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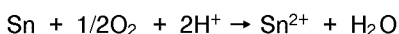
Description

The present invention relates to a method of electroplating of metallic material such as metal strip and metal wire, and particularly to a method of continuous electroplating using an insoluble anode.

5 A known method for continuous electroplating of metallic material such as metal strip and metal wire in an electroplating tank employs an insoluble anode, where the insoluble anode is immersed in electroplating solution containing tin ion. An example of the insoluble anode is titanium coated with platinum. The tin plating layer is formed on the metallic material by applying direct current between the insoluble anode and the metal being plated while supplying tin ion (Sn^{2+}) to the electroplating solution.

10 Such an electroplating method using an insoluble anode maintains stable distance between anode and metallic material and keeps a constant current density level because the anode dissolves little, which provides a uniform coating weight throughout the tin plating layer formed on the metallic material and gives the tin layer having uniform surface gloss. In addition, no adjustment nor exchange of anode is required because the anode dissolves very little.

15 A method of prior art (a) is proposed in JP-A-76735/74, JP-B-54079/81, and JP-B-54080/81 (the term "JP-A-" and "JP-B-" referred to herein signify "unexamined Japanese patent publication" and "examined Japanese patent publication", respectively). In the method (a), metallic tin particles are filled in a metallic tin dissolving tank which is installed separately from the electroplating tank. By charging the plating solution containing dissolved oxygen into the metallic tin dissolving tank which is filled with the metallic tin particles, 20 the metallic tin dissolves following the reaction given below to supply tin ion (Sn^{2+}) to the plating solution.



The plating solution supplied with tin ion (Sn^{2+}) is fed to the plating solution in the electroplating tank to 25 electroplate the metallic material in the electroplating tank.

The method of prior art (a) has, however, a problem. Since the plating solution contains a larger amount of dissolved oxygen, tin ion (Sn^{2+}) in the plating solution is oxidized to yield SnO_2 . The yielded SnO_2 does not dissolve and accumulates in the plating solution as fine sludge. The accumulated fine sludge adheres to the tin plating layer formed on the metallic material and the inside wall surface of the plating solution feed 30 pipe to finally degrade the quality of tin plating and to plug the plating solution feed pipe.

Another method of prior art (b) is presented in JP-A-41799/86 which describes a method of tin supply to electroplating tank. In the method (b), tin ion is supplied to the plating solution by dissolving tin oxide such as SnO into the solution containing components to form the plating solution.

The method (b) also has the disadvantage that the chemicals employed to yield tin oxide such as SnO 35 are expensive and that these chemicals are likely to be contaminated, during the preparation stage, by impurities hazardous for tin plating.

A further method of prior art (c) is presented in JP-A-70087/90 and JP-A-175894/90 which describe a method of electroplating. In the method (c), the electrolytic tank which is installed separately from the electroplating tank contains an anode made of metallic tin and a cathode as the counter electrode. These 40 electrodes are separated each other by a diaphragm such as semipermeable membrane or ion-exchange membrane. By applying direct current between the anode and the cathode, tin ion generates from the metallic tin anode by electrolysis. The generated tin ion is introduced to the plating solution in the electrolytic tank while being prevented to deposit on the cathode by the presence of diaphragm. The prepared electroplating solution containing tin ion is then fed to the plating solution in the electroplating tank. The electroplating of the metallic material in the electroplating tank is carried under the continuous 45 supply of tin ion.

The method (c), however, still has problems. The diaphragm such as semipermeable membrane and ion-exchange membrane separating the anode from the cathode is expensive, has poor strength and insufficient durability. In addition, the method operates at a low current efficiency owing to the limit of 50 electrolytic current density, and consumes a large quantity of power because of the large reduction of electrolytic voltage across the diaphragm. As a result, the method (c) unavoidably raises the production cost and is difficult to commercialize on a large scale.

The object of this invention is to provide a method of electroplating to form a high quality tin plating layer on metallic material at an industrial scale economically and with a high current efficiency. To achieve 55 the object, this invention provides the electrolytic tin plating method which comprises the following steps:

(a) preparing an electrolytic tank containing electroplating solution as electrolytic solution and being provided with an anode of metallic tin and a cathode as a counter electrode;

(b) preparing an electroplating tank containing electroplating solution and being provided with an insoluble anode and a metallic material to be supplied into the electroplating solution;

(c) applying direct current between the anode and the cathode which are placed in the electrolytic tank, the anode being dissolved by electrolysis to generate tin ion and the tin ion then depositing on the cathode;

(d) controlling to keep a tin deposition rate onto the cathode in the electrolytic tank less than the metallic tin dissolving rate of the anode, the dissolved tin ion being fed to the electroplating solution in the electrolytic tank;

(e) supplying the electroplating solution supplied with the tin ion at the electrolytic tank to the electroplating solution in the electroplating tank; and

(f) forming a tin plating layer on surface of the metallic material by applying the direct current between the insoluble anode and the metallic material which are placed in the electroplating tank.

Fig. 1 is schematic diagram illustrating means for carrying the method of the present invention.

The method of the present invention employs an electroplating tank containing electroplating solution and an electrolytic tank containing electroplating solution as electrolytic solution. An anode made of metallic tin is dissolved in the electroplating solution of the electrolytic tank by the electrolysis. During the tin dissolving period, if the tin deposition rate onto a cathode is kept at a lower level than the metallic tin dissolving rate of anode by inducing the tin deposition reaction and the reducing reaction such as hydrogen generation on cathode, then the tin ion dissolved from the anode is efficiently supplied into the electrolytic solution without installing expensive diaphragm in between anode and cathode. Thus the electrolytic solution containing the tin ion is supplied to the electroplating tank. As a result, high quality tin plating layer is formed on the metallic material at an industrial scale economically and with a high current efficiency.

The present invention is performed based on the above described findings. Accordingly, the procedure of the method of the present invention is described below.

The electrolytic tank is prepared, which electrolytic tank contains the electroplating solution as the electrolytic solution and is provided with the anode made of metallic tin and the cathode as the counter electrode against the anode. The electroplating tank is separately prepared, which electroplating tank includes the electroplating solution and is provided with the insoluble anode and the metallic material to be placed into the plating solution. Direct current is applied between the insoluble anode and the metallic material which are placed in the electroplating tank to form the tin plating layer on the surface of the metallic material. Direct current is applied between the anode and the cathode which are placed in the electrolytic tank to dissolve the anode by electrolysis to generate tin ion, which tin ion then deposits on the cathode. Tin ion is supplied to the electroplating solution in the electrolytic tank while controlling to keep the tin deposition rate on the cathode of the electrolytic tank at a lower level than the metallic tin dissolving rate of the anode of the electrolytic tank by inducing the tin deposition reaction and the reducing reaction of hydrogen generation on the cathode. The electroplating solution supplied with the tin ion in the electrolytic tank is supplied to the electroplating solution in the electroplating tank.

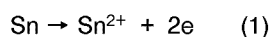
The electroplating solution in the electrolytic tank and the electroplating tank may be either acid or alkaline. In the case of acid electroplating solution, the tin deposition rate on the cathode of the electrolytic tank is preferably controlled to at least 10% lower level than the metallic tin dissolving rate of the anode by inducing the tin deposition reaction and the reducing reaction of hydrogen generation on the cathode.

For the case of alkaline electroplating solution, the tin deposition rate on the cathode of the electrolytic tank is preferably controlled to at least 30% lower level than the metallic tin dissolving rate of the anode by inducing the tin deposition reaction and the reducing reaction of hydrogen generation on the cathode.

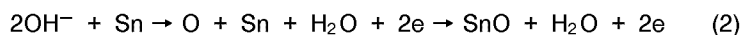
Plating with acid electroplating solution

The invention is described to a greater detail in the following embodiment using acid electroplating solution as the electroplating solution for both electrolytic tank and electroplating tank. The electrolytic tank is installed separately from the electroplating tank to supply tin ion (Sn^{2+}) to the plating solution in the electroplating tank. The electrolytic tank is provided with the anode made of metallic tin and the cathode as the counter electrode. Direct current is applied between these electrodes, and the anode is dissolved by electrolysis. The dissolved anode portion provides the tin ion (Sn^{2+}) to the electrolytic solution of electroplating solution in the electrolytic tank. The electrolysis allows the high efficient dissolving of anode. On the other hand, the reducing reaction such as hydrogen generation occurs on the cathode to suppress the tin deposition on the cathode.

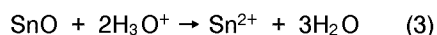
The principle of tin ion (Sn^{2+}) supply to the electrolytic solution is described below. The anode made of metallic tin in the electrolytic tank dissolves following eq.(1).



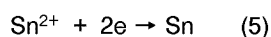
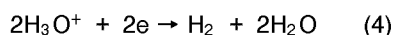
In addition, in the electroplating solution of sulfuric acid series, for example, a slight oxidation reaction such as oxygen generation on the surface of anode made of metallic tin collaterally occurs. Accordingly, SnO is generated on the surface of anode following eq.(2).



The generated SnO is converted to Sn^{2+} following eq.(3), which is then dissolved into the tin plating solution.



On the surface of cathode of the electrolytic tank, reactions at least expressed in eq.(4) and eq.(5) occur.



The difference of the amount of tin between the tin dissolved from anode following the equations of (1), (2), and (3) and the tin deposited on cathode following eq.(5) is supplied to the electrolytic solution as tin ion (Sn^{2+}). In other words, the equivalent amount of tin ion (Sn^{2+}) which is almost the same with the equivalent amount of hydrogen generated on the cathode increases in the electrolytic solution. In concrete terms, the ratio of the current consumed by the reducing reaction such as hydrogen generation on the cathode to the electrolytic current becomes nearly equal to the supply efficiency of tin ion (Sn^{2+}) to the electrolytic solution. Accordingly, the efficient supply of tin ion (Sn^{2+}) to the electrolytic solution needs to enhance the reducing reaction such as hydrogen generation on the cathode to suppress the metallic tin deposition reaction on the surface of cathode as far as possible.

The tin deposition rate on the cathode of electrolytic tank is preferably kept lower by at least 10% than the dissolving rate of the anode made of metallic tin. When the difference is less than 10%, the supply of tin ion (Sn^{2+}) to the electrolytic solution is insufficient and a large quantity of power is consumed to carry the electrolysis, which raises the power cost. More preferably, the tin deposition rate on the cathode of electrolytic tank is kept lower by at least 30% than the dissolving rate of the anode made of metallic tin. The efficiency of the electrolytic current gets 100% and this is most advantageous in the operation cost. Therefore, it is most preferable that the tin deposition rate on the cathode of the electrolytic tank is 0%.

A measure to reduce the tin deposition rate on the cathode below the dissolving rate of the anode made of metallic tin is to decrease the current efficiency for metallic tin deposition. Several means may be adopted to decrease the current efficiency for the tin deposition on cathode, which include increasing the electrolytic current density at cathode and reducing the temperature of electrolytic solution. When a ferrosulfate bath is used, it is preferable that the electrolytic current density on the cathode is about 50 A/dm² so as to control the tin deposition rate on the cathode to be by 10% less than the dissolving rate of the anode made of metallic tin. And so as to make 30% the difference between the tin deposition rate and the dissolving rate of the anode made of metallic tin, it is preferable that the electrolytic current density on the cathode is about 70 A/dm².

To raise the dissolving efficiency of anode made of metallic tin, it is preferable to maintain the high current efficiency for dissolving the anode. When raising the current efficiency at the anode, an adequate electrolytic condition is selected to suppress oxidation reaction such as oxygen generation at the cathode as far as possible except for the tin dissolving reaction. That is to say, the electrolysis is carried out with a current density equal to the critical dissolving current density or less. In case of the ferrosulfate bath, when the electrolytic current density is 30 A/dm² or lower, the dissolution of substantially 100% is obtained. So far as the other operation conditions are concerned, higher the bath temperature, the better the operation is and the higher the stirring flow rate, the more effective the raising the dissolution efficiency is.

In order to reduce the tin deposition rate on the cathode in electrolytic tank lower by at least 10% than the tin dissolving rate of the anode made of metallic tin, the reducing reaction such as hydrogen generation at the cathode is enhanced by raising the electrolytic current density at the cathode higher than the level of electrolytic current density at the anode and by forming the concentration boundary layer of tin ion diffusion in the vicinity of cathode surface in the electrolytic solution during the electrolysis. Several modes of the

method are given below.

In the first mode, the surface of cathode comprises a metallic sheet coated with a passive layer which is difficult to dissolve, which raises the current density at the actual electrolysis region.

In the second mode, the surface of the cathode comprises alternative arrangement of conductive part and insulated parts.

In the third mode, the cathode has a mesh structure, which decreases the total area of conductive part below the surface area of anode.

In the fourth mode, the surface area of cathode is made smaller than that of anode by applying a configuration where a rod or wire cathode is surrounded by a cylindrical anode, for example.

The metallic tin deposition on the cathode is removed from the cathode surface on occasion. The removed metallic tin is reused as the anode and is converted to tin ion.

Examples of the electrolytic solution, or the acid electroplating solution, are acid electroplating solution of sulfuric acid series such as ferrostannate bath, methane sulfonate bath, dimethyl sulfonate bath, and sulfuric acid bath, and acid electroplating solution such as fluoborate bath and halide bath.

According to the method of the present invention, tin ion (Sn^{2+}) is supplied to the acid electroplating solution by electrolysis, as described above. Consequently, there occurs no reverse effect as seen in the method of prior art (a), which reverse effect is the increase of dissolved oxygen in the plating solution and the SnO_2 sludge formation in the plating solution during the process of chemical dissolving of metallic tin particles by the oxygen introduction.

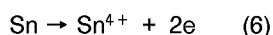
In the method of the present invention, the reaction using a soluble anode is simply divided into the tin deposition in the tin plating process and the tin dissolving in the tin ion supplying process. Consequently, the additional reaction in the sulfuric acid series plating bath such as ferrostannate bath and methane sulfonate bath is basically the electrolytic reaction of water. The composition of electrolytic solution shows very little change during electrolysis. The method of the present invention needs no chemical, which chemical is necessary in the method of prior art (b) to form tin oxide such as SnO . In the halide bath, the electrolytic reaction of hydrochloric acid, etc. is added, so the supply of chlorine and other substances is needed, which chlorine and other substances are generated from the insoluble anode in the plating process and are emitted to outside of the system without caught by the plating solution. Nevertheless, according to the method of the present invention, the supply of such chlorine and other substances is carried easily and inexpensively.

Furthermore, the method of the present invention does not require expensive diaphragm made of semipermeable membrane or ion-exchange membrane which is employed by the method of prior art (c) to separate anode from cathode to prevent the tin deposition on the cathode.

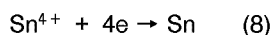
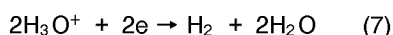
35 Plating with alkaline electroplating solution

The present invention is further described in greater detail in the following embodiment using alkaline electroplating solution as the electroplating solution for both electrolytic tank and electroplating tank. The electrolytic tank is installed separately from the electroplating tank to supply tin ion (Sn^{4+}) to the plating solution in the electroplating tank. The electrolytic tank is provided with the anode made of metallic tin and the cathode as the counter electrode. Direct current is applied between these electrodes, and the anode is dissolved by electrolysis. The dissolved anode portion provides the tin ion (Sn^{4+}) to the electrolytic solution of electroplating solution in the electrolytic tank. The electrolysis allows the high efficient dissolving of anode. On the other hand, the reducing reaction such as hydrogen generation occurs on the cathode to suppress the tin deposition on the cathode.

The principle of tin ion (Sn^{4+}) supply to the electrolytic solution is described below. The anode made of metallic tin in the electrolytic tank dissolves following eq.(6).



On the surface of cathode of the electrolytic tank, reactions at least expressed in eq.(7) and eq.(8) occur.



The difference of the amount of tin between the tin dissolved from anode following eq.(6), and the tin

deposited on cathode following eq.(8) is supplied to the electrolytic solution as tin ion (Sn^{4+}). In other words, the equivalent amount of tin ion (Sn^{4+}) almost the same with the half equivalent amount of hydrogen generated on the cathode increases in the electrolytic solution. In concrete terms, the ratio of the current consumed by the reducing reaction such as hydrogen generation on the cathode to the electrolytic current becomes nearly equal to the supply efficiency of tin ion (Sn^{4+}) to the electrolytic solution. Accordingly, the efficient supply of tin ion (Sn^{4+}) to the electrolytic solution needs to enhance the reducing reaction such as hydrogen generation on the cathode to suppress the metallic tin deposition reaction on the surface of cathode as far as possible.

The tin deposition rate on the cathode of electrolytic tank is preferably kept lower by at least 30% than the dissolving rate of the anode made of metallic tin. When the difference is less than 30%, the supply of tin ion (Sn^{4+}) to the electrolytic solution is insufficient and a large quantity of power is consumed to carry the electrolysis, which raises the power cost. More preferably, the tin deposition rate on the cathode of electrolytic tank is kept lower by at least 50% than the dissolving rate of the anode made of metallic tin. Since the efficiency of the electrolytic current gets 100%, this is most advantageous in the operation cost. Therefore, it is most preferable that the tin deposition rate on the cathode of the electrolytic tank is 0%.

A measures to reduce the tin deposition rate on the cathode below the dissolving rate of the anode made of metallic tin is to decrease the current efficiency for metallic tin deposition. Several means may be adopted to decrease the current efficiency for the tin deposition on the cathode, which include increasing the electrolytic current density at cathode and reducing the temperature of electrolytic solution. When a sodium bath is used, it is preferable that the electrolytic current density on the cathode is about 3A/dm^2 so as to control the tin deposition rate on the cathode to be by 30% less than the dissolving rate of the anode made of metallic tin. And so as to make 50% the difference between the tin deposition rate and the dissolving rate of the anode made of metallic tin, it is preferable that the electrolytic current density on the cathode is about 5A/dm^2 . Further, when a sodium bath is used, it is preferable that the electrolytic current density on the cathode is about 5.5 A/dm^2 so as to control the tin deposition rate on the cathode to be by 30% less than the dissolving rate of the anode made of metallic tin. And so as to make 50% the difference between the tin deposition rate and the dissolving rate made of metallic tin, it is preferable that the electrolytic current density on the cathode is about 7.5 A/dm^2 .

To raise the dissolving efficiency of anode made of metallic tin, it is preferable to maintain the high current efficiency for dissolving the anode. To improve the current efficiency of the anode, it is preferable to maintain the anode current density at below the critical current density and in a range not diminishing the greenish yellow coating film on the anode.

In order to reduce the tin deposition rate on the cathode in electrolytic tank lower by at least 30% than the tin dissolving rate of the anode made of metallic tin, the reducing reaction such as hydrogen generation at the cathode is enhanced by raising the electrolytic current density at the cathode higher than the level of electrolytic current density at the anode and by forming the concentration boundary layer of tin ion diffusion in the vicinity of cathode surface in the electrolytic solution during the electrolysis. Several modes of the method are given below.

In the first mode, the surface of cathode comprises a metallic sheet coated with a passive layer which is difficult to dissolve, which raises the current density at the actual electrolysis region.

In the second mode, the surface of cathode comprises alternative arrangement of conductive part and insulated part.

In the third mode, the cathode has a screen structure, which decreases the total area of conductive part to below the surface area of anode.

In the fourth mode, the surface area of cathode is made smaller than that of anode by applying a configuration where a rod or wire cathode is surrounded by a cylindrical anode, for example.

The metallic tin deposition on the cathode is removed from the cathode surface on occasion. The removed metallic tin is re-used as the anode and is converted to tin ion (Sn^{4+}).

The electrolytic solution, or the alkaline electroplating solution, is a sodium bath or a potassium bath. According to the method of the present invention, tin ion (Sn^{4+}) is supplied to the alkaline electroplating solution by electrolysis, as described above. Consequently, there occurs no reverse effect as seen in the method of prior art (a), which reverse effect is the increase of dissolved oxygen in the plating solution and SnO_2 sludge formation in the plating solution during the process of chemical dissolving of metallic tin particles by the oxygen introduction.

In the method of the present invention, the reaction using a soluble anode is simply divided into the tin deposition in the tin plating process and the tin dissolving in the tin ion supplying process. Consequently, the additional reaction is basically the electrolytic reaction of water in the alkaline plating bath such as sodium bath and potassium bath. The composition of electrolytic solution shows very little change during

electrolysis. The method of the present invention needs no chemical, which chemical is necessary in the method of prior art (b) to form tin oxide such as SnO. Furthermore, the method of the present invention does not require expensive diaphragm made of semipermeable membrane or ion-exchange membrane which is employed by the method of prior art (c) to separate anode from cathode to prevent the tin deposition on the cathode.

Processing therefore to describe the present invention in detail, reference should be made to Fig. 1. The reference character 1 illustrates the vertical electroplating tank containing acid electroplating solution 2. Above the electroplating tank 1, conductor rolls 4 and 4' are positioned at the inlet and outlet of the path of steel strip 3. At the bottom of the electroplating tank 1, a sink roll 5 is located to turn the path of the steel strip 3 introduced into the electroplating tank 1 from downward to upward direction. A pair of insoluble anodes 6 are placed to sandwich the steel strip 3 coming down from the conductor roll 4 to the sink roll 5. A pair of insoluble anodes 6' are placed to sandwich the steel strip 3 coming up to the roll 4'. Both insoluble anodes 6 and 6' are parallel to the steel strip 3, and the strip 3 passes through each pair of insoluble anodes 6 and 6' in the electrolytic tin plating solution 2.

The reference character 7 illustrates the electrolytic tank to supply the electroplating solution to the electroplating tank. The electrolytic tank 7 is provided with a horizontal anode 8 made of metallic tin and having the designed length and a cathode 9 as the counter electrode against the anode 8. The cathode 9 has a cylindrical form having the similar length with the anode 8 and is rotatable around center axis thereof. The surface of cathode 9 is covered with the stainless steel part 9a and the resin part 9b. For example, the surface of cathode 9 is formed in stripes having 1 mm width of stainless steel part 9a and 9mm width of resin part 9b alternatively along the circumference.

The reference character 10 illustrates the re-circulation tank. The electroplating solution conduits 11 and 11' connect the electroplating tank 1 and the re-circulation tank 10. The electroplating solution 2 in the re-circulation tank 10 is fed to the electroplating tank 1 via the pump 13. The electroplating solution conduits 12 and 12' connect the electrolytic tank 7 and the re-circulation tank 10. The electroplating solution 2 in the re-circulation tank 10 is fed to the electrolytic tank 7 via the pump 14.

The electroplating solution 2 is fed to the electrolytic tank 7 as the electrolytic solution. The cathode 9 rotates in arrowed direction. Direct current is applied between the anode 8 and the cathode 8 while the cathode 9 is rotating. The electrolytic current density on the cathode 9 becomes approximately 10 fold or more of the current density dissolving the anode 8 therewith. On the cathode 9, the reducing reaction such as hydrogen generation aggressively occurs. The difference amount of tin dissolved from the anode 8 and tin deposited on the cathode 9 is fed to the electroplating solution as tin ion. The metallic tin deposited on the surface of cathode 9 is removed by the knife installed near the cathode 9 (not shown in the figure) with the rotation of the cathode 9.

The electroplating solution 2 supplied with tin ion is introduced to the re-circulation tank 10 via the conduit 12' and is further fed to the electroplating tank 1 from the re-circulation tank 10 through the conduit 11. The steel strip 3 continuously moves through each pair of 6 and 6' positioned in the electroplating tank 1. While passing through the electroplating tank 1, tin plating layer is formed on the surface of the steel strip 3. The electroplating solution 2 overflowed from the electroplating tank 1 returns to there-circulation tank 10 via the conduit 11', which solution 2 is further recycled to the electrolytic tank 7 from the re-circulation tank 10 via the conduit 12. In this way, the electroplating solution 2 circulates among the electrolytic tank 7, recirculation tank 10, and electroplating tank 1.

Example 1

The means illustrated in Fig. 1 was employed to carry out the tin electrolysis in the electrolytic tank 7 using an acid electroplating solution with supplying tin ion (Sn^{2+}) to the plating solution. The conditions of electrolysis are given in Table 1. The electroplating solution supplied with tin ion (Sn^{2+}) was supplied to the electroplating tank 1. The tin plating layer was continuously formed on the surface of steel strip within the electroplating tank 1. The tin ion supplying current efficiency was determined based on the assumption that the weight difference of tin determined by subtracting the weight of metallic tin deposited on the cathode from the weight reduction of the anode made of metallic tin was supplied to the tin plating solution as tin ion (Sn^{2+}). The amount of tin ion supplying current efficiency which was determined agreed with the resulting increase of tin ion (Sn^{2+}) in the plating solution determined by direct titration.

Example 2

The means illustrated in Fig. 1 was employed to carry out the tin electrolysis in the electrolytic tank 7 using an alkaline electroplating solution with supplying tin ion (Sn^{4+}) to the plating solution. The conditions of electrolysis are given in Table 2. The plating solution supplied with tin ion (Sn^{4+}) was supplied to the electroplating tank 1. The tin plating layer was continuously formed on the surface of steel strip within the electroplating tank 1. The tin ion supplying current efficiency was determined based on the assumption that the weight difference of tin determined by subtracting the weight of metallic tin deposited on the cathode from the weight reduction of the anode made of metallic tin was supplied to the electroplating solution as tin ion (Sn^{4+}). The amount of tin ion supplying current efficiency which was determined agreed with the resulting increase of tin ion (Sn^{4+}) in the plating solution determined by the direct titration.

Table 1

Plating solution	Temperature of plating solution (°C)	Anode dissolving current density (A/dm ²)	Tin ion supplying current efficiency (%)
Sulfuric acid bath	30	30	80
Ferrostannate bath	40	20	71
Methane sulfonate bath	35	40	62
Cresol sulfonate bath	20	10	55
Halide (chlorinated) bath	65	50	69
Fluosilicate bath	30	15	78
Fluoborate bath	35	40	65

Table 2

Plating solution	Temperature of plating solution (°C)	Anode dissolving current density (A/dm ²)	Tin ion supplying current efficiency (%)
Potassium bath	65	8	86
Potassium bath	75	8	82
Potassium bath	85	8	79
Potassium bath	85	10	85
Sodium bath	65	5	81
Sodium bath	75	5	85
Sodium bath	85	7	88

Claims

1. A method of electroplating comprising the steps of:
 - (a) preparing an electrolytic tank (7) containing electroplating solution (2) as electrolytic solution and being provided with an anode (8) made of metallic tin and a cathode (9) as a counter electrode against said anode;
 - (b) preparing an electroplating tank (1) containing electroplating solution (2) and being provided with an insoluble anode (6), (6') and a metallic material (3) to be placed into said electroplating solution;
 - (c) forming a tin plating layer on surface of said metallic material by applying direct current between said insoluble anode and said metallic material both being placed in said electroplating tank;

(d) applying direct current between said anode and said cathode both being placed in said electrolytic tank, said anode being dissolved by electrolysis to generate tin ion to deposit on said cathode;

5 (e) controlling a tin deposition rate onto said cathode of said electrolytic tank to keep lower than the metallic tin dissolving rate of said anode, the dissolved tin ion being fed to said electroplating solution in said electrolytic tank by suppressing a tin deposition reaction and by enhancing a reducing reaction of hydrogen generation on said cathode; and

(f) supplying said electroplating solution supplied with the tin ion at said electrolytic tank to said electroplating solution in said electroplating tank.

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2. The method of electroplating of claim 1, characterized in that:

said electroplating solution in both said electrolytic tank and said electroplating tank is an acid electroplating solution; and

15 the tin deposition rate on said cathode of said electrolytic tank is controlled to be lower by at least 10% than the metallic tin dissolving rate of said anode by suppressing the tin deposition reaction and by enhancing the reducing reaction of hydrogen generation on said cathode.

3. The method of electroplating of claim 2, characterized in that the tin deposition rate on said cathode of said electrolytic tank is controlled to be lower by at least 30% than the metallic tin dissolving rate of said anode.

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4. The method of electroplating of claim 2, characterized in that said acid electroplating solution is a bath selected from the group of sulfuric acid bath, ferrostannate bath, methane sulfonate bath, cresol sulfonate bath, halide bath, fluosilicate bath, and fluoborate bath.

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5. The method of electroplating of claim 1, characterized in that

said electroplating solution in both said electrolytic tank and said electroplating tank is an alkaline electroplating solution; and

30 the tin deposition rate on said cathode of said electrolytic tank is controlled to be lower by at least 30% than the metallic tin dissolving rate of said anode by suppressing the tin deposition reaction and by enhancing the reducing reaction of hydrogen generation on said cathode.

6. The method of electroplating of claim 5, characterized in that the tin deposition rate on said cathode of said electrolytic tank is controlled to be lower by at least 50% than the metallic tin dissolving rate of said anode.

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7. The method of electroplating of claim 5, characterized in that said alkaline electroplating solution is a sodium bath or a potassium bath.

40 8. The method of electroplating of claim 1, characterized in that the controlling of the tin deposition rate on said cathode of said electrolytic tank includes controlling by raising the electrolytic current density of said cathode above the electrolytic current density of said anode made of metallic tin.

9. The method of electroplating of claim 8, characterized in that the tin deposition rate on said cathode is controlled by using a cathode comprising a metallic plate being covered with a passive layer.

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10. The method of electroplating of claim 8, characterized in that the tin deposition rate on said cathode is controlled by using a cathode having a surface structure comprising a conductive part and a insulating part.

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11. The method of electroplating of claim 8, characterized in that the tin deposition rate on said cathode is controlled by making the conductive part area of said cathode smaller than the surface area of said anode by using a cathode comprising a mesh structure.

55 12. The method of electroplating of claim 8, characterized in that the tin deposition rate on said cathode is controlled by making the surface area of said cathode smaller than the surface area of said anode by means of arranging said anode to surround said cathode.

Patentansprüche

1. Verfahren zur Elektroverzinnung, das die folgenden Schritte umfasst:
 - (a) Herstellung eines elektrolytischen Tanks (7), der eine Elektroverzinnungslösung (2) als elektrolytische Lösung enthält und mit einer Anode (8) aus metallischem Zinn und einer Kathode (9) als Gegenelektrode gegen die genannte Anode ausgerüstet ist;
 - (b) Herstellung eines Elektroplattierungstanks (1), der eine Elektroverzinnungslösung (2) enthält und mit einer unlöslichen Anode (6, 6') und mit einem metallischen Material (3), die in der genannten Elektroverzinnungslösung platziert werden, ausgestattet ist;
 - (c) Bildung einer Zinnplattierungsschicht auf der Oberfläche des genannten metallischen Materials durch Anlegen eines direkten Stroms zwischen der genannten unlöslichen Anode und dem genannten metallischen Material in besagtem Elektroplattierungstank;
 - (d) Anlegen eines direkten Stroms zwischen der Anode und der Kathode, die in dem elektrolytischen Tank platziert sind, wobei sich die Anode unter Bildung von Zinnionen elektrolytisch auflöst, die sich auf der Kathode abscheiden;
 - (e) Steuerung der Zinnabscheidungsrate auf der Kathode des elektrolytischen Tanks, so dass sie niedriger ist als die Auflösungsrate des metallischen Zinns der Anode, die aufgelösten Zinnionen werden in die Elektroverzinnungslösung im elektrolytischen Tank eingebracht, indem die Zinnabscheidungsreaktion unterdrückt und die Reduktionsreaktion der Wasserstoffbildung an der Kathode verstärkt wird; und
 - (f) Einbringung der mit Zinnionen beschickten Elektroverzinnungslösung im elektrolytischen Tank in die Elektroverzinnungslösung im Elektroplattierungstank.
2. Verfahren zur Elektroverzinnung gemäß Anspruch 1, dadurch **gekennzeichnet**, dass die Elektroverzinnungslösung sowohl im elektrolytischen Tank als auch im Elektroverzinnungstank eine saure Elektroverzinnungslösung ist, und die Zinnabscheidungsrate an der Kathode des elektrolytischen Tanks so gesteuert wird, dass sie mindestens 10 % kleiner ist als die Auflösungsrate des metallischen Zinns an der Anode durch Unterdrückung der Zinnabscheidungsreaktion und durch Steigerung der Reduktionsreaktion der Wasserstoffbildung an der Kathode.
3. Verfahren zur Elektroverzinnung gemäß Anspruch 2, dadurch **gekennzeichnet**, dass die Zinnabscheidungsrate auf der Kathode im elektrolytischen Tank so gesteuert wird, dass sie um mindestens 30 % kleiner gehalten wird als die Auflösungsrate des metallischen Zinns der Anode.
4. Verfahren zur Elektroverzinnung gemäß Anspruch 2, dadurch **gekennzeichnet**, dass die saure Elektroverzinnungslösung ein Bad ist, ausgewählt aus der Gruppe Schwefelsäurebad, Ferrostannatbad, Methansulfonatbad, Cresolsulfonatbad, Halogenidbad, Fluosilicatbad und Fluorobatbad.
5. Verfahren zur Elektroverzinnung gemäß Anspruch 1, dadurch **gekennzeichnet**, dass die Elektroverzinnungslösung sowohl im elektrolytischen Tank als auch im Elektroverzinnungstank eine alkalische Elektroverzinnungslösung ist, und die Zinnabscheidungsrate an der Kathode des elektrolytischen Tanks so gesteuert wird, dass sie mindestens 30 % kleiner gehalten wird als die Auflösungsrate des metallischen Zinns der Anode durch Unterdrückung der Zinnabscheidungsreaktion und durch Steigerung der Reduktionsreaktion der Wasserstoffbildung an der Kathode.
6. Verfahren zur Elektroverzinnung gemäß Anspruch 5, dadurch **gekennzeichnet**, dass die Zinnabscheidungsrate an der Kathode im elektrolytischen Tank so gesteuert wird, dass sie um mindestens 50 % niedriger ist als die Auflösungsrate des metallischen Zinns der Anode.
7. Verfahren zur Elektroverzinnung gemäß Anspruch 5, dadurch **gekennzeichnet**, dass die alkalische Elektroverzinnungslösung ein Natriumbad oder ein Kaliumbad ist.
8. Verfahren zur Elektroverzinnung gemäß Anspruch 1, dadurch **gekennzeichnet**, dass die Steuerung der Zinnabscheidungsrate auf der Kathode des elektrolytischen Tanks die Steuerung durch Anhebung der elektrolytischen Stromdichte der Kathode über die elektrolytische Stromdichte der Anode aus metallischem Zinn einschliesst.

9. Verfahren zur Elektroverzinnung gemäss Anspruch 8, dadurch **gekennzeichnet**, dass die Zinnabscheidungsrate der Kathode durch Verwendung einer Kathode, die eine metallische Platte umfasst, die mit einer passiven Schicht bedeckt ist, gesteuert wird.
- 5 10. Verfahren zur Elektroverzinnung gemäss Anspruch 8, dadurch **gekennzeichnet**, dass die Zinnabscheidungsrate auf der Kathode gesteuert wird durch Verwendung einer Kathode, die eine Oberflächenstruktur besitzt, die leitende Teile und isolierende Teile umfasst.
11. Verfahren zur Elektroverzinnung gemäss Anspruch 8, dadurch **gekennzeichnet**, dass die Zinnabscheidungsrate auf der Kathode dadurch gesteuert wird, dass die Fläche des leitenden Teils der Kathode durch Verwendung einer Kathode, die eine Gitterstruktur umfasst, kleiner gemacht wird als die Oberfläche der Anode.
12. Verfahren zur Elektroverzinnung gemäss Anspruch 8, dadurch **gekennzeichnet**, dass die Zinnabscheidungsrate an der Kathode dadurch gesteuert wird, dass die Oberfläche der Kathode durch eine Anordnung kleiner als die Oberfläche der Anode gemacht wird, bei der die Anode die Kathode umgibt.

Revendications

- 20 1. Procédé d'électro-étamage comportant les étapes consistant à:
(a) préparer un réservoir d'électrolyse (7) contenant une solution d'électro-étamage (2) sous la forme d'une solution électrolytique et doté d'une anode (8) réalisée en étain métallique et d'une cathode (9) servant de contre-électrode vis-à-vis de ladite anode;
(b) préparer un réservoir d'électro-plaquage (1) contenant une solution d'électro-étamage (2) et doté d'une anode insoluble (6), (6') et d'un matériau métallique (3) à placer dans ladite solution d'électro-étamage;
(c) former une couche de plaquage d'étain à la surface dudit matériau métallique en appliquant un courant continu entre ladite anode insoluble et ledit matériau métallique, tous deux placés dans ledit réservoir d'électro-plaquage;
(d) appliquer un courant continu entre ladite anode et ladite cathode, toutes deux placées dans ledit réservoir d'électrolyse, ladite anode étant dissoute par électrolyse pour produire des ions étain à déposer sur ladite cathode;
(e) contrôler la vitesse de dépôt de l'étain sur ladite cathode dudit réservoir d'électrolyse, pour la maintenir inférieure à la vitesse de dissolution de l'étain métallique de ladite anode, les ions d'étain en solution étant introduits dans ladite solution d'électro-étamage dans ledit réservoir d'électrolyse en freinant une réaction de dépôt de l'étain et en renforçant une réaction de réduction avec production d'hydrogène sur ladite cathode; et
(f) fournir ladite solution d'électro-étamage, approvisionnée en ions d'étain dans ledit réservoir d'électrolyse, à ladite solution d'électro-étamage dans ledit réservoir d'électro-plaquage.
- 40 2. Procédé d'électro-étamage selon la revendication 1, caractérisé en ce que ladite solution d'électro-étamage dans ledit réservoir d'électrolyse et dans ledit réservoir d'électro-étamage est une solution acide d'électro-étamage; et la vitesse de dépôt de l'étain sur ladite cathode dudit réservoir d'électrolyse est contrôlée de manière à être inférieure d'au moins 10% à la vitesse de dissolution de l'étain métallique de ladite anode, en freinant la réaction de dépôt de l'étain et en renforçant la réaction de réduction avec production d'hydrogène sur ladite cathode.
- 45 3. Procédé d'électro-étamage selon la revendication 2, caractérisé en ce que la vitesse de dépôt de l'étain sur ladite cathode dudit réservoir d'électrolyse est contrôlée de manière à être inférieure d'au moins 30% à la vitesse de dissolution de l'étain métallique de ladite anode.
- 50 4. Procédé d'électro-étamage selon la revendication 2, caractérisé en ce que ladite solution acide d'électro-étamage est un bain choisi dans le groupe constitué d'un bain d'acide sulfurique, d'un bain de ferrostannate, d'un bain de sulfonate de méthane, d'un bain de sulfonate de crésol, d'un bain d'halogénure, d'un bain de fluorosilicate et d'un bain de fluoroborate.
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5. Procédé d'électro-étamage selon la revendication 1, caractérisé en ce que ladite solution d'électro-étamage dans ledit réservoir d'électrolyse et dans ledit réservoir d'électro-étamage est une solution alcaline d'électro-étamage; et la vitesse de dépôt de l'étain sur ladite cathode dudit réservoir d'électrolyse est contrôlée de manière à être inférieure à la vitesse d'au moins 30% de dissolution de l'étain métallique de ladite anode, en freinant la réaction de dépôt de l'étain et en renforçant la réaction de réduction avec production d'hydrogène sur ladite cathode.
6. Procédé d'électro-étamage selon la revendication 5, caractérisé en ce que la vitesse de dépôt de l'étain sur ladite cathode dudit réservoir d'électrolyse est contrôlée de manière à être inférieure d'au moins 50% à la vitesse de dissolution de l'étain métallique de ladite anode.
7. Procédé d'électro-étamage selon la revendication 5, caractérisé en ce que ladite solution alcaline d'électro-étamage est un bain de sodium ou un bain de potassium.
8. Procédé d'électro-étamage selon la revendication 1, caractérisé en ce que le contrôle de la vitesse de dépôt de l'étain sur ladite cathode dudit réservoir d'électrolyse comprend un contrôle par augmentation de la densité du courant d'électrolyse à ladite cathode au-delà de la densité du courant d'électrolyse à ladite anode réalisée en étain métallique.
9. Procédé d'électro-étamage selon la revendication 8, caractérisé en ce que la vitesse de dépôt de l'étain sur ladite cathode est contrôlée en utilisant une cathode comportant une plaque métallique recouverte d'une couche passive.
10. Procédé d'électro-étamage selon la revendication 8, caractérisé en ce que la vitesse de dépôt de l'étain sur ladite cathode est contrôlé en utilisant une cathode présentant une structure de surface comportant une partie conductrice et une partie isolante.
11. Procédé d'électro-étamage selon la revendication 8, caractérisé en ce que la vitesse de dépôt de l'étain sur ladite cathode est contrôlé en rendant la superficie de la partie conductrice de ladite cathode plus petite qu'une superficie de ladite anode, en utilisant une cathode comportant une structure maillée.
12. Procédé d'électro-étamage selon la revendication 8, caractérisé en ce que la vitesse de dépôt de l'étain sur ladite cathode est contrôlée en rendant la superficie de ladite cathode inférieure à la superficie de ladite anode, au moyen d'un agencement de ladite anode autour de ladite cathode.

FIG. 1

