SHELL, PREPARING METHOD AND APPLICATION THEREOF IN ELECTRONIC PRODUCT

A shell, a method of preparing the shell and an electronic product comprising the shell are provided. The shell may comprise: a metal shell body; a plastic part made of a resin; and an oxide layer formed between the metal body and the plastic part, joining the plastic part to the metal shell body, wherein the oxide layer contains corrosion pores having an average pore size of about 200nm to about 2000nm in the surface contacting the plastic part, and nanopores having a pore size of about 10 to 100nm in the surface contacting the metal shell body; and a part of the resin is filled in the corrosion pore and corrosion pore.
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CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to and benefits of Chinese Patent Application Serial No. 201210043628.0, filed with the State Intellectual Property Office of P. R. China on February 24, 2012, the entire content of which is incorporated herein by reference.

FIELD

The present disclosure relates to the field of metal-plastic molding, and more particularly to a shell, a method of preparing the shell and an electronic product comprising the shell.

BACKGROUND

With the increasing consumption levels, the electronic products having a special texture are very competitive in market. The metal shell can bring excellent visual impact, at the same time it has advantages of delicate feel, wear-resist, drop-resist and corrosion resist and the like.

The existing method of preparing a shell comprising metal and plastic generally uses an adhesive to integrally join the metal and the plastics. However, the mobile phone shell obtained has poor connection force between the metal and the plastic, without performances of wear-resist and drop-resist. And the adhesive has poor performances of acid-resist and alkali-resist, and the obtained mobile phone shell cannot be subjected to surface treatment such as anodic oxidizing.

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. And the present disclosure aims to provide a shell and a method of preparing the shell, in which the shell may have strong combination force between the metal and plastic, and the shell may have advantages of wear-resist, drop-resist and corrosion resist and the like.
According to a first aspect of the present disclosure, there is provided a shell comprising: a metal shell body; a plastic part made of a resin; and an oxide layer formed between the metal body and the plastic part, joining the plastic part to the metal shell body, wherein the oxide layer contains corrosion pores having an average pore size of about 200nm to about 2000nm in the surface contacting the plastic part, and nanopores having a pore size of about 10 to 100nm in the surface contacting the metal shell body; and a part of the resin is filled in the nanopores and corrosion pores.

According to a second aspect of the present disclosure, there is provided a method of preparing the shell, which may be used to prepare the shell described above. According to embodiments of present disclosure, the method may comprise: S1: anodizing at least a part of the surface of a metal shell body to form an oxide layer, wherein the oxide layer is formed with nanopores; S2: immersing the resulting metal shell body in step S1 in an etching solution, to form corrosion pores in at least a part of the outer surface of the oxide layer; and S3: injection molding a resin onto at least a part of the resulting metal shell body in step S2 to obtain the shell, in which the resin is molded into a plastic part.

According to a third aspect of the present disclosure, there is provided electronic product comprising a shell, wherein the shell is described above.

It was found by the inventors surprisingly that a unique two-layer spatial pore structure may be formed in the oxide layer formed on the surface of metal shell body. By means of the method according to embodiments of present disclosure, an oxide layer may be formed on the surface of the metal shell body and the oxide layer may possess nanopores with excellent properties. By means of the technical solutions according to embodiments of present disclosure, nanopores having an average pore size of about 10 to about 100nm may be formed, which is a unique structure, and has well connection force with resin. Meanwhile, by means of further corrosion treatment, corrosion pores may be formed on the outer surface of the oxide layer, to be contacted with a resin. The corrosion pores may have a larger average pore size than nanopores. By means of the technical solutions according to embodiments of present disclosure, nanopores having an average pore size of about 200nm to about 2000nm may be formed on the outer surface of the oxide layer, which is a unique structure contributing to enhance the connection force of a resin with the metal shell body, then the obtained shell may have performances of wear-resist, drop-resist. In the course of following molding steps, a resin may penetrate into the pores in the
inner layer through the relative bigger pores on the outer surface of metal shell, which will make molding easier. According to embodiments of present disclosure, metal shell body may be joined to a plastic tightly without additional moiety, and a higher strength may be obtained, then improving the anti-corrosion performance. According to embodiments of present disclosure, there is little influence on the size of metal shell body and the appearance of metal shell body, and relatively less heat is produced in the course of processing. Meanwhile, resin may be easily injection molded into the corrosion pores with larger pore size on the surface, and there is no particular requirement on the resin. Then the present technical solution may be used widely, is environment-friendly, and may be adopted for massive production.

Additional aspects and advantages of embodiments of 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.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects and advantages of the disclosure will become apparent and more readily appreciated from the following descriptions taken in conjunction with the drawings in which:

Fig. 1 shows the presence of two-layer spatial pore structure in the oxide layer prepared in one embodiment of present disclosure;

Fig. 2 shows a scanning electron microscopy diagram of aluminum alloy sheet surface after surface treatment 1 in Example 1;

Figs. 3a and 3b show scanning electron microscopy diagrams of aluminum alloy sheet surface after surface treatment 2 in Example 1;

Fig.4 shows a schematic diagram of a metal shell body of a mobile phone shell according to one embodiment of present disclosure;

Fig.5 shows a schematic diagram of a plastic part of a mobile phone shell according to one embodiment of present disclosure; and

Fig.6 shows a schematic diagram of a mobile phone shell according to one embodiment of 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 a first aspect of the present disclosure, there is provided a shell. According to embodiments of present disclosure, the shell may comprise a plastic part, a metal shell body, and an oxide layer formed between the metal body and the plastic part. According to embodiments of present disclosure, the plastic part may be made of a resin, and oxide layer may join the plastic part to the metal shell body. According to embodiments of present disclosure, the oxide layer contains corrosion pores having an average pore size of about 200nm to about 2000nm in the surface contacting the plastic part, and nanopores having a pore size of about 10 to 100nm in the surface contacting the metal shell body. And according to embodiments of present disclosure, a part of the resin is filled in the nanopores and the corrosion pores. Then, the connection force between metal shell body and plastic may be enhanced and stronger, thus the shell may be wear-resist, drop-resist and corrosion-resist.

According to embodiments of present disclosure, the corrosion pores may have an average pore size of about 200nm to about 1000nm, preferably about 400nm to about 1000nm, and the nanopores may have an average pore size of about 20nm to about 80nm, preferably about 20nm to about 60nm. Then, the structure of two-layered pore may be further optimized, and further contribute to the direct injection of resin when molding and improve the combination of resin with the metal sheet body.

According to embodiments of present disclosure, the corrosion pores may have an average pore size of about 0.5µm to about 9.5µm, preferably 0.5µm to 5µm. Then the structure of corrosion pores may be further optimized, which contribute to the penetration of injected resin.

According to embodiments of present disclosure, the corrosion pores may be communicated with the nanopores. Then the structure of two-layered pore may be further optimized, and further contribute to the direct injection of resin and molding, improving the combination of resin with the metal sheet body.

According to embodiments of present disclosure, the oxide layer may have a thickness of about 1µm to about 10µm, preferably about 1µm to about 5µm. Then the oxide layer may have an improved combination with the aluminum alloy body, and further optimize the structure of corrosion pores, thus make it easy to create optimized corrosion pores.

According to embodiments of present disclosure, the nanopores may have an average depth
of about 0.5 \mu m to about 9.5 \mu m, preferably about 0.5 \mu m to 5 \mu m. Then the structure of nanopores may be further optimized, then improve the degree of filling of melt resin in the nanopores, ensuring that the resin may penetrate into nanopores with such depth, decreasing the connection area between resin and oxide layer, and there is no gap in the nanopores, and then the connection force was further enhanced.

According to embodiments of present disclosure, the types of the plastic part is not specially limited, as long as it can be made of resin, and the plastic part can be used as any parts of the shell.

According to embodiments of present disclosure, referring to Fig. 5 the plastic part may comprise a plastic shell body 2 having a similar shape with the metal shell body, and a free space may be defined by the plastic shell body 2 to accommodate other parts for example a display screen or an antenna for a cell phone. The plastic shell body 2 may be provided on an end of the metal shell body 1, and the oxide layer is formed between the plastic shell body 2 and the end of the metal shell body 1, and the oxide layer may join the plastic shell body 2 to the end of the metal shell body 1. According to embodiments of present disclosure, the plastic shell 2 may be provided on one or two end of the metal shell body 1, depending on the specific desired needs. According to embodiments of present disclosure, the plastic shell body 2 may match with the metal shell body 1, namely the plastic shell body 2 may form a whole shell shape together with the metal shell 1. According to embodiments of present disclosure, the plastic shell body 2 is joined to the metal shell body 1’s one end, and an oxide layer may be provided between the metal shell body 1 and the plastic shell body 2, then the plastic shell body 2 may be joined to the metal shell body 1 via the oxide layer made of a metal oxide. According to embodiments of present disclosure, a part of the resin forming the plastic shell body may be filled into the nanopores and corrosion pores, resulting in an integral combination of plastic shell body and metal shell body. According to embodiments of present disclosure, the size of a surface joining the plastic shell body to the metal shell body is not limited. In one embodiment of present disclosure, the width of the surface joining the plastic shell and the metal shell body is about 0.5mm to about 2mm, which is relative small, thus a stronger combination force is required.

According to embodiments of present disclosure, the plastic part may further comprise a strengthening rib 51 made of a resin and the strengthening rib 51 may extend along the inner surface of the metal shell body and is joined to the inner surface of the metal shell body.
According to embodiments of present disclosure, the oxide layer may be formed between the strengthening rib and the inner surface of the metal shell body, and the resin forming the strengthening rib may be filled in the corrosion pores and corrosion pores of the oxide layer. Thus the connection force between the plastic shell and metal shell body is further enhanced, and then shell obtained may have an enhanced drop-resist.

According to embodiments of present disclosure, the plastic part may comprise a plastic patch 3 provided in the inner surface of the metal shell body 1, and the plastic patch3 is joined to the inner surface of the metal shell body 1. According to embodiments of present disclosure, the oxide layer is formed between the plastic patch 3 and the inner surface of the metal shell bodyl, and may join the plastic patch 3 to the inner surface of the metal shell bodyl, and the resin forming the plastic patch 3 is filled in the nanopores and the corrosion pores of the oxide layer. According to embodiments of present disclosure, the shape and size of the plastic patch is not specially limited, for example the plastic patch may be used as a support of antenna. And for the purpose of saving space, the plastic patch may be in a form of sheet, and located on the inner surface of metal shell body, adhering to and contacting the surface of the metal shell body. The plastic patch may be used to mount a WIFI antenna. Thus, for a purpose of avoiding signaling is shielded by a metal, an opening for signaling is provided in the surface joining the plastic patch to metal shell body. The size and shape of the opening is not specially limited in present disclosure, for example the opening may be a small slit located in such a way that a part of the plastic patch is exposed.

According to embodiments of present disclosure, the plastic part may comprise a plastic support provided in the inner surface of the metal shell body, and the plastic support is joined to the inner surface of the metal shell body. According to embodiments of present disclosure, the oxide layer is formed between the plastic support and the inner surface of the metal shell body, joining the plastic support to the inner surface of the metal shell body. According to embodiments of present disclosure, the resin forming the plastic support is filled in the nanopores and corrosion pores of the oxide layer. The structure and function of the support made of resin may be designed depending on desired need. According to embodiments of present disclosure, the plastic support further comprises a buckle and a mounting hole. In one embodiment of present disclosure, the mounting hole may be a screw hole. According to embodiments of present disclosure, the plastic support may be used to accommodate other parts, for example parts of a mobile phone, to firmly mount the components within the space of the shell, thus resulting a performances of firm
mounting, wear-resisting, drop-resisting and beautiful appearance, easiness to assemble.

According to embodiments of present disclosure, the plastic part comprises a plastic basal plate provided on an end of the metal shell body. According to embodiments of present disclosure, the plastic basal plate is vertical to the metal shell body, and an edge of the plastic basal plate is joined to the inner surface or the end of the metal shell body. According to embodiments of present disclosure, the oxide layer is formed between the plastic basal plate and the inner surface or the end of the metal shell body, joining the plastic basal plate to the inner surface or the end of the metal shell body. According to embodiments of present disclosure, the resin forming the plastic basal plate is filled in the nanopores and corrosion pores of the oxide layer. According to embodiments of present disclosure, the plastic plate may be used to mount GPRS, Bluetooth, and infrared antenna.

According to embodiments of present disclosure, the plastic part may comprise at least one of the above described plastic shell body, plastic support, plastic patch to mount an antenna, depending on the desired need. The assembling of antenna is not specially limited, the person skilled in the art, may just attach the antenna in a shape of sheet to the plastic part, or form an antenna through chemical plating.

According to embodiments of present disclosure, the plastic part comprises: a plastic shell body; a plastic support; a plastic patch, provided on the plastic support; and a plastic basal plate. According to embodiments of present disclosure, the plastic shell body is connected with the plastic basal plate via the plastic support, and the plastic shell, the plastic support, the plastic patch and the plastic basal plate are integrally formed.

According to a second aspect of the present disclosure, a method of preparing an aluminum alloy described above is provided. The method comprises steps of:

**SI: anodizing at least a part of the surface of a metal shell body to form an oxide layer, wherein the oxide layer is formed with nanopores;**

According to embodiments of present disclosure, in this step, at least a part of the surface of a metal shell body, optionally pre-treated prior to step SI, may be subjected to anodization treatment, thus an oxide layer may be formed on the part of the surface of the aluminum alloy, and the oxide layer may be formed with nanopores. According to embodiments of present disclosure, the method for the anodization treatment is well known to the skilled person in the art. According
to embodiments of present disclosure, the step SI, namely the anodization treatment may comprise: placing the part of the surface of the metal shell body, optionally pre-treated prior to this step, as an anode in a $\text{H}_2\text{SO}_4$ solution with a concentration of about 10wt% to about 30wt%; and electrolyzing the part of the surface of the metal shell body at a temperature of about 10°C to about 30°C, at a voltage of about 10V to about 100V for about 1min to about 40min, to form the oxide layer with a thickness of about $\text{I}_0\text{mm}$ to about $\text{IO}_0\text{mm}$. According to embodiments of present disclosure, any apparatus well known for the anodization treatment may be applied in present disclosure, for example according to an embodiment of present disclosure, an anodization tank may be applied. According to embodiments of present disclosure, the oxide layer formed by means of anodization treatment may have a preferred thickness of about $\text{I}_0\text{mm}$ to about $\text{IO}_0\text{mm}$, preferably about $\text{I}_0\text{mm}$ to about $5\text{mm}$. According to embodiments of present disclosure, the nanopores of the oxide layer may have an average pore size of about $10\text{nm}$ to about $100\text{nm}$, preferably about $20\text{nm}$ to about $80\text{nm}$, and further preferred about $20\text{nm}$ to about $60\text{nm}$. According to embodiments of present disclosure, the nanopores may have a depth of about $0.5\text{mm}$ to about $9.5\text{mm}$, preferably about $0.5\text{mm}$ to about $5\text{mm}$. It was founded by the inventors surprisingly that with the nanopores, the connection force between the oxide layer and the resin will be stronger.

According to embodiments of present disclosure, the part of the surface of the metal shell body to be subjected to anodization may be any parts to be joined to a plastic part. According to embodiments of present disclosure, the plastic part comprises a plastic shell body, and the part of the surface of the metal shell body to be subjected to anodization may be at least a part of an end of the metal shell body. According to embodiments of present disclosure, the plastic part comprises a plastic support, and the part of the surface of the metal shell body to be subjected to anodization may be at least a part of the inner surface of the metal shell body. According to embodiments of present disclosure, the plastic part comprises a plastic patch, and the part of the surface of the metal shell body to be subjected to anodization may be at least a part of the inner surface of the metal shell body. According to embodiments of present disclosure, the plastic part comprises a plastic basal plate, and the part of the surface of the metal shell body to be subjected to anodization may be at least a part of the inner surface or the end of the metal shell body and the surface around thereof. According to one embodiment of present disclosure, the whole metal shell body may be subjected to anodization to form an oxide layer on the surface of the metal shell.
body, and the oxide layer formed may comprise nanopores having an average pore size of about 10nm to about 100nm. It should be noted the formed nanopores will have no adverse influence on the appearance of the resulting shell, because these pores may be easily removed, for example removed by furnishing treatment.

**S2: immersing the resulting metal shell body in step S1 in an etching solution, to form a corrosion pores in at least a part of the outer surface of the oxide layer**

According to embodiments of present disclosure, in this step, the resulting metal shell body in step S1 may be immersed in an etching solution thus corrosion pores with a pore size of about 200nm to about 2000nm may be formed in the outer surface of the oxide layer formed on the aluminum alloy substrate in step S1.

In this step, an etching solution is used to treat the resulting aluminum alloy substrate in step S1, then corrosion pores may be formed in an outer surface of the oxide layer, and the size of corrosion pores is usually larger than that of nanopores. The type and concentration of the etching solution is not specially limited, as long as the etching solution is a solution being corrosive to the oxide layer. According to embodiments of present disclosure, the etching solution is an acid/alkaline etching solution with a pH of about 10 to about 13. According to embodiments of present disclosure, the etching solution may be an alkaline solution with a pH of about 10 to about 13 of sole alkali or mixture of several alkalis. According to embodiments of present disclosure, the etching solution may comprise an aqueous solution containing at least one selected from a group consisting of Na$_2$CO$_3$, NaHCO$_3$, NaOH, NaH$_2$PO$_4$, Na$_2$HPO$_4$, Na$_3$P0$_4$, Na$_2$S0$_3$ or Na$_2$B$_4$0$_7$.

According to embodiments of present disclosure, the alkaline solution is an aqueous solution containing Na$_2$CO$_3$ and/or NaHCO$_3$. According to embodiments of present disclosure, in the alkaline solution, Na$_2$CO$_3$ and/or NaHCO$_3$ have a mass percent concentration of about 0.1wt%-15wt% respectively. According to embodiments of present disclosure, in the alkaline solution, Na$_2$CO$_3$ and/or NaHCO$_3$ have a mass percent concentration of about 0.1wt%-10wt% respectively. According to embodiments of present disclosure, the etching solution may be a mixture of a soluble alkali with a soluble hydrophosphate or dihydrogen phosphate. According to embodiments of present disclosure, the soluble alkali may be a strong alkali. According to embodiments of present disclosure, the dihydrogen phosphate is at least one selected from a group consisting of sodium dihydrogen phosphate, potassium dihydrogen phosphate, ammonium dihydrogen phosphate, and aluminum dihydrogen phosphate, and the soluble alkali is at least one
selected from a group consisting of sodium hydroxide and potassium hydroxide. Then, with the preferred combination of dihydrogen phosphate and alkali, the corrosion pores formed will distribute evenly in the surface of oxide layer with uniform pore sizes, and pore structure may be excellent, enabling a better connection force performance of a resin layer with the aluminum alloy substrate, resulting in a better tensile strength and a better integral joining of the aluminum alloy-resin composite. According to an embodiment of present disclosure, the dihydrogen phosphate has a concentration of about 50wt% to about 99wt%, and the soluble alkali has a concentration of about 1wt% to about 50wt%, and more preferably, the dihydrogen phosphate has a concentration of about 60wt% to about 99wt%, and the soluble alkali has a concentration of about 1wt% to about 40wt%. Further, the etching solution may be at least one of ammonia solution, hydrazine aqueous solution, hydrazine derivatives aqueous solution, water-soluble amine compound aqueous solution and \( \text{NH}_3\text{-NH}_2\text{Cl} \) aqueous solution and the like. According to an embodiment of present disclosure, step S2 may comprise repeatedly immersing the resulting aluminum alloy in step S1 in an alkaline solution having a pH of about 10 to about 13 for a plurality of times, namely more than one time, for example for about 2-10 times, each immersing may last for about 1 min to about 60 min, and cleaning the aluminum alloy with water after each immersing, for example washing with de-ionized water. According to an embodiment of present disclosure, the cleaning may comprise just placing the part to be cleaned in a washing tank and stand for about 1 min to 5 min, and may comprise washing the part to be cleaned in a washing tank for about 1 min to 5 min.

**S3: injection molding a resin onto at least a part of the resulting metal shell body in step S2 to obtain the shell, in which the resin is molded into a plastic part.**

According to embodiments of present disclosure, in this step, the resulting metal shell body after the treatments in steps S1 and S2 may be placed in a mold, and a resin composition may be injected into the mold to combine with the metal shell body, thus an shell is produced after the molding treatment.

According to embodiments of present disclosure, after injection molding, the resulting shell may be further subjected to annealing under a temperature of about 50°C to about 200°C. According to embodiments of present disclosure, the annealing may comprise keeping the resulting shell after injection molding under a temperature of about 50°C to about 200°C for
about 1 to 2 hours, and then decreasing the temperature. For example, the resulting shell may be kept at about 70°C to about 180°C for about 1 to 1.5 hours, and then decrease the temperature. The annealing apparatus may be any well-known equipment by the person skilled in the art. For example, the resulting shell may be kept in an Electric Thermostatic Drying Oven, and a Multistage heating furnace may also be applied. According to embodiments of present disclosure, the resulting shell may be placed in an annealing apparatus at a temperature of about 50°C to about 200°C directly, or the temperature of about 50°C to about 200°C may be reached gradually, for example at a rate of 1-10 °C/min. And the temperature may be decreased to room temperature, for example 15-28 °C, which may be reached naturally or gradually, for example at a rate of about 1-10 °C/min, and 3-8 °C/min is preferred. Thus the solid resin may be transformed into liquid phase, and penetrate into the nanopores, thus the connection force between the metal shell body and plastic part will be further enhanced.

As mentioned before, prior to the treatment of step SI, the metal shell body may be subjected to a pretreatment, which generally comprises mechanical burnishing or mechanical lapping to remove visible foreign matters from the surface, and degreasing and washing the metal shell body to remove processing oil adhered to the metal surface. Preferably, pretreatment comprises burnishing the surface of an metal shell body, for example further comprises burnishing the surface of an metal shell body using a sand paper of about 100 mesh to about 400 mesh or using a polishing machine, to create small pores of microns. According to embodiments of present disclosure, the burnished metal shell body may be sequentially subjected to oil removing, a first washing with water, alkali etching, a second washing with water, neutralizing, and a third washing with water. According to embodiments of present disclosure, the metal shell body may be cleaned by means of ultrasonic wave using any well-known solvent for about 0.5 hour to about 2 hours to remove oily dirty from the surface of metal shell body, and then place the metal shell body in an acid/alkali aqueous solution, and wash the surface again under ultrasonic wave. The types of the solvents and acid/alkali aqueous solution are not limited, the solvent used may be ethanol or acetone, and the acid/alkali aqueous solution may be at least one selected from a group consisting of hydrochloric acid, sulphuric acid, sodium hydroxide, potassium hydroxide and the like. According to embodiments of present disclosure, the metal shell body is subjected to oil removing treatment using water-free ethanol to remove oil from the surface, and then washing the metal shell body using water. Then, the washed metal shell body is immersed in a sodium hydroxide
solution at a concentration of about 30-70g/L and at a temperature of about 40°C to about 80°C
to alkali etch the aluminum alloy for about 1-5min, and wash using deionized water. Then,
neutralize the metal shell body using a 10-30 wt% HNO₃ to remove trace alkali solution, and
wash using deionized water. Thus, a pore with a size of microns may be formed in the surface of
metal shell body. According to embodiments of present disclosure, the pore size may be about
1-10μm.

There are no special limitations to the metal shell body used in present disclosure, and the
examples may be aluminum alloy of Industry-Standard 1000-7000 series, or various metal shell
body of molded-class. The metal shell body in this disclosure may be commonly-used metal shell
body with various shapes and structures, which is not limited in present disclosure. The various
shapes and structures of the metal shell body may be achieved by mechanical processing.

According to embodiments of present disclosure, the resin used in present disclosure may be
prepared by mixing main resin and polyolefin resin. For example, the resin is prepared by mixing
evenly a main resin and a polyolefin resin, and then granulation with twin-screw extruding
machine. According to embodiments of present disclosure, a flow improver and a filler may be
added to the main resin and mixed evenly, thus the obtained resin has a linear expansion
coefficient similar to the aluminum alloy both in horizontal and vertical direction.

According to embodiments of present disclosure, the conditions to carry out the injection
molding are not limited. For example, according to one embodiment of present disclosure, the
condition of injection molding may be: mold temperature 50 to 300°C, nozzle temperature
200-450°C, pressure maintaining time 1-50s, injection pressure 50-300MPa, injection time 1-30s,
delay time 1-30s, and cooling time 1-60s. According to one embodiment of present disclosure, the
condition of injection molding may be: mold temperature 80 to 200°C, nozzle temperature
200-350°C, pressure maintaining time 1-10s, injection pressure 90-140MPa, injection time
3-10s, delay time 15-30s, and cooling time 15-25s. Then the surface of the prepared composite
may have a resin layer with a depth of 0.5-10mm.

The preparation method of the present disclosure is simple, which simplifies significantly the
production process when compared with existing adhesive technology, and shortens the corrosion
time when compared with the existing amine substance, thus shortens the production time and
significantly reduces the process complexity. All above may be achieved only by directly injection
molding after using the process method of the present disclosure. At the same time, the prepared
aluminum alloy resin composite by the preparation method of the present disclosure has a combination between the resin layer and the aluminum alloy substrate, and has better tensile shear strength.

There is no special limitation to the resin used in present invention, which may be any resin capable of joining with aluminum alloy, in which thermoplastic resin is preferred. According to embodiments of present disclosure, the thermoplastic resin is a mixture of a main resin and a polyolefin resin. According to embodiments of present disclosure, the main resin may be non-crystalline resin, which has a surface gloss and a toughness both superior to those of the highly crystalline resins in the prior art, is used as an injection molding material, and a polyolefin resin with a melting point of about 65°C to about 105°C is also used. Therefore, injection molding at a specific mound temperature may be not required during the molding, subsequent annealing treatment may also be not required, the molding process may be simplified, and it may be ensured that the obtained metal-resin composite structure may have high mechanical strength and good surface treatment characteristics, thus solving the problem of the surface decoration of a plastic part and meet the diverse requirements of customers.

According to embodiments of present disclosure, it has been found by the inventors through many experiments that in the present disclosure, by using a polyolefin resin with a melting point of about 65°C to about 105°C in the non-crystalline main resin, the flowing capability of the resin in the nanoscale micropore in the surface of the metal sheet may be enhanced, thus ensuring strong adhesive force between the metal and the plastic as well as high mechanical strength of the metal-resin composite structure. Preferably, based on 100 weight parts of the thermoplastic resin, the amount of the main resin is about 70 weight parts to about 95 weight parts, and the amount of the polyolefin resin is about 5 weight parts to about 30 weight parts.

It has also been found by the inventors that the flowing capability of the resin may be enhanced by using a flow improver in the thermoplastic resin, thus further enhancing the adhesive force between the metal and the plastic as well as the injection molding performance of the resin. Preferably, based on 100 weight parts of the thermoplastic resin, the thermoplastic resin further contains about 1 weight part to about 5 weight parts of a flow improver. Preferably, the flow improver is a cyclic polycarbonate.
As mentioned before, the resin used in present disclosure may be non-crystalline resin. According to embodiments of present disclosure, the main resin is a mixture of polyphenylene ether (PPO) and polyphenylene sulfide (PPS). According to one embodiment of present disclosure, in the main resin, the weight ratio of polyphenylene ether to polyphenylene sulfide is about 3:1 to about 1:3, preferably about 2:1 to about 1:1. According to embodiments of present disclosure, the main resin is a mixture of polyphenylene oxide and a polyamide. According to one embodiment of present disclosure, in the main resin, the weight ratio of polyphenylene oxide to the polyamide is about 3:1 to about 1:3, preferably about 2:1 to about 1:1. According to embodiments of present disclosure, in the main resin, the main resin is a polycarbonate, which may be linear chain polycarbonate or branched polycarbonate.

According to embodiments of present disclosure, the polyolefin resin has a melting point of about 65 °C to about 105 °C, preferably the polyolefin resin may be grafted polyethylene. Preferably, a grafted polyethylene with a melting point of about 100 °C to about 105 °C may be used as polyolefin resin.

The resin used in present disclosure may further comprise other modifier additives, and there is no special limitation to the additives, for example, the resin may comprise a filler. And there is no special limitation to the filler, the non-limiting example of the filler is fiber filler or powder filler. The fiber filler may be at least one selected from a group consisting of fiberglass, carbon fiber and aromatic polyamide fiber. And the powder filler may be at least one selected from a group consisting of calcium carbonate, magnesium carbonate, silica, heavy barium sulfate, talcum powder, glass and clay. According to embodiments of present disclosure, based on 100 weight parts of the main resin, the content of the fiber filler is 50-150 weight parts and the content of the powder filler is 50-150 weight parts. Then the resin has a linear expansion coefficient similar to the aluminum alloy both in horizontal and vertical direction.

According to embodiments of present disclosure, the resin used in present disclosure may be prepared by mixing main resin and polyolefin resin. For example, the resin is prepared by mixing evenly a main resin and a polyolefin resin, and then granulation with twin-screw extruding machine. According to embodiments of present disclosure, a flow improver and a filler may be added to the main resin and mixed evenly, thus the obtained resin has a linear expansion coefficient similar to the metal shell body both in horizontal and vertical direction.

According to embodiments of present disclosure, the conditions to carry out the injection
molding are not limited. For example, according to one embodiment of present disclosure, the condition of injection molding may be: mold temperature 50 to 300 °C, nozzle temperature 200-450 °C, pressure maintaining time 1-50s, injection pressure 50-300MPa, injection time 1-30s, delay time 1-30s, and cooling time 1-60s. According to one embodiment of present disclosure, the condition of injection molding may be: mold temperature 80 to 200 °C, nozzle temperature 200-350 °C, pressure maintaining time 1-10s, injection pressure 90-140MPa, injection time 3-10s, delay time 15-30s, and cooling time 15-25s. Then the surface of the prepared shell may have a resin layer with a depth of 0.5-10mm.

The preparation method of the present disclosure is simple, which simplifies significantly the production process when compared with existing adhesive technology, and shortens the corrosion time when compared with the existing amine substance, thus shortens the production time, and significantly reduces the process complexity. All above may be achieved only by directly injection molding after using the process method of the present disclosure. At the same time, the prepared shell by the preparation method of the present disclosure has a better combination between the resin layer and the metal shell body, and has better tensile shear strength.

There is no special limitation to the resin used in present invention, which may include any resin capable of joining with metal shell body, in which thermoplastic resin is preferred. According to embodiments of present disclosure, the thermoplastic resin includes a mixture of a main resin and a polyolefin resin. According to embodiments of present disclosure, the main resin may include non-crystalline resin, which has a surface gloss and a toughness both superior to those of the highly crystalline resins in the prior art, is used as an injection molding material, and a polyolefin resin with a melting point of about 65 °C to about 105 °C is also used. Therefore, injection molding at a specific mound temperature may be not required during the molding, subsequent annealing treatment may also be not required, the molding process may be simplified, and it may be ensured that the obtained metal-resin composite structure may have high mechanical strength and good surface treatment characteristics, thus solving the problem of the surface decoration of a plastic part and meet the diverse requirements of customers.

According to embodiments of present disclosure, it has been found by the inventors through many experiments that in the present disclosure, by using a polyolefin resin with a melting point
of about 65°C to about 105°C in the non-crystalline main resin, the flowing capability of the resin in the nanopores in the surface of the metal sheet may be enhanced, thus ensuring strong adhesive force between the metal and the plastic as well as high mechanical strength of the metal-resin composite structure. Preferably, based on 100 weight parts of the thermoplastic resin, the amount of the main resin is about 70 weight parts to about 95 weight parts, and the amount of the polyolefin resin is about 5 weight parts to about 30 weight parts.

It has also been found by the inventors that by using a flow improver in the thermoplastic resin, the flowing capability of the resin may be enhanced, thus further enhancing the adhesive force between the metal and the plastic as well as the injection molding performance of the resin. Preferably, based on 100 weight parts of the thermoplastic resin, the thermoplastic resin further contains about 1 weight part to about 5 weight parts of a flow improver. Preferably, the flow improver is a cyclic polycarbonate.

As mentioned before, the resin used in present disclosure may be non-crystalline resin. According to embodiments of present disclosure, the main resin is a mixture of polyphenylene ether (PPO) and polyphenylene sulfide (PPS). According to one embodiment of present disclosure, in the main resin, the weight ratio of polyphenylene ether to polyphenylene sulfide is about 3:1 to about 1:3, preferably about 2:1 to about 1:1. According to embodiments of present disclosure, the main resin is a mixture of polyphenylene oxide and a polyamide. According to one embodiment of present disclosure, in the main resin, the weight ratio of polyphenylene oxide to the polyamide is about 3:1 to about 1:3, preferably about 2:1 to about 1:1. According to embodiments of present disclosure, in the main resin, the main resin is a polycarbonate, which may be linear chain polycarbonate or branched polycarbonate.

According to embodiments of present disclosure, the polyolefin resin has a melting point of about 65°C to about 105°C, preferably the polyolefin resin may include a grafted polyethylene. Preferably, a grafted polyethylene with a melting point of about 100°C to about 105°C may be used as polyolefin resin.

The resin used in present disclosure may further comprise other modifier additives, and there is no special limitation to the additives, for example, the resin may comprise a filler. And there is no special limitation to the filler, and the non-limiting example of the filler is fiber filler or powder filler. The fiber filler may be at least one selected from a group consisting of fiberglass, carbon
fiber and aromatic polyamide fiber. And the powder filler may be at least one selected from a group consisting of calcium carbonate, magnesium carbonate, silica, heavy barium sulfate, talcum powder, glass and clay. According to embodiments of present disclosure, based on 100 weight parts of the main resin, the content of the fiber filler is 50-150 weight parts and the content of the powder filler is 50-150 weight parts. Then the resin has a linear expansion coefficient similar to the metal shell body both in horizontal and vertical direction.

According to embodiments of present disclosure, the resulting shell after injection molding may be further subjected to finishing treatments. For example, the resulting shell may be subjected to surface burnishing and abrasion blasting, removing the flashes, making the shell brighter, and improving the aesthetic feeling. The burnishing treatment may be carried out using a sand paper of about 100 mesh to about 400 mesh or using a polishing machine. The abrasion blasting may be carried out using a ceramic bead or iron bead of about 100 to about 600 mesh, to form a sandy appearance of the shell.

According to embodiments of present disclosure, after the surface burnishing and abrasion blasting, the resulting shell may be subjected to surface treatments of anodization and dyeing, so as to form a decorative effect of various colors and improve the characteristics of corrosion-resistance and wear-resistance. It may be also comprise performing other surface decorative treatment of shell surface, such as spraying, electrophoresis, PVD, plating, etc.

According to a third aspect of the present disclosure, there is provided electronic product comprising a shell, wherein the shell is described above. The example of the electronic product may include: cell phone, PDA, computer, and the same.

In order to make the technical problem, the technical solution and the advantageous effects of the present disclosure more clear, the present disclosure will be further described below in detail with reference to examples thereof. It would be appreciated that particular examples described herein are merely used to understand the present disclosure. The examples shall not be construed to limit the present disclosure. The raw materials used in the examples and the comparative examples are all commercially available, without special limits.

Example 1

1. Pretreatment:

A commercially available A5052 aluminum alloy shell body with a thickness of 1mm was cut
into 15mm x 80mm rectangular shells (as shown in Fig. 4), which were then polished in a polishing machine, and cleaned with water-free ethanol, and then immersed in a 40g/L NaOH aqueous solution. After 2 min, the rectangular shells were washed with water and dried to obtain pretreated aluminum alloy shells.

2. Surface treatment 1:

Each aluminum alloy shell as an anode was placed in an anodizing bath containing a 20wt% H₂SO₄ solution, the aluminum alloy shell was electrolyzed at a voltage of 20V at 18 °C for 10 min, and then the aluminum alloy shell was blow-dried.

The cross section of the aluminum alloy shell after the surface treatment 1 was observed by a metalloscope, to find out that an aluminum oxide layer with a thickness of 5μm was formed on the surface of the electrolyzed aluminum alloy shell. The surface of the aluminum alloy shell after the surface treatment 1 was observed by an electron microscope (see Fig. 2), to find out that nanopores with an average pore size of about 40nm to about 60nm and a depth of 1μm was formed in the aluminum oxide layer.

3. Surface treatment 2

500ml aqueous solution containing 10wt% Na₂CO₃(pH=12.2) was prepared in a beaker. The aluminum alloy sheet after step (2) was immersed in the sodium carbonate solution at 20 °C, taken out after 5 min, and placed in a beaker containing water to be immersed for 1min. After 5 cycles, after water immersing for the last time, the aluminum alloy shell was blow-dried.

The surface of the aluminum alloy shell after the surface treatment 2 was observed by an electron microscope (see Figs. 3a and 3b), to find out that corrosion pores with an average pore size of 300nm to 1000nm and a depth of 4μm was formed in the surface of the immersed aluminum alloy shell. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores.

4. Molding:

The dried aluminum alloy shell was inserted into an injection mold with a pattern shown in Fig. 5. A resin composition containing a polyphenylene sulfide (PPS) resin and 30wt% fiberglass was injection molded. The shell for cell phone which was a firmly combination of aluminum alloy and resin composite was obtained after being demolded and cooled, as shown in Fig. 6.
As shown in Fig. 5, the formed plastic part comprised a plastic shell body 2, a plastic patch 3, a plastic support 4 and a plastic basal plate 5, which were integrally formed. The plastic shell body 2 was provided on one end of the aluminum alloy shell 1, and the plastic shell body 2 matched with the aluminum alloy shell 1 very well, and the interface between the plastic shell body 2 and the end of the aluminum alloy shell 1 formed a first connection surface 22, and the connection force between the aluminum alloy shell 1 and the plastic shell body 2 was formed by the first connection surface 22. The plastic basal plate 5 was provided on the other end of the aluminum alloy shell 1, and was vertical to the aluminum alloy shell 1, and a second connection surface 52 was formed by the interface between the plastic basal plate 5 and aluminum alloy shell 1, and the connection force between the aluminum alloy shell 1 and the plastic basal plate was formed by the second connection surface 52. A strengthening rib 51 extending along the inner surface of the aluminum alloy shell 1 from the plastic basal plate 5 was formed, and strengthening rib 51 was joined to the inner surface of the aluminum alloy shell 1 strengthening the connection force between the plastic part and the metal shell body. The plastic shell body 2 was connected with the plastic basal plate 5 via a plastic support 4 provided in the inner surface of the metal shell body 1. The plastic support 4 was a framework construct, and a support rod 42 was provided in the middle of the framework, and some screwed holes were formed in the support rod 42, and the rod 42 was joined to the middle area of the inner surface of the aluminum alloy shell body 1. The plastic support 4 was vertical to the plastic basal plate 5, and the framework 44 having a buckle 43 thereon was joined to the edges of the metal shell body 1. The screw hole 41 and buckles 43 disposed in the framework 4 were used to mount the some parts within the cell phone. The plastic patch 3 was provided on the plastic support 4, and was vertical to the support rod 42, forming a cross together, and the end of the plastic patch 3 may also be engaged to the framework 44. And an opening 11 was formed in the outer surface of the shell, i.e. under the surface of the plastic patch 3 to expose a part of the plastic patch 3, avoiding the shielding by the metal, (see Fig. 4). The plastic shell body 3, plastic patch 3, plastic support 4 and the plastic basal plate were integrally formed via injection molding. A strengthening rib 21 extended from the inner surface from the plastic shell body 2, and the strengthening rib 21 were joined to the metal shell body 1, strengthening the connection force between the plastic part and the aluminum shell body. And the plastic shell body 2 may be used to mount some parts such as antenna, display screen, plastic patch 3 may be used to mount WIFI antenna, plastic basal plate 5 may be used to mount antennas
for GPRS, Bluetooth, and infrared.

5. Surface burnishing, and abrasion blasting

The resulting shell after injection molding was subject to surface burnishing using a 400 mesh sand paper, and abrasion blasting suing 500 mesh ceramic beads.

6. Anodization

The resulting shell was placed, as an anode, in an anodizing bath containing a 20wt% H₂SO₄ solution, the shell was electrolyzed at a voltage of 20V at 20°C for 140 min, and then dyed the shell after washing.

Example 2

In this example, a shell for cell phone was prepared by a method which was substantially the same as the method in Example 1, with the following exceptions.

In the step of surface treatment 1, each aluminum alloy shell body as an anode was placed in an anodizing bath containing a 20wt% H₂SO₄ solution, the aluminum alloy was electrolyzed at a voltage of 15V at 18°C for 10 min, and then the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 5µm was formed after electrolysis, and nanopores having a size of 20-40nm was formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-1000nm and a depth of 4µm was formed in the surface of the immersed aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Example 3

In this example, a shell for cell phone was prepared by a method which is substantially the same as the method in Example 1, with the following exceptions.

In the step of surface treatment 1, each aluminum alloy shell body as an anode was placed in an anodizing bath containing a 20wt% H₂SO₄ solution, the aluminum alloy was electrolyzed at a voltage of 40V at 18°C for 10 min, and then the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 5µm was formed after electrolysis, and nanopores having a size of 60-80nm and a depth of 4µm were formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-1000nm and a depth of 4µm was formed in the surface of the immersed
aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Example 4

In this example, a shell for cell phone was prepared by a method which is substantially the same as the method in Example 1, with the following exceptions.

In the step of surface treatment 1, each aluminum alloy shell body as an anode was placed in an anodizing bath containing a 20wt% H₂SO₄ solution, the aluminum alloy was electrolyzed at a voltage of 20V at 18 °C for 15 min, and then the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 7µm was formed after electrolysis, and nanopores having a size of 40-60nm and a depth of 3µm were formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-1000nm and a depth of 4µm was formed in the surface of the immersed aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Example 5

In this example, a shell for cell phone was prepared by a method which is substantially the same as the method in Example 1, with the following exceptions.

In the step of surface treatment 1, each aluminum alloy shell body as an anode was placed in an anodizing bath containing a 20wt% H₂SO₄ solution, the aluminum alloy was electrolyzed at a voltage of 15V at 18°C for 15 min, and then the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 7µm was formed after electrolysis, and nanopores having a size of 20-40nm and a depth of 3µm were formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-1000nm and a depth of 4µm was formed in the surface of the immersed aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Example 6

In this example, a shell for cell phone was prepared by a method which is substantially the
same as the method in Example 1, with the following exceptions.

In the step of surface treatment 1, each aluminum alloy shell body as an anode was placed in an anodizing bath containing a 20wt% H₂SO₄ solution, the aluminum alloy was electrolyzed at a voltage of 40V at 18°C for 15 min, and then the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 7μm was formed after electrolysis, and nanopores having a size of 60-80nm and a depth of 3μm were formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-1000nm and a depth of 4μm was formed in the surface of the immersed aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Example 7

In this example, a shell for cell phone was prepared by a method which was substantially the same as the method in Example 2, with the following exceptions.

100ml aqueous solution containing 5wt% Na₂CO₃ with pH=11.9 was prepared in a beaker. The aluminum alloy shell body after step (2) was immersed in the sodium carbonate solution, taken out after 5 min, and placed in a beaker containing water to be immersed for 1min. After 5 cycles, after water immersing for the last time, the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 5μm was formed after electrolysis, and nanopores having a size of 20-40nm and a depth of 3μm were formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-600nm and a depth of 2μm were formed in the surface of the immersed aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Example 8

In this example, a shell for cell phone was prepared by a method which is substantially the same as the method in Example 2, with the following exceptions.

100ml aqueous solution containing 15wt% NaHCO₃ with pH=10 was prepared in a beaker. The aluminum alloy shell body after step (2) was immersed in the sodium carbonate solution, taken out after 5 min, and placed in a beaker containing water to be immersed for 1min. After 5
cycles, after water immersing for the last time, the aluminum alloy shell body was blow-dried.

It was observed that a layer of aluminum oxide film having a thickness of about 5\(\mu\text{m}\) was formed after electrolysis, and nanopores having a size of 20-40nm and a depth of 3\(\mu\text{m}\) were formed in the aluminum oxide layer. And it was observed that after surface treatment 2, corrosion pores with a size of 300-600nm and a depth of 2\(\mu\text{m}\) was formed in the surface of the immersed aluminum alloy sheet. It may also be observed that there was a double-layer three-dimensional pore structure in the aluminum oxide layer similar to the structure shown in Fig. 1, and the corrosion pores were communicated with the nanopores. And a shell for cell phone was prepared.

Comparative example 1

1. Pretreatment:

A commercially available A5052 aluminum alloy shell body with a thickness of 1mm was cut into 15mm x 80mm rectangular shells, which were then polished in a polishing machine, and cleaned with water-free ethanol, and then immersed in a 2wt% NaOH aqueous solution. After 2 min, the rectangular sheets were washed with water and dried to obtain pretreated aluminum alloy sheets.

2. Adhesion

Coated the hot melt adhesive from 3M Company to the connection surface between the metal and the plastic part, and joined the two parts via hot pressing.

Performance test

The connection force of the aluminum alloy and the resin: the shell for cell phone prepared in Examples 1-8 and Comparative example 1 was fixed in a universal material testing machine to perform tensile test. The test results under maximum load can be regarded as the connection force value between the aluminum alloy and resin, the test results were summarized in Table 1.
It can be seen from Table 1 that the combination between the resin and the metal shell body in shell of the present disclosure can achieve up to 1211 N, and then the combination is excellent. While the combination between the resin and the metal shell body in existing shell is just tens or hundreds of newton. The performance of the shell in the present disclosure has been improved significantly compared the existing ones and the resin molding is easier. The metal shell body in the present disclosure does not need additional moiety to combine firmly to the resin with stronger strength, which has little effect on size of the metal substrate and appearance of the aluminum alloy. At the same time, it is easier to inject mold resin directly into the corrosion holes with a bigger surface. It also has no specific requirement with synthetic resin, so the application scope is wider. And there is no environmental pollution which is more suitable for mass production.

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.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Thickness of oxide layer /μm</th>
<th>Pore size of nanopore /nm</th>
<th>Depth of nanopore /μm</th>
<th>Pore size of corrosion pore /nm</th>
<th>Depth of Nano Pore/μm</th>
<th>Combination /N</th>
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<td>4</td>
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WHAT IS CLAIMED IS:

1. A shell comprising:
   a metal shell body;
   a plastic part made of a resin; and
   an oxide layer formed between the metal body and the plastic part, joining the plastic part to the metal shell body,
   wherein
   the oxide layer contains corrosion pores having an average pore size of about 200nm to about 2000nm in the surface contacting the plastic part, and nanopores having a pore size of about 10 to 100nm in the surface contacting the metal shell body; and
   a part of the resin is filled in the corrosion pore and corrosion pore.

2. The shell according to claim 1, wherein the corrosion pores have an average pore size of about 200nm to about 1000nm, and the nanopores have an average pore size of about 20nm to about 80nm.

3. The shell according to claim 2, wherein the corrosion pore have an average pore size of about 400nm to about 1000nm, and the nanopores have an average pore size of about 20nm to about 60nm.

4. The shell according to claim 1, wherein the corrosion pores have an average pore size of about 0.5μπι to about 9.5μπι.

5. The shell according to claim 1, wherein the corrosion pores are communicated with the nanopores.

6. The shell according to claim 1, wherein the oxide layer has a thickness of about 1μτη to about 10μπι.

7. The shell according to claim 1, wherein the nanopores have an average depth of about 0.5μπι to about 9.5μπι.

8. The shell according to claim 1, wherein the plastic part comprises:
   a plastic shell body, which is provided on an end of the metal shell body;
   wherein,
   the oxide layer is formed between the plastic shell body and the end of the metal shell body, joining the plastic shell body to the end of the metal shell body.
9. The shell according to claim 8, wherein the width of the contacting surface between the plastic shell body and the end of the metal shell body is about 0.2 to about 10mm.

10. The shell according to claim 8, wherein the plastic part further comprises:
   a strengthening rib made of a resin, extending along the inner surface of the metal shell body;

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wherein
the strengthening rib is joined to the inner surface of the metal shell body.

11. The shell according to claim 1, wherein the plastic part comprises:
   a plastic patch provided in the inner surface of the metal shell body, and joined to the inner surface of the metal shell body,

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wherein
the oxide layer is formed between the plastic patch and the inner surface of the metal shell body, joining the plastic patch to the inner surface of the metal shell body.

12. The shell according to claim 11, wherein an opening for signaling is provided in a contacting surface between the plastic patch and the metal shell body.

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13. The shell according to claim 1, wherein the plastic part comprises:
   a plastic support provided in the inner surface of the metal shell body, and joined to the inner surface of the metal shell body,

20

wherein
the oxide layer is formed between the plastic support and the inner surface of the metal shell body, joining the plastic support to the inner surface of the metal shell body.

14. The shell according to claim 13, wherein the plastic support further comprises:
   a buckle; and
   a mounting hole.

15. The shell according to claim 1, wherein the plastic part comprises:

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a plastic basal plate provided on an end of the metal shell body,

wherein,
the plastic basal plate is vertical to the metal shell body, and an edge of the plastic basal plate is joined to the inner surface or the end of the metal shell body,

the oxide layer is formed between the plastic basal plate and the inner surface or the end of the metal shell body, joining the plastic basal plate to the inner surface or the end of the metal shell body.
16. The shell according to claim 1, wherein the plastic part comprises:

a plastic shell body;

a plastic support;

a plastic patch, provided on the plastic support; and

a plastic basal plate,

wherein,

the plastic shell body is connected with the plastic basal plate via the plastic support, and

the plastic shell, the plastic support, the plastic patch and the plastic basal plate are integrally formed.

17. The shell according to claim 1, wherein the resin includes a thermoplastic resin.

18. The shell according to claim 17, wherein the thermoplastic resin comprises a mixture of a main resin and a polyolefin resin.

19. The shell according to claim 18, wherein the main resin comprises a mixture of polyphenylene ether and polyphenylene sulfide, and the polyolefin resin has a melting point of about 65°C to about 105°C.

20. The shell according to claim 19, wherein in the main resin, the weight ratio of polyphenylene ether to polyphenylene sulfide is about 3:1 to about 1:3.

21. The shell according to claim 19, wherein the main resin comprises a mixture of polyphenylene oxide and a polyamide, and the polyolefin resin has a melting point of about 65°C to about 105°C.

22. The shell according to claim 21, wherein in the main resin, the weight ratio of polyphenylene oxide to the polyamide is about 3:1 to about 1:3.

23. The shell according to claim 18, wherein in the main resin, the main resin comprises a polycarbonate, and the polyolefin resin has a melting point of about 65°C to about 105°C.

24. The shell according to claim 18, wherein based on 100 weight parts of the thermoplastic resin, the amount of the main resin is about 70 weight parts to about 95 weight parts, and the amount of the polyolefin resin is about 5 weight parts to about 30 weight parts.

25. The shell according to claim 18, wherein the polyolefin resin comprises a grafted polyethylene.

26. The shell according to claim 17, wherein based on 100 weight parts of the thermoplastic resin, the thermoplastic resin further comprises about 1 weight part to about 5 weight parts of a
flow improver, and the flow improver is a cyclic polyester.

27. The shell according to claim 17, wherein the resin further contains a filler, and the filler comprises at least one of a fiber filler and a powder filler,

wherein the fiber filler is at least one selected from the group consisting of fiberglass, carbon fiber and polyamide fiber, and the powder filler at least one selected from the group consisting of silica, talc, aluminum hydroxide, magnesium hydroxide, calcium carbonate, magnesium carbonate, glass and kaolin.

28. A method of preparing a shell, comprising:

SI: anodizing at least a part of the surface of a metal shell body to form an oxide layer, wherein the oxide layer is formed with nanopores;

S2: immersing the resulting metal shell body in step SI in an etching solution, to form a corrosion pore in at least a part of the outer surface of the oxide layer; and

S3: injection molding a resin onto at least a part of the resulting metal shell body in step S2 to obtain the shell, in which the resin is molded into a plastic part.

29. The method according to claim 28, wherein step S3 further comprises subjecting the resulting metal shell body to annealing under a temperature of about 50 °C to about 200 °C.

30. The method according to claim 28, wherein the plastic part comprises a plastic shell body, and the oxide layer is formed between the plastic shell body and at least a part of an end of the metal shell body.

31. The method according to claim 28, wherein the plastic part comprises a plastic patch, and the oxide layer is formed between the plastic patch and at least a part of the inner surface of the metal shell body.

32. The method according to claim 28, wherein the plastic part comprises a plastic support, and the oxide layer is formed between the plastic support and at least a part of the inner surface of the metal shell body.

33. The method according to claim 28, wherein the plastic part comprises a plastic plate, and the oxide layer is formed between the plastic plate and at least a part of an end of the metal shell body, or the oxide layer is formed between the plastic plate and at least a part of the inner surface of the metal shell body.

34. The method according to claim 28, wherein the corrosion pores have an average pore size of about 200nm to about 2000nm, and the nanopores have an average pore size of about 10nm to
about 100nm.

35. The method according to claim 28, further comprising a step of subjecting the shell to
surface burnishing, and abrasion blasting.

36. The method according to claim 35, further comprising steps of subjecting the shell to
surface treatments of anodization and dyeing after the surface burnishing and abrasion blasting.

37. The method according to claim 28, further comprising step of subjecting the shell to
surface decoration.

38. The method according to claim 28, wherein in step SI, anodizing at least a part of the
surface of the metal shell body further comprises:

placing the part of the surface of the metal shell body as an anode in a H₂SO₄ solution with a
concentration of about 10wt% to about 30wt%; and
electrolyzing the part of the surface of the metal shell body at a temperature of about 10°C to
about 30°C, at a voltage of about 10V to about 100V for about 1min to about 40min, to form the
oxide layer with a thickness of about 1μm to about 10μm.

39. The method according to claim 28, wherein the etching solution is a solution having a pH
of about 10 to about 13.

40. The method according to claim 28, wherein the etching solution comprises at least one
selected from Na₂C₀₃ aqueous solution, NaHC₀₃ aqueous solution, NaOH aqueous solution,
K₂C₀₃ aqueous solution, KHC₀₃ aqueous solution, KOH aqueous solution, NaOH-NaHP₀₄ aqueous
solution, KOH-K₂HP₀₄ aqueous solution, ammonia aqueous solution, hydrazine aqueous aqueous solution,
hydrazine derivatives aqueous solution, water-soluble amine compounds aqueous solution,
HN₃-NH₄Cl aqueous solution, Na₃P₀₄-Na₂HP₀₄ aqueous solution or K₃P₀₄-Na₂HP₀₄ aqueous
solution.

41. The method according to claim 28, wherein step S2 comprises repeatedly immersing the
resulting metal shell body in step SI in an etching solution for more than one times, each
immersing lasts for about 1 min to about 60min, and cleaning the metal shell body with water
after each immersing.

42. The method according to claim 41, wherein step S2 comprises repeatedly immersing the
resulting metal shell body in step SI in an etching solution for about 2-10 times.

43. The method according to claim 28, wherein prior to step SI, the metal shell body is
subjected to polishing, oil removing, a first washing with water, alkali etching, a second washing
with water, neutralizing, and a third washing with water.

44. An electronic product comprising a shell according to any one of claims 1-27.
### INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/CN2012/082029

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### A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

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### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC:** H04M1/02;C25D11/02;B33B7/-

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### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

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Date of the actual completion of the international search 07 Dec. 2012(07.12.2012)

Date of mailing of the international search report 03 Jan. 2013 (03.01.2013)

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Name and mailing address of the ISA/CN
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8 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088
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Authorized officer JIA, Junlin
Telephone No. (86-10)82245732
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**INTERNATIONAL application No.**

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**A. CLASSIFICATION OF SUBJECT MATTER**

- H04M1/02(2006.01)i
- C25D1 1/02(2006.01)i
- B32B7/04(2006.01)i