etching amount of the base material [E: (mg/m^2)] with respect to an amount of Mg in the base material before the acid etching [M (wt%)] satisfies a relationship of $10M \leq E \leq 200M$. Performing the acid etching under the condition satisfying the relationship of $10M \leq E \leq 200M$ can remove a vulnerable layer present on the surface of the aluminum alloy base material, and can improve the adhesion durability. The vulnerable layer is a surface-modified layer generated by mechanical processing such as the rolling step and a mixture of aluminum oxide or magnesium oxide grown on the surface of the aluminum alloy in the heat treatment step. When the adhesion is performed in a state where these vulnerable layers remain, the adhesion durability decreases. In an aluminum alloy containing a large amount of magnesium, which is an easily oxidized element, magnesium oxide is likely to be generated in the heat treatment step, and the vulnerable layer tends to be formed thickly. Here, to optimize the etching amount according to the content of a magnesium alloy in the base material, E/M is set to be 10 to 200. It is preferable that E/M be 20 to 150, and it is more preferable that E/M be 30 to 100. It is preferable that M be 0.3 to 5.0 wt%, it is more preferable that M be 1.0 to 5.0 wt%, and it is further preferable that M be 2.0 to 5.0 wt%. The Mg amount in the base material before the etching can be measured by emission spectroscopy in accordance with H 1305:2005, but it may be any method that can obtain a similar level of accuracy. When a manufactured base material is purchased, the Mg amount can be calculated from a nominal Mg content of the base material. The etching amount E of the base material can be calculated by: using a material to be measured in which the base material is cut in an appropriate size; measuring dry masses before and after the etching; and dividing a difference in the measured results (mass before etching - mass after etching) by the area of the material to be measured to be converted into a numerical value per unit area. At this time, the size of the material to be measured may be any, but when the area is small, a change in the weight becomes small, and affects the measurement accuracy. Thus, it is required that the area of the material to be measured be set to an appropriate size with considering accuracy of a balance used for weighing. As an etching liquid for the acid etching, an acid of nitric acid, sulfuric acid, hydrofluoric acid phosphoric acid, or a mixed solution thereof can be used. The etching liquid may optionally contain an etching auxiliary (oxidizing agent), a surfactant, a chelating agent, and the like. It is preferable that a concentration of the acid in the etching liquid (in case of the mixed solution, a total concentration of each acid solution) be 0.01% by weight to 30% by weight, it is more preferable that it be 0.03% by weight to 25% by weight, and it is further preferable that it be 0.05% by weight to 20% by weight. It is preferable that a temperature of the etching liquid be 30 to 90°C, it is more preferable that it be 40 to 90°C, and it is further preferable that it be 45 to 90°C. It is preferable that a time of the etching be 1 second to 30 seconds, it is more preferable that it be 1 to 25 seconds, and it is further preferable that it be 1 to 20 seconds. It is preferable that a water washing step be performed after the acid etching step. In the water washing step, it is preferable that water having an electroconductivity at a temperature of 20°C of 500 mS/m or less be used. When water having a high electroconductivity is used, each ion contained in the water is absorbed on the surface of the aluminum alloy, and may be a cause of decrease in the adhesion durability. It is preferable that a temperature of water in the water washing step be 30°C to 90°C, it is more preferable that it be 40°C to 85°C, and it is further preferable that it be 45°C to 80°C. This is because solubility of many substances increases in water with a higher temperature and it is effective for washing the surface of the aluminum alloy base material after the etching. The higher the temperature of the washing water, the higher the washing effect, but it may cause an increase in energy cost. When the temperature of washing water is higher than 90°C, a hydration reaction of the aluminum alloy base material with water may occur to form a hydrated oxide film of the aluminum on the surface. In addition, when the time of the water washing step is too long, the aluminum surface and the washing water may gradually react to form an oxide of aluminum. When the time of the water washing step is too short, a treating reagent liquid adhering to the surface cannot be sufficiently removed in some cases. Thus, it is preferable that the time of the water washing step be 0.5 seconds to 30 seconds, and it is more preferable that it be 1 second to 20 seconds.

(Forming Chemical Conversion Film)

[0024] In forming a chemical conversion film, the chemical conversion treatment is applied to the surface of the base material after the acid etching to form the chemical conversion film. Although many sites of the cathode reaction are present on the surface after the acid etching step, the adhesion durability can be improved by forming an appropriate chemical conversion film. As the chemical conversion film, a film formed by an electrochemical reaction between ions dissolved in a treatment liquid and the surface of the aluminum alloy is good, and thereby, an inorganic material-based chemical conversion film is preferable. This is because the sites of the cathode reaction present on the surface of the aluminum alloy base material act as sites that are likely to cause the film formation also in the process of forming the chemical conversion film. Thus, when the chemical conversion film is formed by the electrochemical reaction between the dissolved ions in the solution and the aluminum alloy, the cathode reaction sites on the surface of the aluminum alloy can be efficiently covered. Among the inorganic material-based chemical conversion films, in particular, a film containing both titanium and zirconium is preferable. This is because an oxide or hydroxide of titanium and an oxide or hydroxide of zirconium that are formed as the chemical conversion film are chemically stable, and a chemical change is unlikely to occur even in a deteriorative environment and it is effective for preventing decrease in the adhesion durability. In forming the chemical conversion film on the surface of the aluminum alloy base material, since the film formation gradually proceeds from the cathode reaction sites on the surface, as described above, the electrochemical characteristic on the surface of the aluminum alloy changes moment by moment in this process. Thus, by blending titanium and zirconium, which are elements having different solubility and electrode potential in the solution each other in the treatment liquid, it can widely manage the surface of the aluminum alloy that changes moment by moment during the process of forming the chemical conversion film, and it can cover the surface of the aluminum alloy with the chemical conversion film efficiently and most appropriately.

[0025] It is preferable that no drying nor air blowing be performed between the water washing step in the acid etching step and the step of forming a chemical conversion film and that the surface of the aluminum alloy be a state of wetted with the washing water. This is to prevent that each oxide on the surface of the aluminum alloy removed in the acid etching step grows again thickly by contacting the air. However, with contacting the washing water in a long time, each oxide begins to grow on the surface of the aluminum alloy. Thus, from the end of the water washing step in the acid etching step, it is preferable that the step of forming a chemical conversion film be begun within 30 seconds, it is more preferable that it be begun within 10 seconds, and it is further preferable that it be begun within 5 seconds. It is most preferable that it be begun within 2 seconds.

[0026] In forming a chemical conversion film, it is preferable that the chemical conversion treatment be applied by using a treatment liquid containing a fluorinated titanium compound and a fluorinated zirconium compound such that a total mass concentration of the fluorinated titanium compound and the fluorinated zirconium compound in the treatment liquid [C (ppm, in terms of metal element amount)] and a treating time [t (seconds)] satisfy $50 \leq C \times t \leq 1500$. The $C \times t$ being within the above range can form the chemical conversion film most suitable for the surface of the aluminum alloy after the acid etching step. As the fluorinated titanium compound, hexafluorotitanic acid (H_2TiF_6), salts thereof (particularly, a potassium salt, a sodium salt, and an ammonium salt), and the like can be mentioned. As the fluorinated zirconium compound, hexafluorozirconic acid (H_2ZrF_6), salts thereof (particularly, a potassium salt, a sodium salt, and an ammonium salt), and the like can be mentioned. $50 \leq C \times t \leq 1500$ is preferable, $80 \leq C \times t \leq 1400$ is more preferable, and $100 \leq C \times t \leq 1300$ is further preferable. When the $C \times t$ is less than 50, the chemical conversion film cannot be sufficiently formed on the surface of the aluminum alloy in some cases. When the $C \times t$ exceeds 1500, the chemical conversion film is formed much thickly to cause decrease in the adhesion durability in some cases. It is preferable that the total mass concentration C (in terms of metal element amount) of the fluorinated titanium compound and the fluorinated zirconium compound in the treatment liquid be 20 to 400 ppm, it is more preferable that it be 30 to 350 ppm, and it is further preferable that it be 40 to 300 ppm. It is preferable that the time t be 0.5 to 30 seconds, it is more preferable that it be 1 to 25 seconds, and it is further preferable that it be 1.5 seconds to 20 seconds. It is preferable that a mass concentration of the fluorinated titanium compound in the treatment liquid in terms of metal element be 10 to 400 ppm, it is more preferable that it be 15 to 300 ppm, and it is further preferable that it be 20 to 200 ppm. It is preferable that a mass concentration of the fluorinated zirconium compound in the treatment liquid be 10 to 400 ppm, it is more preferable that it be 15 to 300 ppm, and it is further preferable that it be 20 to 200 ppm. It is preferable that a temperature of the treatment liquid be 30 to 80°C, it is more preferable that it be 35 to 70°C, and it is further preferable that it be 40 to 65°C. When the concentrations of the fluorinated titanium compound and fluorinated zirconium compound in the treatment liquid, the treating time, and the treating temperature are within the above range, and when the [C (ppm, in terms of metal element amount)] and the treating time [t (seconds)] are within the above range, the chemical conversion film on the surface of the aluminum alloy can be adhered most appropriately.

[0027] As the treating area of the aluminum alloy base material increases, Al ions eluted from the base material gradually increase in the treatment liquid for the chemical conversion treatment. When the Al ions increase, it becomes a cause of inhibiting the film formation of the chemical conversion film. The A1 ion concentration in the treatment liquid of up to approximately 800 ppm does not affect the film formation of the chemical conversion film, but it is preferable that the Al ion concentration in the treatment liquid be 600 ppm or less, and it is more preferable that it be 500 ppm or less.

[0028] As an example, after forming a chemical conversion film, the water washing step is further performed immediately. This step rapidly removes the treatment liquid remained on the surface and controls the time of the reaction between the base material surface and the treatment liquid to be able to appropriately regulate the thickness of the chemical conversion film. Furthermore, this step can prevent that the component in the treatment liquid remains on the surface of the chemical conversion film. When the component in the treatment liquid remains on the surface of the chemical conversion film, it becomes a cause of decrease in the adhesion durability and occurrence of discoloration on the base material surface. It is preferable that the time from the step of forming a chemical conversion film to the water washing step be within 2 seconds, and it is more preferable that it be within 1 second. For the water used in the water washing step, it is preferable that an electroconductivity at a temperature of 20°C be set to be 100 mS/m or less, and it is more preferable that it be set to be 50 mS/m or less. When water having a high electroconductivity is used, each ion contained in the water remains on the base material surface, and it becomes a cause of decrease in the adhesion durability and occurrence of discoloration on the base material surface. For the measurement of the electroconductivity, for example, an alternating-current two-terminal method and the like can be used.

[0029] Since the water washing step after forming a chemical conversion film affects the final quality of the base material surface, it is desirable that two or more times, a plurality times, of the water washing steps be provided. When the plurality times of the water washing steps after forming a chemical conversion film are provided, it is preferable that an interval between each of the water washing steps be within 2 seconds, and it is further preferable that it be within 1 second. It is preferable that the electroconductivity of water used in the water washing step performed after the first water washing step be the same as or lower than the electroconductivity of the water used in the first water washing step after forming a chemical conversion film. This can sufficiently remove a component in the chemical treatment liquid that is not removed in the first water washing step. When the time of the water washing step is too long, the surface of the aluminum alloy base material and the washing water gradually react, and an oxide of aluminum may be formed. When the time of the water washing step is too short, the washing effect cannot be sufficiently obtained. Thus, it is preferable that a total time of the water washing steps performed after forming a chemical conversion film be 0.5 seconds to 30 seconds, and it is more preferable that it be 1 second to 20 seconds. Since solubility of many substances increases in water with a higher temperature, the higher the temperature of water in the water washing step after forming a chemical conversion film, the higher the washing effect. When the temperature of water in the water washing step exceeds 90°C, it may cause increase in energy cost, and the aluminum alloy base material may cause a hydration reaction with water and the hydrated oxide film of aluminum may be formed on the surface of the base material. Thus, it is preferable that at least the temperature of water in the first water washing step after forming a chemical conversion film be 30°C to 90°C, it is more preferable that it be 40°C to 85°C, and it is further preferable that it be 50°C to 85°C. A temperature of water in the water washing step after that may be any as long as it is within a range of 10°C to 90°C. After the water washing step, it is desirable that drying by hot blast and the like be performed to remove water droplets remained on the surface of the aluminum alloy base material.

(Treating Method of Each Step)

[0030] For the degreasing step, performing acid etching, forming a chemical conversion film, and the water washing step associated with each step, a method of spraying the treatment liquid to the surface of the aluminum alloy, a method of passing the aluminum alloy through a treating vessel filled with the treatment liquid (immersion method), or the like is preferably used.

(Method of Using Aluminum Alloy Material)

[0031] The aluminum alloy material of the present invention can be used as a member for automobiles, construction machines, and transportation machines by providing the adhesive layer on the surface of the chemical conversion film and subsequently further adhering to another aluminum alloy material. Since the aluminum alloy material of the present invention is excellent in the adhesion durability with another material, the aluminum alloy material can strongly adhere to the other aluminum alloy material via the adhesive, and can maintain the adhesion in a long term. As the adhesive, an epoxy resin, an acrylic resin, a urethane resin, and the like can be mentioned, and a thermosetting epoxy resin is preferably used. A thickness of the adhesive layer provided on the surface of the chemical conversion film is not particularly limited, but it is preferable that it be 10 to 5000 μm, it is more preferable that it be 20 to 3000 μm, and it is further preferable that it be 30 to 1000 μm.

Example

[0032] Hereinafter, the present invention will be described in detail based on Examples. The present invention is not limited to the examples described below, and the constitution can be appropriately changed within a range not impairing the spirit of the present invention.

(Examples 1 to 8)

[0033] Base materials with a size of 1 mm in plate thickness and 7 cm × 15 cm, shown in the following Table 1, were prepared, and acid etching was performed on the base materials under the following conditions. In Examples 1 to 3, the acid etching was performed for 6 seconds under conditions shown in Table 1 by using an etching liquid at 60°C having a composition of 0.5 mass% sulfuric acid + 0.05 mass% hydrofluoric acid. Similarly, in Examples 4 to 7, the acid etching was performed for 4 seconds under conditions shown in Table 1 by using an etching liquid at 60°C having a composition of 0.5 mass% sulfuric acid + 0.05 mass% hydrofluoric acid. In Example 8, the acid etching was performed for 4 seconds under conditions shown in Table 1 by using an etching liquid at 80°C having a composition of 10 mass% sulfuric acid. After the acid etching, the substrate was washed with ion-exchanged water at a temperature of 70°C having an electroconductivity at a temperature of 20°C of 0.2 mS/m. Next, chemical conversion treatment was immediately applied under conditions of temperature, composition, and treating time shown in Table 1 to obtain an aluminum alloy material having a base material and a chemical conversion film with a film amount shown in Table 1. A fluorinated titanium compound and a fluorinated zirconium compound that were used in Examples 1 to 8 were hexafluorotitanic acid and hexafluorozirconic acid, respectively. After the chemical conversion treatment, the base material was immediately washed with ion-exchanged water at 70°C having an electroconductivity at a temperature of 20°C of 0.2 mS/m, further washed with ion-exchanged water at a room temperature (specifically, 20°C) having an electroconductivity at a temperature of 20°C of 0.1 mS/m, and then warm wind at 50°C was blown to dry the base material. The electroconductivity of water was measured with "Portable Conductivity Meter ES-71", manufactured by HORIBA, Ltd.

(Comparative Examples 1 to 2)

[0034] In Comparative Example 1, a base material with the size same as that used in Example shown in Table 1 was prepared, acid etching was performed on the base material for 4 seconds under conditions shown in Table 1 by using an etching liquid at 80°C having a composition of 10 mass% sulfuric acid, and the substrate was washed with ion-exchanged water at a temperature of 70°C having an electroconductivity at a temperature of 20°C of 0.2 mS/m to obtain an aluminum alloy base material. No chemical conversion treatment was performed in Comparative Example 1. In Comparative Example 2, acid etching was performed for 1 second under conditions shown in Table 1 by using an etching liquid at 50°C having a composition of 10 mass% sulfuric acid, after the acid etching, the substrate was washed with ion-exchanged water at a temperature of 70°C having an electroconductivity at a temperature of 20°C of 0.2 mS/m, and then chemical conversion treatment was immediately performed under conditions shown in Table 1 to obtain an aluminum alloy material having a base material and a chemical conversion film with a film amount shown in Table 1. A fluorinated titanium compound and a fluorinated zirconium compound that were used in Comparative Example 2 were hexafluorotitanic acid and hexafluorozirconic acid, respectively. After the chemical conversion treatment, the base material was immediately washed with ion-exchanged water at 70°C having an electroconductivity at a temperature of 20°C of 0.2 mS/m, further washed with ion-exchanged water at a room temperature (specifically, 20°C) having an electroconductivity at a temperature of 20°C of 0.1 mS/m, and then warm wind at 50°C was blown to dry the base material.

[Table 1]

	Aluminum alloy plate		Acid etching		Chemical conversion treatment							
	JIS alloy number	Mg amount (wt%)	Etching amount E (mg/m^2)	E/M	Mass concentration of fluorinated titanium compound in treatment liquid Ti concentration (ppm: in terms of metal element amount)	Mass concentration of fluorinated zirconium compound in treatment liquid Zr concentration (ppm: in terms of metal element amount)	Temperature (°C)	Time (s)	Treatment parameter Cxt	Content of titanium compound in chemical conversion film (mg/m^2: in terms of metal element amount)	Content of zirconium compound in chemical conversion film (mg/m^2: in terms of metal element amount)	Total amount of titanium compound and zirconium compound in chemical conversion film (mg/m^2: in terms of metal element amount)
Example 1	5182	4,5	400	89	100	100	40	4	800	5,1	4,1	9,2
Example 2	5182	4,5	400	89	100	100	30	3	600	1,3	1,4	2,7
Example 3	5182	4,5	400	89	100	100	60	7	1400	17,2	11,9	29,1
Example 4	5182	4,5	250	56	100	100	40	1	200	2,5	5,0	7,5
Example 5	5182	4,5	250	56	100	100	40	7	1400	5,9	11,8	17,7
Example 6	5182	4,5	250	56	20	20	30	1,5	60	1,0	1,0	2,0
Example 7	5182	4,5	250	56	100	100	50	7	1400	13,0	14,0	27,0
Example 8	5052	2,5	150	60	100	100	50	3	600	5,0	5,0	10,0
Comparative Example 1	5182	4,5	150	33	-	-	-	-	-	-	-	-
Comparative Example 2	5182	4,5	40	9	100	100	40	4	800	4,8	5,1	9,9

[0035] A cathodic polarization curve of the aluminum alloy material of each example obtained as above was measured with the above method. Fig. 2 is a graph indicating a cathodic polarization curve of the aluminum alloy material of Example 2 measured as above.

[0036] As an evaluation of adhesion, on the aluminum alloy material obtained in each example, an evaluation was performed with a method based on a modified APGE test described in Japanese National Publication of International Patent Application No. 2018-527467 to measure an adhesion-rupture cycle Cy. A detailed procedure of the modified APGE test is as follows. Two sheets of materials to be measured with 52.5 mm in length × 25 mm in width were adhered so that a length of an adhering part was 12.5 mm and an adhering thickness was 0.2 mm by using an epoxy-based adhesive. To prevent the material to be measured with 1 mm in plate thickness from deforming during the test, a similar plate was adhered with a similar adhesive in advance to be used. Thereafter, six pairs of the materials to be measured produced in the above procedure were bonded at each end portion with a stainless steel bolt. To prevent galvanic corrosion due to a contact between the stainless steel bolt and the material to be measured, the bolt was insulated with an appropriate method such as winding with a sealing tape. The six pairs of the bonds were maintained in a state where a tensile stress of 2400 N was persistently applied to both ends thereof. Further, the bonds with the state of applying the stress were immersed in a 5 mass% NaCl aqueous solution for 15 minutes, taken out to the atmosphere at a room temperature of 25°C to be naturally dried for 105 minutes, and put in a thermohygrostat chamber set at 50°C and a relative humidity of 90%RH to be maintained for 22 hours. According to this method, durability in a highly strict deteriorative environment of the adhesion boundary with both the tensile stress and the corrosive environment can be evaluated. Furthermore, the procedure from applying the tensile stress of 2400 N to finishing the maintenance in the thermohygrostat chamber for 22 hours was counted as one cycle, and one cycle of the test was performed in one weekday. In a holiday, the bonds was kept being put in the thermohygrostat chamber for 48 hours, and not counted as the test cycle. The bonding state of the sample was checked at a start of the next cycle, and when a break was observed in any one pair of the bond in the six pairs of the bonded specimens, the number of cycle at this time was specified as a first break (break of a first pair). When a break of the material to be measured was observed from applying the tensile stress of 2400 N to putting in the thermohygrostat chamber, the number of cycle at this time was also specified as a first break. The broken material to be measured was removed, a single plate having the size same as one pair of the material to be measured was inserted to be bonded to the other material to be measured with a bolt, and the stress was applied again to restart the test cycle. When a plurality of the bonding parts of the specimens were broken at the same time, each of them was counted as the same number of cycle. For example, when there is no break at the end of the 19th cycle and two pairs in the six pairs of the specimens have been broken at the start of 20th cycle, each of the first break and the second break is specified as 20 cycles, and the next break is to be a third break. This procedure was repeated, and the test was continued until a fourth break (a time when any of four pairs in the six pairs of the bonded specimens were broken). Thereafter, an average value of numbers of cycle from the first break to the fourth break was determined (rounded off the decimal place) to be specified as Cy. A case where Cy < 18 was evaluated as "poor", a case where 18 ≤ Cy < 20 was evaluated as "good", and a case where 20 ≤ Cy was evaluated as "excellent". The above measurement results are shown in Table 2.

[Table 2]

	Polarization	Adhesion evaluation (excellent, good, poor)
	Potential at which cathode current density reaches 10 μA/cm^2 (mV vs. 25°C saturated KCl silver-silver chloride electrode)	Cy< 18 :Poor 18≤Cy< 20: Good 20≤Cy: Excellent
Example 1	-1242	Excellent
Example 2	-1201	Excellent
Example 3	-1302	Good
Example 4	-1230	Excellent
Example 5	-1275	Excellent
Example 6	-1150	Good
Example 7	-1295	Excellent
Example 8	-1240	Excellent
Comparative Example 1	-1089	Poor

(continued)

	Polarization	Adhesion evaluation (excellent, good, poor)
	Potential at which cathode current density reaches 10 μA/cm^2 (mV vs. 25°C saturated KCl silver-silver chloride electrode)	Cy< 18 :Poor 18≤Cy< 20: Good 20≤Cy: Excellent
Comparative Example 2	-1130	Poor

[0037] As seen from Table 2, in Examples 1 to 8, the adhesion evaluations were "good" or "excellent", whereas in Comparative Examples 1 to 2, the adhesion evaluations were "poor". From the above, it is found that the excellent adhesion durability can be obtained in the aluminum alloy material of the present invention.

Claims

1. An aluminum alloy material, comprising: a base material made of an aluminum alloy; and a chemical conversion film on a surface of the base material, wherein
   in a cathodic polarization curve measured on the aluminum alloy material in a 5 wt% NaCl static aqueous solution at 25°C having a pH of 5.5 with a saturated KCl silver-silver chloride electrode as a reference electrode at a sweep rate of 20 mV/min, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is -1350 mV to -1150 mV.

2. The aluminum alloy material according to claim 1, wherein the base material is made of an aluminum alloy containing 0.3 to 5.0% by weight of Mg.

3. The aluminum alloy material according to claim 1 or 2, wherein the chemical conversion film contains a Ti compound and a Zr compound,

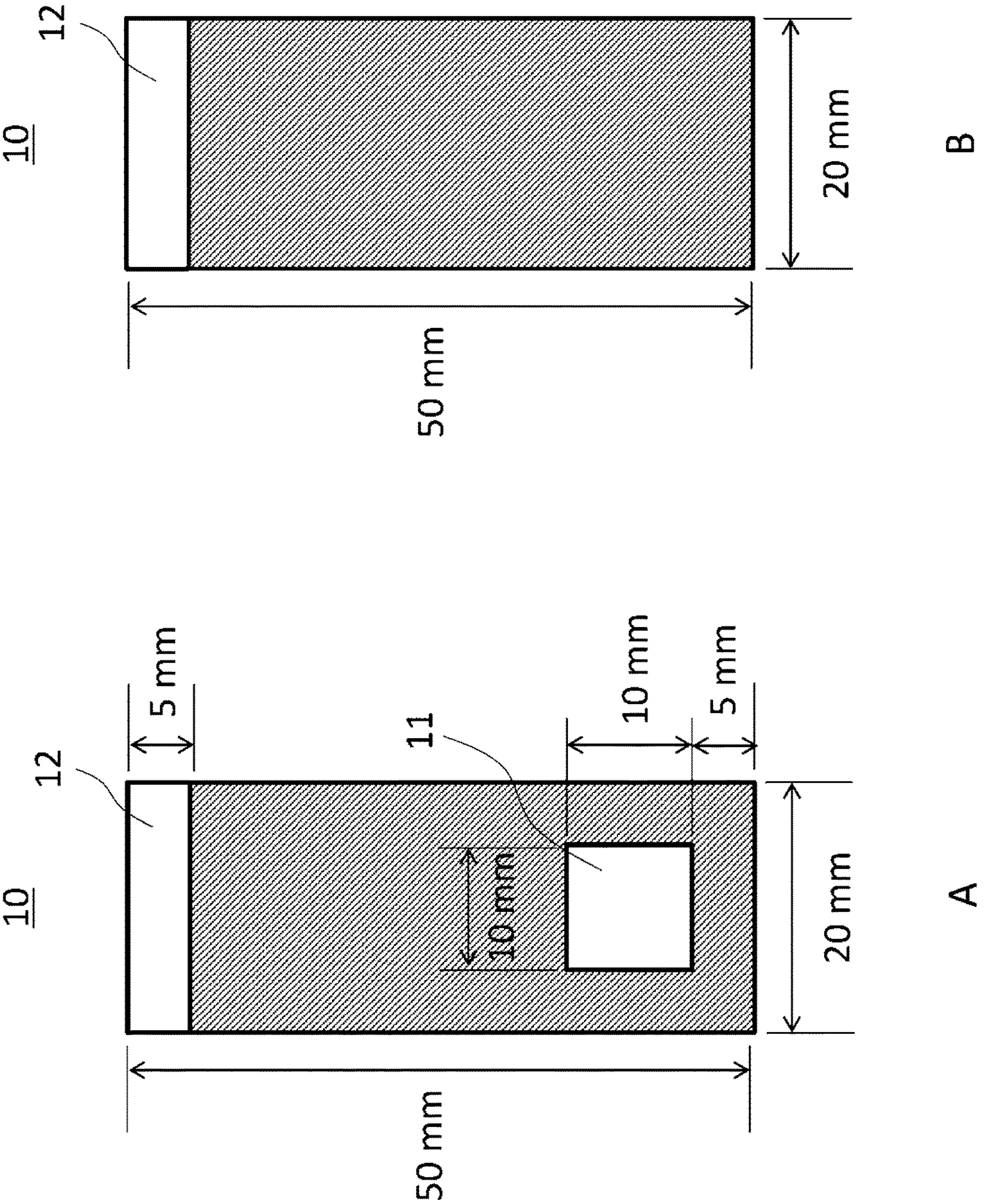
   the Ti compound is at least one of Ti oxide and Ti hydroxide,
   the Zr compound is at least one of Zr oxide and Zr hydroxide, and
   a total amount of the Ti compound and the Zr compound in the chemical conversion film is 2 to 29 mg/m^2 in terms of metal element amount.

4. A method of manufacturing an aluminum alloy material in which, in a cathodic polarization curve measured in a 5 wt% NaCl static aqueous solution at 25°C having a pH of 5.5 with a saturated KCl silver-silver chloride electrode as a reference electrode at a sweep rate of 20 mV/min, an electrode potential at which an absolute value of a current density reaches 10 μA/cm^2 is - 1350 mV to -1150 mV, the method comprising:

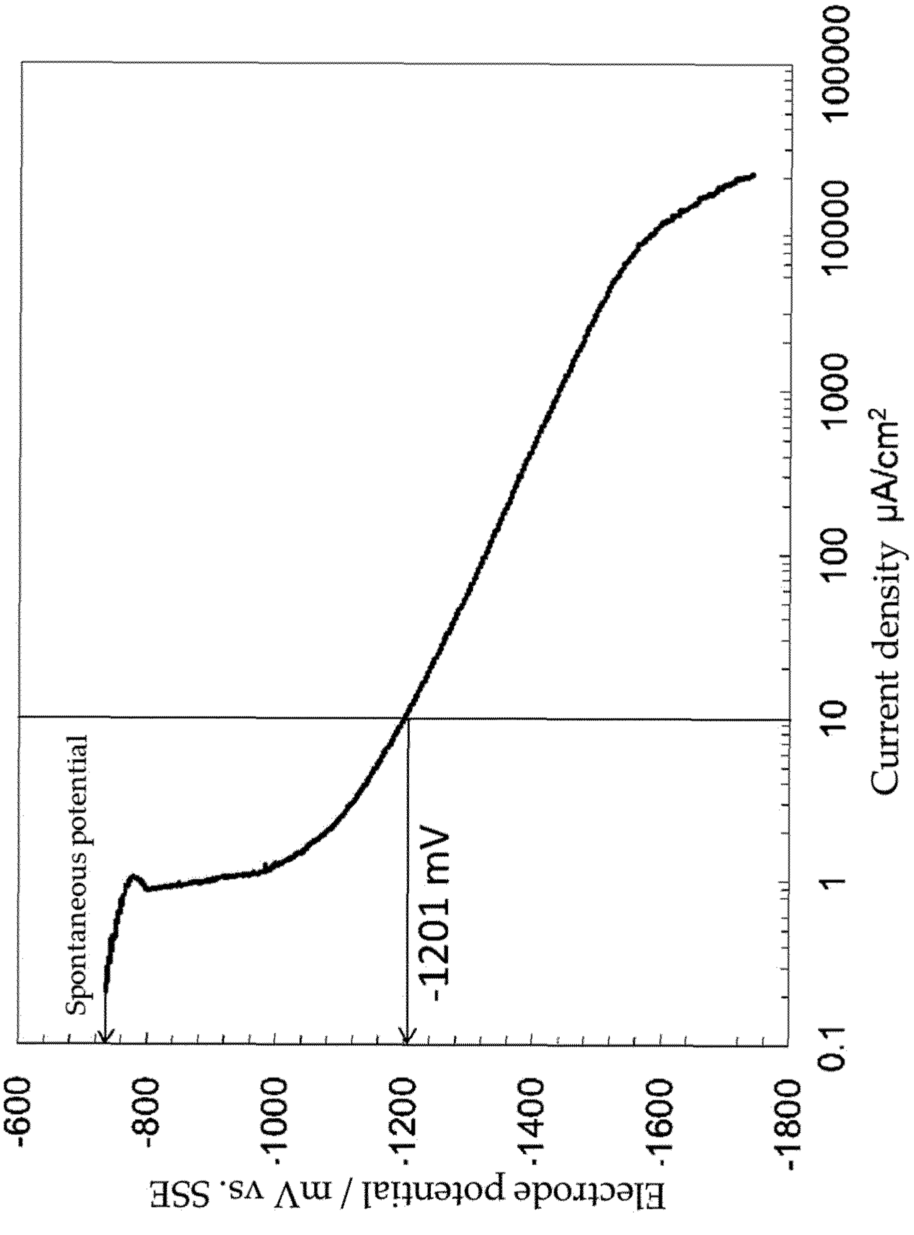
   performing acid etching on a base material made of an aluminum alloy containing Mg; and
   applying chemical conversion treatment to a surface of the base material after the acid etching to form a chemical conversion film, wherein
   an etching amount of the base material in performing acid etching [E: (mg/m^2)] with respect to a Mg amount in the base material [M (wt%)] satisfies a relationship of $10M \leq E \leq 200M$.

5. The method of manufacturing an aluminum alloy material according to claim 4, wherein in forming a chemical conversion film, the chemical conversion treatment is applied by using a treatment liquid containing a fluorinated titanium compound and a fluorinated zirconium compound such that a total mass concentration of the fluorinated titanium compound and the fluorinated zirconium compound in the treatment liquid [C (ppm, in terms of metal element amount)] and a treating time [t (seconds)] satisfy $50 \leq C \times t \leq 1500$.

[Fig. 1]



[Fig. 2]


Spontaneous potential
-1201 mV
-600
-800
-1000
-1200
-1400
-1600
-1800
Electrode potential / mV vs. SSE
0.1
1
10
100
1000
10000
100000
Current density μA/cm²

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/035953

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C23C22/34(2006.01)i
FI: C23C22/34

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C23C22/34

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	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

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.
X Y A	JP 2008-297594 A (NIPPON PAINT CO., LTD.) 11 December 2008 (2008-12-11), paragraph [0039], examples 1, 2	1-2 3 4-5
Y A	JP 2017-179587 A (KOBE STEEL, LTD.) 05 October 2017 (2017-10-05), paragraph [0059]	1-3 4-5
Y A	JP 2009-79252 A (FURUKAWA-SKY ALUMINUM CORP.) 16 April 2009 (2009-04-16), paragraph [0017], examples	1-3 4-5
X Y A	JP 2007-203615 A (FURUKAWA-SKY ALUMINUM CORP.) 16 August 2007 (2007-08-16), paragraph [0015], examples	1-2 3 4-5

☒ 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
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 13 October 2020	Date of mailing of the international search report 02 November 2020
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/035953

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2019-157155 A (KOBE STEEL, LTD.) 19 September 2019 (2019-09-19), paragraphs [0017]-[0020], [0037], examples	1-3 4-5

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/JP2020/035953

JP 2008-297594 A	11 December 2008	(Family: none)
JP 2017-179587 A	05 October 2017	US 2019/0119817 A1 paragraph [0065]
JP 2009-79252 A	16 April 2009	(Family: none)
JP 2007-203615 A	16 August 2007	(Family: none)
JP 2019-157155 A	19 September 2019	(Family: none)

Form PCT/ISA/210 (patent family annex) (January 2015)

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- JP 62277 A **[0002]**
- JP 2015 A **[0003]**
- JP 206117 A **[0003]**
- JP 2014062277 A **[0004]**
- JP 2015206117 A **[0004]**