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(54) **MICRO-NANO PROCESSING METHOD FOR ALUMINUM OR ALUMINUM ALLOY SURFACE, AND ALUMINUM OR ALUMINUM ALLOY STRUCTURE**

(57) A micro-nano processing method of an aluminum or aluminum alloy surface includes a step of placing aluminum or an aluminum alloy as an anode in an electrolyte containing hydrochloric acid, sulfuric acid, phosphoric acid, and an etching inhibitor for DC electrochemical etching, where the concentration of hydrochloric acid is 1.5 to 3 mol/L, the concentration of sulfuric acid is 0.9 to 1.2 mol/L, and the concentration of phosphoric acid is 0.6 to 1 mol/L. A method for integrating aluminum or an aluminum alloy and a plastic includes the following steps: forming a micro-nano porous structure on an aluminum or aluminum alloy surface by using the micro-nano processing method; and closely combining a plastic and the aluminum or aluminum alloy surface by means of the micro-nano porous structure. An aluminum or aluminum alloy structure has a micro-nano porous structure formed on the surface of the aluminum or aluminum alloy structure by using the micro-nano processing method. By using this method, the micro-nano hole processing efficiency is high, the quality is high, and the method is environmental friendly.

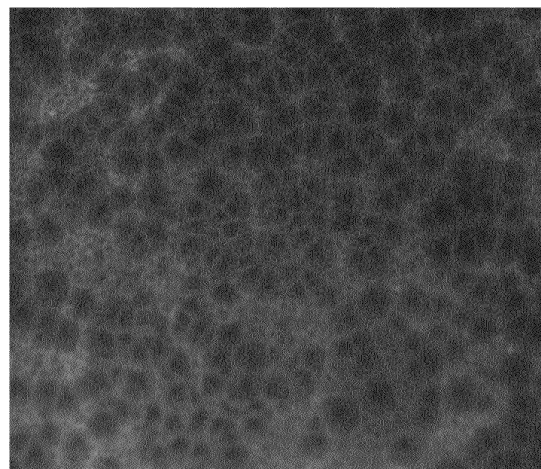


FIG. 2

Description

BACKGROUND

Technical Field

[0001] The present application relates to the technical field of aluminum or aluminum alloy surface processing, and in particular to a micro-nano processing method of an aluminum alloy surface, a method for integrating aluminum or an aluminum alloy and a plastic, and an aluminum or aluminum alloy structure.

Related Art

[0002] In a nano-molding technique, nano-holes are formed on a surface of a metal through chemical or electrochemical etching, and a micro-nano porous structure having a form similar to a coral reef is formed on the surface of the metal by selecting a special etching solution. Next, a treated metal piece is placed in a mold for in-mold injection molding, where a plastic component is directly injected onto the surface of the metal and solidified, and by means of a mechanical interlocking effect of the micro-nano porous structure, a plastic is closely combined to the surface of the metal. Finally, all modification processing for a surface of a metal can be performed on the injection molded piece removed from the mold. Through such micro-nano treatment on the surface of the metal, plane bonding between the metal and the plastic can be achieved, so that a metal-plastic bonding process is omitted. This nano-molding technique is mainly applied in metal-plastic integration bonding. During existing current micro-nano treatment of an aluminum alloy surface, a used etching solution contains a large amount of organic ingredients that may pollute the environment, and the processing efficiency and effect of nano-holes are far from desirable.

SUMMARY

[0003] In order to overcome the deficiencies in the prior art, an object of the present application is to provide a micro-nano processing method of an aluminum or aluminum alloy surface, which effectively solves problems of environmental pollution caused by organics, and meanwhile, improve micro-nano hole processing efficiency and improve processing quality.

[0004] Another object is to provide a method for integrating aluminum or an aluminum alloy and a plastic, which has the advantages described above.

[0005] Yet another object is to provide an aluminum or aluminum alloy structure, having micro-nano holes formed on a surface of the aluminum or aluminum alloy structure by using the method described above.

[0006] In order to achieve the objects, the present application employs the following technical solutions:

A micro-nano processing method of an aluminum or aluminum alloy surface includes a step of placing aluminum or an aluminum alloy as an anode in an electrolyte containing hydrochloric acid, sulfuric acid, phosphoric acid, and an etching inhibitor for DC electrochemical etching, where the concentration of hydrochloric acid is 1.5 to 3 mol/L, the concentration of sulfuric acid is 0.9 to 1.2 mol/L, and the concentration of phosphoric acid is 0.6 to 1 mol/L.

[0007] The following technical solutions may be further employed:

[0008] In some embodiments, the concentration of the etching inhibitor is 0.5 to 2.0 g/L.

[0009] In some embodiments, the etching inhibitor may be an organic etching inhibitor such as thiourea, methyl cellulose, morpholine, butyl amine, cyclohexylamine, cyclohexanol, ethylene diamine, triethylene tetramine, and derivatives thereof, or an inorganic salt such as copper sulfate, potassium iodide, and potassium bromide.

[0010] In some embodiments, the etching current density is 0.1 to 0.4 A/cm², the temperature of the etching solution is 25°C to 70°C, and the powered etching time is 10s to 100s.

[0011] Preferably, the temperature of the etching solution is 40°C to 70°C, and the powered etching time is 30s to 80s.

[0012] In some embodiments, before DC electrochemical etching, the aluminum or aluminum alloy surface is treated with an alkali solution.

[0013] Preferably, the aluminum or aluminum alloy surface is immersed in a NaOH solution having a mass concentration of 2% to 4% for 2 to 6 min.

[0014] In some embodiments, before DC electrochemical etching, the aluminum or aluminum alloy surface is treated with an acid solution.

[0015] Preferably, the aluminum or aluminum alloy surface is immersed in a HNO₃ solution having a mass concentration of 1% to 4% for 1 to 4 min.

[0016] A method for integrating aluminum or an aluminum alloy and a plastic includes the following steps:

forming a micro-nano porous structure on an aluminum or aluminum alloy surface by using the micro-nano processing method; and

closely combining a plastic and the aluminum or aluminum alloy surface by means of the micro-nano porous structure.

[0017] An aluminum or aluminum alloy structure has a micro-nano porous structure formed on the surface of the aluminum or aluminum alloy structure by using the micro-nano processing method.

[0018] The present application has the following beneficial technical effects:

According to the present application, an electrolyte

containing inorganic acid components of 1.5 to 3 mol/L hydrochloric acid, 0.9 to 1.2 mol/L sulfuric acid, and 0.6 to 1 mol/L phosphoric acid and an etching inhibitor is used to perform DC electrochemical etching on aluminum or an aluminum alloy, the hole distribution of the resulting micro-nano porous structure is even and uniform, and the processing is rapid and efficient; moreover, problems of environmental pollution caused by organic components contained in the etching solution used in the prior art are completely eliminated. The processing method of the present application has the advantages of being rapid and safe, simple process and desirable controllability. The micro-nano porous structure formed on the aluminum or aluminum alloy surface by using the present application makes integration of the aluminum or aluminum alloy structure and a plastic easier, and after injection molding, a metal-plastic component having a high bonding strength may be obtained, thereby achieving combined preparation of integration of an aluminum alloy and a plastic in an environmental friendly and high efficient manner.

[0019] According to a preferred embodiment, for the electrolyte containing the special inorganic components, at a temperature of the etching solution of 25°C to 70°C, particularly, 40°C to 70°C and using an etching current density of 0.1 to 0.4 A/cm², powered etching lasts 10s to 100s, and preferably 30s to 80s; in this way, optimal processing effect may be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The present application will become more fully understood from the detailed description given herein below for illustration only, and thus are not limitative of the present application, and wherein:

FIG. 1 is an electron micrograph of an aluminum alloy plate (A5052) after etching obtained according to an embodiment of the present application;

FIG. 2 is a high-power electron micrograph of an aluminum alloy plate (A5052) after etching obtained according to an embodiment of the present application;

FIG. 3 is an electron micrograph of an aluminum alloy plate (A6063) after etching obtained according to an embodiment of the present application;

FIG. 4 is a high-power electron micrograph of an aluminum alloy plate (A6063) after etching obtained according to an embodiment of the present application;

FIG. 5 is an electron micrograph of an aluminum foil after etching obtained according to an embodiment

of the present application; and

FIG. 6 is a high-power electron micrograph of an aluminum foil after etching obtained according to an embodiment of the present application.

DETAILED DESCRIPTION

[0021] In the following, the present application is further described in detail with reference to preferred embodiments.

[0022] In the following, the embodiments of the present application are described in detail with reference to the accompanying drawings. It should be emphasized that the description below is merely exemplary, but not intended to limit the scope and application of the present application.

[0023] Referring to FIG. 1, in some specific embodiments, a micro-nano processing method of an aluminum or aluminum alloy surface includes the following process:

(1) Sample preparation

[0024] Aluminum or an aluminum alloy (such as 1000-7000 series aluminum alloys) is processed into a desired shape and size, and a fit jig is designed according to the product.

(2) Sample pretreatment

[0025] The pretreatment process may be performed in the following manner:

1) The aluminum or aluminum alloy surface is polished by using different types of sandpaper to remove an oxide layer generated during storage of the aluminum or aluminum alloy, so as to obtain a new surface, or the oxide layer on the surface may be removed by using a chemical cleaning method.

2) Degreasing treatment

[0026] The aluminum or aluminum alloy surface is cleaned with a solution of a detergent and water to remove grease from the surface, is then cleaned with distilled water, and then dried in a vacuum oven at 120°C.

3) Treatment with alkali solution

[0027] The part that does not need to be etched may be first protected through coating with paraffin wax, and the aluminum or an aluminum alloy is then immersed in a NaOH solution for several minutes, where the mass concentration of NaOH is preferably 2% to 4%, and the immersion time is preferably 2 to 6 min.

4) Treatment with acid solution

[0028] The aluminum or aluminum alloy is immersed in a HNO_3 solution for several minutes, where the mass concentration of HNO_3 is preferably 1% to 4%, and the immersion time is preferably 1 to 4 min.

[0029] Since the state of the aluminum or aluminum alloy surface has important influence on the subsequent etching process, through the pretreatment on the aluminum or aluminum alloy surface with the above steps, the grease and oxide layer on the surface may be effectively removed, and the surface is activated, thereby improving the effect of subsequent electrochemical etching.

(3) DC electrochemical etching

[0030] This step is a critical step for micro-nano etching of the aluminum alloy surface. An electrolyte of a certain concentration is formulated by hydrochloric acid, sulfuric acid, and phosphoric acid, where the concentration of hydrochloric acid is 1.5 to 3 mol/L, the concentration of sulfuric acid is 0.9 to 1.2 mol/L, the concentration of phosphoric acid is 0.6 to 1 mol/L, a suitable amount of etching inhibitor is added, and preferably, the concentration of the etching inhibitor is 0.5 to 2.0 g/L. The electrolyte of the above formula may achieve the optimal etching inhibition effect. The aluminum alloy sample after pretreatment is placed in the electrolyte as an anode, the cathode may be an inert graphite or platinum electrode, the temperature of the etching solution is controlled to be 25°C to 70°C , and preferably 40°C to 70°C , the current density of the applied DC current is 0.1 A/cm^2 to 0.4 A/cm^2 , and the powered time is 10s to 100s, and preferably 30s to 80s.

(4) Post-treatment

[0031] After etching, post-treatment can be implemented for cleaning and drying. For example, the aluminum foil after DC electrochemical etching is cleaned with distilled water, then immersed in alcohol or acetone for several seconds, and then dried in a drying oven at 70°C .

[0032] Through the nano processing process of the aluminum or aluminum alloy surface according to the embodiments, evenly distributed micro-nano holes whose hole diameters are between 50 nanometer to 20 micrometer are quickly generated on the aluminum or aluminum alloy surface, thereby achieving environmental friendly, high-efficiency, and high-quality nano molding of the aluminum or aluminum alloy surface.

[0033] Some other embodiments relate to a method for integrating aluminum or an aluminum alloy and a plastic, where the method includes the following steps:

forming a micro-nano porous structure on an aluminum or aluminum alloy surface by using the micro-nano processing method; and

closely combining a plastic and the aluminum or aluminum alloy surface by means of the micro-nano porous structure.

[0034] Some other embodiments relate to an aluminum or aluminum alloy structure, having a micro-nano porous structure formed on the surface of the aluminum or aluminum alloy structure by using the micro-nano processing method.

[0035] In the following, features and advantages of the present application are further demonstrated through several examples.

Example 1

[0036] A commercially available aluminum alloy plate A5052 having a thickness of 2 mm was purchased and was evenly cut into aluminum sheets of 20 mm x 10 mm by using line cutting, and the aluminum sheet was polished by using model 360#, 600# and 800# iron sand papers in sequence. During polishing, each time when a sandpaper is changed, the sample needs to be rotated by 900 degrees to ensure that all scratches left in a previous procedure were worn off, so that the thickness of the polished sample reaches a level of about $5\text{ }\mu\text{m}$. Next, the sample was cleaned for 10 min with ultrasonic waves in an ethanol solution to remove the grease from the surface, and was then cleaned with deionized water and dried in a drying oven at 120°C .

[0037] 100 ml NaOH solution having a mass concentration of 2% was formulated with ion exchange water and heated to 40°C in water bath, and the aluminum alloy sheet was immersed in the NaOH solution for 2 min in a suspended manner and then cleaned with deionized water.

[0038] Next, 100 ml HNO_3 solution having a mass concentration of 1% was diluted with ion exchange water and heated to 40°C in water bath, and the aluminum alloy sheet was immersed in the HNO_3 solution for 4 min in a suspended manner and then cleaned with deionized water.

[0039] Then, with the aluminum alloy sheet as an anode, a graphite sheet as a cathode, a mixed solution in an electrolytic cell containing 1.5 mol/L hydrochloric acid, 0.9 mol/L sulfuric acid, and 0.6 mol/L phosphoric acid as an electrolyte, a certain etching inhibitor was added, and the current density was controlled to be 0.15 A/cm^2 by a constant voltage DC source, the temperature of the electrolyte was 40°C , and the powered time was 30s. Next, the aluminum alloy sheet was cleaned with deionized water, then immersed for 5s in acetone, and dried in a drying oven at 70°C . Electron micrographs of the aluminum alloy sheet after etching are shown in FIG. 1 and FIG. 2. It can be seen from the electron micrographs after etching that the hole diameter of a large hole obtained on the etching surface is 1 to 3 micrometers, and a large amount of nano holes having a hole diameter of 30 to 50 nanometers are evenly distributed.

Example 2

[0040] A commercially available aluminum alloy plate A6063 having a thickness of 2 mm was purchased and was evenly cut into aluminum sheets of 20 mm x 10 mm by using line cutting. A small hole was opened on each aluminum alloy sheet, and the surface of the aluminum alloy sheet was polished by using model 360#, 600# and 800# iron sand papers in sequence. During polishing, each time when a sandpaper is changed, the sample needs to be rotated by 90 degrees, so as to ensure that all scratches left in a previous procedure were worn off, so that the thickness of the polished sample reaches a level of about 5 μm . Next, the sample was cleaned for 10 min with ultrasonic waves in an ethanol solution to remove grease from the surface, and then was cleaned with deionized water and dried in a drying oven at 120°C.

[0041] 100 ml NaOH solution having a mass concentration of 2% was formulated with ion exchange water and heated to 40°C in water bath, and the aluminum alloy sheet was immersed in the NaOH solution for 2 min in a suspended manner and then cleaned with deionized water.

[0042] Next, 100 ml mixed solution of HNO_3 having a mass concentration of 1% and HF having a mass concentration of 0.5% was formulated with ion exchange water and heated to 40°C in water bath, and the aluminum alloy sheet was immersed in the mixed solution for 1 min in a suspended manner and then cleaned with deionized water.

[0043] Then, with the aluminum alloy sheet as an anode, the aluminum alloy sheet was treated in an electrolyte formed by mixing 2 mol/L hydrochloric acid, 0.9 mol/L sulfuric acid, 0.8 mol/L phosphoric acid, 2.0 g/L polyethylene glycol, and 1.5 g/L thiourea for 70s, where the etching current density was 0.3 A/cm², and the temperature of the electrolyte was 60°C. Next, the aluminum alloy sheet was cleaned with deionized water, immersed in acetone for 5s, and then dried in a drying oven at 70°C. Electron micrographs of the aluminum alloy sheet after etching are shown in FIG. 3 and FIG. 4. It can be seen from the electron micrographs after etching that the hole diameter of a large hole obtained on the etching surface is 1 to 3 micrometers, and a large amount of nano holes having a hole diameter of 20 to 40 nanometers are evenly distributed.

Example 3

[0044] A commercially available aluminum foil was purchased and was cut into thin sheets of 20 mm x 10 mm. A small hole was opened on each thin sheet, and the surface of the thin sheet was directly polished by using a 800# iron sand paper; next, the thin sheet was cleaned with ultrasonic waves for 10 min in an ethanol solution to remove the grease on surface, and then was cleaned with deionized water and dried in a drying oven at 120°C.

[0045] 100 ml NaOH solution having a mass concentration of 1.5% was formulated with ion exchange water and heated to 40°C in water bath, and the aluminum foil sheet was immersed in the NaOH solution for 2 min in a suspended manner and then cleaned with deionized water.

[0046] Next, 100 ml HNO_3 solution having a mass concentration of 1% was diluted with ion exchange water and heated to 40°C in water bath, and the aluminum foil sheet after being washed with the alkali solution was immersed in the HNO_3 solution for 1 min in a suspended manner and then cleaned with deionized water.

[0047] Then, with the aluminum foil sheet as an anode and a graphite sheet as a cathode, the aluminum foil sheet was treated for 70s in an electrolyte having an etching solution including 2 mol/L hydrochloric acid, 0.9 mol/L sulfuric acid, 0.6 mol/L phosphoric acid, and 0.4 g/L triethylene tetramine, where the temperature was maintained at 60°C, and the applied DC current was 0.15A/cm². Next, the aluminum foil sheet was cleaned with deionized water, immersed in acetone for 5s, and then dried in a drying oven at 70°C. Electron micrographs of the aluminum foil sheet after etching are shown in FIG. 5 and FIG. 6. It can be seen from the electron micrographs after etching that the hole diameter of a large hole obtained on the etching surface is 1 to 5 micrometers, and a large amount of nano holes having a hole diameter of 30 to 60 nanometers are evenly distributed.

[0048] It is verified by numerous other examples (which are not repeated herein), in the electrolyte of the present application, it is feasible that the concentration of hydrochloric acid is 1.5 to 3 mol/L, the concentration of sulfuric acid is 0.9 to 1.2 mol/L, and the concentration of phosphoric acid is 0.6 to 1 mol/L; moreover, in the case that the electrolyte of the present application is used, the temperature of the etching solution is as low as 25°C, the etching current density is as low as 0.1 A/cm², and the continuous powered etching is as short as 10s, although the hole processing effect is not ideal, a nano hole structure with desirable shapes and distribution may be obtained.

[0049] In the above, the present application is further described in detail with reference to the specific preferred embodiments, and it should not be construed that the specific implementation of the present application is limited to these descriptions. Several simple derivations and replacements may be made by persons of ordinary skill in the art without departing from the concept of the present application should be considered as falling within the protection scope of the present application.

Claims

1. A micro-nano processing method of an aluminum or aluminum alloy surface, comprising: placing the aluminum or aluminum alloy as an anode in an electrolyte containing hydrochloric acid, sulfuric acid, phos-

phoric acid, and an etching inhibitor for DC electrochemical etching, wherein the concentration of hydrochloric acid is 1.5 to 3 mol/L, the concentration of sulfuric acid is 0.9 to 1.2 mol/L, the concentration of phosphoric acid is 0.6 to 1 mol/L.

5

micro-nano porous structure formed on the surface by using the micro-nano processing method according to any one of claims 1 to 8.

2. The micro-nano processing method according to claim 1, wherein the concentration of the etching inhibitor is 0.5 to 2.0 g/L, the etching inhibitor is selected from thiourea, methyl cellulose, morpholine, butyl amine, cyclohexylamine, cyclohexanol, ethylene diamine, triethylene tetramine and derivatives thereof, or is selected from copper sulfate, potassium iodide and potassium bromide. 10
3. The micro-nano processing method according to claim 1 or 2, wherein the etching current density is 0.1 to 0.4 A/cm², the temperature of the etching solution is 25°C to 70°C, and the powered etching time is 10s to 100s. 15
4. The micro-nano processing method according to claim 3, wherein the temperature of the etching solution is 40°C to 70°C, and the powered etching time is 30s to 80s. 20
5. The micro-nano processing method according to any one of claims 1 to 4, wherein, before DC electrochemical etching, the aluminum or aluminum alloy surface is treated with an alkali solution. 25
6. The micro-nano processing method according to claim 5, wherein the aluminum or aluminum alloy surface is immersed in a NaOH solution having a mass concentration of 2% to 4% for 2 to 6 min. 30
7. The micro-nano processing method according to any one of claims 1 to 6, wherein, before DC electrochemical etching, the aluminum or aluminum alloy surface is treated with an acid solution. 35
8. The micro-nano processing method according to claim 7, wherein the aluminum or aluminum alloy surface is immersed in a HNO₃ solution having a mass concentration of 1% to 4% for 1 to 4 min. 40
9. A method for integrating aluminum or an aluminum alloy and a plastic, comprising: 45
 - forming a micro-nano porous structure on an aluminum or aluminum alloy surface by using the micro-nano processing method according to any one of claims 1 to 8; and 50
 - closely combining a plastic and the aluminum or aluminum alloy surface by means of the micro-nano porous structure. 55
10. An aluminum or aluminum alloy structure, having a

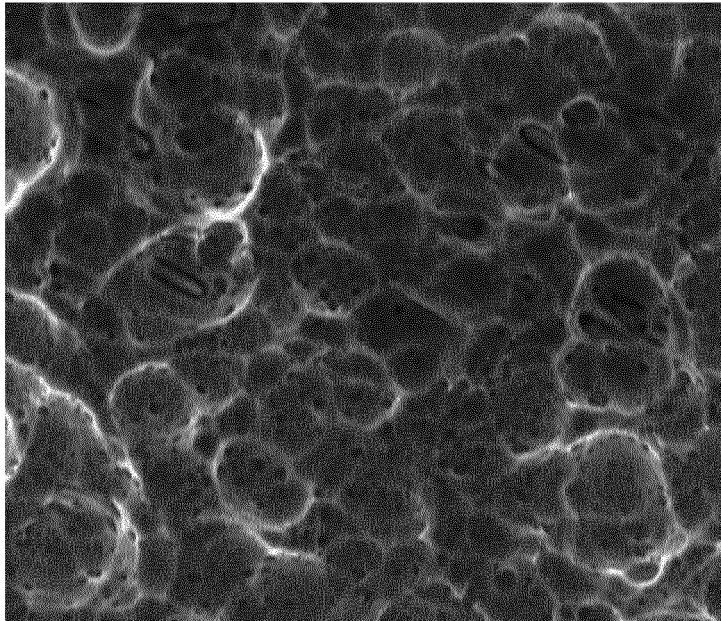


FIG. 1

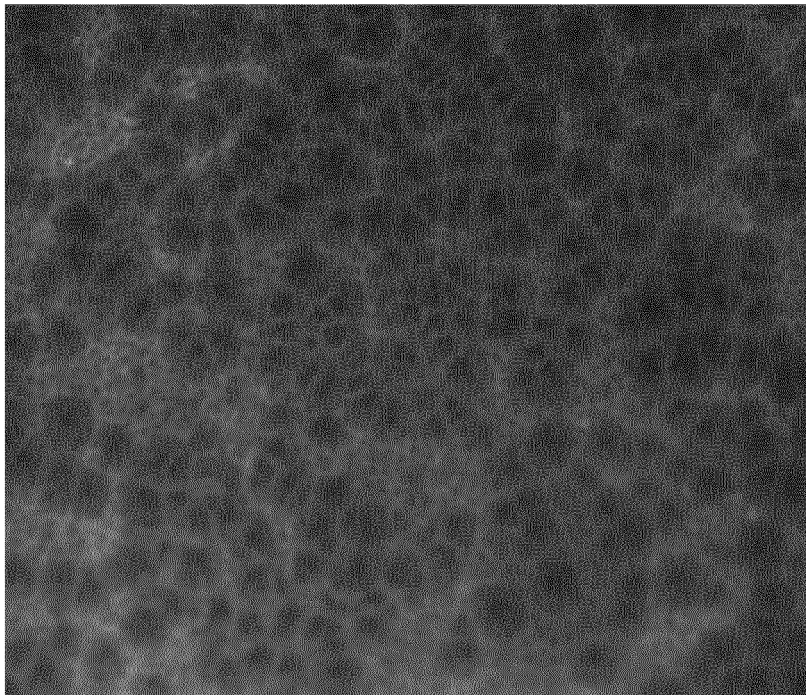


FIG. 2

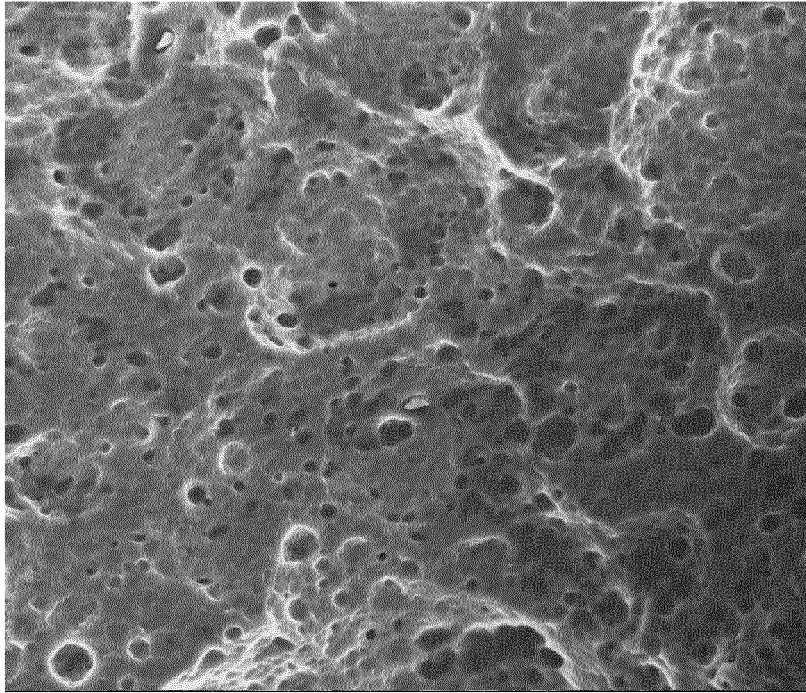


FIG. 3

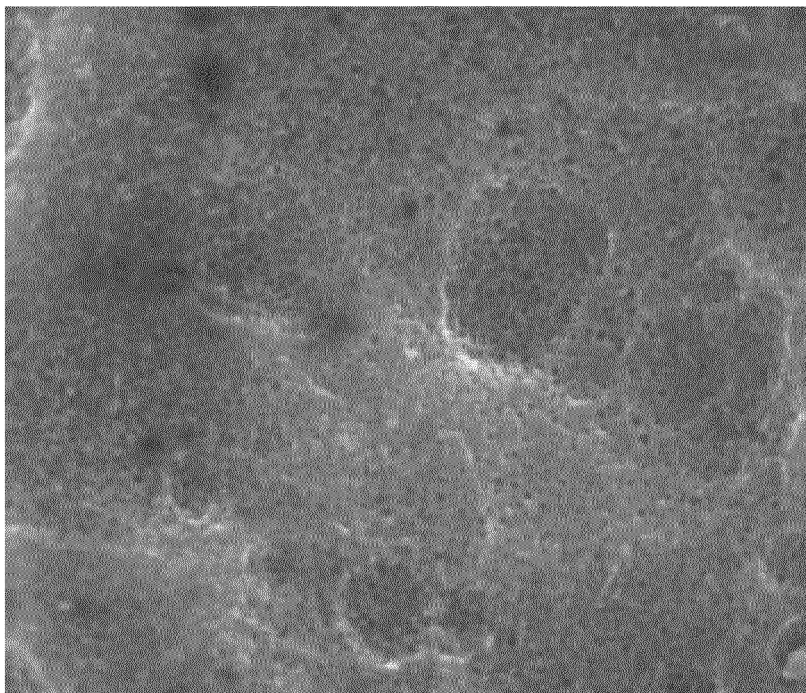


FIG. 4

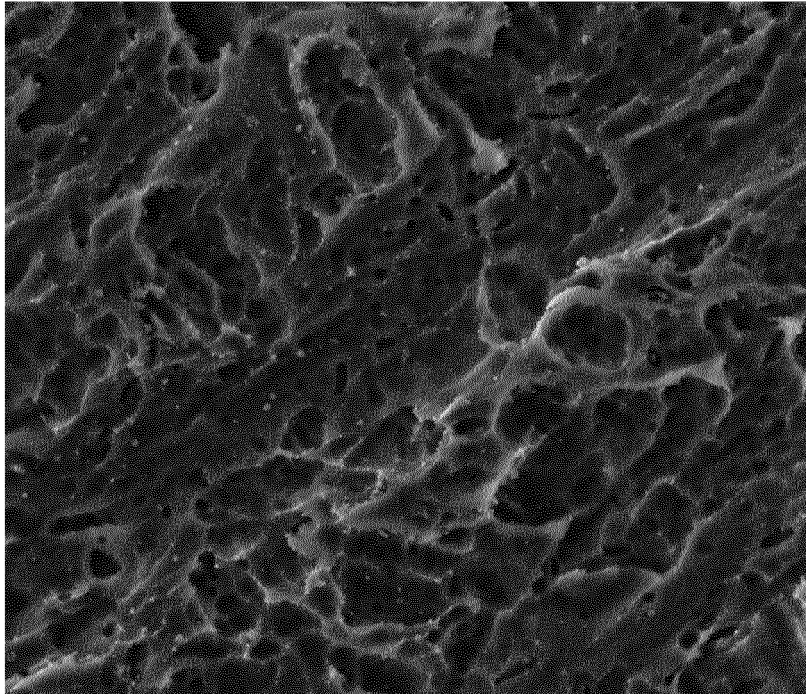


FIG. 5

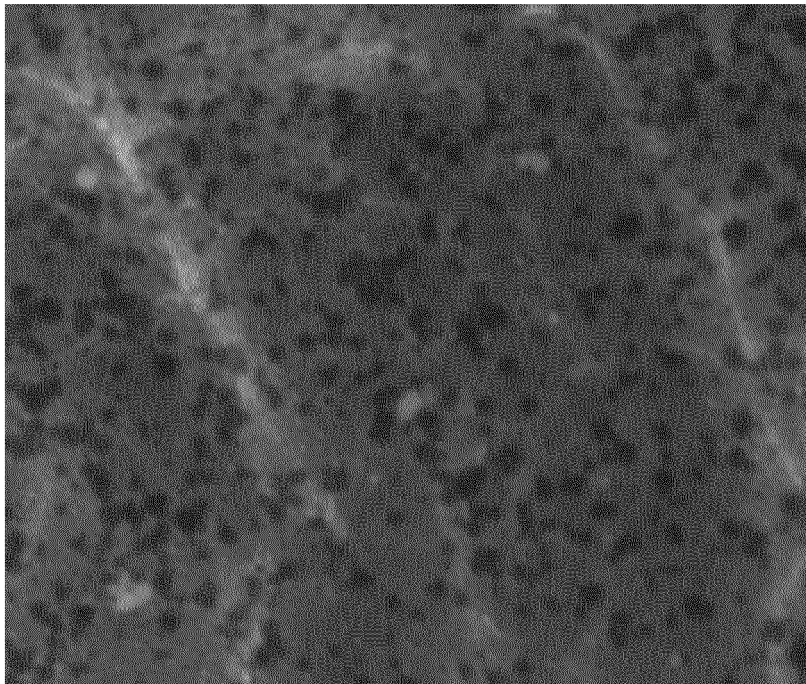


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2013/083591

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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)

IPC: C25F 3/-, B32B 7-, B32B 15/-

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

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

CNPAT, EPODOC, CNKI, WPI, TWABS: aluminium alloy, electrolysis, corrosion, etching, plastic, plastic material, rubber, corrosion mitigation, thiourea, methyl cellulose, morpholino, butylamine, cyclohexylamine, cyclohexanol, ethylene diamine, Triethylene tetramine, copper sulfate, potassium iodide, potassium bromide, Al, aluminium, alloy, galvano-chemistry, chemical etching, inhibitor, inhibitor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"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
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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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INTERNATIONAL SEARCH REPORT
 Information on patent family members

International application No.

PCT/CN2013/083591

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2013/083591

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A. CLASSIFICATION OF SUBJECT MATTER

C25F 3/04 (2006.01) i

B32B 7/08 (2006.01) i

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B32B 15/04 (2006.01) i

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Form PCT/ISA/210 (extra sheet) (July 2009)