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Amended claims in accordance with Rule 137(2) EPC.

(54) **Aluminum alloy surface treatment method, aluminum alloy processed by the method and aluminum alloy composite substrate comprising the aluminum alloy**

(57) An aluminum alloy surface treatment method includes: putting an aluminum alloy (1) into an electrolyte which includes an acidic solution and used for performing an anodic oxidation treatment, an aniline, and a mixed solution of an organic acid capable of reacting with aniline to form polyaniline (21); and performing an anodic oxidation of the aluminum alloy (1) in the electrolyte to form a porous oxide film (2) containing polyaniline (21) and having a plurality of pores (3) on a surface of the aluminum alloy (1), and then removing the aluminum alloy (1) from the electrolyte. The porous oxide film (2) containing polyaniline (21) formed on the surface of the aluminum alloy (1) can reduce the degree of oxidation caused by contamination of the aluminum alloy (1) stored in general environments, so that aluminum alloy composite substrates with high bonding power can be manufactured by plastic injection molding.

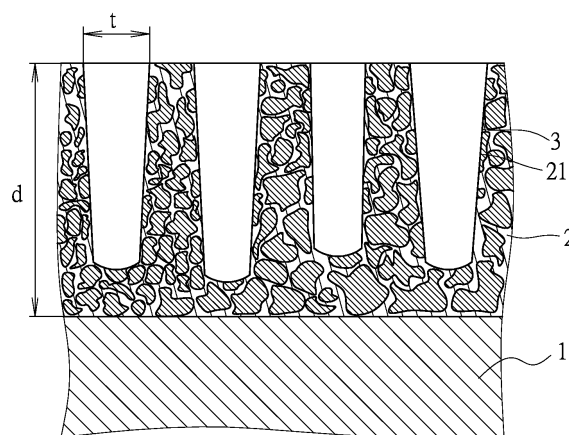


FIG. 2

Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention relates to an aluminum alloy surface treatment method, an aluminum alloy processed by the method, and an aluminum alloy composite substrate comprising the aluminum alloy.

BACKGROUND OF THE INVENTION

10 **[0002]** Plastic layers are generally coated and combined with the housing of metal products such as the housing of 3C products to achieve the effects of heat insulation, collision resistance, and scratch resistance.

[0003] In a conventional method of combining aluminum or aluminum alloy with plastic, pores are formed on the surface of the aluminum or aluminum alloy by a surface etching process in order to inject plastic directly, and thus the surface treatment of aluminum or aluminum alloy is an important processing technique of aluminum materials.

15 **[0004]** The surface treatment of aluminum or aluminum alloy mainly includes anodic oxidation or chemical conversion, and the conventional anodic oxidation of aluminum or aluminum alloy has been disclosed in R.O.C. Pat. Publication No. 201325905 entitled "Aluminum or aluminum alloy surface treatment method and product", and this patent discloses an aluminum or aluminum alloy surface treatment method and a product manufactured thereof, wherein the product comprises an aluminum or aluminum alloy substrate, and an anodic oxide film and an electroplated layer sequentially formed on the aluminum or aluminum alloy substrate, and the anodic oxide film includes a barrier layer and a porous layer sequentially formed on a surface of the aluminum or aluminum alloy substrate, and the anodic oxide film further includes a plurality of second pores, and the second pores penetrate through the barrier layer and the porous layer. The conventional chemical conversion method of aluminum or aluminum alloy has been disclosed in R.O.C. Pat. No. 391988 entitled "Improved aluminum alloy surface treatment method", and this patent discloses an improved aluminum alloy surface treatment method wherein a composite coating of chromate and waterborne polyurethane is formed on the surface of the aluminum alloy.

[0005] The aforementioned prior arts have the following shortcomings:

20 **[0006]** 1. In the "Improved aluminum alloy surface treatment method", a chemical conversion solution containing chromate such as potassium dichromate ($K_2Cr_2O_7$) is used in the chemical conversion surface treatment process of chromate, and thus resulting in heavy metal pollution during the chemical conversion process of the aluminum alloy.

25 **[0007]** 2. In the "Aluminum or aluminum alloy surface treatment method and product", a porous anodic oxide film is formed on the surface of aluminum or aluminum alloy by anodic oxidation, so that the internal surfaces of a large number of pores increase the bonding strength between the surface of aluminum or aluminum alloy and the plastic, but the unsealed pores of the anodic oxide film increase the level of environmental pollution (such as the moisture in air) as the effective surfaces of the aluminum or aluminum alloy exposed in the environment increase, so that the yield rate of a subsequent surface treatment process (such as the surface coating, plastic coating, and plastic injection molding) drops.

SUMMARY OF THE INVENTION

30 **[0008]** Therefore, it is a primary objective of the present invention to overcome the aforementioned problem of the prior art by providing an aluminum alloy surface treatment method, an aluminum alloy processed by the method, and an aluminum alloy composite substrate comprising the aluminum alloy.

35 **[0009]** In the aluminum alloy surface treatment method, the aluminum alloy processed by the method and the aluminum alloy composite substrate comprising the aluminum alloy, a porous oxide film containing polyaniline is formed on a surface of the aluminum alloy to reduce the influence of the environmental pollution (such as moisture) on the aluminum alloy stored in a general environment. In other words, the pores-unsealed porous oxide film containing polyaniline can resist pollutions better than the pores-unsealed conventional anodic oxide film to prevent the pores of the anodic oxide film from being blocked, which may adversely affect the bonding strength between the aluminum alloy and plastic. In addition, the polyaniline-containing porous oxide film is conducive to the bonding strength between the aluminum alloy and plastic, so that the aluminum alloy composite substrate formed by plastic molding injection has a high bonding power.

40 **[0010]** To achieve the aforementioned objective, the present invention provides an aluminum alloy surface treatment method comprising the following steps:

45 **[0011]** A. Put an aluminum alloy into an electrolyte, wherein the electrolyte includes an acidic solution for performing an anodic oxidation treatment of the aluminum alloy, aniline, and a mixed solution of an organic acid capable of reacting with aniline to form polyaniline.

50 **[0012]** B. Perform an anodic oxidation of the aluminum alloy in the electrolyte to form a porous oxide film containing polyaniline and having a plurality of pores formed on a surface of the aluminum alloy, and then remove the aluminum alloy from the electrolyte.

[0013] Wherein, the acidic solution is an aqueous solution selected from the collection of sulfuric acid, phosphoric acid and oxalic acid.

[0014] Wherein, the organic acid is one selected from the collection of benzenesulfonic acid, p-toluenesulfonic acid, n-butyl-benzenesulfonamide, dodecyl benzenesulfonic acid and camphorsulfonic acid.

[0015] Wherein, the acidic solution of the electrolyte is an aqueous solution of sulfuric acid with a concentration by volume of 100 milliliters to 250 milliliters per liter, and aniline with a concentration of 10 grams to 30 grams per liter and dodecyl benzenesulfonic acid with a concentration of 30 grams to 70 grams per liter are added into the aqueous sulfuric acid solution, and the aluminum alloy is put into the electrolyte and electrically conducted to perform an anodic oxidation treatment at a temperature of 15°C to 25°C for 5 minutes to 60 minutes, and the density of current passing through the aqueous sulfuric acid solution is 0.005 ampere to 0.045 ampere per square centimeter of the aluminum alloy and the voltage is 14 volts to 24 volts.

[0016] In the aluminum alloy composite substrate processed by the aluminum alloy surface treatment method of the present invention, the aluminum alloy has a porous oxide film containing polyaniline, and the porous oxide film containing polyaniline has a plurality of pores formed thereon.

[0017] Wherein, the porous oxide film containing polyaniline has a film thickness of 2 microns (μm) to 18 microns (μm).

[0018] Wherein, the pores have an opening diameter of 10 nanometers (nm) to 200 nanometers (nm).

[0019] In the aluminum alloy composite substrate comprising the aluminum alloy of the present invention and a plastic layer, the plastic layer is combined with the porous oxide film containing polyaniline and filled up in the pores.

[0020] The present invention has the following effects:

[0021] 1. The present invention can effectively reduce the influence of the environmental pollution, which may block the pores of the porous oxide film containing polyaniline, on the aluminum alloy stored in a general environment, so as to improve the yield rate of a subsequent surface treatment process (such as surface coating, plastic coating and plastic injection molding).

[0022] 2. The present invention with the porous oxide film containing polyaniline can improve the bonding strength between the aluminum alloy and plastic, so that the aluminum alloy composite substrate formed by plastic injection molding has a high bonding power.

[0023] 3. The present invention can extend the service life of the aluminum alloy composite substrate effectively.

[0024] 4. The present invention provides a simple aluminum alloy surface treatment method without causing any heavy metal pollution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1 is a flow chart of a preferred embodiment of the present invention;

[0026] FIG. 2 is a schematic view of the structure of a polyaniline-containing porous oxide film formed on a surface of aluminum alloy in accordance with a preferred embodiment of the present invention;

[0027] FIG. 3 is a first electronic microscopic view of the surface of an aluminum alloy in accordance with a preferred embodiment of the present invention;

[0028] FIG. 4 is a second electronic microscopic view of the surface of an aluminum alloy in accordance with a preferred embodiment of the present invention;

[0029] FIG. 5 is a graph of the film thickness of a polyaniline-containing porous oxide film versus the time of an anodic oxidation treatment in accordance with a preferred embodiment of the present invention;

[0030] FIG. 6 is a schematic view of the structure of a aluminum alloy composite substrate in accordance with a preferred embodiment of the present invention; and

[0031] FIG. 7 is an infrared spectrogram of a porous oxide film in accordance with a preferred embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0032] description of an illustrative embodiment of this invention described in connection with the drawings. It is intended that the embodiments and drawings disclosed herein are to be considered illustrative rather than restrictive.

[0033] With reference to FIG.1 and FIG.2 for a preferred embodiment of the present invention, the aluminum alloy used in this preferred embodiment is aluminum alloy 6061, and the aluminum alloy surface treatment method of this preferred embodiment comprises the following steps:

[0034] A1. Degrease and clean the surface of an aluminum alloy (1) by a degreasing agent, wherein the aluminum alloy (1) is dipped into the degreasing agent for the degreasing process, and then rinse the aluminum alloy (1) by water after the degreasing process is completed. Make sure that the surface of the aluminum alloy (1) is cleaned.

[0035] A2. Remove oxide and insoluble substances from the surface of the aluminum alloy (1) by a deoxidizer, wherein the aluminum alloy (1) is dipped into the deoxidizer to perform deoxidization, and then rinse the aluminum alloy (1) by

water after the deoxidization is completed. Make sure that the surface of the aluminum alloy (1) is cleaned.

[0036] A3. Put the aluminum alloy (1) into an electrolyte, wherein the electrolyte is an aqueous sulfuric acid solution with a concentration by volume of 100 to 250ml per liter, and aniline with a concentration of 10 to 30g per liter and dodecyl benzenesulfonic acid with a concentration of 30 to 70g per liter are added into the aqueous sulfuric acid solution.

[0037] B. Mix the electrolyte uniformly, and connect a DC power supply with a voltage of 20 volts, and a current density of current passing through the electrolyte is 0.015 ampere per square centimeter of the aluminum alloy (1), and the reaction temperature is 22°C, and dip the aluminum alloy (1) into the electrolyte to perform an anodic oxidation treatment for 30 minutes, and remove the aluminum alloy (1) from the electrolyte after a porous oxide film (2) containing polyaniline (21) and having a plurality of pores (3) is formed on a surface of the aluminum alloy (1). The porous oxide film (2) has a film thickness (d) of 11 to 12μm (as shown in FIG. 3). Wherein, the film thickness (d) is related to the anodic oxidation treatment time and can range from 2μm to 18μm (as shown in FIG. 5). The longer the anodic oxidation treatment time is, the greater the film thickness (d) of the porous oxide film (2) containing polyaniline (21) is. In addition, the pores (3) have an opening diameter (t) of 10 to 80 nanometers (nm) (as shown in FIG. 4).

[0038] C. Rinsing Procedure: Rinse the aluminum alloy (1) by water to wash away the electrolyte remained or attached on the surface of the aluminum alloy (1) after the anodic oxidation treatment is completed.

[0039] D. Drying Procedure: Bake the aluminum alloy (1) at a temperature of 60 to 80°C to remove the moisture remained on the aluminum alloy (1) after the rinsing procedure is completed.

[0040] After all of the aforementioned steps are carried out, the porous oxide film (2) containing polyaniline (21) is formed on a surface of the aluminum alloy (1), and the pores (3) are provided for forming a plastic material (such as Polyvinyl chloride (PVC), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polystyrene (PS), polyethylene (PE), polyether ether keton (PEEK), polyphenylene sulfide (PPS) and high fiberglass etc.) onto the surface of the aluminum alloy (1) by injection molding or plastic coating and tightly coupling the plastic material with the porous oxide film (2) containing polyaniline (21), such that a plastic layer (4) is formed on the porous oxide film (2) containing polyaniline (21) to form the aluminum alloy composite substrate of the present invention as shown in FIG. 6. In addition, polyaniline (21) on the surface of the porous oxide film (2) is conducive to the attachment of the plastic layer (4) onto the porous oxide film (2) containing polyaniline (21) to improve the bonding strength between the aluminum alloy (1) and the plastic layer (4), so that the aluminum alloy (1) and the plastic layer (4) will not be separated from each other easily by external forces or collisions, and the plastic layer (4) can be securely combined with the aluminum alloy (1). On the other hand, the porous oxide film (2) containing polyaniline (21) formed on the aluminum alloy (1) can reduce the degree of block, resulted from the environmental pollution, of the porous oxide film (2) of the aluminum alloy (1) stored in a general environment before injection molding, plastic coating or coating is performed, so that the bonding strength between the aluminum alloy (1) and the plastic is not affected easily, and the yield rate of a subsequent surface treatment process can be improved. In summation of the aforementioned advantages, the present invention can extend the service life of the aluminum alloy composite substrate effectively.

[0041] With reference to FIG. 7 for an infrared spectrogram of a preferred embodiment of the present invention, the absorption peaks at the wave numbers 1645cm⁻¹ and 1456cm⁻¹ correspond to the skeletal vibration of benzene ring ($\nu_{C=C}$); the absorption peak at the wave number 1502cm⁻¹ corresponds to the feature of benzene structure (ν_{NB-N}); the absorption peaks at the wave numbers 1380cm⁻¹ and 1312cm⁻¹ correspond to the bending vibration of carbon-hydrogen bond (C-H) and stretching vibration of carbon-nitrogen bond (C-N) respectively; and the absorption peak at the wave number 1143cm⁻¹ corresponds to the quinone structure (ν_{N-Q-N}); wherein, Q represents quinone ring and B represents benzene ring. The analytic result of the infrared spectrogram definitely shows that the porous oxide film contains polyaniline.

[0042] With reference to the following table for the bonding strength test results of the tensile test of the aluminum alloy composite substrate comprising the aluminum alloy (1) processed by the aluminum alloy surface treatment method of the present invention, the testing conditions include a tensile speed of 10mm/min and a testing temperature of 25°C, and the test results of the tensile test show that the aluminum alloy composite substrate comprising the aluminum alloy (1) processed by the aluminum alloy surface treatment method of the present invention has a high bonding power.

	Maximum Tensile Strength (Kgf/cm ²)	Maximum Deformation (mm)
1	297.47	2.71
2	306.02	2.78
3	374.50	2.55
4	328.88	2.91
5	321.03	3.24

[0043] With the description of the foregoing preferred embodiment, the operation, use and effect of the present invention becomes apparent. While the invention has been described by means of specific embodiments, numerous modifications and variations could be made thereto by those skilled in the art without departing from the scope and spirit of the invention set forth in the claims.

Claims

1. An aluminum alloy surface treatment method, comprising the following steps:

(A) putting an aluminum alloy (1) into an electrolyte, and the electrolyte including an acidic solution for performing an anodic oxidation treatment of the aluminum alloy (1), an aniline, and a mixed solution of an organic acid capable of reacting with aniline to form polyaniline (21); and

(B) performing an anodic oxidation of the aluminum alloy (1) in the electrolyte to form a porous oxide film (2) containing polyaniline and having a plurality of pores (3) on a surface of the aluminum alloy (1), and then removing the aluminum alloy (1) from the electrolyte.

2. The aluminum alloy surface treatment method of claim 1, wherein the acidic solution is an aqueous solution selected from the collection of sulfuric acid, phosphoric acid and oxalic acid.

3. The aluminum alloy surface treatment method of claim 1, wherein the organic acid is one selected from the collection of benzenesulfonic acid, p-toluenesulfonic acid, n-butyl-benzenesulfonamide, dodecyl benzenesulfonic acid and camphor sulfonic acid.

4. The aluminum alloy surface treatment method of claim 1, wherein the acidic solution of the electrolyte is an aqueous solution of sulfuric acid with a concentration by volume of 100 milliliters (ml) to 250 milliliters (ml) per liter (1), and aniline with a concentration of 10 grams (g) to 30 grams (g) per liter (1) and dodecyl benzenesulfonic acid with a concentration of 30 grams (g) to 70 grams (g) per liter (1) are added into the aqueous sulfuric acid solution, and the aluminum alloy (1) is put into the electrolyte and electrically conducted to perform an anodic oxidation treatment at a temperature of 15°C to 25°C for 5 minutes to 60 minutes, and the density of current passing through the aqueous sulfuric acid solution is 0.005 ampere (A) to 0.045 ampere (A) per square centimeter (cm²) of the aluminum alloy, and the voltage is 14 volts (V) to 24 volts (V).

5. An aluminum alloy (1) processed by the aluminum alloy surface treatment method according to any one of claims 1 to 4, **characterized in that** the aluminum alloy (1) has a porous oxide film (2) containing polyaniline (21) formed thereon, and the porous oxide film (2) containing polyaniline (21) has a plurality of pores (3) formed thereon.

6. The aluminum alloy (1) of claim 5, wherein the porous oxide film (2) containing polyaniline (21) has a film thickness (d) of 2 microns (μm) to 18 microns (μm).

7. The aluminum alloy (1) of claim 5, wherein the pores (3) have an opening diameter (t) of 10 nanometers (nm) to 200 nanometers (nm).

8. An aluminum alloy composite substrate comprising the aluminum alloy (1) according to claim 5 and a plastic layer (4), wherein the plastic layer (4) is combined with the porous oxide film (2) containing polyaniline (21) and filled up in the pores (3).

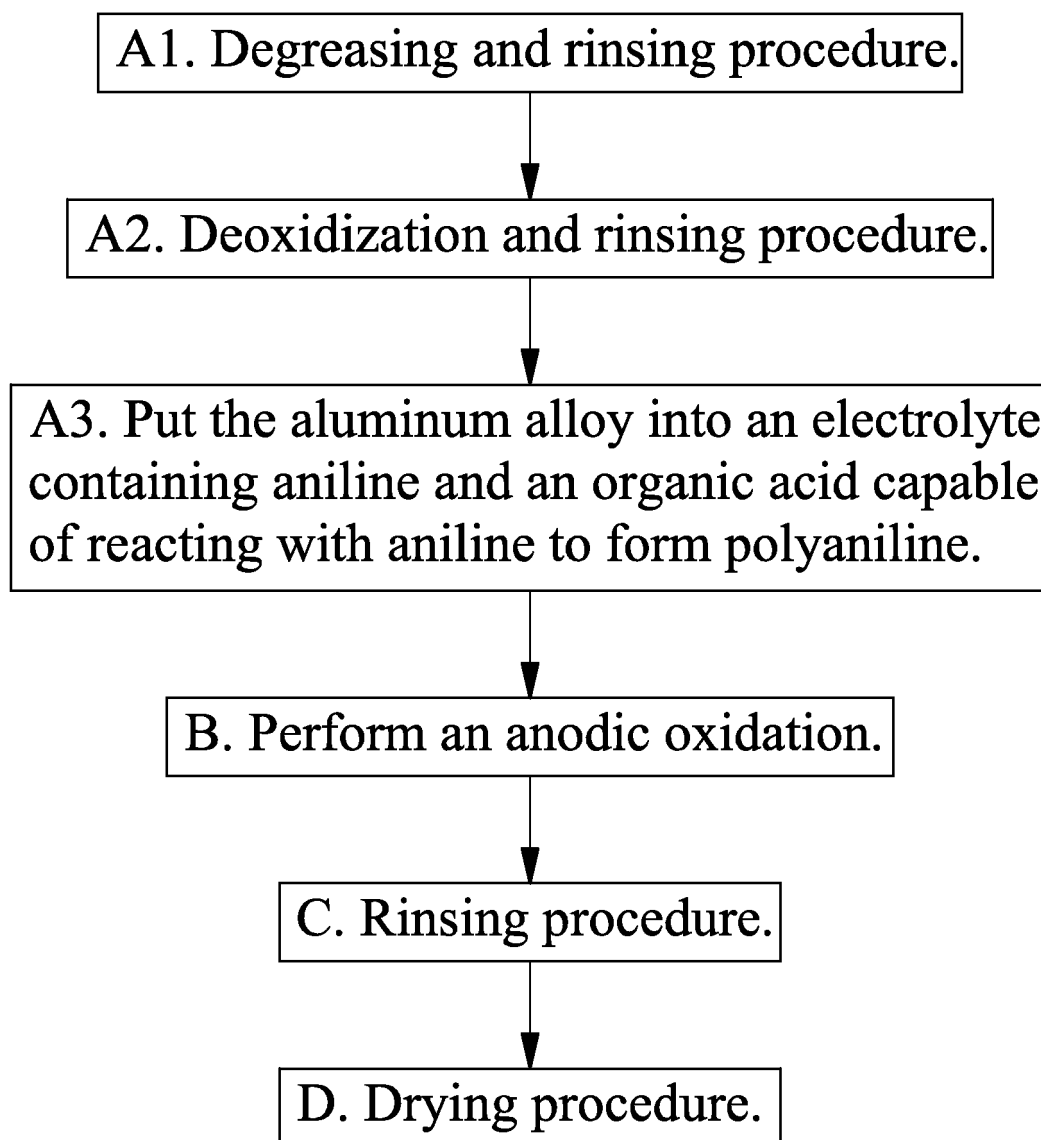
Amended claims in accordance with Rule 137(2) EPC.

1. An aluminum alloy surface treatment method, comprising the following steps:

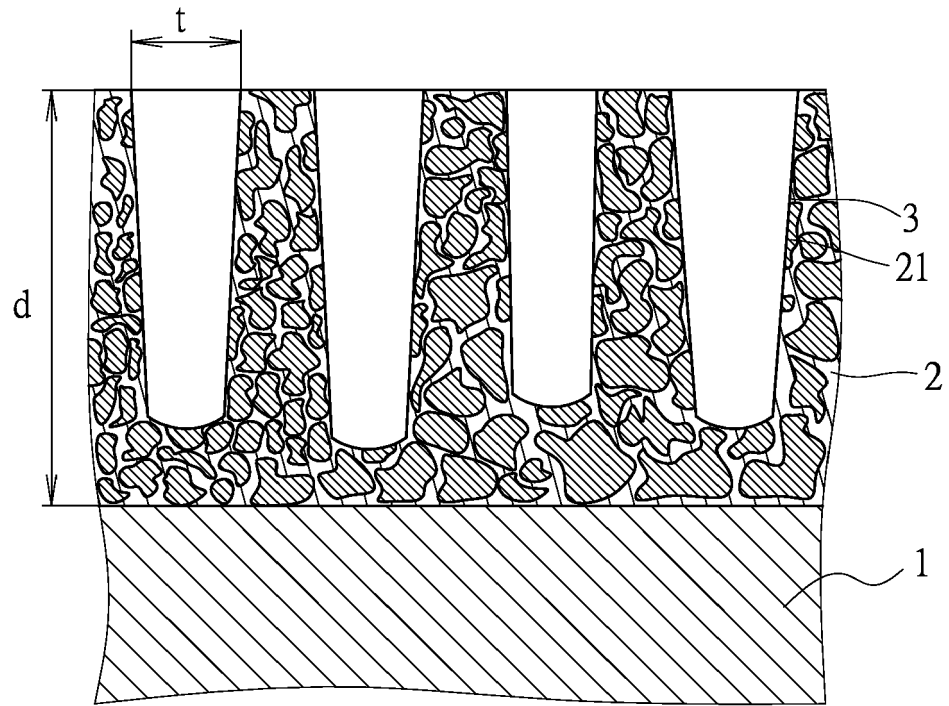
(A) putting an aluminum alloy (1) into an electrolyte, and the electrolyte including an acidic solution for performing an anodic oxidation treatment of the aluminum alloy (1), an aniline, and a solution of an organic acid capable of reacting with aniline to form polyaniline (21); and

(B) performing an anodic oxidation of the aluminum alloy (1) in the electrolyte to form a porous oxide film (2) containing polyaniline and having a plurality of pores (3) on a surface of the aluminum alloy (1), and then removing the aluminum alloy (1) from the electrolyte,

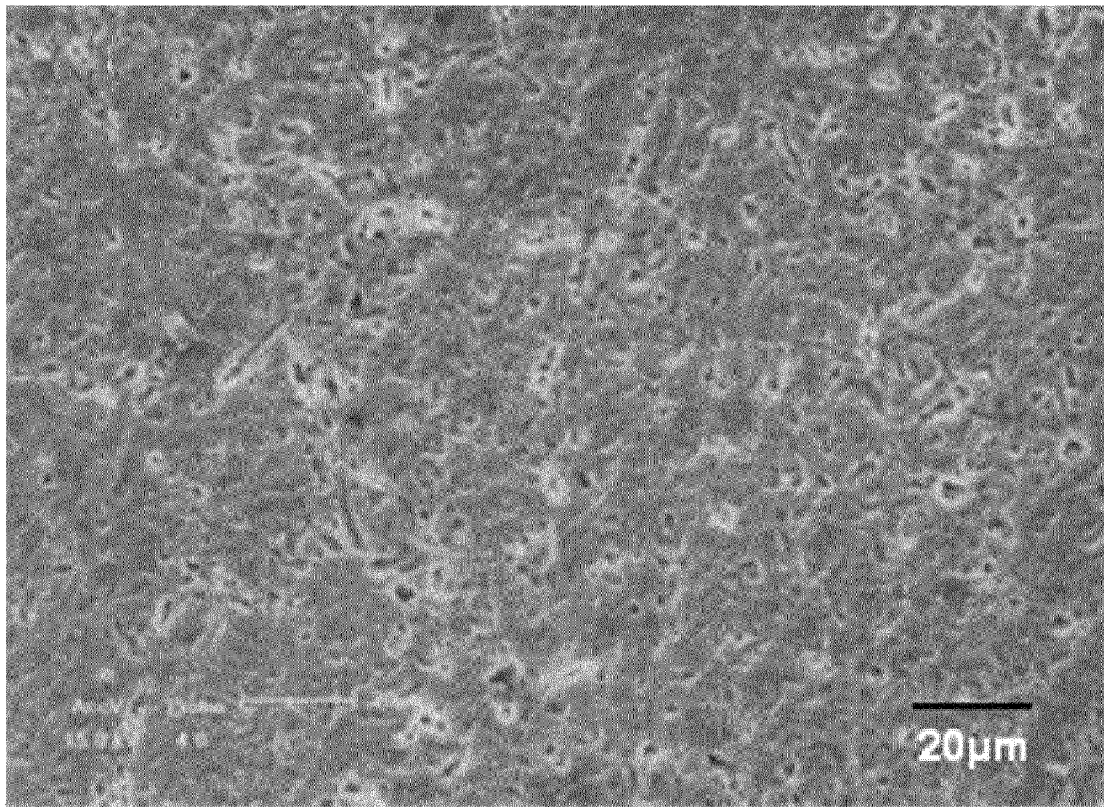
2. The aluminum alloy surface treatment method of claim 1, wherein, the acidic solution is an aqueous solution selected from the collection of sulfuric acid, phosphoric acid and oxalic acid.
3. The aluminum alloy surface treatment method of claim 1, wherein the organic acid is one selected from the collection of benzenesulfonic acid, p-toluenesulfonic acid, n-butyl-benzenesulfonamide, dodecyl benzenesulfonic acid and camphor sulfonic acid.
4. The aluminum alloy surface treatment method of claim 1, wherein the acidic solution of the electrolyte is an aqueous solution of sulfuric acid with a concentration by volume of 100 milliliters (ml) to 250 milliliters (ml) per liter (1), and aniline with a concentration of 10 grams (g) to 30 grams (g) per liter (1) and dodecyl benzenesulfonic acid with a concentration of 30 grams (g) to 70 grams (g) per liter (1) are added into the aqueous sulfuric acid solution, and the aluminum alloy (1) is put into the electrolyte and electrically conducted to perform an anodic oxidation treatment at a temperature of 15°C to 25°C for 5 minutes to 60 minutes, and the density of current passing through the aqueous sulfuric acid solution is 0.005 ampere (A) to 0.045 ampere (A) per square centimeter (cm²) of the aluminum alloy, and the voltage is 14 volts (V) to 24 volts (V).
5. An aluminum alloy (1) processed by the aluminum alloy surface treatment method according to any one of claims 1 to 4, **characterized in that** the aluminum alloy (1) has a porous oxide film (2) containing polyaniline (21) formed thereon, and the porous oxide film (2) containing polyaniline (21) has a plurality of pores (3) formed thereon, wherein the porous oxide film (2) containing polyaniline (21) has a film thickness (d) of 2 microns (μm) to 18 microns (μm), and wherein the pores (3) have an opening diameter (t) of 10 nanometers (nm) to 200 nanometers (nm).
6. An aluminum alloy composite substrate comprising the aluminum alloy (1) according to claim 5 and a plastic layer (4), wherein the plastic layer (4) is combined with the porous oxide film (2) containing polyaniline (21) and filled up in the pores (3).



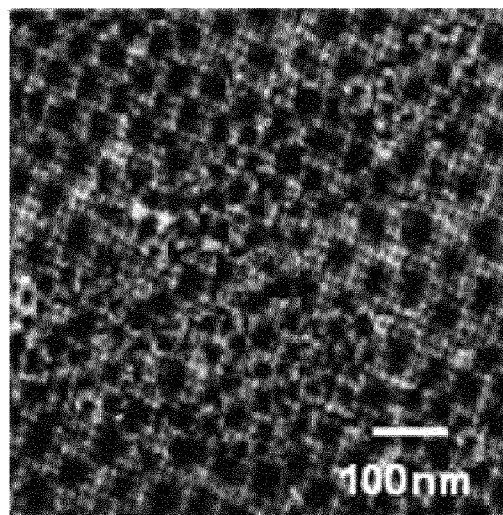
F I G . 1



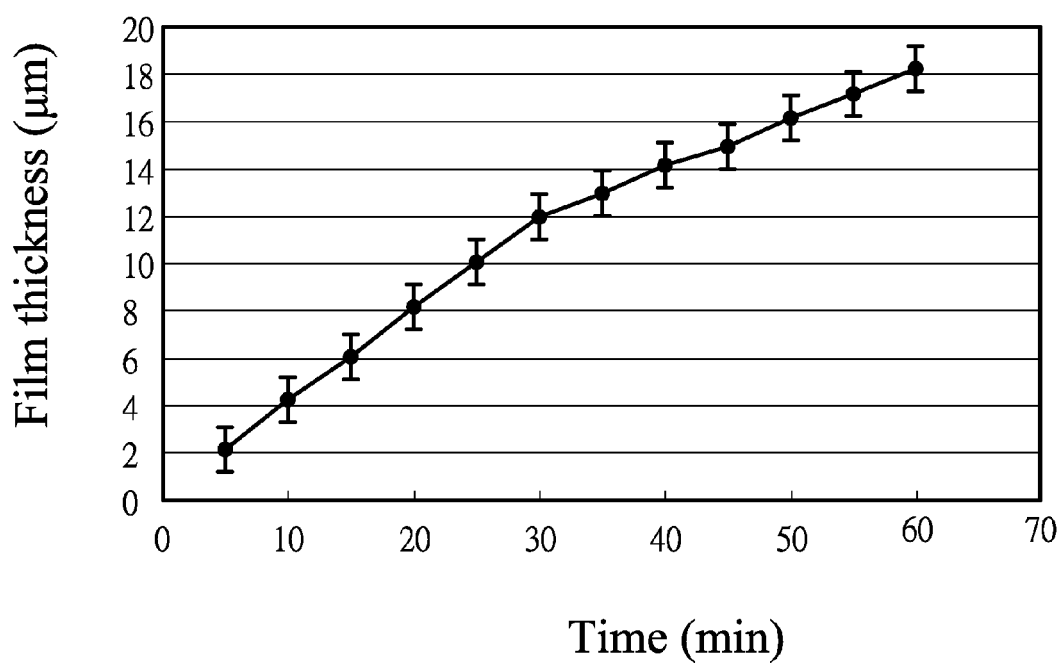
F I G . 2



F I G . 3



F I G . 4



F I G . 5

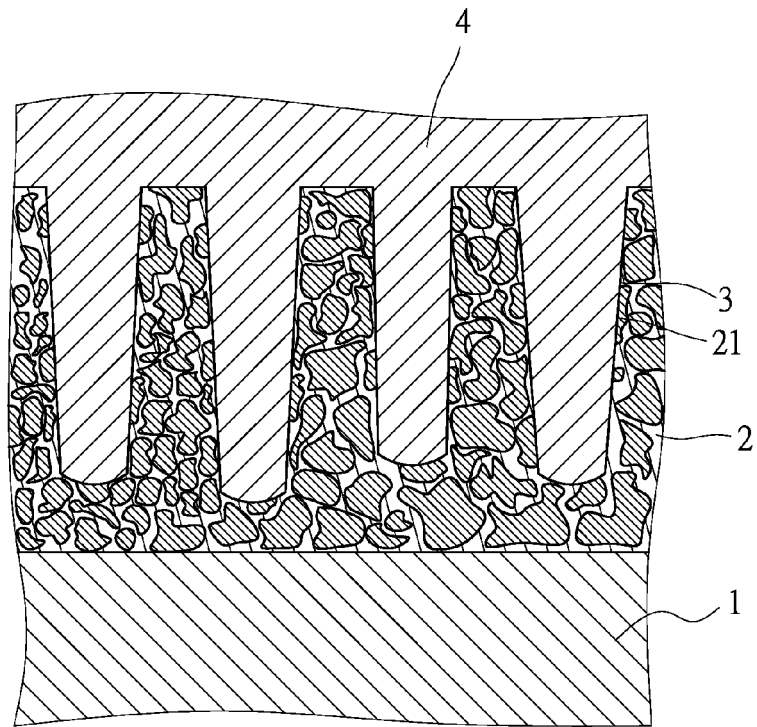
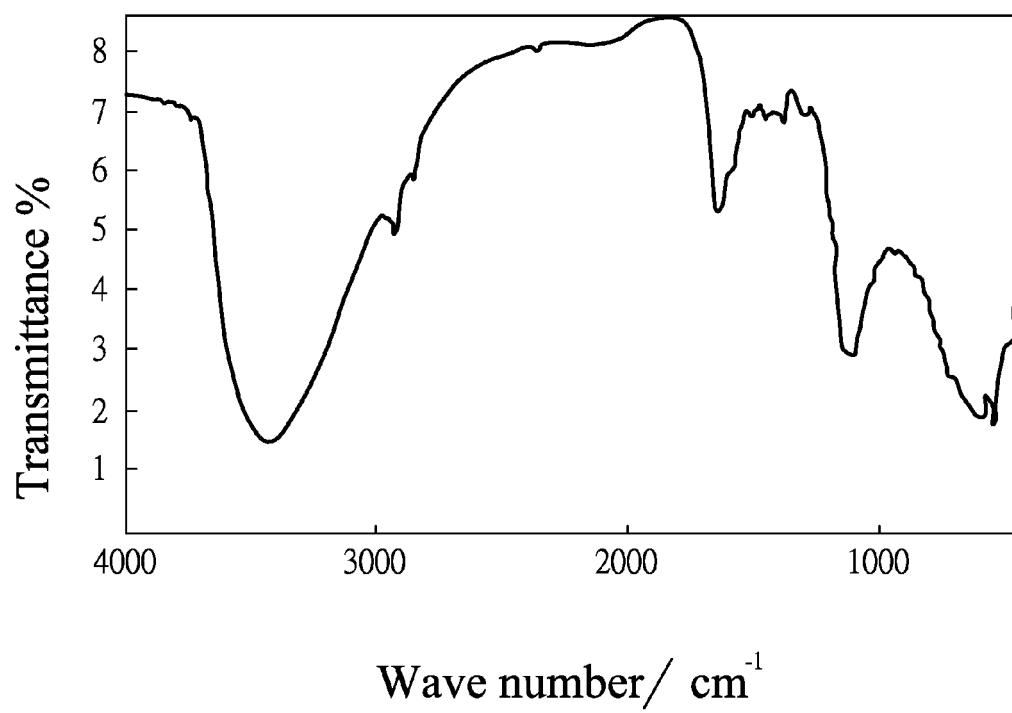


FIG. 6



F I G . 7



EUROPEAN SEARCH REPORT

 Application Number
 EP 13 18 7340

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DOMINGO HUERTA-VILCA ET AL: "Anodic treatment of aluminum in nitric acid containing aniline, previous to deposition of polyaniline and its role on corrosion", SYNTHETIC METALS, vol. 140, no. 1, 1 January 2004 (2004-01-01), pages 23-27, XP055107204, ISSN: 0379-6779, DOI: 10.1016/S0379-6779(02)01314-0 * abstract * * paragraph [0002] * * page 25, left-hand column, last paragraph - page 26, left-hand column, paragraph 1 * * figure 6 *	1-8	INV. C25D11/10 C25D11/24
X	ZUBILLAGA O ET AL: "Synthesis of anodic films in the presence of aniline and TiO ₂ nanoparticles on AA2024-T3 aluminium alloy", THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 517, no. 24, 30 October 2009 (2009-10-30), pages 6742-6746, XP026735947, ISSN: 0040-6090, DOI: 10.1016/J.TSF.2009.05.039 [retrieved on 2009-05-29] * abstract * * paragraph [02.1] * * figures 4, 6 *	1-8	TECHNICAL FIELDS SEARCHED (IPC) C25D
A,D	US 2013/164555 A1 (DING TING [CN]) 27 June 2013 (2013-06-27) * abstract * * figures 1, 3 * * claims 7, 8 *	1-8	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13 March 2014	Examiner Picard, Sybille
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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REFERENCES CITED IN THE DESCRIPTION

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