

SILVER-COATED MATERIAL AND METHOD OF MANUFACTURE THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates to a silver-coated material and a method of manufacture thereof. More specifically, the invention relates to a silver-coated material suitable as a contact in connectors, switches, terminals and electronic components.

2. Description of the Related Art

[0002] Materials obtained by applying a copper or nickel undercoat onto a brass or phosphor-bronze surface and additionally applying on top thereof a silver plating are commonly used in the connectors and switches serving as connection components for electronic equipment. Because silver is a good conductor of electricity and heat, it is used as a plating in such connectors and switches, and also in leadframes and the like.

[0003] It is known that, in recent years, owing to the large number of repeated switching operations carried out on the switches used in cell phones and remote controls, and to the repetition of many switching operations in a short period of time, the silver plating wears away and the contact resistance rises.

[0004] To prevent this from happening, the approach taken to date has been to increase the thickness of the silver plating. However, with the intensifying downward pressure on the cost of electronic components year after year, product specifications which call for thinner silver plating are on the rise. Hence, there exists an urgent need to examine how to improve the abrasion resistance of silver plating.

[0005] In general, increasing the hardness of the coating is effective for enhancing the abrasion resistance. Efforts are being made to increase the coating hardness by adding hardening agents such as antimony to the silver, but such efforts have had the opposite effect of making the coating more brittle, resulting in a deterioration of the abrasion resistance.

[0006] In addition, Japanese Patent Publication No. 2012-49041 discloses a silver-coated material for moving contact components which has an electrically conductive base material made of copper or a copper alloy or of iron or an iron alloy on which are superimposed, in order, an underlayer made of nickel, a nickel alloy, cobalt or a cobalt alloy, an intermediate layer made of copper, a copper alloy, tin or a tin alloy, and an outermost layer made of silver or a silver alloy, and in which an intermediate oxide layer is present as a second intermediate layer between the intermediate layer and the outermost layer. The intermediate oxide layer is a layer of an oxide of the metal making up the intermediate layer. It is claimed that making an intermediate oxide layer present between the intermediate layer and the outermost layer has the effect of keeping the intermediate layer ingredients from diffusing to the surface and forming an oxide within the surface layer, thus preventing a rise in the contact resistance, and moreover has the effect of suppressing peeling of the silver layer at the surface. The intermediate oxide layer is formed by 5 to 60 minutes of heating in open air at a temperature of 250°C after the outermost layer has been formed.

SUMMARY OF THE INVENTION

1. Problems to be Solved by the Invention

[0007] The object of this invention is to provide a silver-coated material of excellent abrasion resistance in which, even when used as, for example, a moving contact and/or a fixed contact in a switch used over an extended period of time under conditions where switching is repeatedly carried out, the silver or silver alloy layer at the surface does not wear away and, moreover, the contact resistance does not rise.

[0008] The inventors have conducted extensive investigations, as a result of which they have discovered that the above problem is resolved by the use of plating to form, as an outermost layer on an electrically conductive base material, a layer made of at least silver or a silver alloy, and heat-treating under specific heating conditions. This discovery led ultimately to the present invention.

[0009] The invention is recited below.

(1) A silver-coated material having a silver coating layer on an electrically conductive base material directly and/or via an underlayer, wherein the silver coating layer is an outermost layer made of silver or a silver alloy, wherein crystals of a columnar structure having an average crystal grain size of 0.2 μm or more and 0.5 μm or less that are made of silver or a silver alloy are included in the layer made of silver or a silver alloy, and wherein the silver-coated material has a coating loss, in an abrasion resistance test, of less than 40 mg and has an initial contact resistance of less than 10 $\text{m}\Omega$ and a contact resistance of less than 10 $\text{m}\Omega$ after a sliding wear test carried out under following conditions.

Sliding wear test conditions:

[Load]	1.6 N
[Sliding range]	0.2 mm
[Sliding speed]	1 mm/s

[Number of cycles] 50,000

[0010] (2) The silver-coated material according to (1) above, characterized in that the coating loss in the abrasion resistance test is less than 30 mg.

[0011] (3) The silver-coated material according to (1) or (2) above, characterized in that the abrasion resistance test is carried out in accordance with JIS H 8682 under conditions of a load of 500 gf (surface area of abrasion, 12 mm × 31 mm), with #1500 emery paper, and 200 back-and-forth cycles.

[0012] (4) A silver-coated material having a silver coating layer on an electrically conductive base material directly and/or via an underlayer, wherein the silver coating layer is an outermost layer made of silver or a silver alloy, wherein the layer made of silver or a silver alloy is formed by plating and heat-treated at 200 to 500°C for 1 to 299 seconds.

[0013] (5) The silver-coated material according to (4) above, characterized in that crystals of a columnar structure that are made of silver or a silver alloy are included in the layer made of silver or a silver alloy.

[0014] (6) The silver-coated material according to (4) or (5) above, characterized in that the silver or silver alloy crystals in the layer made of silver or a silver alloy have an average crystal grain size of 0.2 μm or more and 0.5 μm or less.

[0015] (7) The silver-coated material according to any one of (4) to (6) above, characterized in that the heat treatment is carried out at from 250 to 450°C for 1 to 59 seconds.

[0016] (8) The silver-coated material according to any one of (4) to (6) above, characterized in that the heat treatment is carried out at from 270 to 450°C for 1 to 30 seconds.

[0017] (9) The silver-coated material according to any one of (4) to (6) above, characterized in that the heat treatment is carried out at from 300 to 450°C for 1 to 10 seconds.

[0018] (10) A switch, characterized by using the silver-coated material according to any one of (1) to (9) above as a moving contact and/or fixed contact for the switch.

[0019] (11) A method of manufacturing the silver-coated material according to any one of (1) to (6) above having a silver coating layer on an electrically conductive base material directly and/or via an underlayer, wherein the silver coating layer is an outermost layer made of silver or a silver alloy, and wherein the method includes a step of forming the layer made of silver or a silver alloy by plating, and heat-treating the same at from 200 to 500°C for 1 to 299 seconds.

[0020] (12) The method of manufacturing the silver-coated material according to (11) above, characterized in that the heat treatment is carried out at from 250 to 450°C for 1 to 59 seconds.

[0021] (13) The method of manufacturing the silver-coated material according to (11) above, characterized in that the heat treatment is carried out at from 270 to 450°C for 1 to 30 seconds.

[0022] (14) The method of manufacturing the silver-coated material according to (11) above, characterized in that the heat treatment is carried out at from 300 to 450°C for 1 to 10 seconds.

[0023] According to this invention, there can be provided a silver-coated material of excellent abrasion resistance in which the silver or silver alloy layer at the surface does not wear away and, moreover, the contact resistance does not rise even when used as, for example, a moving contact and/or a fixed contact in a switch used over an extended period of time under conditions where switching is repeatedly carried out.

2. Brief Description of the Drawings

[0024] FIG. 1 is a cross-sectional SIM image of the silver-coated material in Example 1.

[0025] FIG. 2 is a cross-sectional SIM image of the silver-coated material in Comparative Example 1.

[0026] FIG. 3 is a cross-sectional SIM image of the silver-coated material in Comparative Example 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] The silver-coated material of this invention is a silver-coated material that has, as an outermost layer on an electrically conductive base material, a layer made of at least silver or a silver alloy, and is characterized by having a coating loss in an abrasion resistance test of less than 40 mg, and having an initial contact resistance of less than 10 m Ω and a contact resistance of less than 10 m Ω after a sliding wear test carried out under the following conditions.

Sliding wear test conditions:

[Load]	1.6 N
[Sliding range]	0.2 mm
[Sliding speed]	1 mm/s
[Number of cycles]	50,000

[0028] Also, the silver-coated material of the invention is a silver-coated material that has, as an outermost layer on an electrically conductive base material, a layer made of at least silver or a silver alloy, and is characterized in that the layer made of silver or a silver alloy is formed by plating and heat-treated at 200 to 500°C for 1 to 299 seconds.

[0029] The conductive base material is a material having, for example, electrical conductivity, spring characteristics and durability. In this invention, it is preferably made of

copper or a copper alloy, or iron or an iron alloy. Copper alloys that can be preferably used include bronzes, phosphor bronzes, brasses, titanium coppers, copper-nickel-silicon (Corson) alloys and beryllium coppers. Iron alloys that can be preferably used include stainless steels (SUS) and Alloy 42.

[0030] In the outermost layer made of silver or silver alloy, silver alloys such as Ag-Sn alloys, Ag-Cu alloys, Ag-In alloys and Ag-Se alloys have good contact characteristics and thus can be preferably used. The silver alloy is preferably one having a silver content in excess of 50% by mass.

[0031] The outermost layer made of silver or a silver alloy is formed by plating using a known silver plating solution or silver alloy plating solution. The plating solution is not particularly limited, although a plating solution that contains cyanide as a complex is preferred. Prior to plating with a plating solution containing the cyanide as a complex, silver strike plating may be carried out. By using plating to form the outermost layer made of silver or a silver alloy, the layer can be easily and conveniently formed at a low cost.

[0032] The outermost layer has a thickness of preferably from 0.05 to 5 μm , more preferably from 0.1 to 2 μm , and even more preferably from 0.2 to 2 μm .

[0033] The silver-coated material of the invention may have an underlayer between the base material and the outermost layer made of silver or a silver alloy. Examples of the underlayer include a plated Ni layer, a plated copper layer and a plated cobalt layer. These may be formed with a known plating solution and under known plating conditions.

[0034] The plating solution used to form an underlying plated Ni layer is preferably a sulfamate bath.

[0035] The plating solution used to form an underlying plated copper layer is preferably a copper cyanide bath.

[0036] Preferred silver-coated materials of the invention are ones having an outermost layer made of silver or a silver alloy on an electrically conductive base material, and ones having a plated copper or a plated Ni layer as an underlayer between an electrically conductive base material and an outermost layer made of silver or a silver alloy.

[0037] The silver-coated material of the invention, after the outermost layer has been formed, is heat-treated at 200 to 500°C for 1 to 299 seconds. At a low temperature in this temperature range, it is preferable to make the treatment time longer; at a high temperature, it is preferable to make the treatment time shorter. From the standpoint of productivity, heat treatment at 250 to 450°C for 1 to 59 seconds is preferred, heat treatment at 270 to 450°C for 1 to 30 seconds is more preferred, and heat treatment at 300 to 450°C for 1 to 10 seconds is especially preferred.

[0038] When heat treatment is carried out under this range of conditions, the spherical silver or silver alloy crystal grains in the outermost layer grow, enlarging to an average crystal grain size of 0.2 μm or more and becoming columnar in the plating thickness direction, and so the outermost layer includes crystals of a columnar structure that are made of silver or a silver alloy. As a result, the abrasion resistance of the surface was found to greatly improve. It is more preferable for the outermost layer to have an average crystal grain size of 0.2 μm or more and 0.5 μm or less, and to include crystals having a columnar structure. In cases where the temperature was lower and/or the time was shorter than these conditions, the crystals did not grow and an improvement in the abrasion resistance was not observed. Conversely, in cases where the temperature was higher and/or the time was longer than these conditions, the crystals grew

and an improvement in abrasion resistance was observable. However, at an average crystal grain size greater than 0.5 μm , the crystals became horizontally elongated with respect to the plating thickness direction and lamellar, and an increase in abrasion resistance as pronounced as when crystals of a column structure in the plating thickness direction are included was not observed. The shape of the crystal grains was observed from a cross-sectional SIM image in the plating thickness direction obtained after focused ion beam (FIB) milling of a plated substrate that had been heat-treated.

[0039] Given that silver does not readily oxidize, there is no rise in contact resistance with heat treatment in this range of conditions. However, when the heat treatment temperature is higher and/or the heat treatment time is longer than these conditions, the initial contact resistance rises due to surface oxidation.

[0040] Because the purpose of this heat treatment is to make the crystal grains of silver in the outermost layer grow and become columnar, and is not to form an oxide layer, heat treatment may be carried out in an inert gas atmosphere. However, heat treatment in open air is easy and desirable.

[0041] The heating method for heat treatment is not particularly limited. Heat treatment may be carried out using, for example, a hot plate or a circulating hot-air oven.

[0042] Therefore, a silver-coated material with, as the outermost layer, a layer made of silver or a silver alloy, when heat-treated in this way, has a coating loss in an abrasion resistance test of less than 40 mg and has an initial contact resistance of less than 10 $\text{m}\Omega$ and a contact resistance of less than 10 $\text{m}\Omega$ after a sliding wear test has been carried out under the following conditions.

Sliding wear test conditions:

[Load]	1.6 N
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[Sliding range] 0.2 mm

[Sliding speed] 1 mm/s

[Number of cycles] 50,000

[0043] A coating loss in the abrasion resistance test of less than 30 mg is more preferred. The coating loss can be made less than 30 mg by the heat treatment conditions.

[0044] The abrasion resistance test was carried out in accordance with JIS H 8682 under conditions of a load of 500 gf (surface area of abrasion, 12 mm × 31 mm), with #1500 emery paper, and 200 back-and-forth cycles.

[0045] Because the silver-coated material of the invention has, as mentioned above, an excellent peel resistance and abrasion resistance, and the contact resistance does not rise, it can be suitably used in connectors and switches serving as connection components for electronic equipment. Use as a switch moving contact and/or fixed contact utilized in cell phone and remote control switches, such as tactile switches, is especially preferred. Even with long-term use under conditions where switching is repeatedly carried out, the surface silver or silver alloy layer does not wear away and the contact resistance does not rise.

EXAMPLES

[0046] Next, this invention is described more fully based on working examples, although the invention is not limited by these examples.

[0047] Example 1

A plated substrate obtained by successively carrying out, on phosphor bronze (C5210, 25 mm × 20 mm × 0.2 mm (T)): silver strike plating to a thickness of 0.05 μm , and silver plating in a high silver cyanide bath to a thickness of 0.4 μm , was used as the test material.

[0048] This plated substrate was heat-treated in open air using a hot plate under the Example 1 conditions in Table 1. The heat treatment temperature is the temperature of the plated substrate that has been set on a hot plate, as measured with a thermocouple.

[0049] Examples 2 and 3

A plated substrate obtained by successively carrying out, on phosphor bronze (C5210, 25 mm × 20 mm × 0.2 mm (T)): copper plating to a thickness of 3 μm in a copper cyanide bath, silver strike plating to a thickness of 0.05 μm , and silver plating in a high silver cyanide bath to a thickness of 0.4 μm , was used as the test material.

[0050] These plated substrates were heat-treated using a hot plate in open air under the Example 2 and Example 3 conditions in Table 1.

[0051] Example 4

A plated substrate obtained by successively carrying out, on phosphor bronze (C5210, 25 mm × 20 mm × 0.2 mm (T)): nickel plating to a thickness of 3 μm in a sulfamate bath, silver strike plating to a thickness of 0.05 μm , and silver plating in a high silver cyanide bath to a thickness of 0.4 μm , was used as the test material.

[0052] This plated substrate was heat-treated using a hot plate in open air under the Example 4 conditions in Table 1.

[0053] Example 5

[0054] Aside from changing the heat treatment conditions in Example 2 to the conditions indicated in Table 1 and heating in a nitrogen atmosphere (oxygen concentration of less than 1%), a heat-treated plated substrate was obtained in the same way as in Example 2.

[0055] Example 6

Aside from changing the heat treatment conditions in Example 4 to the conditions indicated in Table 1, a heat-treated plated substrate was obtained in the same way as in Example 4.

[0056] Example 7

Aside from changing the heat treatment conditions in Example 2 to the conditions indicated in Table 1, a heat-treated plated substrate was obtained in the same way as in Example 2.

[0057] Example 8

Aside from changing the heat treatment conditions in Example 4 to the conditions indicated in Table 1, a heat-treated plated substrate was obtained in the same way as in Example 4.

[0058] Comparative Example 1

Aside from not carrying out heat treatment, a plated substrate was obtained in the same way as in Example 4.

[0059] Comparative Example 2

Aside from changing the heat treatment conditions in Example 2 to the conditions indicated in Table 1, a heat-treated plated substrate was obtained in the same way as in Example 2.

[0060] Comparative Example 3

Aside from changing the heat treatment conditions in Example 1 to the conditions indicated in Table 1, a heat-treated plated substrate was obtained in the same way as in Example 1.

[0061] Comparative Examples 4 to 6

Aside from changing the heat treatment conditions in Example 4 to the conditions indicated in Table 1, heat-treated plated substrates were obtained in the same way as in Example 4.

[0062] Abrasion resistance tests were carried out on the heat-treated plated substrates. The abrasion resistance test was carried out in accordance with JIS H 8682 and using a Suga Abrasion Tester (NUS-IS03) under the conditions of a load of 500 gf (surface area of abrasion, 12 mm × 31 mm), with #1500 emery paper, and 200 back-and-forth cycles.

Rating Criteria:

Good: Coating loss in abrasion resistance test was less than 30 mg

Fair: Coating loss in abrasion resistance test was 30 mg or more but less than 40 mg

NG: Coating loss in abrasion resistance test was 40 or more

[0063] The heat-treated plated substrate was FIB milled, following which the average crystal grain size and the shape of the crystals were determined from a cross-sectional SIM image (using an SMI3050SE system from SII Nanotechnologies).

[0064] Measurement of the average crystal grain size was carried out via computation from the cross-sectional SIM image by the cutting method in accordance with JIS H 0501.

Rating Criteria:

Small: average crystal grain size < 0.2 μm

Medium: $0.2 \mu\text{m} \leq$ average crystal grain size $\leq 0.5 \mu\text{m}$

Large: average crystal grain size > 0.5 μm

[0065] Cross-sectional SIM images of the plated substrates obtained in Example 1, Comparative Example 1 and Comparative Example 3 are shown in, respectively, FIGS. 1 to 3.

[0066] In the plated substrate of Example 1, as shown in FIG. 1, the plated silver layer includes silver crystals of a columnar structure. Such shapes were referred to as "columnar." In the plated substrate of Comparative Example 1, as shown in FIG. 2, the silver grains in the plated silver layer are rounded. Such shapes were referred to as "round."

In the plated substrate of Comparative Example 3, as shown in FIG. 3, the silver crystals are horizontally elongated. Such shapes were referred to as "horizontally elongated."

[0067] The initial contact resistance and the contact resist after a sliding wear test was carried out under the following conditions were measured for the heat-treated plated substrates.

Contact resistance measurement conditions:

Apparatus: Yamasaki type CRS-1 Contact Simulator

Conditions: contact load, 10 g (Au probe); sliding distance, 1 mm

Sliding wear test conditions:

Apparatus: CRS-G2050-JNS, from Yamasaki Seiki Co.

Conditions:

[Load] 1.6 N

[Sliding range] 0.2 mm

[Sliding speed] 1 mm/s

[Number of cycles] 50,000

[0068] [Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Copper undercoat		No	Yes	Yes	No	Yes	No	Yes	No
Ni undercoat		No	No	No	Yes	No	Yes	No	Yes
Heat treatment conditions	Heat treatment temperature	200°C	250°C	270°C	300°C	350°C	350°C	450°C	500°C
	Heat treatment time	299s	59s	30s	10s	5s	5s	1s	1s
Evaluation results	Abrasion resistance	Fair	Fair	Good	Good	Good	Good	Good	Good
	Crystal grain size	medium	medium	medium	medium	medium	medium	medium	medium
	Crystal shape	columnar	columnar	columnar	columnar	columnar	columnar	columnar	columnar
	Initial contact resistance	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ
	Contact resistance after test	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ	< 10 mΩ

*Heat treatment in Example 5 was carried out in a nitrogen atmosphere (oxygen concentration < 1%)

[0069] [Table 2]

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Copper undercoat		No	Yes	No	No	No	No
Ni undercoat		Yes	No	No	Yes	Yes	Yes
Heat treatment conditions	Heat treatment temperature	no heat treatment	150°C	250°C	300°C	350°C	550°C
	Heat treatment time		600s	600s	350s	320s	1s
Evaluation results	Abrasion resistance	NG	NG	Fair	Fair	Fair	NG
	Crystal grain size	small	small	large	large	large	large
	Crystal shape	round	round	horizontally elongated	horizontally elongated	horizontally elongated	horizontally elongated
	Initial contact resistance	< 10 mΩ	< 10 mΩ	20 mΩ	30 mΩ	30 mΩ	20 mΩ
	Contact resistance after test	> 100 mΩ	> 100 mΩ	> 100 mΩ	> 100 mΩ	> 100 mΩ	> 100 mΩ

WHAT IS CLAIMED IS:

1. A silver-coated material having a silver coating layer on an electrically conductive base material directly and/or via an underlayer, wherein the silver coating layer is an outermost layer made of silver or a silver alloy, wherein crystals of a columnar structure having an average crystal grain size of 0.2 μm or more and 0.5 μm or less that are made of silver or a silver alloy are included in the layer made of silver or a silver alloy, and wherein the silver-coated material has a coating loss, in an abrasion resistance test, of less than 40 mg and has an initial contact resistance of less than 10 $\text{m}\Omega$ and a contact resistance of less than 10 $\text{m}\Omega$ after a sliding wear test carried out under following conditions.

Sliding wear test conditions:

[Load]	1.6 N
[Sliding range]	0.2 mm
[Sliding speed]	1 mm/s
[Number of cycles]	50,000

2. The silver-coated material according to claim 1, characterized in that the coating loss in the abrasion resistance test is less than 30 mg.

3. The silver-coated material according to claim 1 or claim 2, characterized in that the abrasion resistance test is carried out in accordance with JIS H 8682 under conditions of a load of 500 gf (surface area of abrasion, 12 mm $\times$ 31 mm), with #1500 emery paper, and 200 back-and-forth cycles.

4. A silver-coated material having a silver coating layer on an electrically conductive base material directly and/or via an underlayer, wherein the silver coating layer is an outermost layer made of silver or a silver alloy, wherein the layer made of silver or a silver alloy is formed by plating and heat-treated at 200 to 500°C for 1 to 299 seconds.

5. The silver-coated material according to claim 4, characterized in that crystals of a columnar structure that are made of silver or a silver alloy are included in the layer made of silver or a silver alloy.

6. The silver-coated material according to claim 4 or claim 5, characterized in that the silver or silver alloy crystals in the layer made of silver or a silver alloy have an average crystal grain size of 0.2 μm or more and 0.5 μm or less.

7. The silver-coated material according to any one of claims 4 to 6, characterized in that the heat treatment is carried out at from 250 to 450°C for 1 to 59 seconds.

8. The silver-coated material according to any one of claims 4 to 6, characterized in that the heat treatment is carried out at from 270 to 450°C for 1 to 30 seconds.

9. The silver-coated material according to any one of claims 4 to 6, characterized in that the heat treatment is carried out at from 300 to 450°C for 1 to 10 seconds.

10. A switch, characterized by using the silver-coated material according to any one of claims 1 to 9 as a moving contact and/or fixed contact for the switch.

11. A method of manufacturing the silver-coated material according to any one of claims 1 to 6 having a silver coating layer on an electrically conductive base material directly and/or via an underlayer, wherein the silver coating layer is an outermost layer made of silver or a silver alloy, and wherein the method includes a step of forming the layer made of silver or a silver alloy by plating, and heat-treating the same at from 200 to 500°C for 1 to 299 seconds.

12. The method of manufacturing the silver-coated material according to claim 11, characterized in that the heat treatment is carried out at from 250 to 450°C for 1 to 59 seconds.

13. The method of manufacturing the silver-coated material according to claim 11, characterized in that the heat treatment is carried out at from 270 to 450°C for 1 to 30 seconds.

14. The method of manufacturing the silver-coated material according to claim 11, characterized in that the heat treatment is carried out at from 300 to 450°C for 1 to 10 seconds.