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(54) Title: METAL-RESIN COMPOSITE AND METHOD OF PREPARING THE SAME

(57) Abstract: A metal-resin composite and method of producing the same are provided. The method includes : providing a metal substrate, the metal substrate including a metal base made of copper or copper alloy and an oxide layer attached to at least a part of a surface of the metal base; chemically etching the metal substrate to form corrosion pores on a surface of the oxide layer to obtain a surface-treated metal substrate with a treated surface; and injecting a resin composition to fill in the corrosion pores, then molding to obtain a resin layer.

METAL-RESIN COMPOSITE AND METHOD OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to and benefits of Chinese Patent Application Serial No. 201410305849.X, filed with the State Intellectual Property Office of P. R. China on June 30, 2014, the entire content of which is incorporated herein by reference.

FIELD

The present disclosure relates to the field of metal-resin integrally molding, and more particularly to a method for producing a composite of a metal and a resin, and a metal-resin composite obtainable by the same.

BACKGROUND

In the field of vehicles, household electrical appliances, industrial machines and so on, there is an actual requirement for integrating a metal with a resin composition.

Currently, a composite of the metal and the resin composition is normally performed with an adhesion agent at room temperature or under a heating condition. However, metal-resin composites formed with the adhesion agent may have a poor adhesion force between the metal and the resin composition, and the adhesion agent between the metal and the resin composition has poor acid resistance and alkali resistance, which may limit the use field of the metal-resin composites. In addition, the adhesion agent has a certain thickness, which may affect the size of the final product.

However, using the methods mentioned above for preparing metal-resin composite, the adhesion force between the resin and the metal substrate remained to be further improved.

SUMMARY

Embodiments of the present disclosure seek to solve at least one of the problems existing in the prior art to at least some extent, for example, a poor adhesion force between the substrate

made of copper or copper alloy and the resin layer in the current metal-resin composite.

According to a first broad aspect of present disclosure, a method of preparing a metal-resin composite is provided. The method includes: providing a metal substrate including a metal base made of copper or copper alloy and an oxide layer attached to at least a part of a surface of the metal base; chemically etching the metal substrate to form corrosion pores on a surface of the oxide layer to obtain a surface-treated metal substrate; and providing a resin composition on a surface with corrosion pores of the surface-treated metal substrate and molding the resin composition to obtain the metal-resin composite.

According to some embodiments of present disclosure, the method may include: providing a metal substrate, the metal substrate including a metal base made of copper or copper alloy and an oxide layer attached to at least a part of a surface of the metal base; chemically etching the metal substrate to form corrosion pores on a surface of the oxide layer to obtain a surface-treated metal substrate with a treated surface; and injecting a resin composition to fill in the corrosion pores, then molding to obtain a resin layer.

According to a second aspect of present disclosure, a metal-resin composite obtainable by the fore-mentioned method is provided.

According to a third aspect of present disclosure, a metal-resin composite is provided. The metal-resin composite includes: a metal substrate, and a resin layer attached to at least a part of a surface of the metal substrate, wherein the metal substrate includes: a metal base made of copper or copper alloy; and an oxide layer attached to at least a part of a surface of the metal base, corrosion pores formed in the oxide layer and filled with a part of the resin from the resin layer.

According to some embodiments of present disclosure, the metal-resin composite may include: a metal substrate, and a resin layer, attached to at least a part of a surface of the metal substrate, wherein the metal substrate includes a metal base made of copper or copper alloy and an oxide layer attached to at least a part of a surface of the metal base; the oxide layer has a surface thereof formed with corrosion pores, and the corrosion pores are filled with a part of the resin from the resin layer.

The metal-resin composite according to embodiments of the present disclosure, may have a strong adhesion force between the resin and the metal substrate, and the resin layer may be not easy to fall off from the metal substrate, which may enhance a high structure stability of the metal-resin composite, and meet the requirements of using occasions with high structure stability.

The method of preparing the metal-resin composite according to embodiments of the present disclosure, may have good applicability, and is suitable to combine a variety of resins and metal substrates, thus meeting the requirements of a variety of using occasions.

Additional aspects and advantages of embodiments of the present disclosure will be given in part in the following descriptions, become apparent in part from the following descriptions, or be learned from the practice of the embodiments of the present disclosure.

DETAILED DESCRIPTION

Reference will be made in detail to embodiments of the present disclosure. The embodiments described herein are explanatory, illustrative, and used to generally understand the present disclosure. The embodiments shall not be construed to limit the present disclosure.

According to embodiments of the present disclosure, the metal base is made of copper or copper alloy. The copper alloy refers to an alloy using copper as the essential element, and with a combination of other elements. The copper alloy may be some common copper alloys, such as brass. The metal base may be a variety of forming bodies made of copper or copper alloy, which can be any shape according to special requirements.

According to the first aspect of present disclosure, a method of preparing a metal-resin composite is provided. The method includes steps of proving a metal substrate. The metal substrate includes a metal base and an oxide layer attached to at least a part of a surface of the metal base.

In some embodiments of the present disclosure, the oxide layer may be a copper oxide layer, or an oxide layer using copper oxide as a main component. For example, when the metal substrate is made of copper alloy, the oxide layer contains not only copper oxide, but also some oxides of other elements existed in the copper alloy.

In some embodiments of the present disclosure, the oxide layer has a thickness of about 0.1μm to about 50 μm. In some embodiments of the present disclosure, the oxide layer has a thickness of about 1 μm to about 25 μm. In some embodiments of the present disclosure, the oxide layer has a thickness of about 5 μm to about 10 μm. From the viewpoint of further improving the structure stability of the metal-resin composite, a ratio of the thickness of the oxide layer and the metal base may be about 0.001: 1 to about 1:1. In some embodiments of the present disclosure, the ratio of the thickness of the oxide layer and the metal base is about 0.005: 1 to about 0.5:1. In

some embodiments of the present disclosure, the ratio of the thickness of the oxide layer and the metal base is about 0.005: 1 to about 0.01:1.

The oxide layer may be formed by a variety of methods. In one embodiment, the oxide layer is formed by anodizing a surface of the metal base. In other words, the oxide layer is an oxide layer formed by anodic oxidation, which ensure a higher structure stability of the metal-resin composite.

According to embodiments of the present disclosure, the method for anodizing is well known to the skilled person in the art, without special limiting. Preferably, the anodic oxidation method comprises: the metal base is placed in an electrolyte solution, and the metal base is used as an anode, a conductive material which may not react with the electrolyte solution is used as a cathode, the anode and the cathode are electrically connected with the negative electrode and the positive electrode of a power respectively, after turning on the power, an oxide layer may be formed on the metal base.

There's no special limitation to the electrolyte solution. And the electrolyte solution may be any conventional electrolyte solution that may form an oxide layer on the surface of a copper or a copper alloy under the anodizing conditions.

In some embodiments of the present disclosure, the electrolyte solution includes at least one alkaline compound. In some embodiments of the present disclosure, the term "at least one" refers to one or more than one. The alkaline compound may be an alkali or an alkaline salt. In some embodiments of the present disclosure, the alkaline compound may be selected from alkali metal hydroxides (e.g. sodium hydroxide and/or potassium hydroxide), alkali metal carbonate and alkali metal phosphate. In some embodiments of the present disclosure, the alkali metal may be sodium and/or potassium. In some embodiments of the present disclosure, the alkaline compound may be selected from sodium hydroxide, sodium carbonate and sodium phosphate.

The alkaline compound may have a concentration of about 1 wt% to about 50 wt% in the electrolyte solution. In some embodiments of the present disclosure, the alkaline compound may have a concentration of about 10 wt% to about 30 wt% in the electrolyte solution. In some embodiments of the present disclosure, the alkaline compound may have a concentration of about 20 wt% to about 30 wt% in the electrolyte solution.

In a preferred embodiment of the present disclosure, the electrolyte solution further comprises at least a molybdate, which may improve the speed of the anodic oxidation thus

improving the production efficiency, and may provide higher structure stability to the metal-resin composite.

The molybdate may be a water-soluble molybdate. In some embodiments of the present disclosure, the molybdate may be an alkali metal molybdate, such as sodium molybdate or potassium molybdate, preferably sodium molybdate.

The concentration of the molybdate is determined based on the content of the alkaline compound. In some embodiments of the present disclosure, the content of the molybdate is about 1 wt% to about 10 wt%, based on the total weight of the electrolyte solution. In some embodiments of the present disclosure, the content of the molybdate is about 1 wt% to about 5 wt%, based on the total weight of the electrolyte solution.

In some embodiments of the present disclosure, anodizing the surface of the metal base is performed under a voltage of about 10 Volts to about 100 Volts for about 1 minute to about 60 minutes. And in some embodiments of present disclosure, anodizing the surface of the metal base is performed at a temperature of about -20 Celsius degrees to about 80 Celsius degrees. In other words, the electrolyte solution used to perform anodizing the surface of the metal base may have a temperature of about -20 Celsius degrees to about 80 Celsius degrees.

In some embodiments of the present disclosure, the conditions for anodic oxidation may be any conventional conditions which may form an oxide layer with a suitable thickness to meet the actual requirements. In some embodiments of the present disclosure, anodizing the surface of the metal base is performed under a voltage of about 10 Volts to about 100 Volts for about 1 minute to about 60 minutes. And the temperature of the electrolyte solution is about minus 20 Celsius degrees to about 80 Celsius degrees.

In some embodiments of the present disclosure, anodizing the surface of the metal base is performed under a voltage of about 10 Volts to about 50 Volts for about 5 minutes to about 30 minutes. And the temperature of the electrolyte solution is about 20 Celsius degrees to about 60 Celsius degrees.

In some embodiments of the present disclosure, anodizing the surface of the metal base is performed under a voltage of about 15 Volts to about 30 Volts for about 5 minutes to about 20 minutes. And the temperature of the electrolyte solution is about 40 Celsius degrees to about 60 Celsius degrees.

According to embodiments of the present disclosure, the method further includes steps of

chemically etching the metal substrate to form corrosion pores on the surface of the oxide layer to obtain a surface-treated metal substrate with a treated surface.

According to embodiments of the present disclosure, after chemically etching the metal substrate to form corrosion pores on the surface of the oxide layer, then when the resin layer is formed on the surface of the oxide layer, a part of the resin from the resin composition may fill in the corrosion pores, which may improve the adhesion force between the resin layer and the metal substrate in the metal-resin composite.

According to embodiments of the present disclosure, the condition to perform the chemical etching may be selected depending on the desired properties of the corrosion pores on the metal substrate. According to embodiments of the present disclosure, chemically etching the metal substrate is performed until the corrosion pores have a pore diameter of about 200 nm to about 2000 nm, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer is about 0.1-1 to about 1:1.

In some embodiments of the present disclosure, chemically etching the metal substrate is performed until the corrosion pores have a pore diameter of about 800 nm to about 1500 nm, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer is about 0.1:1 to about 0.5:1. Thereby a metal-resin composite obtained may have higher structure stability between the resin layer and the metal substrate.

In some embodiments of the present disclosure, chemically etching the metal substrate is performed until the corrosion pores have a pore diameter of about 1000 nm to about 15000 nm, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer is about 0.2:1 to about 0.4:1.

In some embodiments of the present disclosure, the pore diameter of the corrosion pores refers to the maximum radial dimension of an upper port of the corrosion pores (i.e. the port of the corrosion pores located at the surface of the oxide layer). The depth of the corrosion pores refers to the vertical distance between the two ends of a corrosion hole. The pore diameter and depth of the corrosion pores may be determined by electron microscopy.

In some embodiments of the present disclosure, chemically etching the metal substrate may be performed by any conventional methods which may form corrosion pores on the surface of the oxide layer. In one embodiment, chemically etching the metal substrate is performed by immersing the metal substrate in an acidic etching solution. The acidic etching solution is an

aqueous solution comprising at least an acid. And the acid may be selected from a group consisting of hydrohalic acid, phosphoric acid, sulfuric acid and nitric acid. In some embodiments of the present disclosure, the hydrohalic acid may be hydrochloric acid.

In some embodiments of the present disclosure, the acid has a concentration of about 0.1 wt% to about 50 wt%. In some embodiments of the present disclosure, the acid has a concentration of about 1 wt% to about 30 wt%. In some embodiments of the present disclosure, the acid has a concentration of about 20 wt% to about 50 wt%. Thereby the corrosion pores may be formed on the surface of the oxide layer, with more uniform size and more uniform distribution, which may provide a metal-resin composite with higher structure stability.

In some embodiments of the present disclosure, the acid etching solution further comprises at least a soluble salt, which may improve the stability of the chemically etching, thus ensuring a higher structure stability between the resin layer and the metal base of the metal-resin composite. The content of the soluble salt may be determined by the content of the acid. In some embodiments of the present disclosure, the soluble salt and the acid have a molar ratio of about 0.1:1 to about 1:1.

In some embodiments of the present disclosure, the soluble salt may be at least one selected from a group consisting of hydrohalide, phosphate, sulfate and nitrate. Specific examples of the soluble salt may include, but without no limitation: NaCl, KCl, $AlCl_3$, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, KH_2PO_4, K_2HPO_4, K_3PO_4, Na_2SO_4, K_2SO_4, $NaNO_3$, and KNO_3. In some embodiments of the present disclosure, the soluble salt may be one or more selected from NaCl, NaH_2PO_4, Na_2HPO_4, $NaNO_3$, and Na_2SO_4.

In some embodiments of the present disclosure, the soluble salt has the same acid radicals to the acid of the acid etching solution. For example, when the acid etching solution using a hydrohalic acid as the acid, the soluble salt is one selected from hydrohalide.

The temperature of the acid etching solution may be a conventional choice in the art. Usually, the temperature of the acid etching solution is about 10 Celsius degrees to about 60 Celsius degrees. In some embodiments of the present disclosure, the temperature of the acid etching solution is about 20 Celsius degrees to about 40 Celsius degrees.

The time for chemically etching the metal substrate varies with the type and the concentration of the acid in the acid etching solution. Generally, chemically etching the metal substrate is performed for about 1 minute to about 60 minutes. From the viewpoint of further

improving the dimension uniformity of the corrosion pores, chemically etching the metal substrate is performed for about 10 minutes to about 30 minutes.

According to embodiments of the present disclosure, chemically etching the metal substrate may be carried out for one time or more than one time, such as for 2 times, as long as the total time for chemically etching meet the requirements. While chemically etching the metal substrate may be carried out for more than one time, the etching solution used may be the same or different each time. And, while chemically etching the metal substrate may be carried out for more than one time, the metal substrate should be cleaned to remove the residual etching solution after completion of each chemically etching.

According to embodiments of the present disclosure, the method further includes steps of injecting a resin composition to fill in the corrosion pores, then molding to obtain a resin layer.

The resin from the resin composition (hereinafter referred to the main resin) may be selected according to specific requirements, as long as the resin can be combined with the copper or copper alloy. Usually, the main resin may use any conventional thermoplastic resin, such as polyphenylene sulfide (PPS), polyesters (PE), polyamides (PA), polycarbonates (PC), polyolefins and combinations thereof.

The polyesters (PE) may be a variety of polymers by polycondensation of a dicarboxylic acid with a diol, such as polyethylene terephthalate and/or polybutylene terephthalate (PBT), but without limits.

The polyamides (PA) may be a variety of polymers by polycondensation of a diamine with a dicarboxylic acid, such as polyhexamethylene adipamide, poly-azelaic-methylene adipamide, poly-tetra-methylene adipamide, poly-dodecane-methylene adipamide, poly(hexamethylene sebacamide) (PA-610), poly-sebacamide-decamethylenediamine (PA-1010), polyundecamide, polydodecamide, poly octanamide, poly 9-amino-nonanoic acid, polycaprolactam, poly-p-phenylene isophthalamide, poly-m-phenylene adipamide,poly-p-phenylene adipamide, and poly terephthaloyl nonanediamine, but without limits.

The polyolefins may be at least one selected from a group consisting of polystyrene (PS), polypropylene (PP), polymethyl methacrylate (PMMA) and poly (acrylonitrile-butadiene-styrene) (ABS), but without limits.

Except for the main resin, the resin composition further comprises at least one filler and/or at least one fluidity modifier.

The filler may be any type of fillers selected according to specific requirements. In some embodiments of the present disclosure, the filler may be a fiber filler and/or a powder filler. In some embodiments of the present disclosure, the fiber filler is at least one selected from a group consisting of glass fiber, carbon fiber and aromatic polyamide fiber. The powder filler is at least one selected from a group consisting of calcium carbonate, magnesium carbonate, silicon dioxide, heavy barium sulfate, talcum powder, glass and clay.

The size of the filler may be conventional choice in the art, as long as a compact resin layer can be formed. Usually, the fiber filler may have a length of about 1 mm to about 10mm. The powder filler may have a particle diameter of about 1 μm to about 200 μm.

The content of the filler may be conventional choice in the art. Usually, based on 100 weight parts of the main resin, the content of the filler is about 20 weight parts to 150 weight parts. In some embodiments of the present disclosure, based on 100 weight parts of the main resin, the content of the filler is about 30 weight parts to 60 weight parts.

The fluidity modifier is used to improve the flowing capability of the main resin, further improve the adhesion between the metal substrate and the resin and the processing properties of the resin. The fluidity modifier may be any materials which are able to achieve the above-mentioned effects. In some embodiments of the present disclosure, the fluidity modifier is a cyclic polyester.

The content of the fluidity modifier is determined to ensure the flowing capability of the main resin. In some embodiments of the present disclosure, based on 100 weight parts of the main resin, the content of the fluidity modifier is about 1 weight part to about 5 weight parts.

According to some embodiments of the present disclosure, the resin composition may further comprise other additives according to practical requirements, without special limitations. For example, the additives may comprise a colorant or an antioxidant, which may modify the performance of the resin layer of the metal-resin composite or provide a new performance to the resin layer of the metal-resin composite.

In some embodiments of present disclosure, the resin composition used in present disclosure may be prepared by uniformly mixing the main resin, the filler, the fluidity modifier and other additives. Usually, the resin composition may be prepared by mixing evenly the main resin, the filler, the fluidity modifier and other additives, then granulating and extruding.

According to embodiments of the present disclosure, injecting a resin composition to the

treated surface of the metal substrate may use a conventional method well known in the art, then molding to obtain a resin layer, such as cast molding or injection molding. In one embodiment, the metal substrate is placed in a mold, and then the resin composition is injected into the mold.

The conditions for injecting may be selected according to the types of the main resin of the resin composition. In some embodiments of the present disclosure, the injecting is performed under conditions of: a mold temperature of about 50 Celsius degrees to about 300 Celsius degrees, a nozzle temperature of about 200 Celsius degrees to about 450 Celsius degrees, an injection pressure of about 50 MPa to about 300 MPa, a pressure maintaining time of about 1 s to about 50 s, an injection time of about 1 s to about 30 s, and a delay time of about 1 s to about 30 s. In some embodiments of the present disclosure, the injecting is performed under conditions of: a mold temperature of about 100 Celsius degrees to about 180 Celsius degrees (such as about 120 Celsius degrees to 160 Celsius degrees), a nozzle temperature of about 280 Celsius degrees to about 350 Celsius degrees (such as about 290 Celsius degrees to 320 Celsius degrees), thereby the resin composition may sufficiently fill in the corrosion pores, ensure a higher adhesion force between the resin layer and the metal substrate on one hand; on the other hand, the mold temperature may be easily controlled.

The amount of the injecting of the resin composition may be selected according to the desired thickness of the resin layer. In some embodiments of the present disclosure, the resin composition has an injecting amount for that the resin layer has a thickness of about 0.5 mm to about 10 mm. In some embodiments of the present disclosure, the thickness of the resin layer refers to a vertical distance between the upper surface of the oxide layer and the upper surface of the resin layer, for which the upper surface of the oxide layer refers to a surface contacted to the resin layer.

According to embodiments of the present disclosure, when only a part of the surface of the metal substrate is formed with the resin layer, the surface without the formation of the resin layer may be treated to remove the surface pores and the color changes of the surface caused by chemically etching. These treatments may be carried out before or after the steps of molding, without special limitations.

The metal-resin composite obtained by the method According to embodiments of the present disclosure, has a higher adhesion force between the resin layer and the metal substrate, which may meet the requirements of using occasions with high structure stability.

Therefore, according to the second aspect of present disclosure, a metal-resin composite obtainable by the fore-mentioned method is provided.

According to a third aspect of present disclosure, a metal-resin composite is provided. The metal-resin composite includes: a metal substrate, and a resin layer attached to at least a part of a surface of the metal substrate, wherein the metal substrate comprises: a metal base made of copper or copper alloy; and an oxide layer attached to at least a part of a surface of the metal base, corrosion pores formed in the oxide layer and filled with a part of the resin from the resin layer.

According to some embodiments of present disclosure, the metal-resin composite may include: a metal substrate, and a resin layer, attached to at least a part of a surface of the metal substrate, wherein the metal substrate includes a metal base made of copper or copper alloy and an oxide layer attached to at least a part of a surface of the metal base; the oxide layer has a surface thereof formed with corrosion pores, and the corrosion pores are filled with a part of the resin from the resin layer.

In some embodiments of the present disclosure, the oxide layer has a thickness of about 0.1 μm to about 50 μm. In some embodiments of the present disclosure, the oxide layer has a thickness of about 1 μm to about 25 μm. In some embodiments of the present disclosure, the oxide layer has a thickness of about 5 μm to about 10 μm.

In some embodiments of the present disclosure, a ratio of the thickness of the oxide layer and the metal base is about 0.001: 1 to about 1:1. In some embodiments of the present disclosure, the ratio of the thickness of the oxide layer and the metal base is about 0.005: 1 to about 0.5:1. In some embodiments of the present disclosure, the ratio of the thickness of the oxide layer and the metal base is about 0.005: 1 to about 0.01:1.

In some embodiments of the present disclosure, the corrosion pores have a pore diameter of about 200 nm to about 2000 nm, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer is about 0.1-1 to about 1:1.

In some embodiments of the present disclosure, the corrosion pores have a pore diameter of about 800 nm to about 1500 nm, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer is about 0.1:1 to about 0.5:1.

In some embodiments of the present disclosure, the corrosion pores have a pore diameter of about 1000 nm to about 15000 nm, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer is about 0.2:1 to about 0.4:1.

The main resin may be selected according to specific requirements, as long as the resin can be combined with the copper or copper alloy. Usually, the main resin may use any conventional thermoplastic resin, such as polyphenylene sulfide (PPS), polyesters (PE), polyamides (PA), polycarbonates (PC), polyolefins and combinations thereof.

The polyesters (PE) may be a variety of polymers by polycondensation of a dicarboxylic acid with a diol, such as polyethylene terephthalate and/or polybutylene terephthalate, but without limits.

The polyamides (PA) may be a variety of polymers by polycondensation of a diamine with a dicarboxylic acid, such as polyhexamethylene adipamide, poly-azelaic-methylene adipamide, poly-tetra-methylene adipamide, poly-dodecane-methylene adipamide, poly(hexamethylene sebacamide) (PA-610), poly-sebacamide-decamethylenediamine (PA-1010), polyundecamide, polydodecamide, poly octanamide, poly 9-amino-nonanoic acid, polycaprolactam, poly-p-phenylene isophthalamide, poly-m-phenylene adipamide,poly-p-phenylene adipamide, and poly terephthaloyl nonanediamine, but without limits.

The polyolefins may be at least one selected from a group consisting of polystyrene (PS), polypropylene (PP), polymethyl methacrylate (PMMA) and poly (acrylonitrile-butadiene-styrene) (ABS), but without limits.

Except for the main resin, the resin composition further comprises at least one filler. The filler may be any type of fillers selected according to specific requirements. In some embodiments of the present disclosure, the filler may be a fiber filler and/or a powder filler. In some embodiments of the present disclosure, the fiber filler is at least one selected from a group consisting of glass fiber, carbon fiber and aromatic polyamide fiber. The powder filler is at least one selected from a group consisting of calcium carbonate, magnesium carbonate, silicon dioxide, heavy barium sulfate, talcum powder, glass and clay.

The content of the filler may be conventional choice in the art. Usually, based on 100 weight parts of the main resin, the content of the filler is about 20 weight parts to 150 weight parts. In some embodiments of the present disclosure, based on 100 weight parts of the main resin, the content of the filler is about 30 weight parts to 60 weight parts.

The size of the filler may be conventional choice in the art, as long as a compact resin layer can be formed. Usually, the fiber filler may have a length of about 1 mm to about 10mm. The powder filler may have a particle diameter of about 1 μm to about 200 μm.

According to embodiments of the present disclosure, the thickness of the resin layer may be selected according to specific using occasions. Usually, the resin layer has a thickness of about 0.5 mm to about 10 mm.

The present disclosure will be further described below by way of examples. It would be appreciated that these examples described herein are merely used to understand the present disclosure. These examples shall not be construed to limit the present disclosure.

In the following Examples and Comparative Examples, the average shear strength between the metal substrate and the resin layer of the metal-resin composite was tested according to ASTM D1002-10 with a universal material testing machine INSTRON 3369, and the fracture mode between the metal substrate and the resin layer was observed and recorded.

In the following Examples and Comparative Examples, the thickness of the oxide layer and the depth of the corrosion pores were tested by a metallographic microscope Axio Imager Alm, purchased from ZEISS. Every sample was tested at five different positions thereof, and recorded the depth of the corrosion pores appearing in sight.

In the following Examples and Comparative Examples, the pore diameter of the corrosion pores was tested by a scan electron microscope JSM-7600F, purchased from Japan Electronics Co., Ltd. Every sample was tested at five different positions thereof, and recorded the depth of the corrosion pores appearing in sight.

Examples 1-10 were for instruction of the metal-resin composite and the method of preparing the same According to embodiments of the present disclosure.

Example 1

(1) A commercially available brass plate with a thickness of 1 mm was cut into 15mm × 80mm rectangular sheets, which were then polished in a polishing machine, and cleaned with water-free ethanol, and then immersed in a 2 wt% NaOH aqueous solution. After 2 minutes, the rectangular sheets were washed with water and dried to obtain pretreated brass sheets

(2) Each brass sheet as an anode was placed in an anodizing bath using an aqueous solution containing 20 wt% NaOH and 1 wt% sodium molybdate as an electrolyte solution , a graphite carbon plate was used as a cathode, and the brass sheet was electrolyzed at a voltage of 15 V at 60 ℃ for 5 minutes, and then the brass sheet was blow-dried.

It was determined that an oxide layer with a thickness of 8 μm was formed on the surface of the brass sheet.

(3) The brass sheet after step (2) was immersed in an etching solution containing a hydrochloric acid having a concentration of 30 wt% at 20 ℃, taken out after 10 min, and placed in a beaker containing water to be immersed for 1minute. Then the brass sheet was blow-dried.

It was determined that corrosion pores with a pore diameter of 800 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.1:1 to 0.5:1.

(4) The dried brass sheet after step (3) was inserted into an injection mold. A resin composition containing a polyphenylene sulfide (PPS) resin and fiberglass(length of 5 mm), was injection molded, for which the content of the fiberglass was 30 weight parts, based on 100 weight parts of the PPS, then demolded and cooled. The conditions for injection molding included: a mold temperature of 120 Celsius degrees, a nozzle temperature of 305 Celsius degrees, an injection pressure of 120 MPa, a pressure maintaining time of 5 s, an injection time of 5 s, and a delay time of 5 s.

The cooled product was placed into an oven thermostat keeping 120 Celsius degrees for 1.5h, then cooled to room temperature in the furnace. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Comparative Example 1

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Injection molded the resin composition to the surface of the brass sheet using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Comparative Example 2

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 1.

(3) Injection molded the resin composition to the surface of the brass sheet using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Comparative Example 3

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) The brass sheet was immersed in an etching solution which was an aqueous solution containing 3 wt% H_2SO_4 and 3 wt% H_2O_2 at 30 Celsius degrees for 15 minutes, and placed in a beaker containing water to be immersed for 1minute, then blow-dried. The brass sheet was immersed in a aqueous solution containing 10 wt% NaOH and 5 wt% Na_2SO_3 at 70 Celsius degrees for 1 minute to form oxidation on the surface of the brass, then placed in a beaker containing water to be immersed for 1minute, a brass sheet with a treated surface was obtained.

(3) Injection molded the resin composition to the treated surface of the brass sheet using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 2

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using substantially the same step (2) of Example 1, with the exception that: the electrolyte solution didn't contain the sodium molybdate, and the time for anodic oxidation was 8 minutes.

It was determined that an oxide layer with a thickness of 8μm was formed on the surface of the brass sheet.

(3) The brass sheet after step (2) was immersed in an etching solution containing a hydrochloric acid having a concentration of 30 wt% at 20 ℃, taken out after 10 min, and placed in a beaker containing water to be immersed for 1minute. Then the brass sheet was blow-dried.

It was determined that corrosion pores with a pore diameter of 800 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.1:1 to 0.5:1.

(4) Injection molded the resin composition to the surface of the brass sheet after step (3) using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 3

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 1.

(3) Chemically etched the surface of the brass sheet after step (2) using substantially the same step (3) of Example 1, with the exception that: the etching solution further contained NaCl, and the molar ratio of NaCl and HCl was 1:1. A brass substrate with a treated surface was obtained.

It was determined that corrosion pores with a pore diameter of 1000 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.2:1 to 0.4:1.

(4) Injection molded the resin composition to the surface of the brass substrate using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 4

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 1.

(3) Chemically etched the surface of the brass sheet after step (2) using substantially the same step (3) of Example 1, with the exception that: the time for etching was 40 minutes.

It was determined that corrosion pores with a pore diameter of 200 nm to 2000 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.1:1 to 1:1.

(4) Injection molded the resin composition to the surface of the brass substrate using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 5

(1) A commercially available brass plate with a thickness of 1 mm was cut into 15mm × 80mm rectangular sheets, which were then polished in a polishing machine, and cleaned with water-free ethanol, and then immersed in a 2 wt% NaOH aqueous solution. After 2 minutes, the rectangular sheets were washed with water and dried to obtain pretreated brass sheets

(2) Each brass sheet as an anode was placed in an anodizing bath using an aqueous solution containing 30 wt% Na_3PO_4 and 5 wt% sodium molybdate as an electrolyte solution , a graphite carbon plate was used as a cathode, and the brass sheet was electrolyzed at a voltage of 25 V at 50 ℃ for 15 minutes, and then the brass sheet was blow-dried.

It was determined that an oxide layer with a thickness of 8.5 μm was formed on the surface of the brass sheet.

(3) The brass sheet after step (2) was immersed in an etching solution containing a sulfuric acid having a concentration of 25 wt% at 30 ℃, taken out after 10 min, and placed in a beaker containing water to be immersed for 1minute. Then the brass sheet was blow-dried.

It was determined that corrosion pores with a pore diameter of 800 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.1:1 to 0.5:1.

(4) The dried brass sheet after step (3) was inserted into an injection mold. A resin composition containing a polybutylene terephthalate (PBT) resin and talcum powder (average particle diameter was 4 μm), was injection molded, for which the content of the talcum powder was 40 weight parts, based on 100 weight parts of the PBT, then demolded and cooled. The conditions for injection molding included: a mold temperature of 120 Celsius degrees, a nozzle temperature of 305 Celsius degrees, an injection pressure of 120 MPa, a pressure maintaining time of 5 s, an injection time of 5 s, and a delay time of 3 s.

The cooled product was placed into an oven thermostat keeping 120 Celsius degrees for 1.5h, then cooled to room temperature in the furnace. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 4 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 6

(1) Prepared a brass sheet using the same step (1) of Example 5.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 5.

(3) Chemically etched the surface of the brass sheet after step (2) using substantially the same step (3) of Example 5, with the exception that: the etching solution further contained Na_2SO_4, and the molar ratio of Na_2SO_4 and H_2SO_4 was 0.5:1. A brass substrate with a treated surface was obtained.

It was determined that corrosion pores with a pore diameter of 1000 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.2:1 to 0.4:1.

(4) Injection molded the resin composition to the surface of the brass substrate using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 4 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 7

(1) A commercially available brass plate with a thickness of 1 mm was cut into 15mm × 80mm rectangular sheets, which were then polished in a polishing machine, and cleaned with water-free ethanol, and then immersed in a 2 wt% NaOH aqueous solution. After 2 minutes, the rectangular sheets were washed with water and dried to obtain pretreated brass sheets

(2) Each brass sheet as an anode was placed in an anodizing bath using an aqueous solution containing 25 wt% Na_2CO_3 and 5 wt% sodium molybdate as an electrolyte solution , a graphite carbon plate was used as a cathode, and the brass sheet was electrolyzed at a voltage of 20 V at 40 ℃ for 20 minutes, and then the brass sheet was blow-dried.

It was determined that an oxide layer with a thickness of 10 μm was formed on the surface of the brass sheet.

(3) The brass sheet after step (2) was immersed in an etching solution containing a phosphoric acid having a concentration of 20 wt% at 30 ℃, taken out after 30 min, and placed in a beaker containing water to be immersed for 1minute. Then the brass sheet was blow-dried.

It was determined that corrosion pores with a pore diameter of 800 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.1:1 to 0.5:1.

(4) The dried brass sheet after step (3) was inserted into an injection mold. A resin composition containing a nylon 66 (PA-66) resin and fiberglass (length of 5 mm), was injection molded, for which the content of the fiberglass was 50 weight parts, based on 100 weight parts of the PA-66, then demolded and cooled. The conditions for injection molding included: a mold temperature of 150 Celsius degrees, a nozzle temperature of 305 Celsius degrees, an injection pressure of 120 MPa, a pressure maintaining time of 5 s, an injection time of 5 s, and a delay time of 3 s.

The cooled product was placed into an oven thermostat keeping 120 Celsius degrees for 1.5h, then cooled to room temperature in the furnace. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 5 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 8

(1) Prepared a brass sheet using the same step (1) of Example 7.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 7.

(3) Chemically etched the surface of the brass sheet after step (2) using substantially the same step (3) of Example 7, with the exception that: the etching solution further contained Na_2HPO_4, and the molar ratio of Na_2HPO_4 and H_3PO_4 was 0.2:1. A brass substrate with a treated surface was obtained.

It was determined that corrosion pores with a pore diameter of 1000 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.2:1 to 0.4:1.

(4) Injection molded the resin composition to the surface of the brass substrate using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 5 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 9

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 1.

(3) Chemically etched the surface of the brass sheet after step (2) using substantially the same step (3) of Example 1, with the exception that: the etching solution was a nitric acid having the same concentration as the hydrochloric acid in Example 1. A brass substrate with a treated surface was obtained.

It was determined that corrosion pores with a pore diameter of 800 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.1:1 to 0.5:1.

(4) Injection molded the resin composition to the surface of the brass substrate using the

same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Example 10

(1) Prepared a brass sheet using the same step (1) of Example 1.

(2) Formed an oxide layer on the surface of the brass sheet by an anodic oxidation using the same step (2) of Example 1.

(3) Chemically etched the surface of the brass sheet after step (2) using substantially the same step (3) of Example 9, with the exception that: the etching solution further contained $NaNO_3$, and the molar ratio of $NaNO_3$ and HNO_3 was 1:1. A brass substrate with a treated surface was obtained.

It was determined that corrosion pores with a pore diameter of 1000 nm to 1500 nm was formed in the surface of the oxide layer, and a ratio of the depth of the corrosion pores and the thickness of the oxide layer was 0.2:1 to 0.4:1.

(4) Injection molded the resin composition to the surface of the brass substrate using the same step (4) of Example 1. A metal-resin composite having an oxide layer (the thickness of the oxide layer was 2 mm) was obtained, the average shear strength and fracture mode were listed in Table 1.

Table 1

	average shear strength(MPa)	fracture mode
Example 1	23	A
Comparative Example 1	0.2	B
Comparative Example 2	5	B
Comparative Example 3	11	B
Example 2	20.2	A
Example 3	26.8	A
Example 4	18.1	A
Example 5	20	A
Example 6	23.4	A
Example 7	27	A
Example 8	30.6	A
Example 9	21	A
Example 10	24.5	A

Comment: In the Table 1, the fracture mode A referred to that the fracture place was located at the resin layer. The fracture mode B referred to that the fracture place was located at the combination

part of the resin layer and the metal substrate.

It can be seen from above Table 1 that, the metal-resin composites prepared from the method according to embodiments of the present disclosure, showed higher average shear strength, and the fracture place thereof were located at the resin layer, which demonstrated that the metal-resin composites prepared from the method according to embodiments of the present disclosure had a strong adhesion force between the resin layer and the metal substrate. Meanwhile, the raw materials used in the method according to embodiments of the present disclosure have good applicability and can be used to form various types of resin layers on the surface of the metal substrate.

Although explanatory embodiments have been shown and described, it would be appreciated by those skilled in the art that the above embodiments cannot be construed to limit the present disclosure, and changes, alternatives, and modifications can be made in the embodiments without departing from spirit, principles and scope of the present disclosure.

WHAT IS CLAIMED IS:

1. A method of preparing a metal-resin composite, comprising:

providing a metal substrate comprising a metal base made of copper or copper alloy and an oxide layer attached to at least a part of a surface of the metal base;

chemically etching the metal substrate to form corrosion pores on a surface of the oxide layer to obtain a surface-treated metal substrate; and

providing a resin composition on a surface with corrosion pores of the surface-treated metal substrate and molding the resin composition to obtain the metal-resin composite.

2. The method according to claim 1, wherein the oxide layer is formed by anodizing the surface of the metal base.

3. The method according to claim 2, wherein anodizing the surface of the metal base is performed by using an electrolyte solution comprising an alkaline compound being at least one selected from a group consisting of sodium hydroxide, sodium carbonate and sodium phosphate.

4. The method according to claim 3, wherein the electrolyte solution further comprises a molybdate, and the molybdate has a content of about 1 wt% to about 10 wt% based on a total weight of the electrolyte solution.

5. The method according to claim 4, wherein the molybdate has a content of about 1 wt% to about 5 wt% based on the total weight of the electrolyte solution.

6. The method according to claim 4, wherein the molybdate is an alkali metal molybdate.

7. The method according to claim 6, wherein the molybdate is sodium molybdate.

8. The method according to any one of claims 3 to 7, wherein the alkaline compound has a concentration of about 1 wt% to about 50 wt% in the electrolyte solution.

9. The method according to claim 8, wherein the alkaline compound has a concentration of about 10 wt% to about 30 wt% in the electrolyte solution.

10. The method according to any one of claims 3 to 9, wherein anodizing the surface of the metal base is performed under a voltage of about 10 Volts to about 100 Volts for about 1 minute to about 60 minutes.

11. The method according to any one of claims 3 to 10, wherein anodizing the surface of the metal base is performed at a temperature of about -20 Celsius degrees to about 80 Celsius degrees.

12. The method according to any one of claims 3 to 11, wherein the electrolyte solution has a temperature of about -20 Celsius degrees to about 80 Celsius degrees.

13. The method according to any of claims 1 to 12, wherein the oxide layer has a thickness of about 0.1μm to about 50 μm.

14. The method according to claim 1, wherein chemically etching the metal substrate is performed by immersing the metal substrate in an acidic etching solution.

15. The method according to claim 14, wherein the acidic etching solution is an aqueous solution comprising at least an acid being at least one selected from a group consisting of hydrohalic acid, phosphoric acid, sulfuric acid and nitric acid.

16. The method according to claim 10, wherein the acid etching solution further comprises a soluble salt being at least one selected from a group consisting of hydrohalide, phosphate, sulfate and nitrate.

17. The method according to claim 16, wherein the soluble salt and the acid have a molar ratio of about 0.1:1 to about 1:1.

18. The method according to any o f claims 15 to 17, wherein the acid has a concentration of about 0.1 wt% to about 50 wt% in the acidic etching solution.

19. The method according to claim 18, wherein the acid has a concentration of about 20 wt% to about 30 wt% in the acidic etching solution.

20. The method according to any one of claims 1 to 19, wherein chemically etching the metal substrate is performed for about 1 minute to about 60 minutes.

21. The method according to claim 20, wherein chemically etching the metal substrate is performed for about 10 minutes to about 30 minutes.

22. The method according to any one of claims 1 to 21, wherein the corrosion pores have an average pore diameter of about 200 nm to about 2000 nm.

23. The method according to claim 22, wherein the corrosion pores have an average pore diameter of about 800 nm to about 1500 nm.

24. The method according to claim 23, wherein the corrosion pores have an average pore diameter of about 1000 nm to about 1500 nm.

25. The method according to any one of claims 1 to 21, wherein a ratio of the depth of the corrosion pores and the thickness of the oxide layer ranges from about 0.1-1 to about 1:10.

26. The method according to claim 25, wherein a ratio of the depth of the corrosion pores and the thickness of the oxide layer ranges from about 0.1:1 to about 0.5:1.

27. The method according to claim 25, wherein a ratio of the depth of the corrosion pores and

the thickness of the oxide layer ranges from about 0.2:1 to about 0.4:1.

28. The method according to claim 1, wherein providing the resin composition is performed by cast molding or injection molding.

29. The method according to any one of claims 1 to 28, wherein providing the resin composition with a thickness of about 0.5 mm to about 10 mm on the surface with corrosion pores of the surface-treated metal substrate.

30. A metal-resin composite obtainable by the method according to any one of claims 1 to 29.

31. A metal-resin composite, comprising:

a metal substrate, and

a resin layer attached to at least a part of a surface of the metal substrate, wherein

the metal substrate comprises:

a metal base made of copper or copper alloy; and

an oxide layer attached to at least a part of a surface of the metal base,

corrosion pores formed in the oxide layer and filled with a part of the resin from the resin layer.

32. The metal-resin composite of claim 31, wherein the corrosion pores have an average pore diameter of about 200 nm to about 2000 nm.

33. The metal-resin composite according to claim 32, wherein the corrosion pores have an average pore diameter of about 800 nm to about 1500 nm.

34. The metal-resin composite according to claim 33, wherein the corrosion pores have an average pore diameter of about 1000 nm to about 1500 nm.

35. The metal-resin composite according to any one of claims 31 to 34, wherein a ratio of the depth of the corrosion pores and the thickness of the oxide layer ranges from about 0.1-1 to about 1:10.

36. The metal-resin composite according to claim 35, wherein a ratio of the depth of the corrosion pores and the thickness of the oxide layer ranges from about 0.1:1 to about 0.5:1.

37. The metal-resin composite according to claim 36, whereina ratio of the depth of the corrosion pores and the thickness of the oxide layer ranges from about 0.2:1 to about 0.4:1.

38. The metal-resin composite according to any one of claims 31 to 37, wherein the resin layer has a thickness of about 0.5 mm to about 10 mm.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/082541

A. CLASSIFICATION OF SUBJECT MATTER

B32B 15/20(2006.01)i; B32B 15/08(2006.01)i; B32B 27/06(2006.01)i; C25D 11/34(2006.01)i; C23F 1/18(2006.01)i

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)

B32B; C25D; C23F

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)

CNABS,SIPOABS,DWPI,CNKI: metal, resin, composite, substrate, copper, alloy, etching, corrosion, pores, oxide, layer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103286910 A (BYD CO LTD) 11 September 2013 (2013-09-11) description paragraphs [0027]-[0029], claims 1-13	1-38
X	CN 103448201 A (BYD CO LTD) 18 December 2013 (2013-12-18) claims 1-37	1-38
X	CN 103286908 A (BYD CO LTD) 11 September 2013 (2013-09-11) claims 1-14	1-38

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 August 2015	**22 September 2015**
Name and mailing address of the ISA/CN **STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **WANG,Xiaoyan** Telephone No. **(86-10)62084973**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/082541

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 103286910 A	11 September 2013	US 2014363660 A1	11 December 2014
		EP 2817135 A1	31 December 2014
		JP 2015511188 A	16 April 2015
		KR 20140130195 A	07 November 2014
		WO 2013123754 A1	29 August 2013
CN 103448201 A	18 December 2013	None	
CN 103286908 A	11 September 2013	WO 2013123769 A1	29 August 2013
		KR 20140125845 A	29 October 2014
		US 2014363657 A1	11 December 2014
		EP 2817148 A1	31 December 2014
		JP 2015511190 A	16 April 2015