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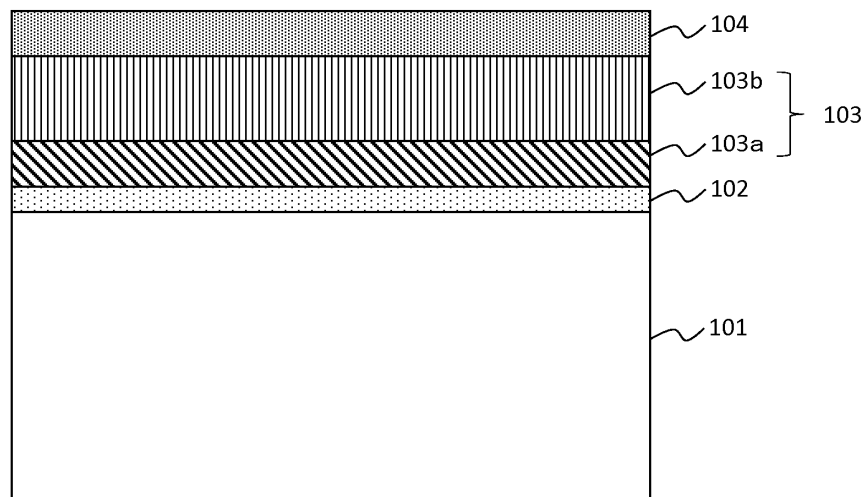
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(54) **MEMBER FOR SLIDE FASTENERS OR BUTTONS, WHICH IS FORMED FROM PLATED ALUMINUM OR ALUMINUM ALLOY**

(57) Provided is a plated member for aluminum or aluminum alloy slide fasteners or buttons, which has both of crack resistance and glossiness. A member for slide fasteners or buttons, the member including: a base material (101) made of aluminum or an aluminum alloy; a zinc diffusion layer (102) having zinc diffused inside a

surface of the base material; and a plurality of plating layers covering the zinc diffusion layer (102), the plating layers including a copper pyrophosphate plating layer (103) and a copper sulfate plating layer (104) in this order from inside.

[FIG. 1]



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Description

TECHNICAL FIELD

- 5 **[0001]** The present invention relates to a plated member for aluminum or aluminum alloy slide fastener or buttons. More particularly, the present invention relates to a plated aluminum or aluminum alloy fastener element.

BACKGROUND ART

- 10 **[0002]** Conventionally, in the field of slide fasteners, products are known in which various kinds of plating are applied to surfaces of base materials of zinc or red brass. In the field of buttons, products are known in which various kinds of plating are applied to surfaces of base material of brass having a good plating property. However, recently, there has been a problem of soaring of material costs, and there also has been a need for weight reduction of buttons and slide fasteners. Therefore, a solution is considered that a slide fastener and a button are produced using aluminum which
- 15 has light weight and is relatively inexpensive. However, it is known that aluminum does not have sufficient gloss, tends to generate a strong oxide film on the surface, and is a material that is difficult to plate. Therefore, when aluminum is used to produce slide fasteners and buttons, there would be need for a technique capable of forming a plated film having good adhesion and glossy appearance.

- [0003]** Conventionally, the following techniques are known to form plating on a surface of aluminum. For example,
- 20 Japanese Patent Application Publication No. 2001-8714 discloses that nickel plating is formed by preparing a deformed wire and a round wire having substantially Y-shaped and circular cross sections, respectively, made of aluminum alloy, and subjecting them to electroless plating in an acid bath containing nickel sulfate and sodium hypophosphite. It also discloses that nickel plating is formed by electrolytic plating in an acid bath containing nickel sulfate, nickel chloride and boric acid.

- 25 **[0004]** Japanese Patent Application Publication No. 2014-19953 A discloses a method for producing a copper plated button or fastener member, comprising a step 1 of profiling an aluminum or aluminum alloy base material to form a semi-product of a member for a button or a slide fastener; a step 2 of forming a first copper plating layer directly on the entire surface of the base material by strike electroplating of copper with a barrel; and then a step 3 of forming a second copper plating layer directly on the first copper plating layer, the second plating layer being thicker than the first copper plating layer, by electroplating of copper with the barrel.
- 30 **[0005]** Japanese Patent Application Publication No. 2012-143798 discloses a method for producing a plated aluminum alloy cast product, comprising casting an aluminum alloy having a predetermined composition to obtain a cast product; electro-polishing a surface of the cast product and then subjecting it to a zincate treatment to form an electroplated copper layer thereon; and forming an electroplated nickel layer thereon. It also discloses that a zincate (zinc-substituted)

- 35 treatment layer as an under layer is formed on the cast surface, thereby enabling adhesion of the plating layer formed on the zincate treatment layer to be improved. It also discloses that a plurality of zincate treatments is preferably carried out in terms of adhesion or glitter of plating.
- [0006]** Japanese Patent Application Publication No. H02-240290 A discloses a method for plating copper directly onto aluminum by carrying out pretreatments such as alkaline degreasing, washing with a surfactant, washing with an acid and washing with water, then carrying out copper plating using a pyrophosphate copper plating bath containing phosphoric acid and/or phosphate, and then subjecting the aluminum to a heat treatment. Example 1 of the publication discloses that the method forms a copper plating layer having a thickness of about 10 μm on an aluminum plate. It also discloses that according to the method, a uniform copper plating layer can be formed, and adhesion of the aluminum substrate to the copper plating layer is excellent, and appearance is also beautiful.
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CITATION LIST

Patent Literatures

- 50 **[0007]**

Patent Document 1: Japanese Patent Application Publication No. 2001-8714 A
 Patent Document 2: Japanese Patent Application Publication No. 2014-19953 A
 Patent Document 3: Japanese Patent Application Publication No. 2012-143798 A
 Patent Document 4: Japanese Patent Application Publication No. H02-240290 A

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SUMMARY OF INVENTION

Technical Problem

[0008] With the method as described in Japanese Patent Application Publication No. 2001-8714 A it is difficult to obtain a plated film having high adhesion. Further, in the method as described in this publication, the plating is carried out on the deformed wire and the round wire before being processed into elements. Therefore, when it is processed into an element shape after plating, a cross section where the plated film is not formed is exposed, so that the appearance is deteriorated. Further, although the method can provide nickel plating with high gloss, the film is hard so that cracking tends to occur, and it also has a risk of allergy. Therefore, there is still room for further improvement.

[0009] The method described in Japanese Patent Application Publication No. 2014-19953 A is to form a copper plated film on the entire surface by barrel plating after shape processing into a fastener element or the like. It is superior to the technique as described in Japanese Patent Application Publication No. 2001-8714 A. However, there is still room for improvement in terms of achieving both prevention of cracking of the plated film and high gloss. In particular, a fastener element requires higher resistance to cracking, because the plated film is subjected to frictional force or bending stress when caulking and fixing the fastener element to a fastener tape.

[0010] Japanese Patent Application Publication No. 2012-143798 A carries out the zincate treatment utilizing substitution reaction of zinc with aluminum as the pretreatment to improve the adhesion of the plated film to aluminum that is a base material. However, the method adopts nickel plating, so that the crack resistance cannot be sufficient, and the problem of allergy also remains.

[0011] With regard to the method as described in Japanese Patent Application Publication No. H02-240290 A, there is still room for improvement in terms of achieving both of prevention of cracking of the plated film and high gloss when caulking and fixing the plated fastener element to the fastener tape. Even if the technique of this publication can prevent cracking of the plated film, this publication does not consider the glossiness. Further, the method as described in the publication is a static plating method, which is not suitable for mass production of small products such as fasteners and buttons.

[0012] The present invention has been made under the above circumstances. An object of the present invention is to provide a plated member for aluminum or aluminum alloy slide fasteners or buttons, which has both of crack resistance and glossiness. Another object of the present invention is to provide a method for producing such a member for slide fasteners or buttons.

Solution to Problem

[0013] The present inventors have intensively studied to solve the above problems, and found that adhesion of plating and cracking resistance can be improved by forming a copper pyrophosphate plating layer after performing the zincate treatment on a material made of aluminum or aluminum alloy, and that high glossiness can be ensured by forming a copper sulfate plating layer on the copper pyrophosphate plating layer. Furthermore, the present inventors have found that the forming of a hard finish plating layer on the copper sulfate plating layer provides appearance of various colors and further improvement of wear resistance, and prevents corrosion of the member for slide fasteners or buttons. The present inventors have completed the present invention based on such findings.

[0014] In one aspect, the present invention relates to a member for slide fasteners or buttons, the member comprising: a base material made of aluminum or an aluminum alloy; a zinc diffusion layer having zinc diffused on an inner surface of the base material; and a plurality of plating layers covering the zinc diffusion layer, the plating layers comprising a copper pyrophosphate plating layer and a copper sulfate plating layer in this order from inside.

[0015] In one embodiment of the member for slide fasteners or buttons according to the present invention, the copper pyrophosphate plating layer has an average thickness of 20 μm or less.

[0016] In another embodiment of the member for slide fasteners or buttons according to the present invention, the copper pyrophosphate plating layer has an average thickness of from 5 to 20 μm .

[0017] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the copper pyrophosphate plating layer comprises a copper pyrophosphate strike plating layer having an average thickness of from 0.1 to 5 μm as an underlayer.

[0018] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the copper sulfate plating layer has an average thickness of 7 μm or less.

[0019] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the copper sulfate plating layer has an average thickness of from 1 to 7 μm .

[0020] In still another embodiment, the member for slide fasteners or buttons according to the present invention has a ratio of an average thickness of the copper sulfate plating layer to an average thickness of the copper pyrophosphate plating layer of from 0.1 to 0.5.

[0021] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the plating layers further comprise a finish plating layer harder than the copper sulfate plating layer outside the copper sulfate plating layer.

[0022] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the finish plating layer is an alloy plating layer containing Cu and Sn.

[0023] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the finish plating layer has an average thickness of from 0.5 to 5 μm .

[0024] In still another embodiment of the member for slide fasteners or buttons according to the present invention, an outermost surface has an arithmetic average roughness of 0.3 μm or less.

[0025] In still another embodiment of the member for slide fasteners or buttons according to the present invention, the plating layers further comprise a plating layer having a different color tone from that of the finish plating layer outside the finish plating layer.

[0026] In still another embodiment of the member for slide fasteners or buttons according to the present invention, an entire surface of the base material is coated with the plating layers.

[0027] In another aspect, the present invention relates to an article comprising the member for slide fasteners or buttons according to the present invention.

[0028] In yet another aspect, the present invention relates to a fastener stringer comprising fastener elements caulked and fixed along one side edge of a fastener tape, wherein at least one of the fastener elements is the member for slide fasteners according to the present invention.

[0029] In yet another aspect, the present invention relates to a method for producing a member for slide fasteners or buttons, comprising:

preparing an aluminum or aluminum alloy base material processed into a shape of a member for slide fasteners or buttons; and

performing a zincate treatment, copper pyrophosphate plating, and copper sulfate plating in this order on at least a part of a surface of the base material.

Advantageous Effects of Invention

[0030] According to the present invention, it is possible to provide a plated member for aluminum or aluminum alloy slide fasteners or buttons, which has both of crack resistance and glossiness. Further, according to a preferred embodiment of the present invention, it is possible to provide a fastener element which has crack resistance and glossiness, as well as low sliding resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0031]

FIG. 1 shows a plated structure according to an embodiment of a member for slide fasteners or buttons of the present invention.

FIG. 2 shows a plated structure according to another embodiment of a member for slide fasteners or buttons of the present invention.

FIG. 3 shows a plated structure according to yet another embodiment of a member for slide fasteners or buttons of the present invention.

FIG. 4 is an example of an elemental mapping image by EDX when observing cross sections of a zinc diffusion layer and a plating layer of a member for slide fasteners or buttons according to the present invention by TEM.

FIG. 5 is a flow chart showing a preferred implementation procedure of a zincate treatment and its pretreatment.

FIG. 6 is a view showing (a) a state before caulking of a fastener element and (b) a state after caulking of the fastener element.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0032] Hereinafter, embodiments of the present invention will be described with reference to the drawings.

[0033] FIG. 1 shows a plating structure according to an embodiment of a member for slide fasteners or buttons of the present invention. The member for slide fasteners or buttons according to the embodiment of FIG. 1 includes: a base material (101) made of aluminum or an aluminum alloy; a zinc diffusion layer (102) having zinc diffused inside a surface of the base material; and a plurality of plating layers covering the zinc diffusion layer (102), the plating layers comprising a copper pyrophosphate plating layer (103) and a copper sulfate plating layer (104) in this order from inside. It is preferable

that the entire surface of the base material (101) be sequentially coated with the plating layers in order to enhance appearance and to improve corrosion resistance.

[0034] FIG. 2 shows a plating structure according to another embodiment of a member for slide fasteners or buttons of the present invention. The member for slide fasteners or button members according to the embodiment of FIG. 2 is different from the embodiment of FIG. 1 in that the plating layers further have a finish plating layer (105) harder than the copper sulfate plating layer (104) outside the copper sulfate plating layer (104). In the present embodiment, it is also preferable that the entire surface of the base material (101) be coated with the plating layers in order to enhance the appearance and to improve the corrosion resistance.

[0035] FIG. 3 shows a plated structure according to yet another embodiment of a member for slide fasteners or buttons of the present invention. The member for slide fasteners or buttons according to the embodiment of FIG. 3 is different from the embodiment of FIG. 2 in that the plating layers further include a plating layer (106) having a different color tone from that of the finish plating layer (105), outside the finish plating layer (105). In the present embodiment, it is also preferable that the entire surface of the base material (101) be coated with the plating layers in order to enhance the appearance and to improve the corrosion resistance.

(1. Base Material)

[0036] The member for slide fasteners or buttons according to the present invention uses aluminum or an aluminum alloy as the base material (101). The aluminum alloy includes, but not limited to, Al-Cu-based alloys, Al-Mn-based alloys, Al-Si-based alloys, Al-Mg-based alloys, Al-Mg-Si-based alloys, Al-Zn-Mg-based alloys and Al-Zn-Mg-Cu-based alloys. Among these, the Al-Mg-based alloys, Al-Mn-based alloys and Al-Mg-Si-based alloys are preferable, and the Al-Mg-based alloys are more preferable, in terms of strength and workability.

[0037] The base material is desirably processed into a shape of the member for slide fasteners or buttons before the various plating layers are formed. For example, fastener elements can be processed into individual element shapes by punching out a flat wire made of aluminum or an aluminum alloy. This can allow elimination of cutting process after forming the plating layers on the base material, so that it is possible to prevent generation of an exposed surface on which the plating layers are not formed. Further, the processing of the base material into the shape of the member for slide fasteners or buttons can allow miniaturization, so that barrel plating can be performed in each of the plating steps as described below. The barrel plating saves time and effort for setting the plating material to a jig, enables mass production as compared to static plating, and also leaves no contact marks when the plating material is set to the jig, so that there is no concern of corrosion from the contact marks. While the barrel plating can plate the entire surface of the product, the static plating does not plate the part that have been covered by the jig.

(2. Zinc Diffusion Layer)

[0038] The member for slide fasteners or buttons according to the present invention includes a zinc diffusion layer (102) having zinc diffused inside the surface of the base material. By providing the zinc diffusion layer, the adhesion of the plating can be improved. The zinc diffusion layer preferably has an average thickness of 50 nm or more, and more preferably 100 nm or more, and even more preferably 200 nm or more, and still more preferably 250 nm or more, in terms of improvement of plating adhesion. Further, the zinc diffusion layer preferably has an average thickness of 500 nm or less, and more preferably 400 nm or less, and even more preferably 350 nm or less, in terms of cost-effectiveness of the zinc diffusion layer.

[0039] The zinc diffusion layer is studded with zinc in the form of island, so that it is difficult to recognize the zinc diffusion layer as a collective layer. Therefore, in the present invention, the average thickness of the zinc diffusion layer is defined as a value obtained by measurement as follows: A thin sample for cross-sectional observation is prepared from a member for a slide fastener or a button by means of a cross-section polisher and a focused ion beam (FIB). The resulting thin sample is then used to measure a cross section of the zinc diffusion layer by TEM and conduct elemental analysis by energy dispersive X-ray spectroscopy (EDX). Then, an element mapping image as shown in FIG. 4 is obtained. There are extremely small objects in the island-shaped Zn mapping image, but in thickness measurement, only islands that can be surrounded by the smallest circle having a diameter of 10 nm or more are to be measured. Then, in the elemental mapping image, among the islands that can be surrounded by the smallest circle having a diameter of 10 nm or more, an island located at the farthest distance from the surface of the base material is identified for every 500 nm of the boundary length of the surface of the base material. The "distance from the surface of the base material" is defined as a distance from the surface of the base material to a distal end of the island (a point of the farthest distance from the surface of the base material in the island) when drawing a normal line from the surface of the base material toward the island. Then, an average value when the distance of the island with the longest distance from the base material surface is measured at ten or more observation visual fields is defined as the average thickness of the zinc diffusion layer.

[0040] In the elemental mapping image of FIG. 4, the boundary length of the surface of the base material is about 500 nm, and in the range, the island located at the farthest distance from the surface of the base material when drawing the normal line from the surface of the material, among the "islands" that can be surrounded by the smallest circle having a diameter of 10 nm or more, is circled in the figure. The distance of the island from the surface of the base material is about 210 nm.

[0041] The zinc diffusion layer can be formed by a zincate treatment. FIG. 5 exemplarily shows a preferred implementation procedure of the zincate treatment and its pretreatment. The zincate treatment itself is known in the art, and although any specific description will not be needed, illustrative examples of the zincate treatment includes a method of cleaning the surface of the aluminum or aluminum alloy member for slide fasteners or buttons and then immersing it in a zinc substitution treatment solution. The zinc substitution treatment solution that can be generally used is a mixed solution containing sodium hydroxide and zinc oxide. Zinc sulfate may be used in place of zinc oxide or in combination with zinc oxide. Further, Rochelle salt (potassium sodium tartrate) or other organic acid salts with complexing ability (e.g., gluconate and salicylate) or other additives (e.g., sodium nitrate, copper, iron or nickel salts) may be added. A bath temperature may be from 10 to 40 °C, and a treatment time may be from 10 to 60 minutes.

[0042] It is preferable that multiple zincate treatments be carried out, because they increase the thickness of the zinc diffusion layer to improve the plating adhesion and they form a smooth plating layer to improve the glossiness of the plated film. Typically, the multiple zincate treatments include double zincate treatment. The double zincate treatment is a method including once immersing an object to be treated in the zinc substitution treatment solution and then immersing the member for slide fasteners or buttons in nitric acid or the like to peel off deposited zinc, and immersing the object to be treated in the zinc substitution treatment solution again. Water washing steps may be appropriately carried out among the respective steps.

[0043] The method of cleaning the surface of the member for slide fasteners or buttons prior to the zincate treatment includes a pretreatment such as degreasing, washing with an acid, washing with a surfactant, washing with water, ultrasonic washing and the like. Among them, a method of sequentially performing degreasing, chemical polishing (etching) and desmutting is exemplified as a preferable method. Washing steps may be appropriately carried out among the respective steps. A degreasing solution includes an alkaline degreasing solution containing an appropriate amount of a surfactant and further containing at least one alkali salt such as sodium hydroxide, sodium carbonate, sodium phosphate, sodium metasilicate, sodium sulfate and sodium borate. The degreasing treatment can be performed by immersing the member for slide fasteners or buttons in the degreasing solution at a temperature of from 70 to 80 °C for 1 to 3 minutes.

[0044] An etching solution used for the chemical polishing includes an alkaline etching solution containing sodium hydroxide, and an acidic etching solution containing at least one of sulfuric acid and phosphoric acid. The chemical polishing can be carried out by immersing the member for slide fasteners or button in the etching solution at a temperature of from 50 to 70 °C for 0.5 to 3 minutes. The chemical polishing can remove an oxide film on the surface of the member.

[0045] When the chemical polishing is carried out, a smut (such as an impurity contained in the base material) remains on the surface of the base material. The desmutting is a treatment for removing the smut. The desmutting may be carried out by immersing the member for slide fasteners or buttons in a treatment solution containing at least one of a strong acid such as nitric acid, sulfuric acid and hydrofluoric acid at a temperature of from 20 to 50 °C for 1 to 60 seconds.

[0046] The various plating layers will be described in detail below. In the following descriptions, an average thickness of the respective plating layers refers to an average value when each of the plating layers are analyzed with an electron microscope or an optical microscope and thickness of the plating layer is measured at arbitrary 10 or more points.

(3. Copper Pyrophosphate Plating layer)

[0047] On the zinc diffusion layer (102), a copper pyrophosphate plating layer (103) is formed. The copper pyrophosphate plating layer is advantageous in terms of an improved crack suppressing effect. For example, fastener elements are attached to a fastener tape by punching out a flat wire made of an aluminum alloy to form individual fastener elements, forming a plating layer on the surface of the fastener elements, and then arranging the fastener tape between a pair of leg portions of the fastener elements, and inwardly caulking the leg portions. FIG. 6 illustrates (b) a state before caulking a fastener element 108 and (b) a state after caulking the fastener element 108 to a fastener tape 109. Typically, before caulking the fastener element, an opening angle θ of the pair of leg portions is from 30 to 50°, and after caulking the fastener element, the pair of leg portions is typically parallel to each other. Therefore, when the fastener element is caulked, the plating layer formed on the surface is extended and easily cracked. By forming a thicker copper pyrophosphate plating layer (103) that has a decreased amount of deformation because it is near the base material and located on the inner side, a copper sulfate plating layer (104) formed outside the copper pyrophosphate plating layer (103) and a hard finish plating layer (105), which will be described below, can be formed so as to be thinner, so that cracking can be suppressed. Further, the copper pyrophosphate plated solution is weakly alkaline and is also advantageous in terms of improved plating coverage after the zincate treatment. The copper pyrophosphate plating layer is a plating layer

obtained by using a plating solution containing copper pyrophosphate and contains Cu and P in the plating layer.

[0048] An average thickness of the copper pyrophosphate plating layer (103) is preferably 20 μm or less, and more preferably 15 μm or less, and even more preferably 11 μm or less, in order to shorten the treatment time (cost reduction) or to reduce sliding resistance. Further, the average thickness of the copper pyrophosphate plating layer (103) is preferably 5 μm or more, and more preferably 6 μm or more, and still more preferably 8 μm or more, for the reason of corrosion resistance.

[0049] The copper pyrophosphate plating layer (103) is preferably provided by forming a thinner copper pyrophosphate strike plating layer (103a) as an underlayer for the purpose of preventing substitution of the zinc diffusion layer, and then forming a thicker copper pyrophosphate main plating layer (103b), in terms of improving plating adhesion and leveling. An average thickness of the copper pyrophosphate strike plating layer (103a) is preferably 5 μm or less, and more preferably 3 μm or less, and even more preferably 2 μm or less, in order to shorten the treatment time (cost reduction) or to reduce the sliding resistance. Further, the average thickness of the copper pyrophosphate strike plating layer (103a) is preferably 0.1 μm or more, and more preferably 0.5 μm or more, and even more preferably 0.8 μm or more, for the reason of corrosion resistance. When the copper pyrophosphate strike plating layer (103a) is formed, the thickness of the copper pyrophosphate plating layer refers to the total thickness of the copper pyrophosphate strike plating layer and the copper pyrophosphate main plating layer.

[0050] The copper pyrophosphate strike plating can be carried out by electroplating in a weak alkaline plating bath containing copper pyrophosphate at a temperature of from 40 to 70 °C at a current density of from 2 to 15 A/dm² for about 0.5 to 30 minutes. The copper pyrophosphate main plating can be carried out by electroplating in a weak alkaline plating bath containing copper pyrophosphate at a temperature of from 40 to 70 °C at a current density of 1 to 10 A/dm² for about 1 to 120 minutes. Since Zn in the zinc diffusion layer is an amphoteric metal, it tends to be dissolved in an acidic or alkaline solution. However, since the copper pyrophosphate plating can be performed in a plating solution that is near neutral, it has an advantage that less damage is given to the zinc diffusion layer.

(4. Copper Sulfate Plating layer)

[0051] On the copper pyrophosphate plating layer (103), a copper sulfate plating layer (104) is formed. The copper sulfate plating layer is advantageous in that high gloss can be obtained. Therefore, it is important to laminate the copper pyrophosphate plating layer (103) and the copper sulfate plating layer (104) in this order, to achieve both of the plating adhesion and the glossiness. The copper sulfate plating layer is a plating layer obtained by using a plating solution containing copper sulfate and contains Cu and S in the plating layer.

[0052] An average thickness of the copper sulfate plating layer (104) is preferably 7 μm or less, and more preferably 5 μm or less, and even more preferably 4 μm or less, in order to shorten the treatment time (cost reduction), to prevent cracking or to reduce sliding resistance. The average thickness of the copper sulfate plating layer (104) is preferably 1 μm or more, and more preferably 2 μm or more, and even more preferably 3 μm or more, in order to obtain high glossiness.

[0053] A ratio of the thickness of the copper sulfate plating layer (104) to the thickness of the copper pyrophosphate plating layer (103) affects a balance between the plating adhesion and the glossiness. Therefore, in terms of achieving both improved plating adhesion and high glossiness, the ratio of the average thickness of the copper sulfate plating layer (104) to the average thickness of the copper pyrophosphate plating layer (103) is preferably from 0.1 to 0.5, and more preferably from 0.3 to 0.4.

[0054] The copper sulfate plating can be carried out by electroplating in an acid plating bath containing copper sulfate at a temperature of from 10 to 40 °C at a current density of from 0.5 to 10 A/dm² for about 1 to 120 minutes. A brightener may be added to the plating bath as needed.

(5. Finish Plating layer)

[0055] On the copper sulfate plating layer (104), a finish plating layer (105) harder than the copper sulfate plating layer (104) is formed. The finish plating layer (105) also has the purpose of providing appearance of a desired color tone, and the forming of a thinner hard finish plating layer (105) can effectively produce a sliding resistance reducing function, a corrosion preventing function, and a crack preventing function. Here, the finish plating layer (105) harder than the copper sulfate plating layer (104) means that a Vickers hardness of the surface of the member having the finish layer (105) formed on the copper sulfate plating layer (104) is higher than that of the surface of the member having the copper sulfate plating layer (104) before the finish layer (105) is formed thereon. Typically, the Vickers hardness Hv of the surface of the member having the copper sulfate plating layer (104) is about 100 (load of 50 g).

[0056] Types of the finish plating layer (105) harder than the copper sulfate plating layer (104) include, for example, a Cu-Sn alloy plating layer, a Cu-Zn alloy plating layer, a Sn-Co alloy plating layer, a Sn-Ni alloy plating layer, a Cu-Sn-Zn alloy plating layer, a Cu-Zn-Sn alloy plating layer, a Cu-Ag-Zn alloy plating layer, a Cu-Zn-Ag alloy plating layer, a Sn-Ni-Cu alloy plating layer, a Co plating layer, a Cr plating layer, and a Cr-Mo alloy plating layer. Among them, an alloy

plating layer containing Cu and Sn such as the Cu-Sn alloy plating layer and the Cu-Sn-Zn alloy plating layer is preferable. Although Ni may cause allergy, the use of the Cu-Sn-Zn alloy plating layer can allow the same color as that of Ni plating to be expressed, and the changing of the plating composition can allow various color tones such as silver white color, brass color and gold color to be expressed. The finish plating layer can be formed by adopting known plating conditions according to the types.

[0057] After forming the finish plating layer, the Vickers hardness Hv of the surface of the member for slide fasteners or buttons is preferably 300 or more, and more preferably 400 or more, and still more preferably 500 or more, for example, from 300 to 800. In one embodiment, the Vickers hardness of the surface of the member after forming a silver-colored finish plating layer (from 50 to 55% by mass of copper, from 30 to 35% by mass of tin, and from 13 to 17 by mass % of zinc) can be about 600 Hv (a load of 50 g). In another embodiment, the Vickers hardness of the surface of the member after forming a gold-colored finish plating layer (from 76 to 86% by mass of copper, from 2 to 6% by mass of tin, and from 12 to 17% by mass of zinc) can be about 400 Hv (a load of 100 g). The Vickers hardness Hv is measured in accordance with JIS Z2244: 2009.

[0058] From a viewpoint of effectively preventing cracking, the finish plating layer is preferably formed so as to be thinner. Further, from a viewpoint of reducing the sliding resistance, the finish plating layer is preferably formed to be thinner. From these viewpoints, an average thickness of the finish plating layer is preferably 5 μm or less, and more preferably 3 μm or less, and still more preferably 2 μm or less. However, if the finish plating layer is too thin, the underlying copper sulfate plating layer may be exposed to promote corrosion. Therefore, the average thickness is preferably 0.5 μm or more, and more preferably 0.7 μm or more, and even more preferably 0.8 μm or more. Further, the average thickness of the finish plating layer (105) is preferably from about 5 to 15% relative to the total average thickness of the underlying copper pyrophosphate plating layer (103) and copper sulfate plating layer (104).

(6. Plating layer Having Different Color Tone)

[0059] On the finish plating layer (105), a plating layer (106) having a different color tone from that of the finish plating layer (105) (hereinafter, referred to as a "color tone adjustment plating layer") may be further formed. This can enhance the color variation. The color tone adjustment plating layer includes, but not particularly limited to, a Cu-Sn-Zn alloy plating layer, a Cu-Sn alloy plating layer, and a Cu-Zn alloy plating layer (a brass plating layer). An average thickness of the color tone adjustment plating layer is preferably 10 μm or less, and more preferably 5 μm or less, and still more preferably 2 μm or less, in order to reduce the sliding resistance. Also, in place of Ni which may cause allergy, a Cu-Sn-Zn alloy plating layer can be used as the color tone adjustment plating layer. The color tone adjustment plating layer can be formed by adopting known plating conditions according to the types.

(7. Thickness of Entire Plating layer)

[0060] In the field of slide fasteners, one of the important matters is to suppress sliding resistance when manipulating the slider. Since the sliding resistance tends to be increased as the total thickness of the various plating layers from the copper pyrophosphate plating layer to the plating layer having the different color tone is increased, the total thickness is preferably reduced. Therefore, the total thickness of all of the plating layers of the copper pyrophosphate plating layer, the copper sulfate plating layer, the finish plating layer where present, and color tone adjustment plating layer where present is preferably 50 μm or less on average, and more preferably 30 μm or less on average, and even more preferably 20 μm or less on average.

(8. Surface Roughness)

[0061] A degree of gloss can be determined by comparison based on a surface roughness. A lower surface roughness decreases surface irregularities and produces the gloss. In one embodiment of the member for slide fasteners or buttons according to the present invention, an arithmetic average roughness (Ra) of the outermost surface can be from 0.3 μm or less, and preferably 0.15 μm or less, and more preferably 0.1 μm or less, and even more preferably 0.08 μm or less, for example, from 0.02 to 0.15 μm . In the present invention, the arithmetic mean roughness (Ra) is measured by means of a noncontact type surface roughness measuring apparatus in accordance with JIS B0601: 2001.

(9. Member for Slide Fasteners or Buttons)

[0062] After thus completing plating on the surface of the material, the resulting member for slide fasteners or buttons can be used to assemble a slide fastener or button by any known means. Non-limiting examples of the member for buttons include a rivet and a button body that is attached to a fabric by the rivet. The member for slide fasteners includes a slider (a body and/or a pull tab), fastener elements, an upper stopper, and a lower stopper. The fastener elements can

be caulked and fixed along one side edge of a fastener tape to produce a fastener stringer, and a pair of the fastener stringers can be connected to each other via a row of the fastener elements to produce a fastener chain. Further, the slider as well as optionally the upper stopper and the lower stopper can be attached to the fastener chain to produce a slide fastener. The slide fastener can be attached to opening and closing parts of various articles including daily necessities such as clothing, bags, shoes and commodities.

EXAMPLES

<1. Production of Plated Products>

(Comparative Example 1)

[0063] A number of slide fastener elements produced by punching out a flat wire made of aluminum by means of a press were prepared and subjected to a pretreatment and a zincate treatment according to the procedure as described in FIG. 5. Subsequently, a copper pyrophosphate plating layer (a strike plating layer → a main plating layer) having the average thickness as described in Table 1 was formed by electric barrel plating. Finally, a finish plating layer (a Cu-Sn-Zn alloy plating layer) having the average thickness as described in Table 1 was formed by electric barrel plating. A measuring method of the average thickness of each plating layer is described below.

(Comparative Example 2)

[0064] Under the same conditions as those of Comparative Example 1, a number of slide fastener elements produced by punching out a flat wire made of aluminum by a press were subjected to a pretreatment and a zincate treatment. Subsequently, a copper cyanide plating layer (a strike plating layer → a main plating layer) and a copper sulfate plating layer each having the average thickness as described in Table 1 were formed in this order by electric barrel plating. Finally, a finish plating layer (a Cu-Sn-Zn alloy plating layer) having the average thickness as described in Table 1 was formed by electric barrel plating.

(Examples 1 to 5)

[0065] Under the same conditions as those of Comparative Example 1, a number of slide fastener elements produced by punching out a flat wire made of aluminum by a press were subjected to a pretreatment and a zincate treatment. Subsequently, a copper pyrophosphate plating layer (a strike plating layer → a main plating layer) and a copper sulfate plating layer each having the average thickness as described in Table 1 were formed in this order by electric barrel plating. Subsequently, for Examples 2 to 4, a finish plating layer (a Cu-Sn-Zn alloy plating layer) having the average thickness as described in Table 1 was formed by electric barrel plating. For Example 5, a black Cu-Sn plating layer (a color tone adjustment plating layer) having the average thickness as described in Table 1 was formed on the finish plating layer by electrical barrel plating. For Example 1, the finish plating layer was not formed.

<2. Average Thickness of Zinc Diffusion Layer and Each Plating Layer>

(1) Zinc Diffusion Layer

[0066] For each plated element of Examples and Comparative Examples obtained under the above conditions, an ultrathin section sample for cross section observation (a thickness of 200 nm or less) was prepared from a cross section sample prepared by the CP method using FIB (Scios Dual Beam from FEI) while adjusting an electric current and a treatment time. Subsequently, using the resulting section sample, a cross section of the zinc diffusion layer was observed with STEM using Hitachi HD-2300A, and elemental analysis was performed with EDX to obtain an element mapping image (an acceleration voltage: 200 kV).

[0067] By the method as described above, in the elemental mapping image, among islands indicating the presence of zinc and that can be surrounded by the smallest circle having a diameter of 10 nm or more, the island located at the farthest distance from the surface of the base material was identified for every 500 nm of the boundary length of the surface of the base material, and the distance of the island with the longest distance from the base material surface was measured at ten or more observation visual fields to calculate an average value. The results are shown in Table 1.

(2) Each Plating layer

[0068] Each plated element of Examples and Comparative Examples obtained under the above conditions were

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embedded in a resin, and a surface of the element was polished to prepare a sample for cross-sectional observation. Each plating layer was analyzed by a metallographic microscope (Model GX 51 from Olympus Corporation), and plated thicknesses at ten points or more were measured to calculate an average value. The results are shown in Table 1.

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[Table 1]

	Zinc Diffusion Layer Average Thickness	Copper Plating		Gloss Copper Plating	Finish plating		Color Tone Adjustment Plating		Total Thickness
		Copper Pyrophosphate (Strike)	Copper Pyrophosphate		Average Thickness	Average Thickness	Type	Average Thickness	
Example 1	300 nm	1 μm	7 μm	3.5 μm	-	-	-	-	11.5 μm
Example 2	300 nm	1 μm	7 μm	3.5 μm	1 μm	Cu- Sn-Zn	-	-	12.5 μm
Example 3	250 nm	1 μm	10 μm	3.5 μm	1 μm	Cu- Sn-Zn	-	-	15.5 μm
Example 4	300 nm	1 μm	7 μm	1.5 μm	1 μm	Cu- Sn-Zn	-	-	10.5 μm
Example 5	250 nm	1 μm	7 μm	1.5 μm	1 μm	Cu- Sn-Zn	0.1 μm	Black Cu- Sn Plating	10.6 μm
Comparative Example 1	250 nm	1 μm	10 μm	-	1 μm	Cu- Sn-Zn	-	-	12 μm
Comparative Example 2	250 nm	Cuprous Cyanide Strike 1 μm	Cuprous Cyanide 7 μm	3.5 μm	1 μm	Cu- Sn-Zn	-	-	12.5 μm

<3. Adhesion Test>

[0069] For each plated element of Examples and Comparative Example obtained under the above conditions, adhesion of the plating layer was confirmed by surface observation (Stereoscopic microscope SZ60 from Olympus Corporation). Results were evaluated by the following criteria. The results are shown in Table 2.

- (a single circle): No peeling of the plating layer was observed; and
- X (a cross): Peeled part(s) of the plating layer was/were observed.

<4. Sliding Resistance>

[0070] A plurality of plated elements of each of Examples and Comparative Examples obtained under the above conditions were caulked and fixed to side edges of a pair of fastener tapes to form element rows, and a pair of the element rows was engaged to each other to form a fastener chain. Using a tensile tester (in accordance with JIS-B-7721), the fastener chain was opened and closed via a slider and the sliding resistance was measured in accordance with JIS-S-3015: 2007. As the sliding resistance, an integral average value was adopted. The results are shown in Table 2. If the sliding resistance is 4.9 N or less, it is determined that there is no problem in practical use. Comparative Example 2 resulted in a plated element having poor adhesion and a partially swollen surface, and thus did not provide any data of the sliding resistance comparable to other examples with no swollen surface.

<5. Glossiness (Surface Roughness)>

[0071] For each plated element of Examples and Comparative Examples obtained under the above conditions, an arithmetic average surface roughness (Ra) of the outermost surface was measured by a noncontact three-dimensional surface shape measuring apparatus (Zygo NewView 6300 from Zygo Corporation, Pa., U.S.) according to JIS B 0601: 2001. The results are shown in Table 2. In addition, Comparative Example 2 resulted in a plated product having poor adhesion and a partially swollen surface, and thus did not provide any data of the surface roughness comparable to other examples with no swollen surface.

<6. Surface Hardness>

[0072] A hardness of each plated element of Examples and Comparative Examples obtained under the above conditions was measured by a Vickers hardness tester (JIS-Z-2244: in accordance with 2009). A load was 50 g. The measurement was performed three times, and an average value of the measurements was determined to be a measured value. The results are shown in Table 2.

<7. Caulking Test>

[0073] Each plated element of Examples and Comparative Examples obtained under the above conditions was caulked and fixed to the side edge of the fastener tape using a jig, and a surface condition of the element was then observed with a stereoscopic microscope (SZ60 from Olympus Corporation). Results were evaluated by the following criteria. The results are shown in Table 2.

- (a single circle): No crack was observed on the plated surface; and
- X (a cross): Crack(s) was/were observed on the plated surface.

<8. Corrosion Test>

[0074] Each plated element of Examples and Comparative Examples obtained under the above conditions was subjected to saltwater spraying for 24 h, and the presence or absence of corrosion was visually checked. Results were evaluated by the following criteria. The results are shown in Table 2.

- (a single circle): No corrosion was observed on the plated surface; and
- X (a cross): Corrosion was observed on the plated surface.

[Table 2]

	Adhesion	Sliding Resistance (Standard 4.9N)	Surface Roughness	Surface Hardness	Caulking (Crack)	Corrosion
			Ra (μm)	Vickers Hardness (Hv)		
Example 1	○	2.93 N	0.07	100	○	×
Example 2	○	3.12 N	0.08	600	○	○
Example 3	○	4.31 N	0.04	650	○	○
Example 4	○	2.87 N	0.13	550	○	○
Example 5	○	2.90 N	0.12	660	○	○
Comparative Example 1	○	3.05 N	0.17	600	○	○
Comparative Example 2	×	-	-	600	○	○

<9. Discussion>

[0075] As can be seen from the above results, the plated elements according to Examples 1 to 5 had both of crack resistance and glossiness. It was also confirmed that the corrosion resistance was improved by carrying out the finish plating. On the other hand, Comparative Example 1 had insufficient glossiness because the gloss copper plating was not carried out. Comparative Example 2 led to poor adhesion of the plating and hence poor appearance, because the copper cyanide plating was carried out in place of the copper pyrophosphate plating.

[0076] While the embodiments of the present invention have been described in detail with reference to the drawings, the present invention is not limited to the above embodiments, and various modifications may be made within the scope of the present invention.

DESCRIPTION OF REFERENCE NUMERALS

[0077]

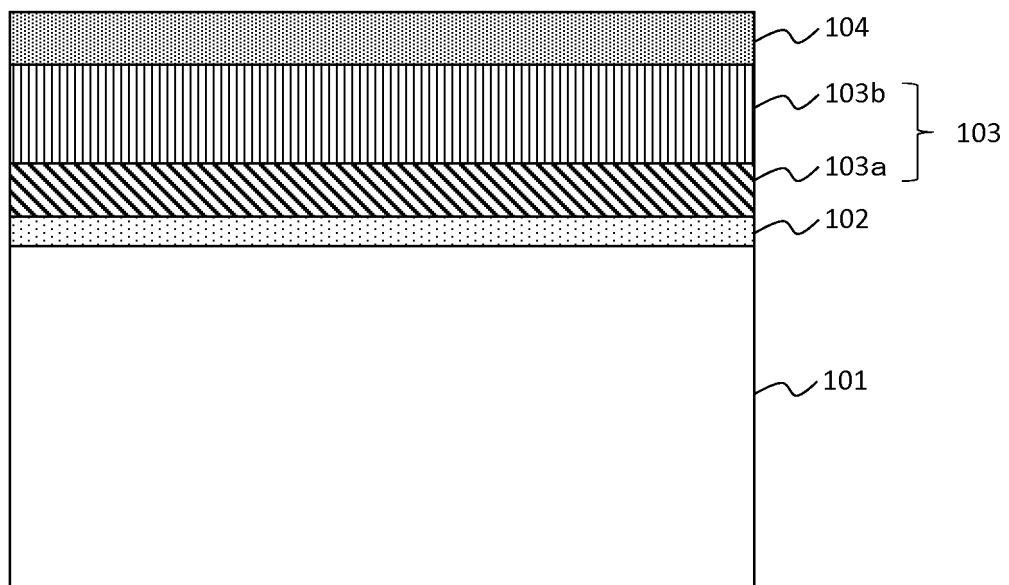
- 101 base material
- 102 zinc diffusion layer
- 103 copper pyrophosphate plating layer
- 103a copper pyrophosphate strike plating layer
- 103b copper pyrophosphate main plating layer
- 104 copper sulfate plating layer
- 105 finish plating layer
- 106 color tone adjustment plating layer
- 108 fastener element
- 109 fastener tape

Claims

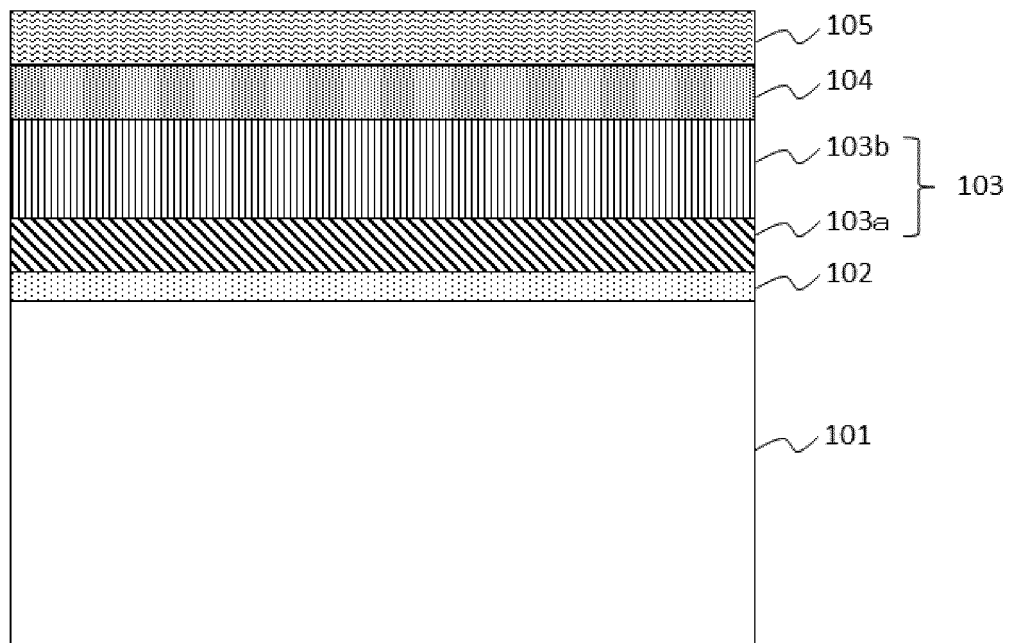
1. A member for slide fasteners or buttons, the member comprising: a base material (101) made of aluminum or an aluminum alloy; a zinc diffusion layer (102) having zinc diffused inside a surface of the base material; and a plurality of plating layers covering the zinc diffusion layer (102), the plating layers comprising a copper pyrophosphate plating layer (103) and a copper sulfate plating layer (104) in this order from inside.
2. The member for slide fasteners or buttons according to claim 1, wherein the copper pyrophosphate plating layer (103) has an average thickness of 20 μm or less.

3. The member for slide fasteners or buttons according to claim 1, wherein the copper pyrophosphate plating layer (103) has an average thickness of from 5 to 20 μm .
- 5 4. The member for slide fasteners or buttons according any one of claims 1 to 3, wherein the copper pyrophosphate plating layer (103) comprises a copper pyrophosphate strike plating layer (103a) having an average thickness of from 0.1 to 5 μm as an underlayer.
- 10 5. The member for slide fasteners or buttons according to any one of claims 1 to 4, wherein the copper sulfate plating layer (104) has an average thickness of 7 μm or less.
- 15 6. The member for slide fasteners or buttons according to claims 1 to 4, wherein the copper sulfate plating layer (104) has an average thickness of from 1 to 7 μm .
- 17 7. The member for slide fasteners or buttons according to any one of claims 1 to 6, wherein the member has a ratio of an average thickness of the copper sulfate plating layer (104) to an average thickness of the copper pyrophosphate plating layer (103) of from 0.1 to 0.5.
- 20 8. The member for slide fasteners or buttons according to any one of claims 1 to 7, wherein the plating layers further comprise a finish plating layer (105) harder than the copper sulfate plating layer (104) outside the copper sulfate plating layer (104).
- 25 9. The member for slide fasteners or buttons according to claim 8, wherein the finish plating layer (105) is an alloy plating layer containing Cu and Sn.
- 30 10. The member for slide fasteners or buttons according to claim 8 or 9, wherein the finish plating layer (105) has an average thickness of from 0.5 to 5 μm .
- 32 11. The member for slide fasteners or buttons according to any one of claims 1 to 10, wherein an outermost surface has an arithmetic average roughness (Ra) of 0.3 μm or less.
- 34 12. The member for slide fasteners or buttons according to any one of claims 8 to 11, wherein the plating layers further comprise a plating layer (106) having a different color tone from that of the finish plating layer (105) on an outer side of the finish plating layer (105).
- 36 13. The member for slide fasteners or buttons according to any one of claims 1 to 12, wherein an entire surface of the base material (101) is coated with the plating layers.
14. An article comprising the member for slide fasteners or buttons according to any one of claims 1 to 13.
- 40 15. A fastener stringer comprising fastener elements caulked and fixed along one side edge of a fastener tape, wherein at least one of the fastener elements is the member for slide fasteners according to any one of claims 1 to 13.
16. A method for producing a member for slide fasteners or buttons, comprising:
 - 45 preparing an aluminum or aluminum alloy base material (101) processed into a shape of a member for slide fasteners or buttons; and
 - performing a zincate treatment, copper pyrophosphate plating, and copper sulfate plating in this order on at least a part of a surface of the base material (101).

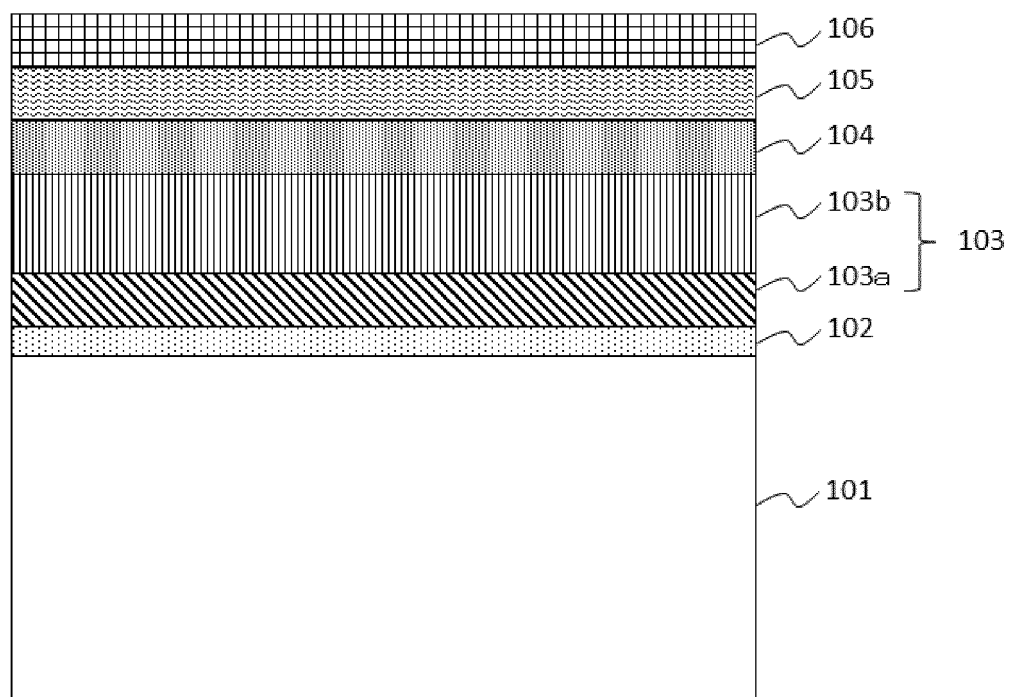
[FIG. 1]



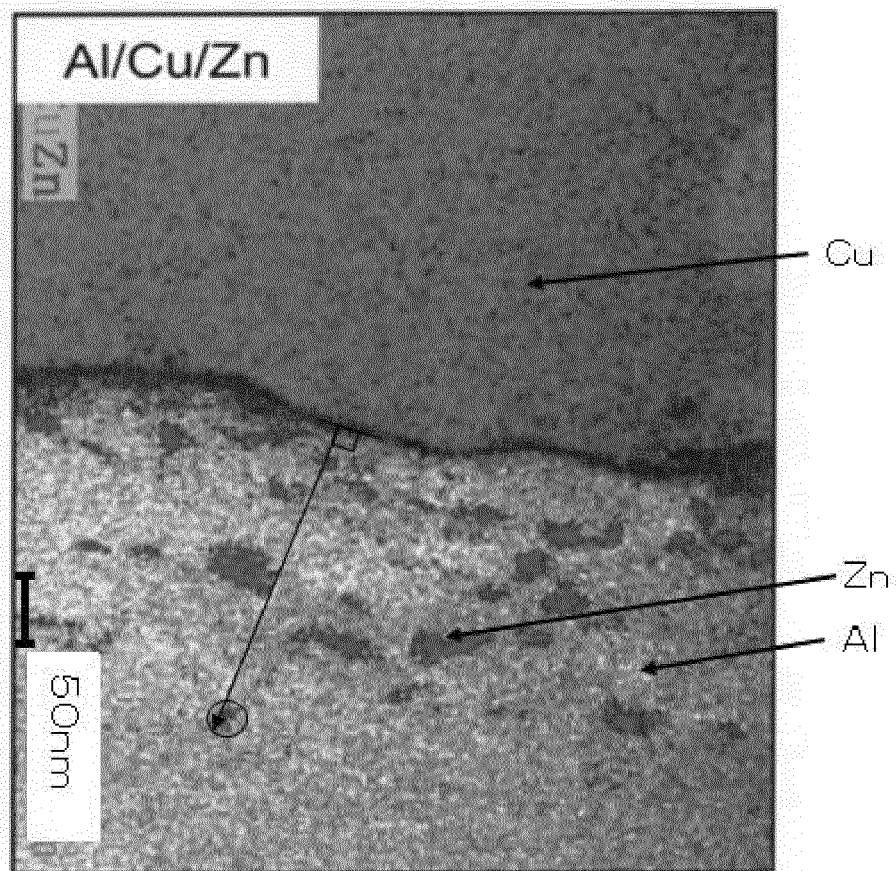
[FIG. 2]



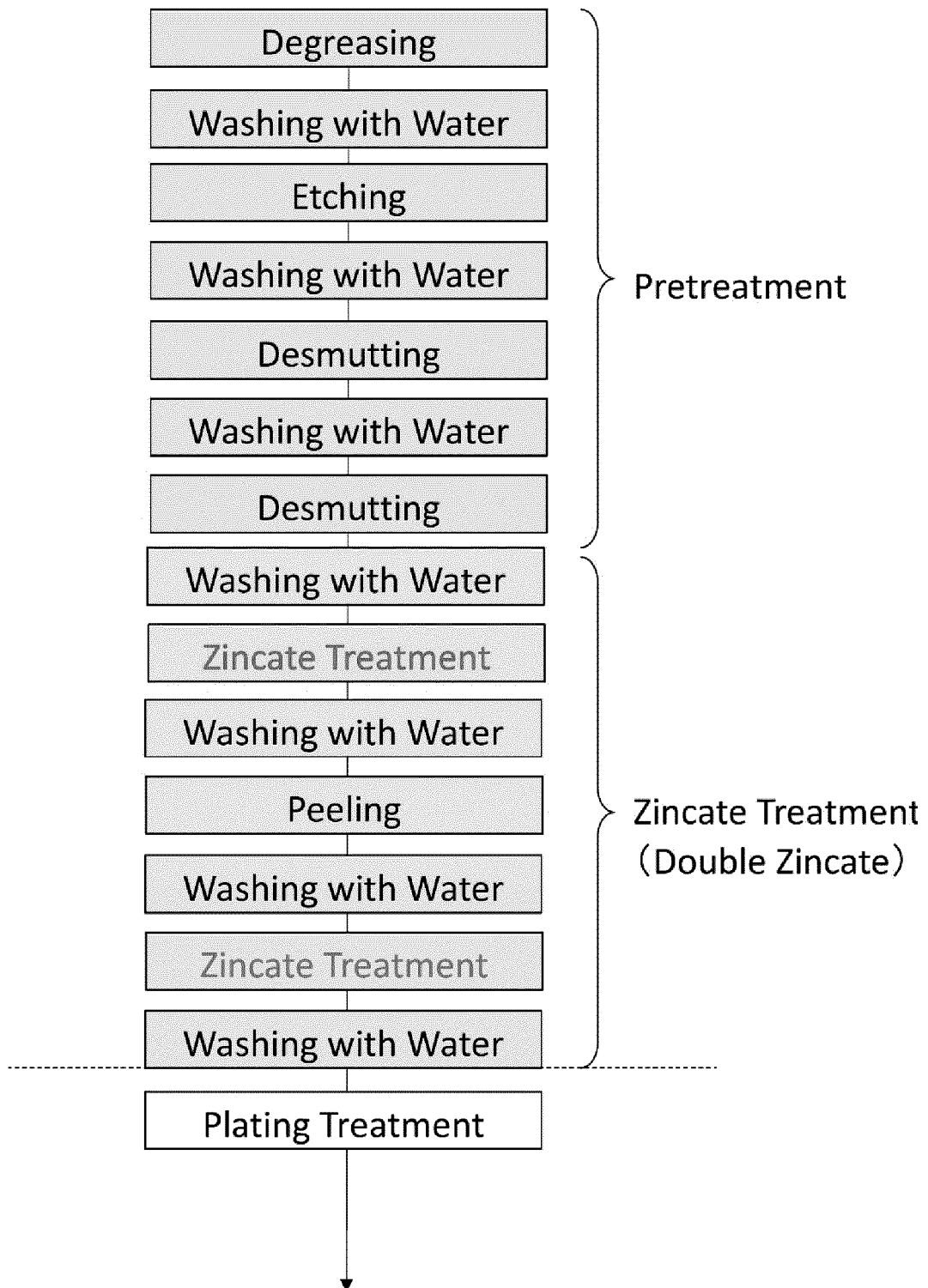
[FIG. 3]



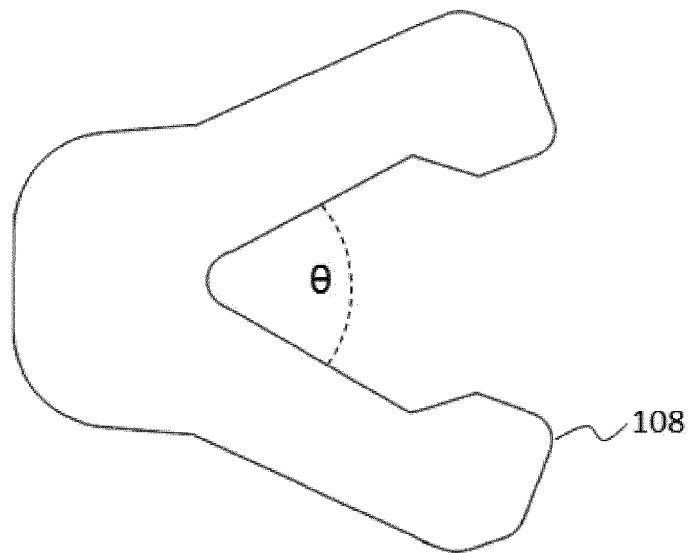
[FIG. 4]



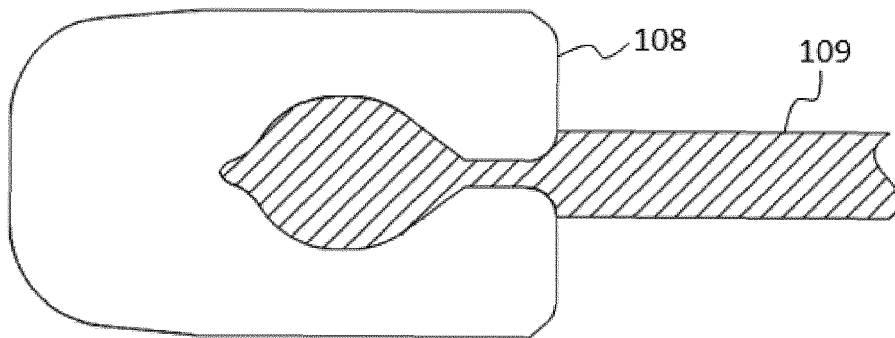
[FIG. 5]



[FIG. 6]



(a) Before Caulking



(b) After Caulking

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/088769

A. CLASSIFICATION OF SUBJECT MATTER

A44B19/00(2006.01)i, A44B1/04(2006.01)i, C25D7/02(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)

A44B19/00-19/64, A44B1/00-9/20, C25D7/02

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017

Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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

JSTPlus/JMEDPlus/JST7580 (JDreamIII), CAPLUS/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/077567 A1 (YKK Corp.), 30 June 2011 (30.06.2011), & US 2012/0297583 A1 & EP 2517593 A1 & CN 102665473 A	1-15
A	JP 1-113001 A (Kabushiki Kaisha Osumi Riko), 01 May 1989 (01.05.1989), (Family: none)	1-15
A	JP 61-129236 A (Iba Kogyo Kabushiki Kaisha), 17 June 1986 (17.06.1986), (Family: none)	1-15
A	JP 49-36856 B1 (Katsumi MORISHIGE), 03 October 1974 (03.10.1974), (Family: none)	1-15

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

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"&" document member of the same patent family

Date of the actual completion of the international search

20 February 2017 (20.02.17)

Date of mailing of the international search report

28 February 2017 (28.02.17)

Name and mailing address of the ISA/

Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/088769

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 6-13753 A (Showa Aluminum Corp.), 21 January 1994 (21.01.1994), (Family: none)	1-15
A	JP 11-181593 A (Totoku Electric Co., Ltd.), 06 July 1999 (06.07.1999), & US 6178623 B1 & EP 924320 A2	1-15

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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