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(54) ALUMINUM METAL MATERIAL HAVING EXCELLENT CONDUCTIVITY, AND PRODUCTION METHOD THEREFOR

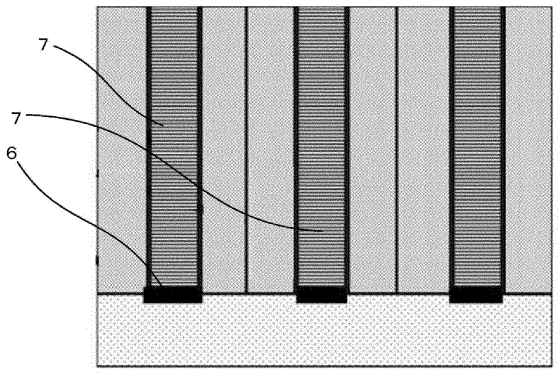
(57) [Problem to be Solved]

To develop material by providing electronic conductivity to an anode-oxidization film while having hardness than that of hard-anodized aluminum.

[Means for Solving Problem]

The present invention provides an excellent material keeping an electric resistance not more than $1 \times 10^{-2}\ \Omega$ while having hardness not less than HV 470 as a film by removing a barrier layer used for an insulation material in the anode-oxidization film, and then forming a film with good electric conductivity by further depositing metal. The material has low resistance suitable to practical use and the excellent hardness, which have not been conventionally known as an aluminum material. This material can be produced by applying four-step electrolysis.

Fig. 5



EP 4 428 270 A1

Description

Technical Field

[0001] The present invention relates to an aluminum metal material having good conductivity and a production method thereof.

Background Art

[0002] Aluminum anode-oxidation films (hereinafter referred to as alumite) have been developed as electrical insulation materials and have played a role in current development of aluminum by improving decoration technologies, corrosion resistance technologies, hardness and abrasion resistance technologies, and the like. Aluminum have come into use in various ways including color panels of buildings, color sashes of window frames, coloration of daily goods, etc. by decoration and corrosion-resistance technologies; weight reduction of machinery parts requiring sliding performance by technologies for hardness; and weight reduction of outdoor exteriors, underwater cameras, etc. by corrosion technologies. Further development of aluminum in future is demanding advance into fields of electricals, electrics, and semiconductors by not only exploration of materials, but also overcoming insulation materials, which is a primary characteristic of anode-oxidation films, and taking advantage of conductivity, magnetism, etc. plus light weight and ease of processing, and thus there have been expected development and practical implementation of an anode-oxidation film having conductivity in addition to conventional characteristics. For example, anode-oxidation films have suffered from troubles of an electronic circuit damaged by a spark due to static electricity, and failure in a magnetic shield effect of medium waves to hyper-ultrashort waves used in smartphones, satellite broadcasting, taxi wireless communications, etc., and have dealt with them by surface plating. However, heavy metal is generated at handling, disposal, and regeneration of a plating liquid and causes a problem in view of measure for LCA, and thus an LCA-conforming film capable of solving the problem has been demanded.

[0003] In regard to providing an anode-oxidation film of alumite with conductivity, a method of treatment in an anode-oxidation bath containing nitrate ions has been proposed (Patent Literature 1). This method is described to achieve conductivity at a level of a resistance value of $10^{5\text{-}6}$ Ω or more, and to provide an antistatic function and be applicable to a variety of computer-related products, but in view of practical use, the performance is too insufficient to prevent troubles of an electronic circuit damaged by a spark due to static electricity, and to exert a magnetic shield effect of medium waves to hyper-ultrashort waves used in smartphones, satellite broadcasting, taxi wireless communications, etc. This literature has no description on surface hardness, but actually, can only provide a hardness of about HV 280, thus cannot be employed in a field of hard alumite application because of shortage of hardness, and has needed improvement.

[0004] An anode-oxidation film of alumite is formed of a porous layer and a barrier layer (nonporous layer). Alumite was originally developed as an insulation material in Institute of Physical and Chemical Research and leads to today. However, in 1970-80s, National Research Institute for Metals reported in a paper, to confirm presence of conductivity upon removal of a barrier layer and deposition of metal to a surface by an electrolysis coloring technique as a technique of hardening a sulfuric acid film (Non-patent Literature 1)

[0005] Non-patent Literature 1 describes that an increase in hardness to about HV50-100 was achieved with use of sulfuric acid as an electrolysis solution, by lowering voltage from the final voltage of 15-20 V at a film production to near 0.05 V at one time, further followed by switching off, dissolution of a barrier layer, and then Ni electrodeposition. Non-patent Literature 1 further reports presence of electrical continuity between an Al base substrate and a film surface as detected by a tester. However, this production method provides nickel electrodeposit with a film hardness of HV450 at most, and furthermore has the greatest disadvantage of complete lack of corrosion resistance, which is the greatest feature of alumite, thus leading to a product practically less likely to be used. Meanwhile, for zinc electrodeposition, which has no impact on corrosion resistance of an anode-oxidation film, this method has little or no contribution to improve film hardness, and only achieve HV330 at most, which is a quite insufficient hardness as for a hard alumite.

Citation List

Patent Literature

[0006] Patent Literature 1 Re-publication WO 00/01865

Non-patent Literature

[0007] Non-patent Literature 1 Journal of the Surface Finishing Society of Japan, Vol. 33, No. 5, 232-237 (1982)

Summary of Invention

Technical Problem

[0008] An object of the present invention is to provide a production method for providing alumite with electric conductivity and hardness, which has not been applied so far as a light-weight material.

Solution to Problem

[0009] In an embodiment, provided are a material having an anode-oxidation film formed of aluminum that has performance as an electric resistance of $1 \times 10^{-2}\ \Omega$ or less and further has hardness as a film sectional hardness of HV470 or more or an alloy thereof, and a production thereof.

[0010] In an embodiment, provided are a material having an anode-oxidation film formed of aluminum or an alloy thereof that has performance as an electric resistance of $1 \times 10^{-2}\ \Omega$ or less between a surface and a base substrate and has a film sectional hardness of HV470 or more, and a production method thereof, wherein the electric resistance was measured by an electric resistance measurement method with an ohmmeter RM3548 (manufactured by Hioki E.E. Corporation) using direct-current four-terminal sensing (voltage drop method), which is well-suited for low resistance measurement, and wherein the hardness is measured in accordance with the method of JIS-Z2244 (Vickers hardness test) at a load of 0.098 N (10 grf) with a retention time of 15 seconds.

[0011] In an embodiments, performance thus provided includes an electric resistance of $1 \times 10^{-2}\ \Omega$ or less between a surface and a base substrate, and a film sectional hardness of HV470 or more; furthermore, the color difference (ΔE) between before and after heating in a two-week heat resistance test at 300°C is 3.0 or less, preferably 2.5 or less; the color difference (ΔE) between before and after heating in a 1 hour heat resistance test at 500°C is also 3.0 or less, preferably 2.5 or less; and a crack on the surface of a film is not observed visually from an anterior view after heating in air at 200°C for 30 minutes. A film in the present invention is derived from a material formed of aluminum having good conductivity, hardness, and thermal resistance, or alloy thereof, and a production method thereof.

Advantageous Effect of Invention

[0012] The disclosure can provide an aluminum metal material having high conductivity and relatively good hardness and durability, and a production method thereof.

Brief Description of Drawings

[0013]

Fig. 1 shows a whole view of an anode-oxidation film produced by the embodiments.
Fig. 2 depicts a cross section and surface condition of an anode-oxidation film produced by the embodiments.
Fig. 3 shows a schematic view of removal of a barrier layer in second electrolysis in a production step in the embodiments.
Fig. 4 shows a schematic view illustrating film formation at the bottoms of micropores in third electrolysis in the production step in the embodiments.
Fig. 5 shows a schematic view illustrating metal deposition in fourth electrolysis in the production step in the embodiments.
Fig. 6 shows a schematic view illustrating a measurement method of electric resistance of aluminum including an anode-oxidation film in the embodiments.
Fig. 7 illustrates various characteristics of anode-oxidation films produced by the embodiments.

Embodiments for Practicing Invention

[0014] The disclosure will be described based on the embodiments below, but the disclosure is not limited to the following embodiments.

[0015] A corrosion-resistance test in the embodiments is performed by continuous spraying for a month (720 hours) using a JIS-Z2371 neutral salt-water spraying test machine STP-90V-4 (Suga Test Instruments Co., Ltd.), followed by assessment according to JIS-H8679-1 (Assessment Method of Pitting Corrosion Generated in Anode-oxidation Film of Aluminum and Aluminum Alloy - Section 1: Rating Numbering (RN)).

[0016] Rating numbering is applied only to pitting corrosion that passes through a film and reaches a metal substrate; the assessment is not directed to neither surface defect not passing through a film, such as discoloration, and corrosion

generated in a test piece. In relation of rating numbering to a corrosion area ratio of pitting corrosion, RN 10 indicates 0% (no pitting corrosion); RN 9.8 indicates more than 0.00 to 0.02% or less; RN 9.5 indicates more than 0.02% to 0.05% or less; and RN 9.3 indicates more than 0.05% to 0.07% or less. The criteria is according to JIS-H8603-5.6 (Hard Anode-oxidation Film of Aluminum and Aluminum Alloy-Corrosion Resistance), which provides groups as shown in Table 1 in accordance with H8603-4: Type (Quality of Material).

[Table 1]

Type	
Type	Material
Type 1	Expanded materials as defined in JIS H4000, 4040, 4080, 4100, and 4140 except for alloys in Type 2
Type 2(a)	2000 series expanded materials
Type 2(b)	7000 series expanded materials, and 5000 series expanded materials containing 2% or more of magnesium
Type 3(a)	Alloys having less than 2% of copper or less than 8% of silicon, belonging to cast materials as defined in JIS H5202 and H5302
Type 3(b)	Other cast materials except for Type 3(a) materials

[0017] In Table 1, type 1 is defined to have no corrosive pitting (pitting corrosion) after a spray test for 336 hours with a neutral salt-water spraying test machine (RN 10), and qualities of materials other than type I is defined to depend on an agreement between parties in delivery. In the embodiments, the aforementioned rule was applied and the other criteria for a process for 720 hours (one month) are added. Actually, after removal from a salt-water spraying test machine, a corrosion product on the surface is physically or chemically removed and thoroughly washed out, and then confirmation is made that the surface has no attachment, followed by drying and assessment of the size and quantity of pitting corrosion compared to a standard chart of rating numbering.

[0018] The material in the embodiments has electric conductivity and a cross-sectional hardness of HV470 or more. Non-Patent Document 1 only described a material that has electric conductivity and large hardness, but no corrosion resistance as described for corrosion as "A 24 hours salt-water spraying test generates a pit, and 240 hours spraying results in significant coating with a corrosion product on a surface".

[0019] The material in the present invention has corrosion resistance that achieves RN 9.5 or more for Type 1 and 2(a) materials, RN 7 or more for Type 2(b) materials, and RN 8 or more for Type 3(a) materials.

[0020] An anode-oxidation film has a thickness of 6-50 pm, preferably 10-30 pm, and more preferably 20-30 pm as measured after calibration in a calibration standard plate (plastic film) using JIS-H8680-2 (eddy-current measurement) and takes a form of a film having a light amber-based or dark amber-based or black-based tone. Typically, an alumite film tends to change in color from amber to black when having a thicker film and is black-colored when having more than 80pm thickness, but has in heating at 100°C, cracks throughout the whole surface to form a reticulate pattern. The film in the embodiments has a thinner film form and darker and black-based tone than those of conventional films, has a certain hardness, and further carries a characteristic providing no visible observation of cracking.

[0021] A production step in the embodiments includes four electrolysis steps and a post-treatment: a first electrolysis including production of a film to serve as a matrix (Figs. 1 and 2), a second electrolysis including removal of a barrier layer on the bottom of a film in a micropore with use of an electrolysis solution that is the same as or different from that of the first electrolysis (Fig. 3), a third electrolysis including reproduction of a film (Fig. 4), and a fourth electrolysis including deposition of metal into a micropore (Fig. 5).

[0022] Furthermore, a production method in the disclosure enables, through an operation such as sealing as a post-treatment, production of a material containing aluminum or an alloy thereof that forms an anode-oxidation film having an electric resistance of $1 \times 10^{-2}\ \Omega$ or less, a film sectional hardness of HV470 or more in a Vickers hardness test, and a color tone of pale brown-dark brown-black bases.

[0023] Hereinafter each step in a production method will be described in detail.

<First Electrolysis>

[0024] Although the first electrolysis requires addition of certain or more hardness on the film, a sulfuric acid-system alone provides only a hardness of HV350-400 even including an additive. When more hardness is required, an organic acid-based solution can be used alone or with addition of an additive, thereby improving a film hardness of about HV450. However, such an electrolysis condition needs complicated control of a solution and will not be practically used except

for special processes. Additionally, in production of such a film, a second electrolysis method in a process of the embodiments fails to remove a barrier layer in a short time; too long time leads to degradation of the film to form a covering, and too short time causes failure in removal of a barrier layer and thus provides higher resistance, resulting in unevenness in metal deposition in the fourth electrolysis, or generation of spalling (film breakage to expose a base substrate).

[0025] The first electrolysis in the embodiments is a process of production of a film to serve as a matrix, and electrolysis is performed in an electrolysis solution having a solution composition that preferably primarily contains a solution of an organic acid, and further contains inorganic acid and/or an organic acid other than the organic acid used as a primary component, and as appropriate, an additive.

[0026] An electrolysis system applies the anode-oxidization processing with a direct-current waveform at a solution temperature of 0-40°C and a current density of 0.6-3.0A/dm^2 for 10-120 minutes, preferably at the solution temperature of 0-30°C and the current density of 0.8-2.0A/dm^2 for electrolysis duration of 20-90 minutes; alternatively, with a pulsed waveform, a PR pulsed waveform, or an alternative waveform under an average current density of 0.1-10A/dm^2 for the positive current and an average current density of 0.0-10A/dm^2 for the negative current in one cycle at the solution temperature of 0-40°C, preferably under the average current density of 0.6-3.0A/dm^2 for the positive current and the average current density of 0.0-3.0A/dm^2 for the negative current in one cycle at the solution temperature of 10-30°C with using one, two or more combination of the direct-current waveform, the alternative-pulsed waveform and the PR pulsed waveform.

[0027] An anode-oxidation film is formed with a hardness of HV470 or more as measured by a Vickers sectional hardness test, and a color tone of pale brown-dark brown-black bases. Fig. 1 shows a whole image of the anode-oxidation film thus formed, and Fig. 2 shows a cross section (Fig. 2 (A)) and a surface visual field diagram (Fig. 2 (B)) thereof.

<Second Electrolysis>

[0028] Once the film thickness reaches a specified thickness in the first electrolysis, the second electrolysis in the embodiments is performed by keeping power on for 1-5 minutes, and then reducing a voltage to 0 V by stepwise. A method therefor is reducing a voltage to 10V by reducing a final voltage by 1-10 V and retaining the reduced voltage for 10-120 seconds and repeating a cycle of further reducing a voltage by 1-10V and retaining the reduced voltage for 10-120 seconds; and then sequentially reducing to 5V, 3V, 2V, 1V, and 0V. This process is desirably conducted with each retention time of 40 seconds and total voltage effect time of 5-60 minutes, preferably with reducing a voltage by 2-5V and retaining it for 20-120 seconds to reach 0 V for 10-40 minutes. This process removed a barrier layer on the lower part of a micropore. Fig. 3 shows a schematic view thereof.

<Third Electrolysis>

[0029] In the third electrolysis in the embodiments, anode oxidation is desirably performed in an electrolysis solution containing an alkali solution plus an additive, with a direct current waveform at a voltage of 1-30 V for a period of 5-20 minutes at a solution temperature of 0-20°C, preferably at a voltage of 5-15V for a period of 10-15 minutes at 10-15°C. This process forms a film having an alkali film-specific cell-shape (160nm) with about four times larger than that of the size of sulfuric acid film (44nm), and good electric conductivity while having a thickness of 2 pm or less on the bottom of a micropore. Fig. 4 shows a schematic view thereof.

<Fourth Electrolysis>

[0030] The fourth electrolysis is performed in an electrolysis solution derived by including an acidic solution containing a metal salt, and an additive. In the electrolysis solution, the metal salt is dissolved and used as metal ions. Electrolysis is performed using only one or combination of two or more of an alternating current waveform, a pulse waveform, and a PR pulse waveform, at a voltage of 5-40 V for a period of 3-30 minutes at a solution temperature of 10-40°C, preferably at 10-25 V for 5-15 minutes at 16-30°C. When a power supply has polarity, electrolysis is carried out with setting up a cathode (with a member to be treated) and using a carbon plate anode electrode for an anode. Washing in water before and after electrolysis stain is thoroughly performed in deionized water or pure water. This process results in deposition of metal inside a micropore in the anode-oxidation film. Fig. 5 shows a schematic view thereof.

[0031] The electrolysis solutions used in the first and second electrolysis in the embodiments preferably primarily contain an aliphatic or aromatic sulfonic acid- and/or carboxylic acid-based organic acid alone or in a mixture. Alternatively, the solution is an electrolysis solution further containing an inorganic acid and/or an organic acid other than the organic acid used as a primary component as described above, or an additive as appropriate. Their concentrations in the solution are preferably 0.1-4.5 mol/L.

[0032] An electrolysis solution used in the third electrolysis in the embodiments is an alkaline solution that contains a single one or two or more of alkaline compounds and further contains an organic substance as an additive. Specific

examples include sodium hydroxide, sodium carbonate, and sodium phosphate, which are used alone as one species or in combination of two or more species as an electrolysis solution for anode oxidation. Their concentrations in the solution are 0.05-2.0 mol/L, and preferably 0.1-0.5 mol/L.

[0033] As the additive in the third electrolysis solution in the embodiments, carboxylate, carbonate, phosphate, fluoride and aluminate, etc. are used alone as one species or in combination of two or more species. Specific examples include ammonium tartrate, sodium tartrate, ammonium carbonate, sodium carbonate, sodium polyphosphate, sodium fluoride, ammonium fluoride, and sodium aluminate. Their concentrations in the solution are 0.05-1.0 mol/L, and preferably 0.1-0.5 mol/L.

[0034] An electrolysis solution used in the fourth electrolysis is formed of an acidic solution containing a metal salt, and an additive, and the metal salt is used in form of a soluble metal ion. A representative of the acidic solution is a solution primarily containing a sulfuric acid compound or an oxalic acid compound and further containing a carboxylic acid-based organic acid or boric acid as an additive, and the metal salt compound to be used for addition thereto is a compound of gold, silver, copper, platinum, tin, cobalt, nickel, iron, tungsten, molybdenum, chromium, zinc, palladium, zirconium, rhodium, ruthenium, vanadium, titanium, manganese or the like. Zinc is the most preferable to maintain good corrosion resistance of an anode-oxidation film made of a resulting material.

[0035] In the embodiments, a film having a thickness of 6-50 pm, particularly 10-30 pm also includes an anode-oxidation film formed in coloration with pale brown-dark brown-black bases; this black-based film is not derived by stain with a dye, a pigment or the like, but is formed by metal deposition in the fourth electrolysis. This film exhibits little change in color tone visually even in heating both at 300°C for 2 weeks and at 500°C for 1 hour and has high stability.

[0036] Meanwhile, black alumite produced by a common staining system begins to become discolored within a short period after heating at 200°C, and there has recently been few black alumite products produced by a staining system that allows prolonged use without discoloration under an environment of use at higher than 200°C.

[0037] A reason to use a temperature of 300°C in the embodiments for the purpose of detection of color difference ΔE, an indicator of discoloration, is as follows.

[0038] Aluminum has a recrystallization temperature of approximately 250°C, at which temperature a crude crystal to cause work-hardening (work-strain generated in deformation processing such as rolling in normal temperature) remains within an aluminum processed product, and then softens at 250°C or higher and recrystallizes to generate a crystal particle, which has no internal strain and is stable. Practical process requires an operation of softening at approximately 350°C to reduce internal stress, so-called annealing.

[0039] In processing of aluminum, processing at recrystallization temperature or less is referred to as cold working. This processing method always generates work-hardening and thus needs annealing. However, a processed product is rarely used at recrystallization temperature or higher for long periods of time, and therefore, when a thermal resistance test at 300°C, an origin point of softening, reveals no abnormality in discoloration, this temperature can also be used in regard to discoloration in practical use without problems.

[0040] A reason to set a temporary thermal resistance test at 500°C for 1 hour in the embodiments is that a prolonged test at 300°C or higher, an origin point of softening, causes abnormality in a material itself and thus practically has time limitation of 1 hour, therefore, during which it is only necessary to exhibit thermal resistance.

[0041] The organic acid preferably used in the first electrolysis and the second electrolysis in the embodiments is an aliphatic or aromatic sulfonic acid- and/or carboxylic acid-based substance alone or in a mixture. Specific examples include oxalic acid, malonic acid, succinic acid, malic acid, maleic acid, citric acid, tartaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid and terephthalic acid, and sulfonic acid-based substance such as sulfosalicylic acid, sulfophthalic acid and sulfoacetic acid, and these are used alone as one species or in combination of two or more species as an electrolysis solution in anode oxidation.

[0042] Their concentrations in the solution are preferably 0.1-4.5 mol/L. The electrolysis system applies the anode-oxidization processing to produce the anode-oxidation film having the thickness of 6-50 pm with a direct-current waveform at a solution temperature of 0-40°C and a current density of 0.6-3.0A/dm^2 for 10-120 minutes, preferably at the solution temperature of 10-30°C and the current density of 0.8-2.0A/dm^2 for electrolysis duration of 20-90 minutes; alternatively, with a pulsed waveform, a PR pulsed waveform, or an alternative waveform under an average current density of 0.1-10A/dm^2 for the positive current and an average current density of 0.0-10A/dm^2 for the negative current in one cycle at the solution temperature of 0-40°C, preferably under the average current density of 0.6-3.0A/dm^2 for the positive current and the average current density of 0.0-3.0A/dm^2 for the negative current in one cycle at the solution temperature of 10-30°C with using one, two or more combination of the direct-current waveform, the alternative-pulsed waveform and the PR pulsed waveform at the solution temperature of -10-60°C.

[0043] A current density of direct current electrolysis commonly used refers to a value derived by dividing a quantity of electricity (A*secs) by electrolysis time (secs) and the surface area of a material to be treated (dm^2). Since direct current constant-current electrolysis (commonly referred to as direct current electrolysis) has no time-dependent change in current for a material to be treated, current density and average current density are used as synonyms, and have a unit indicated by A/dm^2. However, since a waveform such as a pulse or PR pulse waveform involves, depending on

time, "positive current", "0 (time with no current)" or "negative current", which has reversed polarity, the average current density in a waveform requires to be indicated as the average current density of a positive current and the average current density of negative current that represent values derived by separating one pitch (cycle) of a current waveform into a positive current part and a negative current part and dividing each quantity of electricity (A. sec) by electrolysis time and the surface area of a material to be treated.

[0044] For instance, in electrolysis of a material to be treated having an electrolysis area of 2 dm^2 with a PR waveform, when during a cycle of waveform defined as 10 seconds, a positive current of 2 A flows for 4 seconds, followed by flow of a negative current of 1 A for 6 seconds, the average current density of positive current and negative current are 0.4 A/dm^2 and 0.3 A/dm^2, respectively. In use of positive current only, the average current density of negative current is 0.0 A/dm^2.

[0045] An additive(s) to be added to an electrolysis solution primarily containing an organic acid can be solely one species or two or more species of inorganic acid-based or organic acid-based compounds. Examples of the organic acid-based compounds include the aliphatic or aromatic sulfonic acid- and/or carboxylic acid-based compounds as described above but note that an organic acid other than the organic acid used in the electrolysis solution is used as the additive. In addition, an alcohol-based compound such as ethylene glycol, diethylene glycol, or glycerin can also be used as a solvent and in an amount of not more than 60%. These alcohol-based compounds can be used as a part of solvents in combination with water. The inorganic acid-based compounds to be used can be solely one species or two or more species of boric acid, silicic acid, hydrofluoric acid, sulfuric acid, phosphoric acid, nitric acid and salts thereof pyrophosphoric acid, sulfamic acid and salts thereof and fluoride salts, perfluoride salts, permanganates, and the like. The usage of these additive is less than the usage of the organic acid primarily used in an electrolysis solution, and preferably provides a concentration of 0.001-0.9 mol/L in the solution.

[0046] The fourth electrolysis in the embodiments can produce an anode-oxidation film having coloration with pale brown-black bases, good resistance to weather and discoloration, and good surface hardness. Electrolysis conditions of the fourth electrolysis in that case is use of only one or combination of two or more of an alternating current waveform, a direct current waveform, a pulse waveform, a PR pulse waveform as a current or voltage waveform(s), at a voltage of 5-40 V for a period of 3-30 minutes at a solution temperature of 10-40°C, preferably at 10-25 V for 5-15 minutes at 16-30°C. When a power supply has polarity, electrolysis is carried out with setting up a cathode (with a member to be treated) and using a carbon plate anode electrode for an anode. Washing in water before and after electrolysis stain is thoroughly performed in deionized water or pure water.

[0047] Color difference (ΔE), which is used as a scale for indicating poor discoloration in the embodiments, represents quantifiably "difference in color" that could conventionally be derived only by sensory evaluation. For example, even in the visually same appearance to human eyes, a difference is provided by a method by measuring three-dimensionally hue, saturation and luminosity of a point of a standard color using a colorimeter, also measuring them for a point of a sample color in the same manner, and then indicating a three-dimensional distance of these two points as a color difference. The color difference in the embodiments is derived in a thermal resistance test by setting a color before heating as a standard point, measuring a post-heating color with a spectral calorimeter, and indicating a three-dimensional distance of two points as ΔE, and presently, a numerical value thereof can be displayed automatically by a colorimeter. Generally, a color difference ΔE of about 1 represents a difference allowing discrimination of two colors placed side by side in visual comparison, and a ΔE of about 2-3 represents a difference allowing discrimination of two colors placed apart in visual comparison.

[0048] One of expression methods for colors is the Mansell system (1905), which expresses colors by hue, luminosity and saturation. During an attempt to represent these factors by numerical values, the International Commission on Illumination (CIE) established the XYZ colorimetric system in 1931 and the L*u*v* color space in 1976, which have also been employed in JISZ8781-4 in Japan. Later, it is modified as the L*a*b*color space and employed as the JIS standard. For the color difference in the embodiments, a distance between two points represented by the L*a*b*color space is indicated as color difference (ΔE). The color difference (ΔE) in the embodiments was derived by measuring the same face of samples by a L*a*b*color space method with a spectral calorimeter (CM-700d) manufactured by Konica Minolta, Inc., and calculating each color difference thereof.

[0049] Conventional products begins to discolor to brown by heat at a temperature of higher than 200°C and has a color difference ΔE of above 3.0 at 300°C for approximately 1 hour, However, the anode-oxidation film in the embodiments can retain a ΔE of 3.0 or less even in a thermal resistance test at the same temperature for 2 weeks, and when heated for a short time, it also provides a similar result in a thermal resistance test at 500°C for 1 hour. Meanwhile, in the art of electrolytic colored film, it has been proposed that a film having deposition of nickel or cobalt into micropores of a porous material remains unchanged in brown coloring at 400°C for 100 hours (4 days), but no material has been found yet that has a ΔE of 3.0 or less in heat treatment at 300°C for 2 weeks, among black-based anode-oxidation films. Furthermore, a surface hardness of about HV470 leads to prevention of damage in practical use.

[0050] The anode-oxidation film in the embodiments also has a hardness of HV470 or more in a Vickers hardness test, and further has a good characteristic of having electromagnetic field properties similar to that of an aluminum base

substrate in an electromagnetic shield effect of 500 KHz-1000 MHz.

[0051] Measurements of an electromagnetic shield effect of the anode-oxidation film produced in the embodiments was caried out by measuring an electric field and a magnetic field in the range of 100 KHz-1000 MHz (1 GHz) by the KEC method in the testing division, General Incorporated Association of KEC Electronic Industry Development Center. The results gave 30 dB or more in 500 KHz-1000MHz (1 GHz) as a certifiable numerical value, which is the same value as that of an aluminum base substrate and represents a shield effect comparable with the limit value of aluminum. This adds a function as a material with thermal resistance, less corrosion due to corrosion resistance, long-term stable retention of a shield effect, and further, resistance to damage, and good thermal absorption and emission, and the film thus obtained is expected to be a non-conventional material.

[0052] An electromagnetic wave is a wave (wave motion) formed by change of an electric field and a magnetic field in a space. Light and radio waves are types of electromagnetic waves, which are roughly classified into and generally respectively referred to as: radio waves, having a wavelength longer than infrared rays (having a size of mm or more); infrared rays, having a wavelength of up to about 1 pm; visible light, having a wavelength of up to 0.7-0.3 pm; ultraviolet rays having a shorter wavelength of several nm; and X-rays, having a wavelength of 10nm -1 pm. An electromagnetic wave also has both characteristics of a wave and a particle, and exhibits various properties as a wave, such as scattering, refraction and interference, corresponding to wavelength, as well as can be counted for the number as a particle.

[0053] In the embodiments, radio waves to be used are roughly categorized into longwave (low frequency, LF), mediumwave (medium frequency, MF), shortwave (high frequency, HF), very short wave (very high frequency: VHF), ultrashort wave (ultrahigh frequency: UHF), centimeter wave (super high frequency: SHF), millimeter wave (extremely high frequency: EHF), and submillimeter wave. Among these, in the range of mediumwave to ultrashort wave of 500 KHz-1000 MHz (1 GHz), one object is to provide, as a primary application, a shield for a wavelength range used in cellular-phones, smartphones, TVs, taxi radio, in-flight telephone, AM radio, FM broadcast, ships, international broadcast, beacons for ships and planes.

[0054] Recently, cellular phones become smartphones; many devices such as robots and drones etc. becomes to start wireless communications and electronic devices becomes much familiar about us. These ones require much more electromagnetic compatibility (EMC measures) for receiving necessary electro-magnetic wave while omitting (shielding) unnecessary electro-magnetic wave. Furthermore, in addition to noise countermeasure between devices, there are practically many people that worry about effects to human body such as electro-magnetic hypersensitivity.

[0055] Now, generally the electro-magnetic shield addresses to 300Hz-3THz frequency so called to RF. Basic strategy of the electro-magnetic shield stands on multi-reflection losses provided by reflection loss, absorption loss and combinations thereof to improve shield performance. The term "reflection loss" refers to loss (attenuation) by reflection on the shield surface when the electro-magnetic wave enters and passes through the shield material; the term "absorption loss" refers to absorption due to conversion to induction current in the shield material when the electro-magnetic wave enters the shield material; and the term "multiple-reflection loss" refers to attenuation by combination of layered shield-materials in which the electro-magnetic wave penetrating to the inside of the shield material is partly reflected; partly pass through; then reaches the next shield material; and the reflection and penetration are repeated again and again to improve the shield effect.

[0056] The effect of the electromagnetic shield may be represented by using decibel (dB). This is a unit that represents how much the electro-magnetic wave is attenuated before and after the shield and derived by the following calculation equation.

[Eq. 1]

$$\text{Decibel(dB)} = 20\text{Log}_{10}(E_0/E_1)$$

E_0: Electric Field Intensity without shield material (V/m)
E_1: Electric Field Intensity after passing shield material (V/m)

[0057] There are popular methos for evaluation of electro-magnetic shield performance and one is a "KFC method" that has been developed by Incorporated Association KANSAI ELECRTONIC INDUSTORY CENTER and another is an "ADVANTEST method" that has been developed by ADVANTEST CORPORATION and in the present embodiment, both method may be applied. Here, relations between decibel, shield rate, and attenuation rate is shown in Table 2.

[Table 2]

Relation between Decibel (dB) and Shield Rate		
SHEILD EFFECT	SHIELD RATE	ATTENUATION RATIO
-20 dB	90%	1/10
-40 dB	99%	1/100
-60 dB	99.90%	1/1000
-80 dB	99.00%	1/10000

[0058] An aluminum anode-oxidization film has been firstly developed as insulation material and becomes the current anode-oxidization layer by multiple improvements after passing long years so that there is no doubt for contribution to development of aluminum; however, an implementation density becomes much increased by recent development of semiconductors, and accordingly, electronic devices have become rapidly smaller and smaller. With this reason, spaces becomes narrow extremely, which have not raised problems so far, such that the sparks by static electricity occur and the spark damages severely the electronic devices. For addressing to this problem, the film has been required, which is a conductor that the static electricity can be constantly leaked to a ground level without storing on the surface, has hardness and furthermore may satisfy LCA. According to the present embodiment, the film of an anode-oxidization film, which has electronic conductivity and hardness as well as heat resistance, electro-magnetic shield effect, heat dissipation and heat absorption, has been developed. When these features are combined, it is expected that further small-sized electronic devices, shield effect in the 5G communication, and usage for chargers of smartphones.

Examples

[0059] Hereafter, embodiments of the present disclosure will be described using specific examples. Now, in examples, a method for measuring electric resistance was performed by using a direct-current type four-terminals method (voltage drop method) as shown in Fig. 6, which is superior in low resistance measurements. Electrodes 11 of an ohmmeter 6 RM3548 (available from Hioki E.E. Corporation), which were prepared by plating gold to 1cm^2 cupper, were placed to a surface 12 of anode-oxidization film and a base substrate 3, and then the electric resistance was measured by applying weight of 50g/cm^2. Vickers Hardness Test represents an averaged film hardness measured using a micro hardness meter (HMV-G-XY-D) available from Shimadzu Co. with a microscope cross-section measurement method under a weight load of 10gf for 15 seconds.

[0060] Here, when a film thickness not more than 20 pm, the hardness values were those measured under the same load and time duration using a knoop-type indenter. The film thickness values represent average thickness values measured using an eddy-current film thickness meter (LH-373) available from Kett Electric Laboratory Co. Ltd. A corrosion resistance test was performed using a neutral salt-water spraying test machine STP-90V-4 defined by JIS-Z2371 (available from Suga Test Instruments Co., Ltd.) after continuous spraying duration of one month (720 hours) under the measurement method regulated in "Evaluation method of point Corrosion Occurred on Anode-oxidized film of Aluminum and Aluminum alloy"; Rating Number Method (RN) defined by JIS-H8679-1 as an evaluation method.

[0061] A practical evaluation was performed by comparing specimens with a rating number standard drawing and table after taking out from the salt-water spraying test machine, then removing physically chemically corrosion products, and drying them. There are two heat resistance tests; one is performed by the heat-treatment of 300°C for two weeks and the other is performed by the heat-treatment of 500°C for one hour and then measurements were performed by a spectral colorimeter (CM-700d) available from KONICA MINOLTA, INC. under room temperature; color difference values after heat treatment were represented by color difference value (ΔE) in the L*a*b* color space coordinate. Measurements of electro-magnetic shield effect represent the results of electric and magnetic field measurements of 100KHz-1000MHz (1GHz) according to the KFC method conducted by a Testing Division of Incorporated Association KANSAI ELECRTONIC INDUSTORY CENTER. Thermal emission rates are total emission rates of middle wave infrared light of 3-6 pm and of the wavelength of 3-25 pm-far infrared light range represented in percentages (%) when the emission rate of full radiator is to be 100% measured by using a spectrophotometric emission rate measurement system (IRTracer-100) as an infrared emission rate measurement device and holding the temperature of specimens at 100 °C.

[Example 1]

[0062] A testing piece of aluminum A1050 composition (Si 0.25%, Mn not more than 0.05%) having 50×100×t1.0mm was applied to a pre-processing comprising emulsion cleaning of 45°C ×5 minutes-5% nitrous acid at room temperature

×3 minutes-etching with 20% sodium hydroxide at room temperature × 1 minute-desmutting with 10% sulfuric acid at room temperature × 3 minutes; then a first electrolyte solution was prepared as an admixture of malonic acid 0.7mol/L and an additive of sulfuric acid of 0.05mol/L and a first electrolyzation was performed at the solution temperature of 25±1°C and at the current density of 1.4 ± 0.4A/dm^2 for 70 minutes using a direct current waveform power source.

[0063] A second electrolysis was performed as follows: keeping the last voltage 70V of the first electrolysis for 2 minutes while not turn-off the power source; then decreasing the voltage for 5V and keeping for 60 seconds; next decreasing the voltage for 5V and keeping for 60 seconds again; repeating this cycle to the voltage of 10V; further then decreasing the voltage as 7V, 5V, 3V, 2V, 1V, and 0V, sequentially. The holding time was 60 seconds, respectively and it takes 17 minutes to reaching 0V.

[0064] After completing the second electrolysis, water rinsing was performed sufficiently, and a third electrolysis was performed in a solution composition including sodium hydroxide of 0.3mol/L with an additive of ammonium tartrate of 0.05mol/L at the solution temperature of 5°C and at a current density of 0.8 A/dm^2 for 10 minutes using the direct current waveform.

[0065] Then, after sufficient rinsing, a fourth electrolysis was performed by alternative current using the solution having the solution composition of Zinc sulfate of 300g/L, ammonium sulfate of 28g/L, boric acid of 25g/L at pH=2-3.5, a bath temperature of 29±1°C, and a current density of 1.0A/dm^2 for 20 minutes.

[0066] Then, further a boiling water pore-sealing treatment was performed at 95-98°C for 20 minutes and as the results, an anode-oxidization film with an electric resistance value of 8 × $10^{-3}\Omega$ between a film surface and an aluminum base substrate; an average film hardness of HV475 by the microscope cross-section measurement method; an average film thickness of 21 pm; a color tone of black near to dark brown region, a corrosion resistance of RN9.8 at 720 hours; an electro-magnetic shield effect not less than 43 dB for electric field and not less than 36dB for magnetic field; a heat resistance with the color difference (ΔE) of 2.6 in the L*a*b* color space at about 300 °C and 2.2 at 500°C; a total emission rates of middle wave infrared light of 3-6 pm of 78.3% and of the wavelength 3-25pm-far infrared light range of 86.9% was obtained. Furthermore, any crack was not observed in the obtained anode-oxidization film.

[Comparable Example 1]

[0067] Using a test piece of A1050 composition with 100×50×t1.0 mm and after cleaning organic materials and after etching of 30 second by a sodium hydroxide of 50g/dm^3 at 70 °C, a first electrolysis was performed in a sulfuric acid of 98 g/dm^3 and a voltage of 20V (approximately 3A/dm^2) for 30 minutes while using carbon as a counter electrode. A second electrolysis for removing a barrier was performed by decreasing a bath voltage to 0.08V within 3 minutes before the termination of electrolysis; then the power source was turned off and further then a galvanic-type dissolution was performed for 15 minutes with connecting the test piece and the counter electrode (carbon) by a conductive line. The third electrolysis was performed for electrolytic deposition of Zinc and a solution composition was Zinc sulfate of 350g/L-ammonium sulfate of 30g/L-boric acid of 30g/L-Dextrin of 15g/L, and a counter electrode of Zinc at pH=2-3, bath temperature 30±1 °C, and current density of 1.0A/dm^2 for 20 minutes.

[0068] The resulting anode-oxidization film had the electric resistance value of 4×$10^{-1}\Omega$, the cross-sectional film hardness of HV380, the cross-sectional film thickness of 26 pm, and the corrosion resistance of RN 9.0 and mesh-shaped cracks appeared after heating and cooling to 200°C. In the Comparable Example 1, the targeted material was not obtained with regard to insufficient resistance, corrosion resistance, electro-magnetic shield effect, heat resistance, and infrared emission rate.

[Comparable Example 2]

[0069] Using a test piece of A1100 composition with 100×50×t1.0 mm and after cleaning organic materials and after etching of 30 second by a sodium hydroxide of 50g/L at 70°C-etching for 30 minutes-30% nitric acid at room temperature, and desmutting by immersing 10 seconds; a first electrolysis was performed in a sulfuric acid of 100g/L and a voltage of 20V for 20 minutes while using carbon as a counter electrode. A second electrolysis for removing a barrier was performed by decreasing a bath voltage to 0V immediately; then the voltage of 0.1V was applied. The third electrolysis was performed for electrolytic deposition and a solution composition was Nickel sulfate of 280g/L, Nickel chloride of 45g/L, boric acid of 30g/L, Cobalt sulfate of 15g/L, saccharine 1g/L at pH=4.0, bath temperature 50-60°C, current density 0.15 A/dm^2 and a Ni counter electrode for 10 minutes. The fourth electrolysis was performed using nickel acetate of 5 g/L, boric acid of 5g/L at 70°C for 20 minutes, and furthermore boiled water treatment with pure water not less than 98°C was performed for 20 minutes.

[0070] The resulting anode-oxidization film had the cross-sectional film thickness of 22pm, the electric resistance value of 1.67×$10^{-1}\Omega$ in average, the hardness in the knoop type of HV380, the corrosion resistance of RN 8; the heat resistance with the color difference (ΔE) of 3.8 at 300°C for 2 weeks and of 3.5 at 500°C for 1 hour; a total emission rates of middle wave infrared light of 3-6μm of 0.631 (63.1%) and of wavelength 3-25pm-far infrared light range of 72.8% was obtained.

Furthermore, any crack was not observed in the obtained anode-oxidization film. Furthermore, when the obtained anode-oxidization film was heated and cooled to 200°C, mesh-shaped cracks appeared such that the targeted material was not obtained with regard to insufficient resistance, corrosion resistance, electro-magnetic shield effect, heat resistance, and infrared emission rate.

[Comparable Example 3]

[0071] The materials, pre-processing, first electrolysis, fourth electrolysis, pore-sealing treatment and measurements of films were performed similar to Example 1. The second electrolysis and the third electrolysis were omitted and then the fourth electrolysis was performed. When the surface was observed, spalling was generated, and the film was found likely to craters of a volcano such that subsequent processing was stopped.

[Comparable Example 4]

[0072] The materials, pre-processing, fourth electrolysis, pore-sealing treatment and measurements of films were performed similar to Example 1. The first electrolysis was performed in sulfuric acid of 15% under the condition of current density of 1.0-1.1 A/dm^2, electrolysis voltage of 14-16V, bath temperature of 19-20°C and electrolysis duration 60 minutes. After the electrolysis, sufficient rinsing was applied; the second and fourth electrolysis were omitted; and the fourth electrolysis and pore-sealing treatment were performed to obtain an anode-oxidization film.

[0073] The resulting anode-oxidization film was even dark brown; an insulator with the electric resistance not less than $10^6\Omega$ between the film surface and the aluminum base substrate; the hardness in the knoop type of HV290; the average film thickness of 20um; the corrosion resistance of RN 10 with no corrosion; an electro-magnetic shield effect not less than 45 dB for electric field and not less than 28dB for magnetic field; a heat resistance with the color difference (ΔE) of 3.2 in the L*a*b* color space at about 300 °C for 14 days and the color difference (ΔE) of 3.1 at 500°C for 1 hour; the total emission rates of middle wave infrared light of 3-6 pm of 65.3% and of the wavelength 3-25pm-far infrared light range of 75.2%; and mesh-like cracks appeared. According to this method, except for the hardness, the targeted material was not obtained with regard to insufficient resistance, corrosion resistance, electro-magnetic shield effect, heat resistance, and infrared emission rate.

[Comparable Example 5]

[0074] The materials, pre-processing, first electrolysis, second processing, fourth electrolysis, pore-sealing treatment and measurements of films were performed similar to Example 1 with omitting the third electrolysis and an anode-oxidization film was produced. The obtained anode-oxidization film had the electric resistance of 36.2Q between the film surface and the aluminum base substrate; the hardness by the microscope cross-section measurement method of HV438; the average film thickness of 21μm; the color tone of black near dark brown; the corrosion resistance of RN 8 for 720 fours (corrosion area rate exceeded 0.10% and was not more than 0.25%); an electro-magnetic shield effect not less than 42 dB for electric field and 27dB for magnetic field; a heat resistance with the color difference (ΔE) of 3.3 in the L*a*b* color space before and after heating to 300 °C and the color difference (ΔE) of 3.1 at 500°C; a total emission rates of middle infrared-light wavelength region of 3-6 pm of 65.7% and of the wavelength 3-25pm-far infrared light range of 73.4%; and mesh-like cracks did not appear. In Comparative Example 5, the targeted material was not obtained with regard to insufficient resistance, hardness, corrosion resistance, electro-magnetic shield effect, heat resistance, and infrared emission rate.

[Comparable Example 6]

[0075] The materials, pre-processing, first electrolysis, second processing, third electrolysis, pore-sealing treatment and measurements of films were performed similar to Example 1 with omitting the fourth electrolysis. As the result, the electric resistance was not less than $10^6\Omega$ between the film surface and the aluminum base substrate; the hardness by the microscope cross-section measurement method was HV437; the average film thickness was 19um; the color region was dark brown; the corrosion resistance was RN 6 for 720 fours (corrosion area rate exceeded 0.50% and was not more than 1.00%); an electro-magnetic shield effect was not less than 43 dB for electric field and was 26dB for magnetic field; a heat resistance with the color difference (ΔE) was 3.2 in the L*a*b* color space before and after heating to 300 °C and the color difference (ΔE) was 2.8 at 500°C; a total emission rates of middle infrared-light wavelength region of 3-6μm was 71.3% and of the wavelength 3-25pm-far infrared light range was 78.5%; and mesh-like cracks did not appear. However, in Comparative Example 6, the targeted material was not obtained with regard to insufficient resistance, hardness, corrosion resistance, electro-magnetic shield effect, heat resistance, and infrared emission rate.

[Comparable Example 7]

[0076] The materials, pre-processing, first electrolysis, second processing, third electrolysis, pore-sealing treatment and measurements of films were performed similar to Example 1 and the fourth electrolysis was applied by a direct current waveform and the solution composition included Tin sulfate 10g/l, Nickel sulfate 6 hydrate 15g/L, sulfuric acid 15g/L, tartaric acid, and 8g/L under the condition of pH=1, bath temperature 23°C , electrolysis voltage 16V for 20 minutes as a secondary electrolysis. Furthermore, boiling water pore-sealing at 95°C for 20 minutes was applied as the pore-sealing processing. As the result, the electric resistance was not less than 0.3Q between the film surface and the aluminum base substrate such that the sufficient electric resistance was not obtained. The hardness by the microscope cross-section measurement method was HV478; the average film thickness was 21μm; the color region was deep dark brown; the corrosion resistance was RN 8 for 720 fours (corrosion area rate exceeded 0.10% and was not more than 0.25%); an electro-magnetic shield effect was not less than 33 dB for electric field and was 30dB for magnetic field; a heat resistance with the color difference (ΔE) was 3.5 in the L*a*b* color space before and after heating to 300°C and the color difference (ΔE) was 33 at 500°C; a total emission rates of middle infrared-light wavelength region of 3-6 pm was 64.8% and of the wavelength 3-25pm-far infrared light range was 87.5%; and mesh-like cracks did not appear. However, in Comparative Example 7, the targeted material was not obtained with regard to insufficient resistance, hardness, corrosion resistance, electro-magnetic shield effect, heat resistance, and infrared emission rate except for the hardness and the middle-far infrared emission rate.

[Example 2]

[0077] The materials, pre-processing, second processing, third electrolysis, fourth electrolysis, pore-sealing treatment; measurements of films were performed similar to Example 1; and the solution composition for the first electrolysis was same. The electrolysis condition was changed to comprise; using PR pulse waveform; setting a plus side current density to be 2.0A/dm^2 while setting a minus side current density to be 0.5A/dm^2; setting the maximum voltage at the plus side to be 70V while setting the maximum voltage at the minus side to be -15V; setting one pulse to be 3.3ms; applying 20 pulses at the plus side and applying 3 pulses at the minus side; inserting an idle period of three pulses length when polarity changed; and setting the above pulse combination to be one cycle. As the result of the processing under the bath temperature of 25±1°C and the processing of 70 minutes, the color of film was deep dark brown and subsequently the processing was followed as the second, third, fourth electrolysis and pore-sealing processing. The resulting electric resistance was not less than $2\times10^{-3}\Omega$ between the film surface and the aluminum base substrate; the average hardness was HV480; the average film thickness was 21μm; the color tone was black near deep dark brown; the corrosion resistance was RN 9.8 for 720 fours; an electro-magnetic shield effect was not less than 38 dB for electric field and 32dB for magnetic field; a heat resistance with the color difference (ΔE) was 2.6 in the L*a*b* color space before and after heating to 300 °C and the color difference (ΔE) was 2.2 at 500 °C ; a total emission rates of middle wave infrared light of 3-6 pm was 90.7% and of the wavelength 3-25pm-far infrared light range was 93.4%; and mesh-like cracks did not appear and an anode-oxidization film having excellent performances was obtained.

[Example 3]

[0078] The materials, pre-processing, second processing, third electrolysis, fourth electrolysis, pore-sealing treatment; measurements of films were performed similar to Example 1; and the solution composition for the first electrolysis was changed to tartaric acid 3%. The electrolysis condition was changed to comprise; applying alternative and direct currents altogether; setting a "+" side current density to be 1.5A/dm^2 while setting a "-" side current density to be 0.5A/dm^2; setting the voltage of the direct component to be 50V while setting the voltage of the alternative component to be 90V; setting the bath temperature to be 25°C and setting the electrolysis duration to be 60 minutes. As the result the electric resistance was not less than $3\times10^{-3}\Omega$ between the film surface and the aluminum base substrate; the average hardness was HV475; the color tone was black near deep dark brown; the average film thickness was 36pm; the corrosion resistance was RN 9.5 for 720 fours; an electro-magnetic shield effect was not less than 35 dB for electric field and 32dB for magnetic field; a heat resistance with the color difference (ΔE) was 2.7 in the L*a*b* color space before and after heating to 300°C and the color difference (ΔE) was 2.4 at 500°C; a total emission rates of middle infrared- light wavelength region of 3-6 pm was 76.3% and of the wavelength 3-25pm-far infrared light range was 82.1%; and mesh-like cracks did not appear and an anode-oxidization film having excellent performances was obtained.

[0079] Here, the results of the above experiments are summarized in Table of Fig. 7. In the table, signs "-" means the measurements were not conducted or measurements were impossible.

Industrial Availability

[0080] The material of the present invention is the anode-oxidization film having the film of low resistance not more than $1 \times 10^0\ \Omega$ and the hardness not less than HV450, and hence, the material may be expected to be used to a light-weight casing with electric conductivity while being hard to scratches, damage protection from the spark discharge of static electricity in electronic devices, shield effects, specifically to the magnetic field of 500kHz-1000MHz, the material for un-used energy temperature band having the heat resistance providing the color difference not more than ΔE3.0 under 300 °C for two weeks and 500°C for one hour, and a light-weight, hard and slidable conductive material.

Description of Numerals and Signs

[0081]

1.	fine pore	2.	wall
3.	base substrate (aluminum)	4.	porous layer
5.	barrier layer	6.	re-coated film
7.	metal deposition in fine pores	8.	ohmmeter: R3548
9.	DC constant voltage power source	10.	voltage meter
11.	metal plated electrode	12.	anode-oxidization film

Claims

1. A material consisting of aluminum or an aluminum alloy including an anode-oxidization film which has a performance of an electric resistance not more than $1\times10^{-2}\Omega$ and a film cross-sectional hardness not less than HV470 in a Vickers hardness test.

2. The material consisting of aluminum or an aluminum alloy of claim 1, wherein the material has the anode-oxidization film having corrosion resistance of the material not less than RN (rating number) 7 under a salt-water spraying test for 720 hours.

3. The material consisting of aluminum or an aluminum alloy of claim 1 or 2, wherein the material includes the anode-oxidization film without appearing cracks after heating at 200°C for 30 minutes when viewed from a front side.

4. The material consisting of aluminum or an aluminum alloy of claims 1, 2, or 3, wherein the material includes the anode-oxidization film of which an electro-magnetic shield effect of the material having the anode-oxidization film of aluminum or aluminum alloy is not less than 30 dB in a range of 500KHz-1GHz.

5. The material consisting of aluminum or an aluminum alloy of any one of claims 1-4, wherein the material includes the anode-oxidization film of which heat resistance provides a color difference (ΔE) not more than 3.0 in a heat resistance test at 300°C for two weeks before and after heating and cooling.

6. The material consisting of aluminum or an aluminum alloy of any one of claims 1-5, wherein the material includes the anode-oxidization film of which heat resistance provides a color difference (ΔE) not more than 3.0 in a heat resistance test at 500°C for one hour before and after heating and cooling.

7. The material consisting of aluminum or an aluminum alloy of any one of claims 1-6, wherein the material includes the anode-oxidization film of which total emission rate is not less than 75% (0.75) in a middle far infrared region in a wavelength of 3-6pm and is not less than 80% (0.80) in a middle far infrared - far infrared in a wavelength of 3-25pm when a measurement temperature of measured substance is set to 100°C and an emission rate of a full radiator is to be 100% (1.00).

8. The material consisting of aluminum or an aluminum alloy of any one of claims 1-6, wherein a thickness of a film is 6-50μm and a color tone ranges from pale dark brown, deep dark brown to black.

9. A production method for a material consisting of aluminum or an aluminum alloy including an anode-oxidization film, the method comprising the steps of:

applying a first electrolysis using a first electrolysis solution including one, two or more kind selected from an organic compound selected from aliphatic or aromatic sulfonic acid, carboxylic acid and/or an anhydrate thereof or a salt thereof and/or an inorganic compound of sulfuric acid or sulfuric acid;
applying a second electrolysis in an electrolysis solution which is same with the first electrolysis solution or is different from the first electrolysis solution while decreasing voltages stepwise and substantially to 0V and then taking out an anode-oxidization product after completing the second electrolysis;
applying a third electrolysis in an alkalic electrolysis solution for 5-20 minutes; and
applying a fourth electrolysis in an acidic solution including a metal element.

10. The production method of claim 9, wherein the material includes an anode-oxidization film which has a performance of an electric resistance not more than $1\times10^{-2}\Omega$ and a film cross-sectional hardness not less than HV470 in a Vickers hardness test.

11. The production method of claim 9 or 10, wherein a current or voltage waveform for an anode-oxidization processing of the aluminum or an aluminum alloy uses the waveforms selected from one, two or more combined waveform consisting of a direct current waveform, an alternative current waveform, an overlapped waveform of the direct current waveform and the alternative current, a pulsed waveform, and a PR-pulse waveform.

12. The method of any one of claims 9-11, wherein the first electrolysis is performed using the organic and/or inorganic electrolysis solution at a solution temperature of 0-40°C, a current density of 0.6-3.0A/dm^2 for 10-120 minutes; the second electrolysis decreases the voltage from a final voltage to 0V by 1-10V while holding the voltage for 10-120 seconds, decreases the voltage by 1-10V while holding the voltage for 10-120 second, repeats a cycle of decreasing and holding stepwise to 10V, after holding the voltage for 10-60 seconds, then decreases the voltage to be 5V, 3V, 2V, 1V, and 0V sequentially while setting a holding duration to be 20-120 seconds within 5-60 minutes in total, and after that sufficient water rinsing is applied; the third electrolysis is performed in an alkaline electrolysis solution at a solution temperature of 0-30°C and a voltage of 1-100V for a time duration 2-20 minutes and sufficient water rinsing is applied; and the fourth electrolysis is performed in the acidic solution including the metal element at a solution temperature of 10-40°C and a current density of 0.1-2.0A/dm^2 for a time duration 2-60 minutes.

Fig. 1

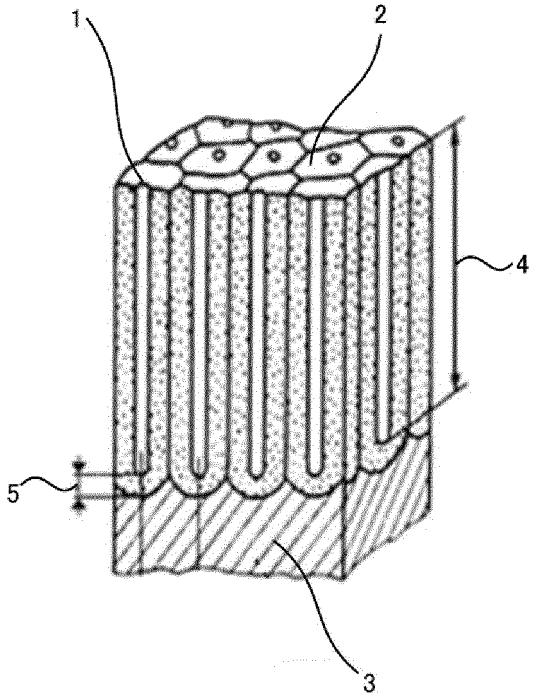


Fig. 2

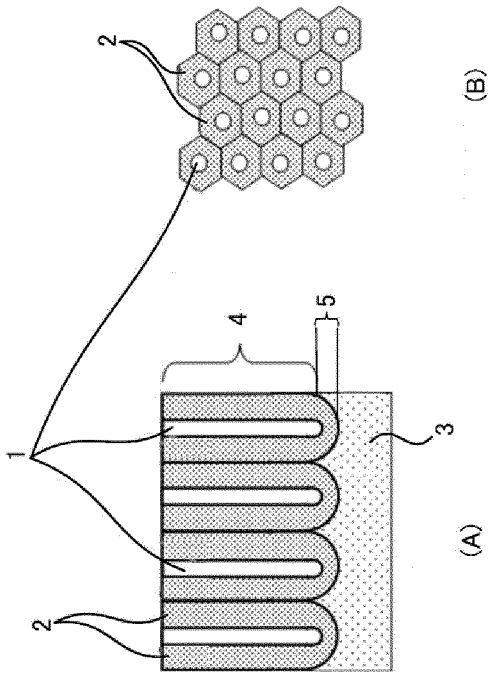


Fig. 3

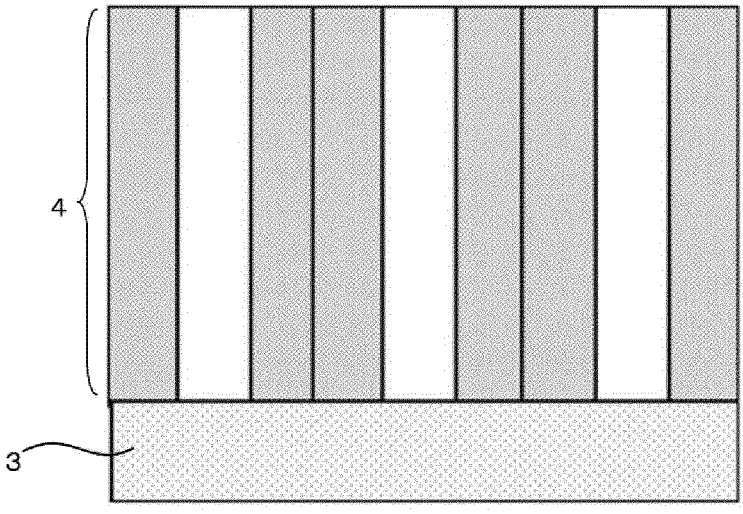


Fig. 4

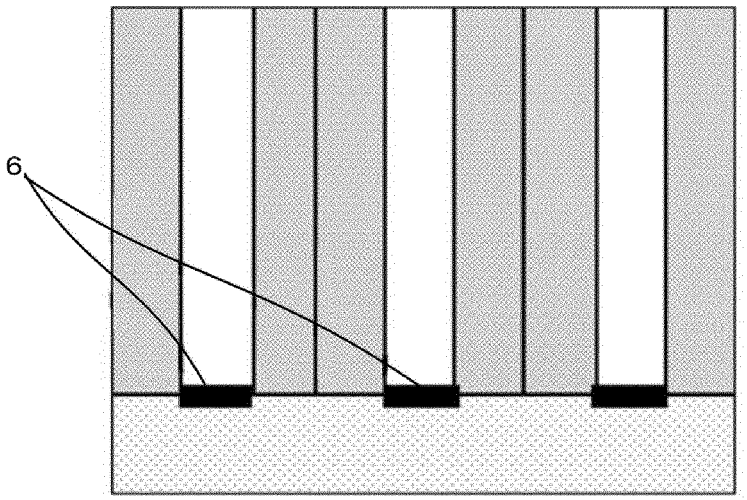


Fig. 5

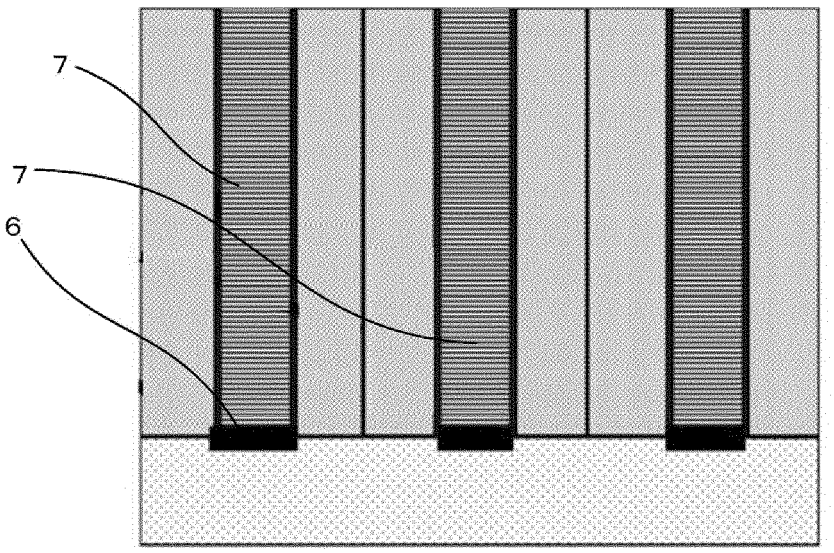


Fig. 6

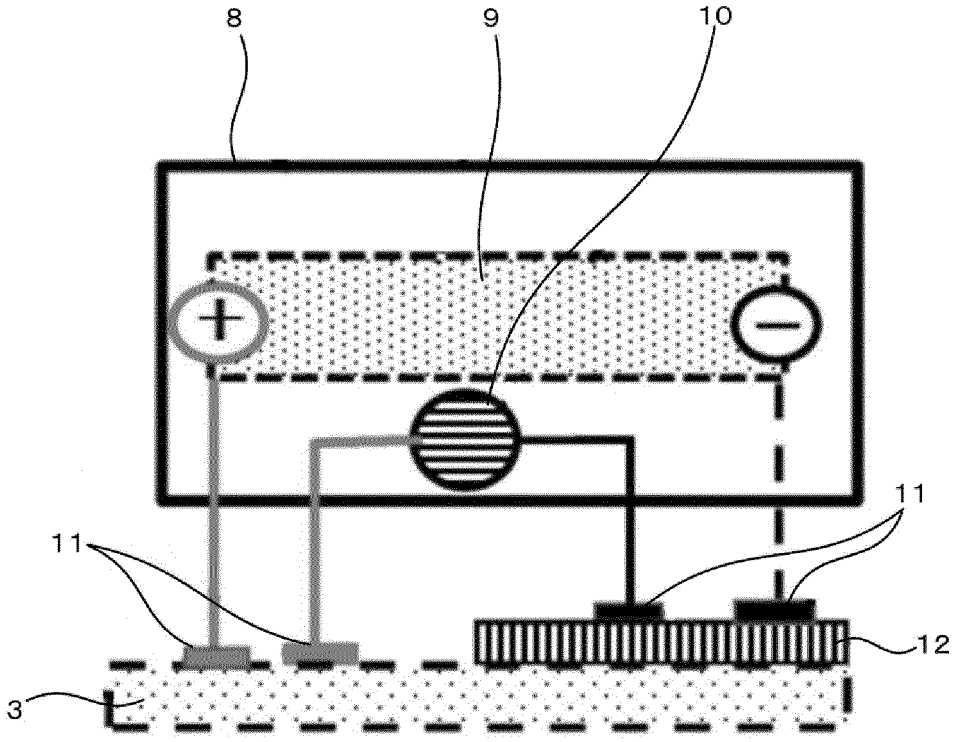
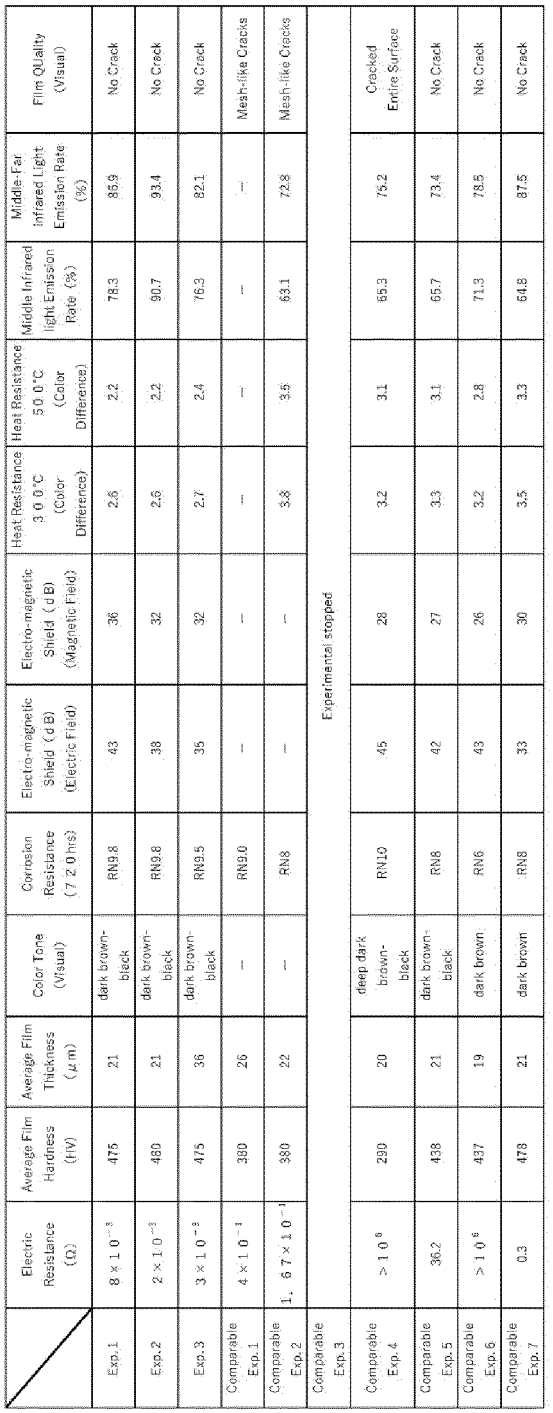


Fig. 7



	Electric Resistance (Ω)	Average Film Hardness (HV)	Average Film Thickness (μm)	Color Tone (Visual)	Corrosion Resistance (720 hrs)	Electro-magnetic Shield (dB) (Electric Field)	Electro-magnetic Shield (dB) (Magnetic Field)	Heat Resistance 300°C (Color Difference)	Heat Resistance 500°C (Color Difference)	Middle Infrared light Emission Rate (%)	Middle-Far Infrared Light Emission Rate (%)	Film QUality (Visual)
Exp.1	8×10^{-3}	475	21	dark brown-black	RN9.8	43	36	2.6	2.2	78.3	85.9	No Crack
Exp.2	2×10^{-3}	480	21	dark brown-black	RN9.8	38	32	2.6	2.2	90.7	93.4	No Crack
Exp.3	3×10^{-3}	475	36	dark brown-black	RN9.5	35	32	2.7	2.4	76.3	82.1	No Crack
Comparable Exp.1	4×10^{-1}	380	26	—	RN9.0	—	—	—	—	—	—	Mesh-like Cracks
Comparable Exp.2	1.67×10^{-1}	380	22	—	RN8	—	—	3.8	3.6	63.1	72.8	Mesh-like Cracks
Comparable Exp.3	Experimental stopped											
Comparable Exp.4	$> 10^{6}$	290	20	deep dark brown-black	RN10	45	28	3.2	3.1	65.3	75.2	Cracked Entire Surface
Comparable Exp.5	36.2	438	21	dark brown-black	RN8	42	27	3.3	3.1	65.7	73.4	No Crack
Comparable Exp.6	$> 10^{6}$	437	19	dark brown	RN6	43	26	3.2	2.8	71.3	78.5	No Crack
Comparable Exp.7	0.3	478	21	dark brown	RN8	33	30	3.5	3.3	64.8	87.5	No Crack

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2021/040703

A. CLASSIFICATION OF SUBJECT MATTER

C25D 11/04(2006.01)i; ***C25D 11/06***(2006.01)i; ***C25D 11/18***(2006.01)i; ***C25D 11/24***(2006.01)i
FI: C25D11/04 302; C25D11/06 C; C25D11/18 311; C25D11/24 302

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)

C25D11/04; C25D11/06; C25D11/18; C25D11/24

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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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.
Y	JP 2019-147988 A (FUJIFILM CORP) 05 September 2019 (2019-09-05) claims, paragraphs [0049]-[0092]	9, 11, 12
A		1-8, 10
Y	JP 2002-332578 A (CANON INC) 22 November 2002 (2002-11-22) paragraphs [0060]-[0069]	9, 11, 12
A	JP 2006-291259 A (KUMABO METAL KK) 26 October 2006 (2006-10-26) entire text, all drawings	1-12
A	WO 00/01865 A1 (IZUMI TECHNO INC) 13 January 2000 (2000-01-13) entire text, all drawings	1-12
A	JP 2021-70865 A (ART FIRST CO LTD) 06 May 2021 (2021-05-06) entire text, all drawings	1-12
E, X	JP 2021-181609 A (ART FIRST CO LTD) 25 November 2021 (2021-11-25) claims	1-12

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

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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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
11 January 2022	**18 January 2022**
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/JP2021/040703

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2019-147988 A	05 September 2019	(Family: none)	
JP 2002-332578 A	22 November 2002	(Family: none)	
JP 2006-291259 A	26 October 2006	(Family: none)	
WO 00/01865 A1	13 January 2000	(Family: none)	
JP 2021-70865 A	06 May 2021	(Family: none)	
JP 2021-181609 A	25 November 2021	(Family: none)	

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 0001865 A **[0006]**

Non-patent literature cited in the description

- *Journal of the Surface Finishing Society of Japan,* 1982, vol. 33 (5), 232-237 **[0007]**