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(54) **PROCESS FOR THE NON-GALVANIC TIN PLATING OF COPPER OR COPPER ALLOYS**

VERFAHREN ZUR STROMLOSEN VERZINNUNG VON KUPFER ODER KUPFERLEGIERUNGEN

PROCEDE DESTINE A L'ETAMAGE NON GALVANIQUE DU CUIVRE OU D'ALLIAGES DE CUIVRE

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Description

[0001] The invention deals with a use of a foreign metal as diffusion barrier.

[0002] Non-galvanic tin precipitation is known from the current state of the art and is commonly used, based both on acidic and alkaline electrolytes. Primarily, copper and copper alloys are tin plated in an ion exchange process, for example pipes, pipe sections and fittings for cold and hot water, battery posts, sanitary connectors as well as conductor frames. As the source of the tin for the electrolytes especially bivalent tin salt is used, such as for example tin chloride, tin sulfate, tin tetrafluoroborate or tin methanesulphonate.

[0003] The formation of non-galvanically precipitated tin layers on copper and copper alloys is effected by the exchange of copper for tin atoms, whereby the removal of the copper is made possible by a complexing agent.

[0004] A generic process is described in DE 197 49 382 A1. The process described there refers to the tin plating of pipes, pipe sections and fittings of copper or a copper alloy by the chemical precipitation of a tin layer. Methanesulphonic acid, tin methanesulphonate, a complexing agent as well as a wetting agent are suggested as electrolyte.

[0005] The tin layers produced with the tin precipitation processes known heretofore only grow until no more surface copper can pass through the porous tin layer. The achievable layer thickness is therefore limited to a maximum of 2 μm . The disadvantage is that a diffusion of metals from the base material, especially of alloy components, can occur which may lead to undesirable effects. For example, copper of a potable water pipe may dissolve and diffuse through the tin and can enter the water, which may have effects detrimental to health. Also, the liberation of lead and zinc from brass base materials, for example, can not be prevented by the precipitation of a generic tin layer. In addition, difficulties with soldering of the surface of tin plated base materials due to the diffusion are a disadvantage.

[0006] US 5,435,838 discloses a method comprising the deposition of a tin-bismuth plate onto a surface formed of copper. Large amounts of bismuth, however, are required and the metal plate is prone to corrosion.

[0007] US 4,749,626 discloses a tin coating solution comprising an addition for inhibiting the growth of tin whiskers. The addition is a metal salt of the group consisting of palladium chloride or silver sulfate.

[0008] JP H09-302476 discloses an electroless plating method of a tin-silver alloy onto a copper substrate in order to replace harmful tin-lead solder. Certain additions are necessary for the plating bath in order to dissolve stably the silver ions in the solution of the plating bath and the suppress preferential deposition of silver. A diffusion barrier is not used.

[0009] In order to avoid the above disadvantages it is the purpose of the invention to improve non-galvanic tin plating of copper or copper alloys so that a durable tin

layer, which can easily be soldered, can be produced which, at the same time, prevents the liberation of the basic material.

[0010] As a solution, it is proposed by the invention a use according to the subject matter of attached claim 1.

[0011] With the use described in the invention, a tin bath is suggested for the formation of a tin layer by chemical precipitation, which contains at least one foreign metal. The addition of foreign metals to the tin bath achieves an advantageous suppression of the diffusion processes, and thus a diffusion barrier is built which prevents the liberation of metals from the base material to a large extent. The advantages thus gained are good soldering characteristics at the surface and good durability of the tin layer.

[0012] The formation of a tin layer by the above use therefore not only creates the possibility to produce effective corrosion protection but, moreover, by the use of foreign metals a diffusion-stable tin layer is produced which prevents the liberation of materials from the base layer to a large extent. This is an advantage especially in view of the copper liberation from potable water carrying copper tubing. However, an out-diffusion of lead and zinc from basic brass materials is prevented by a diffusion-stable tin layer.

[0013] In accordance with one feature of the invention, a metal of the group silver, bismuth, nickel, titanium, zirconium and indium is suggested as the foreign metal, whereby the use of indium has shown to be especially effective. For the formation of a diffusion barrier within the tin layer, at least one of the above metals is added to the tin bath as a foreign metal.

[0014] In accordance with an additional feature of the invention, thiourea and/or its derivative is used as the complexing agent. Thiourea as the complexing agent enables the liberation of positively charged copper ions. A copper thiourea complex forms which is soluble in electrolytes at a temperature of $>28^{\circ}\text{C}$. As a result of the complexing of the copper, its potential compared to that of tin is reduced. The then more noble tin precipitates, forming a layer of tin on the copper. The liberated copper ions concentrate in the electrolyte, whereby at a copper concentration above 7g/l economical working is no longer possible since at these concentrations tin is no longer precipitated at satisfactory rates. It is therefore suggested to remove the copper by precipitation of the copper-thiourea compounds in solution in the electrolyte. In this manner, a substantial increase in the useful life of the tin bath may be achieved. The precipitation of the copper-thiourea compounds can be achieved by means of another feature of the invention by filtration. Finally, the electrolytic bath further comprises an antioxidant.

[0015] For the application of the non-galvanic precipitation of diffusion-stable tin layers in accordance with the invention a tin bath is of advantage, which preferably contains the following components:

1. A source of tin,

preferably a bivalent tin salt, for example tin methanesulfonate,
with 1 to 30 g/l of tin in the tin bath;

2. An acid,

preferably methanesulphonic acid with 5 to 200 g/l in the tin bath,

whereby the tin bath assumes a pH value of 0 to 3;

3. A complexing agent,

preferably thiourea or a derivative in quantities of 10 to 200 g/l;

4. A wetting agent in quantities of 1 to 10 g/l;

5. At least one foreign metal,

preferably a metal in the group Ag, Bi, Ni, Ti, Zr and In in a proportion of 1 to 500 mg/l in the tin bath;

6. an antioxidant.

To apply the process described in the invention, a working temperature of the tin bath of 35 to 80°C is suggested. In addition, already known measures common to the state of the art can be taken when using the process described. This includes, for example, rinsing, pickling and drying of the work pieces.

[0016] Further details regarding the invention follow from the examples below in each of which an electrolyte composition is suggested.

Example 1

[0017]

Thiourea	100 g/l
Methanesulphonic acid	100 g/l
Tin methanesulphonate	15 g/l tin
Wetting agent	3 g/l
Antioxidant	5 g/l
Titanium	5 mg/l

Example 2

[0018]

Thiourea	120 g/l
Methanesulphonic acid	140 g/l
Tin methanesulphonate	15 g/l tin
Wetting agent	5 g/l
Antioxidant	5 g/l
Indium	50 mg/l

The use described by the invention makes it possible to produce diffusion-stable tin layers by means of chemical precipitation, whereby the diffusion barrier generated by the addition of foreign metals prevents the liberation of metals from the base materials in an advantageous manner. In addition, by using thiourea as complexing agent it becomes possible to remove the copper ions liberated

from the copper from the electrolyte by filtration, and thus to achieve a substantially extended useful life. Furthermore, in this manner a substantial acceleration of the process is achieved.

Claims

1. Use of a foreign metal of the group consisting of Ag, Bi, Ni, Ti, Zr, and In as diffusion barrier for suppressing the diffusion of a base layer material through a tin layer, wherein the base layer is a copper or copper alloy layer and the tin layer is non galvanically precipitated on the base layer.
2. Use according to claim 1, wherein the tin layer is precipitated from an electrolyte comprising 5 to 200 g/l methane sulfonic acid, whereby the tin bath assumes a pH value of 0 to 3, 1 to 30 g/l tin and 1 to 500 mg/l of the foreign metal used as diffusion barrier.
3. Use according to claim 2, wherein the electrolyte comprises an antioxidant.
4. Use according to claim 2 or 3, wherein the electrolyte comprises thiourea and/or its derivate as a complexing agent.
5. Use according to one of the claims 2 to 4, wherein the electrolyte is reconditioned by removing the copper soluted in the electrolyte by precipitation as a copper-thiourea compound.
6. Use according to claim 5 wherein the copper-thiourea precipitate is removed from the electrolyte by filtration, thereby accelerating the precipitation process.
7. Use according to any of claims 1 to 6 wherein said foreign metal comprises silver.
8. Use according to any of claims 1 to 6 wherein the foreign metal comprises bismuth.
9. Use according to any of claims 1 to 6 wherein the foreign metal comprises indium.
10. Use according to any of claims 2 to 9 wherein the electrolyte comprises a bivalent tin salt.
11. Use according to claim 10 wherein the bivalent tin salt comprises tin methanesulfonate.
12. Use according to any of claims 2 to 11 wherein the electrolyte comprises 10 to 200 g/L thiourea or a thiourea derivative.

13. Use according to any of claims 2-12 wherein the electrolyte comprises 1 to 10 g/L wetting agent.
14. Use according to any of claims 2-13 wherein the temperature of the electrolyte is between 35° and 80°C during precipitation of tin.

Patentansprüche

1. Verwendung eines Fremdmetalls aus der Gruppe, die aus Ag, Bi, Ni, Ti, Zr und In besteht, als Diffusionsbarriere zur Unterdrückung der Diffusion eines Basisschichtmaterials durch eine Zinnschicht hindurch, wobei es sich bei der Basisschicht um eine Kupfer- oder Kupferlegierungsschicht handelt und die Zinnschicht stromlos auf der Basisschicht abgeschieden wird.
2. Verwendung nach Anspruch 1, wobei die Zinnschicht aus einem Elektrolyt abgeschieden wird, der 5 bis 200 g/l Methansulfonsäure, wodurch das Zinnbad einen pH-Wert von 0 bis 3 annimmt, 1 bis 30 g/l Zinn und 1 bis 500 mg/l des Fremdmetalls umfasst, das als Diffusionsbarriere verwendet wird.
3. Verwendung nach Anspruch 2, wobei der Elektrolyt ein Antioxidationsmittel umfasst.
4. Verwendung nach Anspruch 2 oder 3, wobei der Elektrolyt Thioharnstoff und/oder ein Derivat desselben als Komplexbildner umfasst.
5. Verwendung nach einem der Ansprüche 2 bis 4, wobei der Elektrolyt wiederaufbereitet wird, indem das in dem Elektrolyt gelöste Kupfer durch Ausfällen als Kupfer-Thioharnstoff-Verbindung entfernt wird.
6. Verwendung nach Anspruch 5, wobei der Kupfer-Thioharnstoff-Niederschlag durch Filtration aus dem Elektrolyt entfernt wird, wodurch der Ausfällungsprozess beschleunigt wird.
7. Verwendung nach einem der Ansprüche 1 bis 6, wobei das Fremdmetall Silber umfasst.
8. Verwendung nach einem der Ansprüche 1 bis 6, wobei das Fremdmetall Bismut umfasst.
9. Verwendung nach einem der Ansprüche 1 bis 6, wobei das Fremdmetall Indium umfasst.
10. Verwendung nach einem der Ansprüche 2 bis 9, wobei der Elektrolyt ein zweiwertiges Zinnsalz umfasst.
11. Verwendung nach Anspruch 10, wobei das zweiwertige Zinnsalz Zinnmethansulfonat umfasst.

12. Verwendung nach einem der Ansprüche 2 bis 11, wobei der Elektrolyt 10 bis 200 g/l Thioharnstoff oder ein Thioharnstoff-Derivat umfasst.
13. Verwendung nach einem der Ansprüche 2 bis 12, wobei der Elektrolyt 1 bis 10 g/l Benetzungsmittel umfasst.
14. Verwendung nach einem der Ansprüche 2 bis 13, wobei die Temperatur des Elektrolyten während der Zinnabscheidung 35 °C bis 80 °C beträgt.

Revendications

1. Utilisation d'un métal étranger du groupe constitué par Ag, Bi, Ni, Ti, Zr et In comme barrière de diffusion pour supprimer la diffusion d'un matériau de couche de base à travers une couche d'étain, dans laquelle la couche de base est une couche de cuivre ou d'alliage de cuivre et la couche d'étain est précipitée de manière non galvanique sur la couche de base.
2. Utilisation selon la revendication 1, dans laquelle la couche d'étain est précipitée à partir d'un électrolyte comprenant 5 à 200 g/l d'acide méthanesulfonique, moyennant quoi le bain d'étain prend une valeur pH de 0 à 3, 1 à 30 g/l d'étain et 1 à 500 mg/l de métal étranger utilisés comme barrière de diffusion.
3. Utilisation selon la revendication 2, dans laquelle l'électrolyte comprend un antioxydant.
4. Utilisation selon la revendication 2 ou 3, dans laquelle l'électrolyte comprend de la thiourée et/ou son dérivé comme agent complexant.
5. Utilisation selon l'une quelconque des revendications 2 à 4, dans laquelle l'électrolyte est reconditionné en éliminant le cuivre en solution dans l'électrolyte par précipitation en tant que composé de cuivre-thiourée.
6. Utilisation selon la revendication 5, dans laquelle le précipité de cuivre-thiourée est éliminé de l'électrolyte par filtration, accélérant ainsi le processus de précipitation.
7. Utilisation selon l'une quelconque des revendications 1 à 6, dans laquelle ledit métal étranger comprend de l'argent.
8. Utilisation selon l'une quelconque des revendications 1 à 6, dans laquelle ledit métal étranger comprend du bismuth.
9. Utilisation selon l'une quelconque des revendications 1 à 6, dans laquelle ledit métal étranger com-

prend de l'indium.

10. Utilisation selon l'une quelconque des revendications 2 à 9, dans laquelle l'électrolyte comprend un sel d'étain bivalent. 5
11. Utilisation selon la revendication 10, dans laquelle le sel d'étain bivalent comprend du méthanesulfonate d'étain. 10
12. Utilisation selon l'une quelconque des revendications 2 à 11, dans laquelle l'électrolyte comprend 10 à 200 g/L de thiourée ou de dérivé de thiourée.
13. Utilisation selon l'une quelconque des revendications 2 à 12, dans laquelle l'électrolyte comprend 1 à 10 g/L d'agent mouillant. 15
14. Utilisation selon l'une quelconque des revendications 2 à 13, dans laquelle la température de l'électrolyte est comprise entre 35 et 80 °C pendant la précipitation de l'étain. 20

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REFERENCES CITED IN THE DESCRIPTION

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