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Lescure

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[54] BATH FOR ELECTROPLATING TIN-BISMUTH ALLOY

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **C23b 5/38**

[58] **Field of Search** 204/43

[56] **References Cited**

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[57] **ABSTRACT**

Bath for electroplating tin-bismuth alloy upon a metal object such as a frame of a computer, including fluoboric acid in order to maintain the pH acid, tin fluoborate and a bismuth oxide-bismuth sulphate mixture of low quantity. The utilized method is of the soluble anode type and the cathode is formed of the object to be coated.

6 Claims, No Drawings

BATH FOR ELECTROPLATING TIN-BISMUTH ALLOY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention concerns an electroplating method and bath. More particularly, it concerns a method for depositing, through an electroplating process, a tin-bismuth alloy as well as the bath used for its implementation.

2. Description of the Prior Art

It is well known for the man skilled in the art that it is possible to electrodeposit (or electroplate) metal tin upon various metal surfaces. For instance, it can be deposited upon aluminum, nickel, etc... The use of tin as a coating is preferred when casings, frames, etc., must be built which must show a high compatibility and a time-constant and frequency-independent contact impedance lower than 1 ohm. These properties are due to the fact that the tin oxide has the same impedance as the metal tin.

Unfortunately, tin coatings have a drawback. Indeed, at temperatures near the room temperature, a temperature lower than 13° C., tin is submitted to an allotropic transformation: the deposited white tin is changed into a grey tin. This phenomenon is known as tin pest. This tin pest appears as a non-adherent powder which separates from the deposit, thereby exposing the underlying metal to corrosion.

In order to avoid tin pest, it has been proposed to add bismuth or antimony to tin.

The prior art has disclosed an electroplating method and bath for electroplating bismuth-tin-alloy. The bath is basic and, therefore, bismuth must be introduced in the form of organic bismuthates which are not much soluble. In addition, the operating temperature is near 90° C. This method is difficult as to its implementation and is relatively expensive and does not make it possible to obtain a sufficient bismuth concentration.

SUMMARY OF THE INVENTION

Therefore, one object of this invention is to obtain an acid bath for electroplating tin-bismuth alloy.

Another object of the invention is the implementation of a tin-bismuth electroplating method with which it is possible to obtain a constant bismuth concentration in the tin.

Another object of the invention is the implementation of a method with which it is possible to obtain a uniform coating of the tin-bismuth alloy upon another metal and this in a simple and cheap manner.

This invention will be further explained with reference to the following preferred embodiments of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In each embodiment of the invention, the object to be coated is immersed into the bath where it acts as a cathode. A tin anode is used which is wrapped in a polypropylene bag the texture of which is very close in order to prevent the non ionized metal particles from moving which are pulled out of the anode during dissolution of the anode used to regenerate the tin-contents in the bath.

The proportion of tin contained in the bath is within 20–80 g. of metal tin per liter which is introduced in the form of tin salt, namely, tin fluoborate.

It contains from 100 to 200 g. of free fluoboric acid; it may also contain in appropriate proportions a buffer solution such as boric acid. The concentration of the bismuth ions in the bath, which is within 0.01 and 0.05 g. of bismuth per liter, is obtained in the bath by introducing therein from 0.1 to 0.5 g. per liter of a mixture formed of bismuth sulphate, $Bi_2(So_4)_3$ and of bismuth oxide (Bi_2O_3) the composition of which may vary from 15 to 50 percent by weight of bismuth sulphate and from 85 to 50 percent by weight of bismuth oxide, the preferred ratio of the mixture being, 30 percent by weight of $Bi_2(So_4)B3$, 70 percent of Bi_2O_3. This soluble mixture, but with which it is however possible to obtain the necessary concentration of bismuth ions in the bath, is inserted into close texture polypropylene bags which prevent non dissolved molecules from being drawn into the bath while making it possible to obtain a concentration of bismuth ions which is constant and near saturation.

The bath contains also about 1g. of formol per liter in order to avoid the anodic oxidation of the stannous ions (Sn^{++}) into stannic ions (Sn^{4+}). Besides, this bath may include gelatine the proportions of which are 2 to 7 g. per liter and β-naphtol the proportions of which are 0.5 to 1.5 g. per liter in order to improve the quality of the deposit.

The bath may also contain brighteners in appropriate proportions.

The so-formed bath has an acid pH and its acidity corresponds to the acidity of a solution containing 100 g./liter of sulphuric acid. The density is about 13° B.

The electroplating process is carried out at a temperature within 20°–50° C. The voltage is between 1 and 3 volts and the current density is between 0.8 and 3A/dm². For a current density of 1A/dm², the obtained deposit ratio is 0.5 μ/minute. The anode-cathode surface ratio may be between 1 and 1.5. The following examples are only given by way of a non limitative example. Six deposit tests have been made upon a steel sheet coated with a nickel layer which is of the Watt type and 15 μ thick, by varying the potential. The bath had the following composition:

tin fluoborate	30g/liter of metal tin
fluoboric acid	130g/liter
boric-acid	30g/liter
mixture: bismuth sulphate 30% by weight bismuth oxide 70% by weight	0.3g/liter
formol	1g/liter
equivalent acid H_2SO_4	100g/liter

The tests have been made at 25° C. and are gathered in the following table.

Tests No.	Voltage, v.	Current density, a./dm.²	Time, hours	Percent by weight of Bi in the deposit
1	2	3	1	0.54
2	2.5	2.5	1	
3	1.5	1	1	
4	1.5	1.5	1	
5	1	1	1¼	
6	0.8	0.8	1	0.25

The so-prepared plates, after a stay of 90 days at 0° C., showed no trace of tin pest or oxidation.

The preferred percentage of bismuth in tin is 0.4 percent.

When performing the electroplating operation, it should be advisable to empty the container every 24 hours in order to prevent tin from getting enriched with tin at rest, to check the bags containing bismuth and to clean the container.

Though the description makes use of tin fluoborate, it is obvious for the man skilled in the art that another tin salt can be used. The man skilled in the art will also recognize that bismuth can be inserted in forms different from that used in the invention.

It is clear that the previous description has only been given as an unrestrictive example and that numerous alternatives may be considered without departing from the spirit and scope of the invention.

What is claimed is:

1. An aqueous bath for electroplating tin-bismuth alloy, characterized in that it includes acid ions in order to maintain pH acid, and characterized in that the bismuth is inserted in the form of a bismuth sulphate-bismuth oxide mixture, the concentration of which relative to the entire bath is between 0.1 and 0.5 grams per liter and in which the relative proportion of bismuth sulphate to bismuth oxide is in the range between 15/85 and 1.

2. An aqueous electroplating bath characterized in that it includes:

1. tin fluoborate equivalent to 30g/liter of metal tin
2. 130g/liter of fluoboric acid
3. 30g/liter of boric acid
4. 0.3g/liter of the bismuth sulphate-bismuth oxide mixture the respective proportions by weights of which are 30%–70%.
5. 1g/liter of formol

3. An aqueous acid fluoborate tin-bismuth alloy electroplating bath containing stannous ions, free fluoboric acid and an acid soluble mixture of bismuth sulphate and bismuth oxide in which the relative proportion of bismuth sulphate to bismuth oxide is in the range between 15/85 and 1.

4. A tin plating bath according to claim 3 wherein said bismuth mixture comprises bismuth sulphate and bismuth oxide in relative weight proportions of approximately 30 to 70 percent.

5. A tin plating bath according to claim 4 including approximately 1 gram per liter of formol as additive to inhibit anodic oxidation of the stannous ions.

6. A tin plating bath according to claim 4 wherein the concentration of said bismuth mixture in proportion to the total volume of the bath is between 0.1 and 0.5 grams per liter.

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