

Method for coating surfaces on copper or on a copper alloy with a tin or tin alloy layer

Description:

The invention relates to a method for coating surfaces on copper or on a copper alloy, for example on brass, with a tin or tin alloy layer, furthermore to a layer combination including a tin or tin alloy layer as well as applications of the method for producing surfaces on copper or on a copper alloy which are suitable for soldering even after thermal treatment, and for producing layers to protect such surfaces against corrosion. Moreover the invention also relates to a bath solution for the electroless deposition of a tin layer or a tin alloy layer.

For surface treatment of workpieces on copper or copper alloys with the aim of creating corrosion-resistant surfaces, tin layers have, for a long time now, been applied in an electroless method by the basic metal decomposing in favour of the deposited tin ions. The tin layers can in principle also be deposited on other metals, such as iron. In order to be able to form a sufficiently thick layer, the workpiece must here be treated for two to three hours at 90 to 100°C.

For example, in US 2,891,871 A a method is described for the direct coating of workpieces on a copper or on a copper alloy, in which method a tin layer is formed on the workpiece through charge exchange by dipping it into a solution composed of a tin salt, a carboxylic acid and thiourea or a derivative of thiourea.

In US 2,282,511 A a method for coating copper surfaces is described in which a solution is used which contains compounds containing tin-II ions, dissolved thiocarbamide and a small amount of an alkali metal carbonate. With this solution, too, a tin layer can be directly formed on the copper surfaces. For example, solutions of this kind can be used for the electroless deposition of tin on the inner surfaces of copper pipes, in order to prevent the decomposition of copper.

Also, in US 2,369,620 A, an electroless tin-plating method for the coating of copper surfaces is described. The aqueous coating solution described in this

document is acid and contains besides a tin-II salt, preferably SnCl_2 , thiourea in addition.

According to DE-AS 1 521 490, an aqueous dipping bath for the deposition of tin also contains hypophosphorous acid or its alkali salts in order to improve the stability of the depositing solution and in order to obtain purer, brighter, denser tin layers which are more resistant to etching agents than with the previously known depositing solutions. Furthermore, it is stated that the depositing solution can also contain an organic acid, such as for example ethanoic acid, citric acid, malic acid, maleic acid and similar aliphatic mono-, di- and tricarboxylic acids. Thiourea is also contained in this solution and in addition a wetting agent. Layers with a thickness of several μm could be deposited with this bath.

In DE 30 11 697 A1 is described an acid chemical tin- plating bath, for example for coating copper surfaces, which contains a source for tin-II ions, thiourea, and an inhibitor as a further component, an organic sulphonic acid being preferably used as the inhibitor. The pH value of the solution is kept under 1. Moreover, this solution also contains a hypophosphite.

For application in the manufacture of printed circuit boards, a method is described in US 4,657,632 A in which a portion of the copper surface on the base material is removed by etching, by an etch-resist being applied to the copper surfaces which are not to be removed, and the portions of the copper surfaces which are to be removed remaining free. The etch-resist layer is formed by electroless deposition of a tin layer on the copper layers. The depositing solution used for this contains besides the tin-II salt and thiourea or a thiourea derivative, urea or a derivative of urea in addition. Furthermore, the solution can also contain a chelating agent, for example amino- and hydroxycarboxylic acids, a reducing agent, e.g. an aldehyde, and an acid. In addition, a wetting agent can be contained in the solution.

In EP 0 503 389 A2 is described a method for the electroless coating of workpieces with surfaces on copper or on a copper alloy with tin or a tin/lead alloy. The acid coating bath contains, in addition to the metal salts, a reducing

agent such as hypophosphite or its acid, and a complexing agent, for example organic carboxylic acids or thiourea or its derivatives.

In EP 0 521 738 A2 is described a solution for the electroless coating with tin or with a tin/lead alloy of copper surfaces preferably contained on printed circuit boards, which solution contains, besides tin salts, thiourea, an acid and a reducing agent, such as hypophosphite, in addition one or more nonionic wetting agents, preferably a polyoxyalkyl ether, for example polyoxynonylphenol ether.

In DE 40 01 876 A1 is described a composition for a bath for electroless coating with tin or with a tin/lead alloy, which contains alkane or alkanol sulphonic acids as well as their tin and lead salts, and in addition thiourea and thiourea derivatives as well as mono-, di-, tricarboxylic acids or their salts as a chelating agent for tin and lead. The composition serves to coat copper or copper alloys. Contained in the composition can be, amongst other things also nonionic wetting agents, for example polyoxyalkylene alcohol ether.

The use of tin layers as the solderable layer has been tested again and again for the manufacture of printed circuit boards. The conductor tracks obtained after the structuring of the copper layers has to be solderable for the fitting of components, the requirement existing that the exposed metal surfaces must have, even after lengthy storage time of several days to weeks, good wettability with the solder, mostly tin/lead solder.

However, it has emerged that the wettability of the tin layers during soldering is generally substantially worse than with the use of tin/lead alloys. Through storage of printed circuit boards with conductor tracks which are covered with tin layers, it emerged that large regions of the printed circuit board could not be wetted after its storage, whilst other regions did not present any problems of this kind. The electroless deposition of tin/lead layers is expensive, however, such that the use of purely tin layers seems advantageous as a soldering aid.

An attempt has been made, for example, to avoid this phenomenon through the application of temporarily applied organic protective varnishes. This protective coating is intended to dissolve within the first minutes in the tin/lead solder.

Varnishes of this kind are expensive however. In addition, they cause problems during processing since, during the soldering, they reach the soldering bath and contaminate it. In addition to this, tin layers on printed circuit boards provided with a temporary protective varnish have disadvantageous properties.

Moreover, it has also emerged that with the known methods no sufficiently high-quality layer surfaces can be obtained from tin or a tin alloy, such that, in the subsequent processing steps, problems arose for the printed circuit boards.

The problem underlying the present invention, therefore, is to avoid the disadvantages of prior art and especially to find a method and a bath solution with which it is possible to form tin and, if necessary, also tin alloy layers on surfaces on copper or on a copper alloy, which surfaces are, even after a lengthy storage time, easily wettable with liquid tin/lead solder.

This problem is solved by the features of claims 1 and 8, 9, 12 and 13. Preferred embodiments of the invention are quoted in the sub-claims.

It has been shown that, for the inadequate solderability of tin layers on printed circuit boards, which had been stored for several days to weeks, the formation of an intermetallic phase is responsible. Through the storage, at the boundary surface between the copper substrate and the tin layer, a copper/tin alloy forms which is the thicker, the longer the printed circuit board is stored and the higher the temperature is during storage. These intermetallic phases are formed very quickly. The capacity for soldering sinks rapidly if the whole tin layer, which has for example a thickness of 0.7 μm , is converted into the intermetallic phase.

If the electroless deposition of tin is observed accurately in the first seconds of the depositing process, it can be ascertained that "states" which were visible before tin plating on the copper surface, are "frozen" by the tin layer. On specific morphological structures, which are located on the copper surface, the

tin or respectively tin alloy layer is more quickly deposited than at points on the copper surfaces at which these structures are not located. For example, at rinsing water lines or oxidised portions of the copper surfaces, structures are formed which are distinguished at least optically from adjacent regions. If the printed circuit board is tempered after the tin plating of such points, very quickly intermetallic phases form at these points. These are more easily oxidised in air than pure tin layers or copper surfaces. During oxidation, these intermetallic phases lose the capacity for wetting with liquid solder.

The problems described above were solved by the method according to the invention which has the following essential method steps:

- a. the copper or copper alloy surfaces are treated with a solution which contains at least one noble metal compound, in order to deposit noble metal in a first step. The thickness of this metal can be extremely small. It is for example sufficient to form a noble metal layer which is not visible with the naked eye. The solution of the above-mentioned problems in carrying out this first method step and a subsequent tin plating alone shows that the noble metal treatment leads to the formation of a noble metal layer on the surfaces on copper or on a copper alloy.
- b. the surfaces coated with noble metal as per step a. are then treated with a solution which contains at least one tin compound and, if necessary, at least one compound of a further metal to be deposited, at least one acid and at least one complexing agent for copper from the group consisting of thiourea and its derivatives. During this treatment, the tin or tin alloy layer is formed.

The bath solution according to the invention for the electroless deposition of a tin layer or a tin alloy layer is characterised in that it

- a. contains at least one tin compound and, if necessary, at least one compound of a further metal to be deposited,
- b. at least one acid,
- c. at least one complexing agent for copper from the group consisting of thiourea and its derivatives, and

- d. if necessary, at least one wetting agent.

Just like the tin or tin alloy layer, the noble metal layer is formed by charge exchange, as a result of which copper ions go into solution at the same time as the metal deposition. It is assumed that the noble metal coating formed prevents the further oxidation of copper and the formation of the intermetallic phase between copper and tin. By this means, the further oxidation of the tin layer is probably suppressed, such that the wettability of the surfaces with solder is preserved even after lengthy heat treatment.

During the soldering process itself, the tin and the noble metal layers are extremely quickly decomposed by the liquid solder. This process advances very quickly, such that sufficient time remains for the desired intermetallic tin/copper phase, typical for the soldering process, to form between the liquid tin/lead solder and the copper.

The following method steps are preferably carried out:

1. The copper or copper alloy surfaces are cleaned or etched.
2. The treated surfaces are thoroughly rinsed.
3. Noble metal is then deposited by cementation.
4. Thereafter the workpieces are brought into contact with an aqueous acid solution.
5. Following this, tin is deposited in an electroless manner, preferably at a temperature of roughly 60°C; the treatment time is preferably roughly 4 minutes to roughly 30 minutes.

To clean the copper or copper alloy surfaces, conventional cleaning and etching solutions are used, for example solutions containing wetting agents, and which can additionally contain, for example, hydrogen peroxide and sulphuric acid. In the bath used for the noble metal deposition, one or more noble metal compounds from the group consisting of silver, gold, platinum, palladium, ruthenium, rhodium, osmium and iridium are used. The concentration of the noble metals in the solution is preferably roughly 0.1 to 2000 ppm (parts by

weight noble metal per 1 million parts by weight solution), preferably roughly 1 to roughly 100 ppm.

The printed circuit boards are only treated for a short time in the noble metal bath, for example within a period of roughly 60 seconds to roughly 120 seconds.

Longer treatment times can naturally also be chosen.

The treatment temperature during the deposition of noble metal is preferably roughly 20 to roughly 30°C.

After the deposition of noble metal, the boards are brought into contact with an acid solution. An acid contained in the tin-plating bath can preferably be used as the acid. Naturally, a different acid can also be used. During this treatment, the copper or respectively copper alloy surfaces are prepared for tin-plating; simultaneously, the acid forms a protection for the subsequent tin bath before dilution.

The electroless tin bath must have as high stability as possible against decomposition. In particular, with known baths there exists the tendency for precipitates to form within a very short time (within days).

As acids contained in the tin bath, preferably mineral acids, organic acids and sulphonic acids are selected.

The tin-plating bath is operated at a temperature of roughly 50 to roughly 70°C. Under these conditions, adhesive and evenly bright tin layers with a thickness of between roughly 0.6 and roughly 1.4 μm can be deposited on copper or respectively on a copper alloy.

As the tin alloy, a tin/lead alloy can be deposited for example. The deposition bath contains in this case in addition a lead-II salt, for example PbCl_2 or $\text{Pb}(\text{OCOCH}_3)_2$.

To carry out the process, the printed circuit boards are dipped in the standard method one after the other in containers in which the individual treatment

solutions are contained. Since the treatment times are extraordinarily short, the printed circuit boards can also be treated in a continuous treatment plant, through which the boards are led in horizontal or vertical alignment and in a horizontal conveying direction.

The method according to the invention is particularly well suited for the production of surfaces on copper or on a copper alloy which are suitable for soldering even after thermal treatment, as well as for the manufacture of layers to protect surfaces on copper or on a copper alloy against corrosion. The method can also serve to form the layer combination according to the invention on workpieces other than printed circuit boards, for example for coating pipes against corrosion.

The following examples serve to explain the invention further:

Example 1:

A wiring board, provided with copper structures and especially with connection places for electrical components, was, after cleaning and etching of the copper with an aqueous solution of sodium peroxodi- sulphate in a silver complexing solution, which contained 50 ppm silver, treated for a minute at room temperature. After the board had been rinsed with water and subsequently treated with a solution of 2% by wt. acid in water, it was tin-plated in an electroless tin-plating bath for 15 minutes at 60°C.

The tin-plating bath had the following composition:

Tin-II fluoroborate	15g tin
Fluoboric acid	100 ml
Thiourea	100 g
Sodium lauryl sulphate	2 mg
Fill up with water to 1 l.	

The tin layer obtained after treatment with the bath was bright metallic and had a thickness of 1.05 µm. The plate was thereafter tempered for 8 hours at 155°C

in air and finally subjected to a wave soldering process. As the fluxing agent, a low-solids (2%) no-clean fluxing agent (Kester® product of the company Litton-Kester, USA) was used.

The soldering result on the connection places was excellent, since the wetting behaviour was perfect on the tin-plated copper surfaces. The rise of the solder into the bores contained in the printed circuit board was 80 – 90% perfect (the printed circuit board was not fitted with components).

Example 2:

A printed circuit board pre-treated as in Example 1, was coated with platinum in a platinum solution which contained 15 ppm platinum, for 1 minute at room temperature, and thereafter treated further as in Example 1.

The bright tin layer obtained had, after a dipping time of 30 minutes in the tin-plating bath at 55°C, a thickness of 1 µm.

Then the board was tempered for 4 hours at 155°C and, analogously to Example 1, subjected to a solder test. Neither faults during the wetting with the liquid solder nor problems as the solder rose in the bores were apparent; this was 100%.

Example 3:

A printed circuit board, pre-treated as in Example 1, was treated for 2 minutes in a ruthenium solution which contained 50 ppm ruthenium. The copper layers which were coated with the extremely thin ruthenium layer, were tin-plated at 50°C in a chemical tin bath of the composition:

Tin (II) chloride	5 g
N-methyl thiourea	55 g
Conc. sulphuric acid	20 g
Isopropyl alcohol	500 ml
Water	500 ml

The tin layer was subjected to a solder test (solder spread test). The soldering capability was excellent with 9° contact angle.

Patent Claims



1. Method for coating surfaces on copper or on a copper alloy with a tin or tin alloy layer, with the following essential method steps:
 - a. treatment of the surfaces with a solution containing at least one noble metal compound in order to deposit the noble metal;
 - b. treatment of the surfaces coated with the noble metal according to step a. with a solution containing at least one tin compound, at least one acid and at least one complexing agent for copper, selected from the group consisting of thiourea and its derivatives, in order to form the tin or tin alloy layer.
2. Method according to claim 1, characterised in that compounds of the noble metal, selected from the group consisting of silver, gold, platinum, palladium, ruthenium, rhodium, osmium and iridium, are used.
3. Method according to one of the preceding claims, characterised in that the solution for depositing the noble metal contains in addition at least one compound of a further metal to be deposited.
4. Method according to one of the preceding claims, characterised in that the concentration of the noble metal in the solution as per step a. is set at 0.1 to 2000 ppm (weight/weight), preferably at 1 to 200 ppm (weight/weight).
5. Method according to one of the preceding claims, characterised in that the solution for depositing the noble metal contains in addition to the noble metal compounds at least one solvent, selected from the group consisting of water and an organic solvent.
6. Method according to one of the preceding claims, characterised in that acids, selected from the group consisting of mineral acids, organic acids and sulphonic acids, are selected for the solution for forming the tin or tin alloy layer.

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7. Method according to one of the preceding claims, characterised in that, in addition, a wetting agent is added to the solution for depositing the tin or tin alloy layer.
8. Layer combination on a surface on copper or on a copper alloy, comprising a noble metal layer adjacent to the surface and a tin or tin alloy layer applied to same.
9. Bath solution for the electroless deposition of a tin or tin alloy layer, containing
 - a. at least one tin compound
 - b. at least one acid and
 - c. at least one complexing agent for copper, selected from the group consisting of thiourea and its derivatives.
10. Bath solution according to claim 9, characterised in that the solution contains in addition at least one compound of a further metal to be deposited.
11. Bath solution according to one of claims 9 and 10, characterised in that the solution contains in addition at least one wetting agent.
12. Application of the method according to one of claims 1 to 7 for producing surfaces on copper or on a copper alloy which are suitable for soldering even after thermal treatment.
13. Application of the method according to one of claims 1 to 7 for producing layers to protect surfaces on copper or on a copper alloy against corrosion.

