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(54) **ELECTROPLATING ADDITIVE SOLUTION AND PREPARATION METHOD THEREFOR, AND ELECTROPLATING MIXED SOLUTION OF HARD SILVER AND GRAPHENE**

(57) An electroplating additive solution, a preparation method thereof, and a hard silver-graphene electroplating mixture liquid are provided. The electroplating additive solution includes metal oxide, glycerol, alkali metal hydroxide and water. The metal oxide, the glycerol,

the alkali metal hydroxide and the water have a mass ratio of 1:(1-3):(3-6):(8-15). When the electroplating additive of the present disclosure is used in an electroplating mixture liquid, it can increase the hardness of the finally formed plating layer.

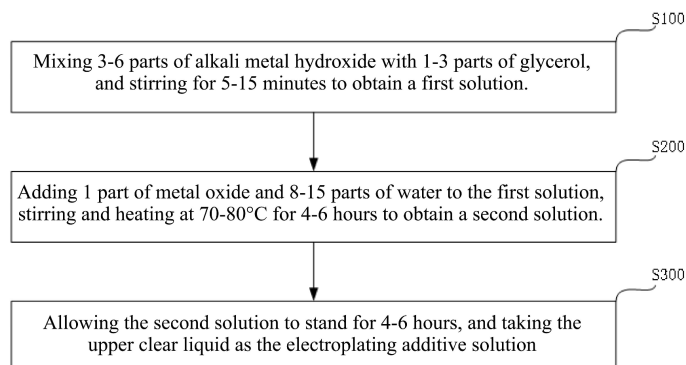


FIG. 1

Description

[0001] The present disclosure claims a priority of Chinese patent application No. 202311386283.3 filed with China National Intellectual Property Administration on October 23, 2023, the entire disclosure of which is incorporated into the present disclosure by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to a technical field of electroplating, in particular to an electroplating additive solution, a preparation method thereof, and a hard silver-graphene electroplating mixture liquid.

BACKGROUND

[0003] A silver layer is usually plated on an outer portion of a traditional connector. With a development of science and technology, plating a silver-graphene composite coating on the outer portion of the connector has become a better option, which can further improve an electrical conductive property of the connector.

SUMMARY

[0004] The connector is subjected to a high number of plugging and unplugging cycles, while the silver-graphene coating in the related art have low hardness, resulting in a short service life of the connector. Therefore, there is an urgent need for a silver-graphene coating with high hardness and excellent electrical conductive property.

[0005] In view of the above problem, the present disclosure provides an electroplating additive solution, a preparation method thereof, and a hard silver-graphene electroplating mixture liquid, aiming to remedy the problem of low hardness of the silver-graphene coating in the related art.

[0006] In a first aspect, an embodiment of the present disclosure provides an electroplating additive solution, including metal oxide, glycerol, alkali metal hydroxide and water.

[0007] A mass ratio of the metal oxide, the glycerol, the alkali metal hydroxide and the water is 1:(1-3):(3-6):(8-15).

[0008] Optionally, in some embodiments, the metal oxide includes one or more of antimony trioxide, bismuth oxide and manganese oxide.

[0009] Optionally, in some embodiments, the mass ratio of the metal oxide, the glycerol, the alkali metal hydroxide and the water is 1:(1-3):(3-6):(8-15).

[0010] In a second aspect, an embodiment of the present disclosure provides a preparation method for the electroplating additive solution as described above, including:

Mixing the alkali metal hydroxide with the glycerol and performing stirring to obtain a first solution;
Adding the metal oxide and the water to the first solution, performing stirring and heating to obtain a second solution;
Allowing the second solution to stand, and taking an upper clear liquid as the electroplating additive solution.

[0011] Optionally, in some embodiments, the first solution is stirred for 5-15 minutes.

[0012] The second solution is heated for 4-6 hours at a heating temperature of 70-80°C.

[0013] The second solution is stood for 4-6 hours.

[0014] In a third aspect, an embodiment of the present disclosure provides a hard silver-graphene electroplating mixture liquid including the electroplating additive solution as described above, the electroplating mixture liquid further includes a silver salt, a complexing agent, a graphene and a dispersant.

[0015] Optionally, in some embodiments, the silver salt includes potassium silver cyanide; and/or

The complexing agent includes potassium cyanide; and/or

The dispersant includes one or more of benzene sulfonate condensate sodium salt and sulfonate sodium salt.

[0016] Optionally, in some embodiments, the benzene sulfonate condensate sodium salt includes one or more of sodium monobenzene sulfonate condensate, sodium o-benzene sulfonate condensate and sodium tribenzene sulfonate condensate.

[0017] Optionally, in some embodiments, the sulfonate sodium salt includes one or more of sodium 2-ethylhexyl sulfonate, sodium diethyl triacetate sulfonate and sodium benzene sulfonate.

[0018] Optionally, in some embodiments, in the electroplating mixture liquid, the silver salt has a concentration of 10-30 g/L; and/or

In the electroplating mixture liquid, the graphene has a concentration of 0.5-4 g/L; and/or

In the electroplating mixture liquid, the dispersant has a concentration of 3-7 g/L; and/or

In the electroplating mixture liquid, the electroplating additive solution has a concentration of 3-10 mL/L; and/or

In the electroplating mixture liquid, the complexing agent has a concentration of 155-190 g/L.

[0019] Optionally, in some embodiments, the dispersant includes benzene sulfonate condensate sodium salt having a concentration of 1-2 g/L and sulfonate sodium salt having a concentration of 2-5 g/L.

Advantageous Effects

[0020] The electroplating additive of the present disclosure includes metal oxide and glycerol. When the additive is used in an electroplating mixture liquid, the metal oxide can stably and reliably refine the coating crystals and enhance the cathodic polarization reaction, thereby increasing the hardness of the finally formed coating. The alkali metal hydroxide can react with glycerol, and the product resulting from the reaction complexes with the metal oxide, such that the metal oxide is not precipitated in the electroplating mixture liquid, facilitating subsequent electroplating operation.

[0021] In addition, the electroplating mixture liquid of the present disclosure contains graphene and a dispersant. After adding the aforementioned electroplating additive to the electroplating mixture liquid, glycerol can also play a lubricating role on the graphene surface to prevent graphene from agglomeration. Glycerol and the dispersant also have a synergistic effect, both of which synergistically disperse the graphene and the metal oxide. This not only reduces the dosage of the dispersant, but also enables various ions, the metal oxide and graphene to reach an ideal migration rate in the electroplating mixture liquid, thereby being conducive to prepare and obtain a coating with excellent thermal conductivity, electrical conductivity and hardness.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] In order to explain the technical solutions in the embodiments of the present disclosure more clearly, the drawings required for describing the embodiments will be briefly introduced below. Obviously, the drawings described below are only some embodiments of the present disclosure, and those skilled in the art can obtain other drawings according to these drawings without creative work.

FIG. 1 is a flow diagram of a preparation method for an electroplating additive solution provided in an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0023] In the first aspect, an embodiment of the present disclosure provides an electroplating additive solution, which is mainly used in a hard silver-graphene electroplating mixture liquid to improve the hardness of the coating prepared by using the electroplating mixture liquid.

[0024] The electroplating additive solution of the present disclosure includes metal oxide, glycerol, alkali metal hydroxide and water. The metal oxide can stably and reliably refine the coating crystals and enhance the cathodic polarization reaction, thereby increasing the hardness of the finally formed coating. Optionally, the metal oxide includes, but is not limited to, one or more of antimony trioxide, bismuth oxide and manganese oxide. The alkali metal hydroxide can react with glycerol, and the product resulted from the reaction complexes with the metal oxide, such that the metal oxide is not precipitated in the electroplating mixture liquid, facilitating subsequent electroplating operation. When the electroplating mixture liquid is used to prepare a plated part, the silver ion, metal oxide and graphene can be migrated synchronously in a certain proportion, and in turn the silver ion, metal oxide and graphene can be uniformly dispersed in the coating, thereby improving the overall hardness of the coating. Optionally, the alkali metal hydroxide includes, but is not limited to, one or more of sodium hydroxide and potassium hydroxide.

[0025] In the electroplating additive solution, the mass ratio of the metal oxide, glycerol, alkali metal hydroxide and water is 1:(1-3):(3-6):(8-15), for example, 1:(1-2.8):(3-5):(8-13), 1:(1-2.4):(4-6):(10-12), 1:(2-2.5):(3-4):(13-15), 1:(2-3):(5-6):(9-11), 1:(1-1.5):(3-6):(8-10), 1:(1.2-2.6):(4-5):(11-13), 1:(1.8-2.2):(3.5-4.5):(10-14), etc. Within the aforementioned ratio range, when the electroplating additive is used in the hard silver-graphene electroplating mixture liquid, the reaction product of the alkali metal hydroxide and glycerol can fully prevent the precipitation of the metal oxide, and glycerol has good dispersibility, which is conducive to the dispersion of the metal oxide by glycerol and the synchronous migration of the silver ion, metal oxide and graphene in a certain proportion. The metal oxide can be uniformly distributed in the coating and can stably and reliably refine the coating crystals, increasing the hardness of the finally formed coating.

[0026] In a second aspect, please refer to FIG. 1. An embodiment of the present disclosure also provides a preparation method for an electroplating additive solution, including the following steps:

Step S100: Mixing 3-6 parts of alkali metal hydroxide with 1-3 parts of glycerol and stirring for 5-15 minutes to obtain a first solution;

Step S200: Adding 1 part of metal oxide and 8-15 parts of water to the first solution, stirring and heating at a heating temperature of 70-80°C for 4-6 hours to obtain a second solution;

Step S300: Allowing the second solution to stand for 4-6 hours, and taking the upper clear liquid as the electroplating additive solution.

[0027] In this embodiment, after the alkali metal hydroxide is mixed and reacted with glycerol, the reaction product will complex with the metal oxide, such that the metal oxide is not precipitated in the electroplating mixture liquid.

[0028] In the third aspect, an embodiment of the present disclosure also provides a hard silver-graphene electroplating mixture liquid. The electroplating mixture liquid includes a silver salt, a complexing agent, graphene, a dispersant and the electroplating additive solution described above.

[0029] The silver salt includes, but is not limited to, potassium silver cyanide.

[0030] The complexing agent includes, but is not limited to, potassium cyanide.

[0031] The dispersant includes, but is not limited to, one or more of benzene sulfonate condensate sodium salt and sulfonate sodium salt.

[0032] In the hard silver-graphene electroplating mixture liquid of this embodiment, the silver salt has a concentration of 10-30 g/L, for example, 15-25 g/L, 10-18 g/L, 22-30 g/L, 18-23 g/L, 11-14 g/L, etc. Within the above concentration range, it is conducive to obtaining an electroplating mixture liquid with the well dispersed silver ion, graphene and metal oxide, which effectively refines the coating crystals and enhances the cathodic polarization reaction, thereby improving the hardness and wear resistance of the coating.

[0033] Optionally, in the electroplating mixture liquid of this embodiment, the complexing agent has a concentration of 155-190 g/L, for example, 170-185 g/L, 155-165 g/L, 175-190 g/L, 175-180 g/L, 157-163 g/L, 180-190 g/L, etc. Within the above concentration range, the complexing agent helps to obtain an electroplating mixture liquid with the well dispersed silver ion, graphene and metal oxide, which effectively refines the coating crystals and enhances the cathodic polarization reaction, thereby improving the hardness and wear resistance of the coating.

[0034] In the hard silver-graphene electroplating mixture liquid of this embodiment, the graphene has a concentration of 0.5-4 g/L, for example, 1-3 g/L, 2-4 g/L, 0.5-1.5 g/L, 1.8-3 g/L, 2.4-3.5 g/L, 3.2-4 g/L, etc. Within the above concentration range, it is conducive to obtaining an electroplating mixture liquid with the well dispersed silver ion, graphene and metal oxide, which effectively refines the coating crystals and enhances the cathodic polarization reaction, thereby improving the hardness and wear resistance of the coating.

[0035] In the hard silver-graphene electroplating mixture liquid of this embodiment, the dispersant has a concentration of 3-7 g/L, for example, 4-6 g/L, 3-4 g/L, 6-7 g/L, 3.5-4.5 g/L, 5-6.5 g/L, 3.5-4.8 g/L, etc. Within the above concentration range, it is conducive to obtaining an electroplating mixture liquid with the well dispersed silver ion, graphene and metal oxide, which effectively refines the coating crystals and enhances the cathodic polarization reaction, thereby improving the hardness and wear resistance of the coating.

[0036] In the electroplating mixture liquid of this embodiment, the electroplating additive solution has a concentration of 3-10 mL/L, for example, 5-8 mL/L, 3-5 mL/L, 8-10 mL/L, 4-6 mL/L, 7-9 mL/L, 6-7 mL/L, etc. Within the above concentration range, it is conducive to obtaining an electroplating mixture liquid with the well dispersed silver ion, graphene and metal oxide, which effectively refines the coating crystals and enhances the cathodic polarization reaction, thereby improving the hardness and wear resistance of the coating.

[0037] Optionally, in the electroplating mixture liquid of this embodiment, the dispersant includes benzene sulfonate condensate sodium salt and sulfonate sodium salt. The benzene sulfonate condensate sodium salt has a concentration of 1-2 g/L, for example, 1-1.5 g/L, 1.5-2 g/L, 1.2-1.8 g/L, 1.4-1.6 g/L, 1.2-1.5 g/L, 1.7-2.0 g/L, etc.; the sulfonate sodium salt has a concentration of 2-5 g/L, for example, 3-4 g/L, 2-3 g/L, 4-5 g/L, 2.5-3.5 g/L, 3.5-4.5 g/L, 2.8-3.8 g/L, etc. Within the above concentration range, the benzene sulfonate condensate sodium salt and sulfonate sodium salt can cooperate synergistically, which is conducive to obtaining an electroplating mixture liquid with the well dispersed silver ion, graphene and metal oxide, which effectively refines the coating crystals and enhances the cathodic polarization reaction, thereby improving the hardness and wear resistance of the coating.

[0038] Optionally, the benzene sulfonate condensate sodium salt includes one or more of sodium monobenzene sulfonate condensate, sodium o-benzene sulfonate condensate and sodium tribenzene sulfonate condensate; the sulfonate sodium salt includes one or more of sodium 2-ethylhexyl sulfonate, sodium diethyl triacetate sulfonate and sodium benzene sulfonate.

[0039] The electroplating mixture liquid of the present disclosure includes a dispersant and the electroplating additive solution described above, and the electroplating additive solution includes glycerol and metal oxide. The metal oxide can stably and reliably refine the coating crystals and enhance the cathodic polarization reaction, thereby increasing the hardness of the finally formed coating. The alkali metal hydroxide can react with glycerol, and the product resulted from the reaction complexes with the metal oxide, such that the metal oxide is not precipitated in the electroplating mixture liquid,

facilitating subsequent electroplating operation. Furthermore, when the electroplating mixture liquid is used to prepare a plated part, it is possible to allow the metal oxide to be uniformly dispersed in the coating, thereby improving the overall hardness of the coating. Glycerol can also play a lubricating role on the graphene surface to prevent agglomeration of graphene. Glycerol and the dispersant also have a synergistic effect, both of which synergistically disperse the graphene and metal oxide. This not only reduces the dosage of the dispersant, but also enables various ions, metal oxide and graphene to reach an ideal migration rate in the electroplating mixture liquid. As such, it is conducive to preparing and obtaining a coating with the excellent thermal conductivity, electrical conductivity and hardness.

[0040] In the fourth aspect, an embodiment of the present disclosure also provides a plated part, at least one surface of which is bonded with a plating layer, and the plating layer is prepared from the hard silver-graphene electroplating mixture liquid described above by the method such as electroplating.

[0041] The present disclosure will be specifically described below through specific examples. The following examples are only partial examples of the present disclosure, without limitation of the scope of the present disclosure.

Electroplating Mixture Liquid Example 1

[0042] Preparation of the electroplating additive solution:

[0043] 4.5 parts of potassium hydroxide is mixed with 2 parts of glycerol and stirred for 5-15 minutes to obtain a first solution.

[0044] 1 part of metal oxide and 11 parts of water are added to the first solution, stirred and heated at a heating temperature of 70-80°C for 4-6 hours to obtain a second solution.

[0045] The second solution is allowed to stand for 4-6 hours, and the upper clear liquid is taken as the electroplating additive solution.

[0046] 1 part of the metal oxide includes 0.4 part of antimony trioxide, 0.4 part of bismuth oxide and 0.2 part of manganese oxide.

[0047] The hard silver-graphene electroplating mixture liquid is prepared using the electroplating additive solution. The hard silver-graphene electroplating mixture liquid includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate.

Electroplating Mixture Liquid Example 2

[0048] The present Electroplating Mixture Liquid Example includes 8 mL/L of the electroplating additive solution, 15 g/L of potassium silver cyanide, 185 g/L of potassium cyanide, 3.5 g/L of graphene, 2 g/L of sodium monobenzene sulfonate condensate, and 3 g/L of sodium 2-ethylhexyl sulfonate; the electroplating additive solution includes 1 part of metal oxide, 5 parts of potassium hydroxide, 3 parts of glycerol and 10 parts of water, where 1 part of the metal oxide includes 0.5 part of antimony trioxide, 0.2 part of bismuth oxide and 0.3 part of manganese oxide.

Electroplating Mixture Liquid Example 3

[0049] The present Electroplating Mixture Liquid Example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerol, and 11 parts of water, where 1 part of metal oxide includes 0.6 parts of antimony trioxide and 0.4 parts of manganese oxide, without containing bismuth oxide.

Electroplating Mixture Liquid Example 4

[0050] The present Electroplating Mixture Liquid Example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerol, and 11 parts of water, where 1 part of metal oxide includes 0.7 parts of antimony trioxide and 0.3 parts of bismuth oxide, without containing manganese oxide.

Electroplating Mixture Liquid Example 5

[0051] The present Electroplating Mixture Liquid Example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide,

4.5 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.5 parts of bismuth oxide and 0.3 parts of manganese oxide, without containing antimony trioxide.

Electroplating Mixture Liquid Example 6

[0052] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 1 part of antimony trioxide, without containing bismuth oxide and manganese oxide.

Electroplating Mixture Liquid Example 7

[0053] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 1 part of bismuth oxide, without containing antimony trioxide and manganese.

Electroplating Mixture Liquid Example 8

[0054] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 1 part of manganese oxide, without containing antimony trioxide and bismuth oxide.

Electroplating Mixture Liquid Example 9

[0055] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 1 part of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 10

[0056] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 1.5 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 11

[0057] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2.5 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 12

[0058] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 3 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 13

[0059] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 6 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 14

[0060] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 8 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 15

[0061] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 15 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 16

[0062] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1 g/L of sodium monobenzene sulfonate condensate, and 2 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, where 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Example 17

[0063] The present Electroplating Mixture Liquid Example includes 6 ml/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 2 g/L of sodium monobenzene sulfonate condensate, and 5 g/L of sodium 2-ethylhexyl sulfonate. The electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerin, and 11 parts of water, wherein 1 part of metal oxide includes 0.4 parts of antimony trioxide, 0.4 parts of bismuth oxide, and 0.2 parts of manganese oxide.

Electroplating Mixture Liquid Comparative Example 1

[0064] The electroplating mixture liquid of this comparative example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate; the electroplating additive solution only includes 4.5 parts of potassium hydroxide and 11 parts of water. The present electroplating mixture liquid does not contain metal oxide and glycerol.

Electroplating Mixture Liquid Comparative Example 2

[0065] The electroplating mixture liquid of this comparative example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate; the electroplating additive solution includes 4.5 parts of potassium hydroxide, 2 parts of glycerol and 11 parts of water. The present electroplating mixture liquid does not contain metal oxide.

Electroplating Mixture Liquid Comparative Example 3

[0066] The electroplating mixture liquid of this comparative example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 1.5 g/L of sodium monobenzene sulfonate condensate, and 4 g/L of sodium 2-ethylhexyl sulfonate; the electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide and 11 parts of water, where 1 part of the metal oxide includes 0.4 part of antimony trioxide, 0.4 part of bismuth oxide and 0.2 part of manganese oxide. The present electroplating mixture liquid does not contain glycine.

Electroplating Mixture Liquid Comparative Example 4

[0067] The electroplating mixture liquid of this comparative example includes 6 mL/L of the electroplating additive solution, 22 g/L of potassium silver cyanide, 175 g/L of potassium cyanide, 2 g/L of graphene, 3 g/L of sodium monobenzene sulfonate condensate, and 6 g/L of sodium 2-ethylhexyl sulfonate; the electroplating additive solution includes 1 part of metal oxide, 4.5 parts of potassium hydroxide, 2 parts of glycerol and 11 parts of water, where 1 part of the metal oxide includes 0.4 part of antimony trioxide, 0.4 part of bismuth oxide and 0.2 part of manganese oxide.

Plated Part Example 1

[0068] A plating layer is provided on at least one surface of the plated part of this example, and the plating layer is obtained by electroplating the hard silver-graphene electroplating mixture liquid of the electroplating mixture liquid Example 1 on the surface of the plated part.

Plated Part Examples 2~17

[0069] The Plated Part Examples 2 to 17 are basically the same as Plated Part Example 1, with exception that the hard silver-graphene electroplating mixture liquid of the electroplating mixture liquid Examples 2 to 17 are used for the plating layers of Plated Part Examples 2~17.

Plated Part Comparative Examples 1~4

[0070] The Plated Part Comparative Examples 1~4 are basically the same as Example 1, with exception that the hard silver-graphene electroplating mixture liquids of the electroplating mixture liquid Comparative Examples 1~4 are used for the plating layers of Plated Part Comparative Examples 1~4.

[0071] The plating layers of the Plated Part Examples 1~17 and Plated Part Comparative Examples 1 to 4 are subjected to a wear resistance test and a hardness test respectively, to obtain the average number of friction withstandable per micron and the hardness of the coating. The wear resistance test is performed on the plating layer by a steel wool friction resistance tester; the hardness test is performed by using a hardness tester. The test results are shown in Table 1.

Table 1:

[Table 1_sm_0001]		
	Average number of friction withstandable per micron	Hardness (HV)
Plated Part Example 1	937.8	155
Plated Part Example 2	913.7	152
Plated Part Example 3	903.7	151
Plated Part Example 4	925.3	152
Plated Part Example 5	894.4	150
Plated Part Example 6	897.0	151
Plated Part Example 7	884.9	149
Plated Part Example 8	855.4	148
Plated Part Example 9	846.9	145
Plated Part Example 10	901.2	150
Plated Part Example 11	888.1	151

(continued)

[Table 1_sm_0001]

	Average number of friction withstandable per micron	Hardness (HV)
Plated Part Example 12	883.1	149
Plated Part Example 13	891.9	150
Plated Part Example 14	898.0	151
Plated Part Example 15	850.5	147
Plated Part Example 16	840.8	145
Plated Part Example 17	852.4	148
Plated Part Comparative Example 1	661.2	130
Plated Part Comparative Example 2	674.9	131
Plated Part Comparative Example 3	691.6	134
Plated Part Comparative Example 4	749.0	137

[0072] It can be seen from Table 1 that:

Compared with the average number of friction withstandable per micron of the coating in Plate Part Comparative Examples 1~4, the plating layers of the Plated Part Examples 1~17 have a higher average number of friction withstandable per micron, with the wear resistance times increasing by 12% or more. The reason is that the hard silver-graphene electroplating mixture liquid used in preparation of the plating layers of the Plated Part Examples 1~17 contains the electroplating additive solution of the present disclosure, and the electroplating additive solution contains alkali metal hydroxide, glycerol and metal oxide. The metal oxide can stably and reliably refine the coating crystals and enhance the cathodic polarization reaction, thereby increasing the wear resistance of the finally formed plating layer. The alkali metal hydroxide can react with glycerol, and the product resulted from the reaction complexes with the metal oxide, such that the metal oxide is not precipitated in the electroplating mixture liquid, thus endowing the plating layer with good hardness.

[0073] Compared with the hardness of the plating layers of the Plated Part Comparative Examples 1~4, the plating layers of the Plated Part Examples 1~17 have higher hardness. The reason is that the hard silver-graphene electroplating mixture liquid used in the preparation of the plating layers of the Plated Part Examples 1~17 contains the electroplating additive solution of the present disclosure, and the electroplating additive solution contains glycerol and metal oxide. The metal oxide can stably and reliably refine the coating crystals and enhance the cathodic polarization reaction, thereby increasing the hardness of the finally formed plating layer. The alkali metal hydroxide can react with glycerol, and the product resulted from the reaction complexes with the metal oxide, such that the metal oxide is not precipitated in the electroplating mixture liquid, thus endowing the plating layer with good hardness.

[0074] Compared with the Plated Part Comparative Example 4, the plating layer of the Plated Part Example 1 has higher hardness and the higher average number of friction withstandable per micron, while the dosages of benzene sulfonate condensate sodium salt and sulfonate sodium salt are lower. The reason is that the hard silver-graphene electroplating mixture liquid used in the preparation of the plating layer of the Plated Part Example 1 contains the electroplating additive solution of the present disclosure, and the electroplating additive solution contains glycerol. Glycerol and the dispersant have a synergistic effect, both of which synergistically disperse graphene and metal oxide. This not only reduces the dosage of the dispersant, but also enables various ions, metal oxide and graphene to reach an ideal migration rate in the electroplating mixture liquid. Thus, it is conducive to preparing a coating with excellent thermal conductivity, electrical conductivity and hardness.

Claims

1. An electroplating additive solution, wherein

the electroplating additive solution comprises metal oxide, glycerol, alkali metal hydroxide and water;

a mass ratio of the metal oxide, the glycerol, the alkali metal hydroxide and the water is 1:(1-3):(3-6):(8-15).

2. The electroplating additive solution according to claim 1, wherein:

the metal oxide comprises one or more of antimony trioxide, bismuth oxide and manganese oxide.

3. A preparation method for the electroplating additive solution according to any one of claims 1 to 2, wherein the method comprises:

mixing alkali metal hydroxide with glycerol and performing stirring to obtain a first solution; adding metal oxide and water to the first solution, performing stirring and heating to obtain a second solution; allowing the second solution to stand, and taking an upper clear liquid as the electroplating additive solution.

4. The preparation method for the electroplating additive solution according to claim 3, wherein:

the first solution is stirred for 5-15 minutes;
the second solution is heated for 4-6 hours at a temperature of 70-80°C;
the second solution is stood for 4-6 hours.

5. A hard silver-graphene electroplating mixture liquid comprising the electroplating additive solution according to any one of claims 1-2, wherein

the electroplating mixture liquid further comprise a silver salt, a complexing agent, a graphene and a dispersant.

6. The hard silver-graphene electroplating mixture liquid according to claim 5, wherein:

the silver salt comprises potassium silver cyanide; and/or
the complexing agent comprises potassium cyanide; and/or
the dispersant comprises one or more of benzene sulfonate condensate sodium salt and sulfonate sodium salt.

7. The hard silver-graphene electroplating mixture liquid according to claim 6, wherein:

the benzene sulfonate condensate sodium salt comprises one or more of sodium monobenzenesulfonate condensate, sodium o-benzene sulfonate condensate and sodium tribenzene sulfonate condensate.

8. The hard silver-graphene electroplating mixture liquid according to claim 6, wherein:

the sulfonate sodium salt comprises one or more of sodium 2-ethylhexyl sulfonate, sodium diethyl triacetate sulfonate and sodium benzene sulfonate.

9. The hard silver-graphene electroplating mixture liquid according to claim 5, wherein

in the electroplating mixture liquid, the silver salt has a concentration of 10-30 g/L; and/or
in the electroplating mixture liquid, the graphene has a concentration of 0.5-4 g/L; and/or
in the electroplating mixture liquid, the dispersant has a concentration of 3-7 g/L; and/or
in the electroplating mixture liquid, the electroplating additive solution has a concentration of 3-10 mL/L; and/or
in the electroplating mixture liquid, the complexing agent has a concentration of 155-190 g/L.

10. The hard silver-graphene electroplating mixture liquid according to claim 9, wherein:

the dispersant comprises benzene sulfonate condensate sodium salt having a concentration of 1-2 g/L and sulfonate sodium salt having a concentration of 2-5 g/L.

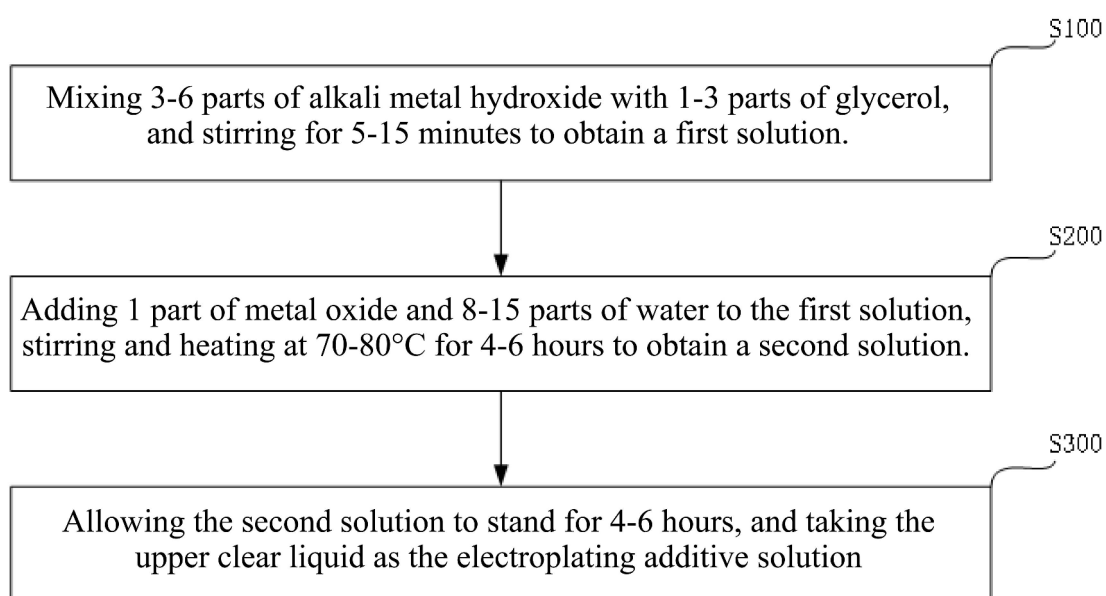


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2024/088613

A. CLASSIFICATION OF SUBJECT MATTER

C25D3/46(2006.01)i; C25D3/64(2006.01)i; C25D7/00(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)

IPC: C25D

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

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

VCN, CNTXT, DWPI, ENTXT, ENTXTC, CNKI, ISI: 丙三醇, 电镀, 甘油, 氢氧化钾, 氢氧化钠, 三氧化二锑, 石墨烯, 氧化锰, 氧化锑, 氧化铟, 银, Ag, Bi2O3, BiO, glycerol, graphene, hardness, KOH, MnO2, NaOH, Sb2O3, hard+, electroplat+, potassium hydroxide, sodium hydroxide, antimony trioxide, manganese oxide, antimony oxide, bismuth oxide, silver

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2018199839 A (TOYOTA MOTOR CORP.; TOYOHASHI PLATING CO., LTD.) 20 December 2018 (2018-12-20) see description, paragraphs [0010]-[0033]	1-10
A	CN 115182023 A (ZHEJIANG CHINT ELECTRICS CO., LTD.) 14 October 2022 (2022-10-14) see entire document	1-10
A	CN 115807248 A (SHENZHEN XINGJIAFENG TECHNOLOGY DEVELOPMENT CO., LTD.) 17 March 2023 (2023-03-17) see entire document	1-10
A	US 2021310142 A1 (ABB POWER GRIDS SWITZERLAND AG) 07 October 2021 (2021-10-07) see entire document	1-10

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

* Special categories of cited documents:

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

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/CN2024/088613

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 202311386283 [0001]