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(54) TIN-ZINC ALLOY ELECTROPLATING METHOD
VERFAHREN ZUR GALVANISCHEN ABSCHEIDUNG VON ZINN-ZINK-LEGIERUNG
MÉTHODE DE GALVANOPLASTIE À L’ALLIAGE ETAIN-ZINC

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(73) Proprietor: DIPSOL CHEMICALS CO., LTD.
Tokyo 104-0061 (JP)

(72) Inventor: YUASA, Satoshi,
Techn. Ctr., DIPSOL CHEM. CO., LTD
Tokyo 1240025 (JP)

(74) Representative: Boult Wade Tennant
Verulam Gardens
70 Gray’s Inn Road
London WC1X 8BT (GB)

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The present invention relates to a method for electroplating with a tin-zinc alloy.

Because electroplating with tin-zinc alloys produces coatings that excel in corrosion resistance, processability and solderability, this method has attracted attention and been widely applied to automobile parts and electronic components. Alkali cyan baths, pyrophosphoric acid baths, borofluoride baths, sulfonic acid baths and carboxylic acid baths have been suggested for use as plating baths in electroplating with tin-zinc alloys, and some of these baths have been practically used.

With the conventional methods using such electroplating baths, when the treatment is carried out at a high current density to shorten the treatment time, coarse precipitates, burns, and scorches appear in the plated layer and characteristics of the tin-zinc alloy coating are degraded. As a result, the practical use of high-speed electroplating is made difficult. The systems that are still used include a rack system (maximum current density about 3 A/dm²) in which the articles to be plated are treated upon mounting them on a jig and a barrel system (maximum current density 1 A/dm²) in which the articles to be plated are treated in a barrel. Further, when plating with a tin-zinc alloy is performed within a short interval, a method by which tin and zinc are electroplated separately and then alloyed and a melt plating method using a molten salt of a tin-zinc alloy are used.

It is an object of the present invention to provide an electroplating method enabling the treatment of articles to be plated within a short interval that was difficult to achieve with the conventional methods for electroplating with tin-zinc alloys.

The present invention is based on a discovery that electroplating with a tin-zinc alloy can be carried out within a short interval by using a specific tin-zinc alloy plating bath at a plating bath temperature and plating bath stirring rate above the predetermined values.

Thus, the present invention provides a method for electroplating with a tin-zinc alloy according to claim 1.

With the present invention, electroplating with a tin-zinc alloy can be carried out within a short interval by using a specific tin-zinc alloy plating bath at a plating bath temperature and plating bath stirring rate above the predetermined values.

The temperature of the plating bath in the electroplating method in accordance with the present invention is 30 to 90°C, preferably 40 to 60°C, and the stirring rate of the plating solution is 5 to 300 m/min, preferably 10 to 100 m/min. Stirring of the plating solution is specifically carried out by a plating apparatus of a jet flow system in which the solution is circulated with a pump or by a plating apparatus for steel sheets. The plating apparatus can be made from any material, provided it has heat resistance and chemical resistance, and metals such as stainless steel and titanium or polyvinyl chloride, Teflon (registered trade name), and an ABS resin can be used. Furthermore, a device enabling the stirring of the plating solution that is uniform with respect to the entire plated article is preferred from the standpoint of increasing the uniformity of the plated alloy composition and plated film thickness.

A compound having one or more hydroxyl groups and one or more carboxyl groups in a molecule is preferred as the hydroxycarboxylic acid. Specific examples of such hydroxycarboxylic acids include citric acid, tartaric acid, malic acid, glycolic acid, glyceric acid, lactic acid, β-hydroxypropionic acid, and gluconic acid. The preferred among them are citric acid, tartaric acid, malic acid, and gluconic acid. Specific examples of hydroxycarboxylic acid salts include alkali metal salts (sodium, potassium, lithium salts) alkaline earth metal salts (magnesium, calcium, barium salts, and the like),
The pH of the plating bath comprising the hydroxycarboxylic acid or salt thereof is 2 to 10, preferably 3 to 9.

When a hydroxycarboxylic acid salt is used as a divalent tin salt and/or zinc salt, the hydroxycarboxylic acid which is a counterion of the metal ions also constitutes part of the aforementioned concentration. The preferred among them are sodium salts, potassium salts, lithium salts, divalent tin salts, and zinc salts of citric acid, tartaric acid, malic acid, and gluconic acid. These hydroxycarboxylic acids and salts thereof may be used individually or in a mixture of two or more thereof, and the concentration thereof in the plating bath is 0.25 to 3 mol/L, preferably 0.3 to 1.5 mol/L. When a hydroxycarboxylic acid salt is used as a divalent tin salt and/or zinc salt, the hydroxycarboxylic acid which is a counterion of the metal ions also constitutes part of the aforementioned concentration.

A plating bath comprising at least one species selected from the group consisting of amphoteric surfactants and water-soluble compounds obtained by a reaction of an aliphatic amine an organic acid ester, and phthalic anhydride also can be utilized as the tin-zinc alloy electroplating bath used in the electroplating method in accordance with the present invention. More specifically, for example, a water-soluble compound can be used that is obtained by reacting 0.2 to 3 moles of an organic acid ester per 1 mole of an aliphatic amine for 10 to 60 min. at a temperature of 50 to 99°C and then reacting phthalic anhydride with the obtained reactive product at a weight ratio of 0.1 to 1 ; 1 for 30 to 180 min at a temperature of 60 to 130°C. Examples of suitable amphoteric surfactants include imidazoline-type, betaine-type, alanine-type, glycine-type, and amide-type surfactants. Examples of aliphatic amines suitable for the reaction of the water-soluble compound include ethylenediamine, triethylenetetramine, isobutylamine, 3-methoxypropylamine, iminobispropylamine, diethylamine, hexamethylenetetramine, and dimethylaminopropylamine. Examples of suitable organic acid esters include dimethyl manolate, diethyl succinate, diethyl maleate, dimethyl fumarate, diethyl tartarate, dimethyl maleate, and diethyl tartronate. These water-soluble compounds and amphoteric surfactants may be used individually or in a mixture of two or more thereof, and the content thereof in the plating bath is 0.001 to 50 g/L, preferably 0.01 to 30 g/L.

The pH of the plating bath comprising at least one species selected from the group consisting of amphoteric surfactants and water-soluble compounds obtained by a reaction of an aliphatic amine an organic acid ester, and phthalic anhydride is preferably 2 to 10, more preferably 3 to 9. The pH of the plating bath can be adjusted by using an alkaline compound such as a hydroxide and carbonate, or an acidic compound such as an inorganic acid or organic acid. Specific examples of suitable compounds include sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, and ammonia water and acidic compounds such as sulfuric acid, hydrochloric acid, sulfamic acid, methanesulfonic acid, and phenolsulfonic acid.

Further, a plating bath comprising at least one species selected from the group consisting of tertiary amine compounds and quaternary amine compounds also can be used as the tin-zinc alloy electroplating bath employed in the electroplating method in accordance with the present invention. Examples of tertiary amine compounds include imidazole compounds and aliphatic amine compounds, and examples of quaternary amine compounds include reaction products of tertiary amine compounds and halogenated alyks. Specific examples of tertiary amine compounds include imidazole compounds, such as imidazole, 1-methylimidazole, 1-ethylimidazole, 2-methylimidazole, 1-ethyl-2-methylimidazole, 1-oxyethylimidazole, 1-vinylimidazole, and 1, 5-dimethylimidazole, and aliphatic amines such as monoethanolamine, diethanolamine, triethanolamine, dimethylamine, ethylenediamine, diethylenetriamine, iminobispropylamine, triethylenetetramine, tetraethylenepentamine, and N,N-bis-(3-aminoethyl)ethylenediamine. Further, specific examples of halogenated alyks that can be reacted with tertiary amine compounds include monochloroacetic acid, benzyl chloride, chloroacetamide, 3-aminobenzylchloride, allyl chloride, dichlorethane, monochloropropane, dichloroglycerin, ethylene chlorohydrine, and epichlorohydrine. These tertiary amine compounds and quaternary amine compounds may be used individually or in a mixture of two or more thereof, and the content thereof in the plating bath is 0.1 to 30 g/L, preferably 0.2 to 20 g/L.

The pH of the plating bath comprising at least one species selected from the group consisting of tertiary amine compounds and quaternary amine compounds is preferably 10 to 14, more preferably 12 to 14. The pH of the plating bath can be adjusted by using an alkaline compound such as a hydroxide and carbonate. Specific examples of suitable compounds include sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, and ammonia water.

The plating bath used in the electroplating method in accordance with the present invention can additionally contain at least one surfactant selected from the group consisting of a nonionic surfactant, anionic surfactant, and cationic surfactant. Introducing such surfactants into the plating bath enables denser precipitation at a high current density and, therefore, makes it possible to implement more smoothly the electroplating method in accordance with the present invention.

In the plating bath used in the plating method in accordance with the present invention, the divalent tin ion...
concentration is 1 to 100 g/L, preferably 5 to 80 g/L, and the zinc ion concentration is 0.2 to 80 g/L, preferably 1 to 50 g/L. Examples of sources of such metal ions include various metal hydroxides, oxides, sulfates, chlorides, sulfamates, pyrophosphates, hydroxyxcarboxylates, sulfonates, and amino acid salts. Various metal oxides, sulfates, chlorides, and hydroxides are preferred. Specific examples of hydroxyxcarboxylic acid salts are presented hereinabove. Specific examples of sulfonates include alkanesulfonates, alkanolsulfonates, and phenolsulfonates. Specific examples of alkanesulfonic acids include methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, iso-propanesulfonic acid, butanesulfonic acid, pentanesulfonic acid, and hexanesulfonic acid. Specific examples of alkanolsulfonic acids include 2-hydroxyethanesulfonic acid, 3-hydroxypropanesulfonic acid, and 2-hydroxybutanesulfonic acid. Specific examples of phenol-sulfonic acids include methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, isopropanesulfonic acid, butanesulfonic acid, pentanesulfonic acid, and hexanesulfonic acid. Specific examples of phenol-sulfonic acids include phenolsulfonic acid, cresolsulfonic acid, and dimethylphenolsulfonic acid. Specific examples of amino acids include glycine, glutamic acid, and alanine.

In order to improve electric conduction during plating, alkaline earth base metal salts (sodium, potassium, lithium salts), alkaline earth metals, salts, ammonium salts, and organic amine salt compounds (monomethylamine, dimethylamine, trimethylamine, methylamine, isopropylamine, ethylenediamine, diethylenetriamine, etc.) of sulfurous acid, hydrochloric acid, sulfamic acid, pyrophosphoric acid, sulfonic acid, hydroxides and carbonates can be introduced in the plating bath used in the electroplating method in accordance with the present invention. Specific examples of such salts include ammonium sulfate, ammonium chloride, sodium pyrophosphate, monomethyl sulfamate, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, and among these especially preferred are ammonium sulfate, ammonium chloride, potassium hydroxide, and potassium carbonate. The content of these salts is 10 to 300 g/L, preferably 50 to 200 g/L.

The plating bath used in the electroplating method in accordance with the present invention can contain water in addition to the above-described components and also can contain additives that have been used as a brightener for tin and zinc. Examples of suitable additives include synthetic polymers (polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene glycol, and the like), ketones (benzalacetone, acetophenone, and the like), aliphatic aldehydes (formalin, acetaldehyde, crotonaldehyde, and the like), aromatic aldehydes (vanillin, salicylaldehyde, orthochlorobenzaldehyde, and the like), reaction products of unsaturated aliphatic aldehydes and amine compounds, sulfur compounds (thiourea, mercaptotetrazol, and the like), and also Cu, Ni, Mn, Bi, In, and the like. These additives are contained at 0.001 to 50 g/L, preferably 0.005 to 30 g/L. Furthermore, hydroxyphenyl compounds such as catechol, pyrogallol, hydroquinone, sulfosalicylic acid, potassium dihydroxybenzenesulfonate and salts thereof and L-ascorbic acid, sorbitol and the like can also be used as oxidation preventing agents for tin.

The articles to be plated by the plating method in accordance with the present invention are metal materials such as Fe, Ni, Cu, or alloys based thereon, and the plating is carried out by using them as cathodes. A carbon electrode and insoluble electrode obtained by plating Pt on a Ti material or tin-zinc alloy can be used as a counter electrode thereof. When an insoluble anode is used, the concentration of metals in the plating bath that is being used can be maintained by directly dissolving the aforementioned tin and zinc salts in the plating bath or by supplying an aqueous solution in which tin and zinc salts are dissolved into a high concentration. The high-concentration aqueous solution of the metals may contain the above-described hydroxyxcarboxylic acid or salt thereof and an alkali hydroxide compound.

The cathode current density is 10 to 120 A/dm². The film thickness can be within a wide range, but is generally 0.5 to 500 μm, preferably 2 to 20 μm.

Tin-zinc alloy plating can be performed within a wide range of alloy compositions by changing the ratio of tin ions and zinc ions in the plating bath that is being used. For example, tin-zinc alloy coatings with a zinc content of 3 to 15% can be obtained on electronic components. When resistance to salt water or corrosion resistance is to be improved, a tin-zinc alloy coating with a zinc content of 15 to 45% can be obtained. Furthermore, when a film with high corrosion resistance that is to be exposed to the atmosphere is obtained, a tin-zinc alloy coating with a zinc content of 50 to 90% can be produced.

With the plating method in accordance with the present invention, the article to be plated is subjected to plating after a pretreatment conducted by the usual method. At least one operation selected from immersion degreasing, pickling, electrolytic washing, and activation is performed in the pretreatment process. After the plating, the film obtained may be washed with water and dried, or can be further coated by a chromating and conversion treatment, or with an inorganic or organic material by the usual method.

The present invention will be described below based on embodiments thereof, but the present invention is not limited to the embodiments, and the plating solution temperature, flow rate of the plating solution, and the composition of the plating bath can be freely changed according to the article to be plated.

Examples

Example 1

A steel sheet was pretreated and then electroplated by using the following plating solution under the conditions...
of a plating bath temperature of 60°C and a plating bath stirring rate of 50 m/min.

Example 2

A steel sheet was pretreated, Nymin NAG-1001 manufactured by Nippon Oils & Fats Co., Ltd. was added as a nonionic surfactant at 5 g/L to the plating solution of Embodiment 1, and electroplating was conducted under the conditions of a plating bath temperature of 60°C and a plating bath stirring rate of 30 m/min.

Example 3

A steel sheet was pretreated and then electroplated by using the following plating solution under the conditions of a plating bath temperature of 60°C and a plating bath stirring rate of 30 m/min.

Example 4

A phosphorus bronze sheet was pretreated and then electroplated by using the following plating solution under the conditions of a plating bath temperature of 50°C and a plating bath stirring rate of 60 m/min.

Example 5

A phosphorus bronze sheet was pretreated and then electroplated by using the following plating solution under the conditions of a plating bath temperature of 60°C and a plating bath stirring rate of 60 m/min.
Comparative Example 1

A steel sheet was pretreated and then electroplated by using the plating solution of Embodiment 1 under the conditions of a plating bath temperature of 23°C and a plating bath stirring rate of 50 m/min.

Comparative Example 2

A steel sheet was pretreated and then electroplated by using the plating solution of Embodiment 1 under the conditions of a plating bath temperature of 60°C and a plating bath stirring rate of 2 m/min.

Comparative Example 3

A steel sheet was pretreated and then electroplated by using the plating solution of Embodiment 3 under the conditions of a plating bath temperature of 60°C and a plating bath stirring rate of 3 m/min.

The plated precipitate state, alloy composition (wt.%) of the precipitated film, treatment time, and film thickness in Examples 1 to 5 and Comparative Examples 1 to 3 are shown in Tables 1 to 2.
<table>
<thead>
<tr>
<th>Example 1</th>
<th>Plated precipitate state</th>
<th>Sn/Zn (wt.%)</th>
<th>Treatment time</th>
<th>Film thickness (μm)</th>
<th>Example 2</th>
<th>Plated precipitate state</th>
<th>Sn/Zn (wt.%)</th>
<th>Treatment time</th>
<th>Film thickness (μm)</th>
<th>Example 3</th>
<th>Plated precipitate state</th>
<th>Sn/Zn (wt.%)</th>
<th>Treatment time</th>
<th>Film thickness (μm)</th>
</tr>
</thead>
<tbody>
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<td>70/30</td>
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<td>8.9</td>
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The treatment time is measured in seconds in all the above cases.
○: dense and smooth precipitate
Δ: local occurrence of coarse precipitate
×: powder-like coarse precipitate
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<th>Example 4</th>
<th>Example 5</th>
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<td>Plated precipitate state</td>
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<tr>
<td>Sn/Zn (wt.%)</td>
<td>Sn/Zn (wt.%)</td>
</tr>
<tr>
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<td>Treatment time</td>
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<td>Film thickness (μm)</td>
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</table>

The treatment time is measured in seconds in all the above cases.
- ○: dense and smooth precipitate
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<table>
<thead>
<tr>
<th>Plated precipitate state</th>
<th>Sn/Zn (wt.%)</th>
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<th>Film thickness (μm)</th>
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</tbody>
</table>

The treatment time is measured in seconds in all the above cases.
○: dense and smooth precipitate
Δ: local occurrence of coarse precipitate
×: powder-like coarse precipitate
Claims

1. A method for electroplating with a tin-zinc alloy performed under the following conditions:

   - plating bath temperature: 30 to 90°C;
   - plating bath stirring rate: 5 to 300 m/min; and
   - cathode current density: 10 to 120 A/dm²;

   wherein, in the tin-zinc alloy plating bath, the divalent tin ion concentration is 1 to 100 g/L and the zinc ion concentration is 0.2 to 80 g/L;

   the tin-zinc alloy plating bath comprises a hydroxycarboxylic acid or a salt thereof and/or at least one species selected from amphoteric surfactants and water-soluble compounds obtained by a reaction of an aliphatic amine, an organic acid ester, and a phthalic anhydride; and

   a pH of the tin-zinc alloy plating bath is 2 to 10.

2. The method according to claim 1, wherein the tin-zinc alloy plating bath comprises at least one species selected from nonionic surfactants, anionic surfactants, and cationic surfactants.

Patentansprüche

1. Verfahren zum Elektroplattieren mit einer Zinn-Zink-Legierung, das unter den folgenden Bedingungen durchgeführt wird:

   - Temperatur des Plattierungsbad: 30 bis 90 °C;
   - Rührgeschwindigkeit des Plattierungsbad: 5 bis 300 m/min; und
   - Kathodenstromdichte: 10 bis 120 A/dm²;

   wobei in dem Zinn-Zink-Legierungs-Plattierungsbad die Konzentration von zweiwertigen Zinnionen 1 bis 100 g/l beträgt und die Zinkionenkonzentration 0,2 bis 80 g/l beträgt;

   das Zinn-Zink-Legierungs-Plattierungsbad umfasst eine Hydroxycarbonsäure oder ein Salz davon und/oder wenigstens eine Spezies ausgewählt aus amphoteren oberflächenaktiven Stoffen und wasserlöslichen Verbindungen, die durch eine Reaktion von einem aliphatischen Amin, einem organischen Säureester und einem Phthalsäureanhydrid erhalten werden; und

   ein pH des Zinn-Zink-Legierungs-Plattierungsbad ist 2 bis 10.

2. Verfahren nach Anspruch 1, wobei das Zinn-Zink-Legierungs-Plattierungsbad wenigstens eine Spezies, ausgewählt aus nicht-ionischen oberflächenaktiven Stoffen, anionischen oberflächenaktiven Stoffen und kationischen oberflächenaktiven Stoffen, umfasst.

Revendications

1. Procédé pour le dépôt électrolytique avec un alliage étain-zinc mis en oeuvre dans les conditions suivantes:

   - température du bain de dépôt : 30 à 90°C ;
   - vitesse d‘agitation du bain de dépôt : 5 à 300 m/min ; et
   - densité de courant cathodique : 10 à 120 A/dm² ;

   où, dans le bain de dépôt d’alliage étain-zinc, la concentration des ions étain étaient fixées à 1 à 100 g/L et la concentration des ions zinc est 0,2 à 80 g/L ;

   le bain de dépôt d’alliage étain-zinc comprend un acide hydroxyacrylique ou un sel de celui-ci et/ou au moins une espèce choisie parmi les tensioactifs amphotères et les composés solubles dans l’eau obtenus par une réaction d’une amine aliphatique, d’un ester d’acide organique et d’un anhydride phthalique ; et

   un pH du bain de dépôt d’alliage étain-zinc est 2 à 10.

2. Procédé selon la revendication 1, où le bain de dépôt d’alliage étain-zinc comprend au moins une espèce choisie parmi les tensioactifs non ioniques, les tensioactifs anioniques et les tensioactifs cationiques.