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(54) Process for electroplating zinc alloy and apparatus employed therefor.

(57) Disclosed herein are a process for electroplating a zinc alloy which comprises disposing in an electrolytic cell (10) a gas diffusion electrode apparatus (g) comprising a plurality of gas diffusion electrodes (1) which function as an anode and are formed by a gas diffusion layer (2) and a reaction layer (3) being attached together, and an electroconductive reinforcing frame (4) to which the gas diffusion electrodes (1) are supported; forming a zinc alloy plating bath on the reaction layer side of the electrolytic cell which functions as anode chamber; supplying electricity to the gas diffusion electrodes through the reinforcing frame while supplying a hydrogen gas to the electrolytic cell of the gas diffusion layer side; and electroplating a steel (16) with the zinc alloy by passing the steel as a cathode material through the zinc alloy bath; and an apparatus employed therefor.

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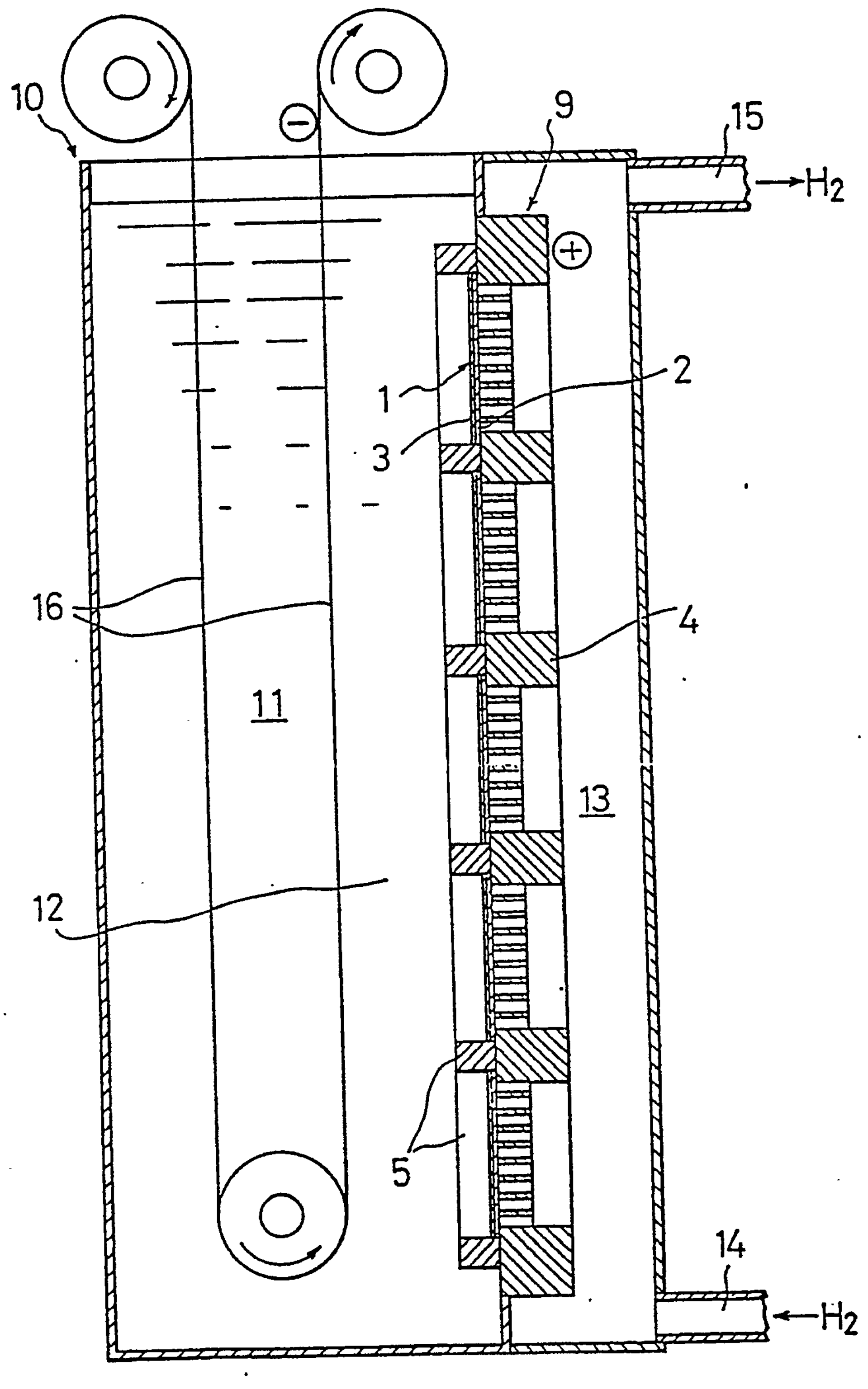
Fig. 2



PROCESS FOR ELECTROPLATING ZINC ALLOY AND APPARATUS EMPLOYED THEREFOR

Background of the Invention

The present invention relates to a process for electro plating a zinc alloy and a gas diffusion electrode apparatus employed therefor.

In these days, as a surface treated steel having a soft plating surface, stretchablity, good affinity for a paint coating and excellent rust prevention effect which require no heat treatment in a field of automobiles, construction materials, appliances and the like, steels which are electroplated with such an alloy as zinc-iron, zinc-cobalt, zinc-nickel and zinc-manganese have attracted public attention. Zinc-iron plating will be described.

There are two processes for electroplating of a zinc-iron alloy, one of which employs a plating bath containing sulfates of zinc and iron while the other employs a plating bath containing chlorides of zinc and iron. In case of the sulfate bath, such problems exist that liquid resistance is high and the deposition efficiency on a cathode is low because the pH is as low as 1.0. On the other hand, in case of the chloride bath, such advantages exist that liquid resistance is lower than that of the sulfate bath, the deposition efficiency on a cathode is good and the appearance is smooth.

However, in case of the chloride bath, a chlorine gas which is harmful to an anode evolves.

In case of the process for electroplating the zinc-iron alloy in which a titanium electrode plated with iridium or platinum is employed as an anode, the life of the electrode is as short as several thousand hours because the oxygen evolution occurs on the iridium or platinum-plated anode. The valency of the iron ion in the plating bath increases in spite of the supplement of the plating solution because the iron ion is oxidized on the anode. For this reason, the plating solution in the plating bath is circulated to an electrolytic reduction apparatus equipped with an ion exchange membrane to reduce Fe^{3+} to Fe^{2+}. Even by this procedure, the zinc, the iron ion and the pH of the plating bath become unbalanced so that, because the plating thickness may change and part of the surface may become rough, large steel companies discharge about two ton/day of the plating solution that causes serious loss.

Since the steel electroplated with the zinc-iron alloy moves at high speed of 200 m/min. in the small plating bath, the anode cannot be used if the mechanical strength is insufficient. The anode may be scratched and sparks when the anode contacts the steel.

Summary of the Invention

An object of the present invention is to provide a process for electroplating a steel with a zinc alloy and a gas diffusion electrode apparatus employed therefor which do not evolve an oxygen gas nor a harmful chlorine gas on an anode.

Another object of the invention is to provide the said process and apparatus which do not require the discharge of a plating solution.

A further object of the invention is to provide the said process and apparatus which do not produce a scratch nor a spark.

The process for electroplating a zinc-iron alloy according to the present invention for overcoming the above problems comprises disposing in an electrolytic cell a gas diffusion electrode apparatus comprising a plurality of gas diffusion electrodes which function as an anode and are formed by a gas diffusion layer and a reaction layer being attached together, and an electroconductive reinforcing frame to which the gas diffusion electrodes are supported ; forming a zinc alloy plating bath on the reaction layer side of the electrolytic cell which functions as anode chamber ; supplying electricity to the gas diffusion electrodes through the reinforcing frame while supplying a hydrogen gas to the electrolytic cell of the gas diffusion layer side ; and electroplating a steel with the zinc alloy by passing the steel as a cathode material through the zinc alloy bath.

The gas diffusion electrode apparatus of this invention comprises a plurality of gas diffusion electrodes supported in an electroconductive reinforcing frame ; the gas diffusion electrode comprising a gas diffusion layer formed by hydrophobic carbon black and fluorine resin, and a reaction layer formed by hydrophilic carbon black supported with a catalyst or catalyst particles and hydrophobic carbon black and fluorine resin attached together.

Since in the process for electroplating the zinc alloy of this invention the gas diffusion electrode is employed as an anode and the hydrogen gas is supplied to the gas diffusion layer side of the gas diffusion electrode to make an anode reaction of the plating bath to a hydrogen oxidation reaction, no oxygen evolves on the anode in case of the sulfate bath and no chlorine gas evolves on the anode so that a smooth and gorgeous zinc alloy plating layer without burning can be formed on the steel passing through the plating bath. Further, ions in the plating bath such as iron, cobalt, manganese and the like are not oxidized on the anode, and even if they are oxidized on the anode to be contaminated in the plating bath in the form of their ions, these ions are reduced by the gas diffusion electrode to lower their ionic valency so that the zinc ion and the pH of the plating bath are never unbalanced. Accordingly, the plating bath can be effectively employed without the discharge of the plating solution, and the plating thickness of the zinc-iron alloy applied to the steel does not change and the surface does not partially become rough.

Since a plurality of the gas diffusion electrodes are supported in the electroconductive reinforcing frame employed in the process for electroplating such an alloy as zinc-iron, zinc-cobalt, zinc-manganese and the like as mentioned before, the mechanical strength of the gas diffusion electrode functioning as an anode is elevated. Therefore, if the steel moves at high speed in the small plating bath, the gas diffusion electrode is never flapped nor scratched and does not generate a spark.

Brief Description of the Drawings

Figs. 1 a and b show one embodiment of a gas diffusion electrode apparatus according to the present invention, Fig. 1 a being its plan view and Fig. 1 b being an A-A sectional view of Fig, 1 a ; and

Fig. 2 shows one embodiment of a zinc-alloy electroplating bath employing the gas diffusion electrode apparatus of Fig. 1.

Detailed Description of the Invention

One embodiment of the gas diffusion electrode apparatus is explained referring to Figs. 1a and 1b in which 1 designates a rectangular gas diffusion electrode. The gas diffusion electrode 1 is formed by a gas diffusion layer 2 and a reaction layer 3 attached together, the gas diffusion layer 2 consisting of hydrophobic carbon black and polytetrafluoroethylene, and the reaction layer 3 consisting of hydrophilic carbon black carrying a platinum catalyst, hydrophobic carbon black and polytetrafluoroethylene. A plurality of the gas diffusion electrodes 1, 10 electrodes in this embodiment, are installed and supported in an electroconductive reinforcing frame made of titanium, copper, stainless and the like, in a lattice reinforcing frame 4 made of titanium in this embodiment. A protection member 5 is formed on the front surface of the reinforcing frame 4 at the reaction layer 3 side of the gas diffusion electrode 1.

A gas diffusion electrode apparatus 9 employing the thus constructed gas diffusion electrode is disposed as an anode in an electrolytic cell 10, and a chloride bath 12 was filled in the cell 11 formed in the reaction layer 3 side of the gas diffusion electrode 1 functioning as an anode chamber. A hydrogen gas was successively introduced into the cell 13 in the gas diffusion layer 2 side of the gas diffusion electrode 1 from an introducing port 14 so as to successively suplly the hydrogen gas to the gas diffusion layer 2 side of the gas diffusion electrode apparatus 9 and to simultaneously discharge the hydrogen gas from the gas diffusion electrode 1 to a discharge port 15 through the cell 13. At the same time, the current is flown to the respective gas diffusion electrodes 1 through the reinforcing frame 4. Under this circumstance, a steel 16 as a cathode material is passed through the plating bath 12 of the cell 11 at a relatively high speed.

Since the gas diffusion electrode 1 is employed as an anode while supplying the hydrogen gas to the gas diffusion layer 2 side of the gas diffusion electrode 1 so as to make the anode reaction of the chloride plating bath 12 to the hydrogen oxidation reaction, no chlorine gas was evolved on the anode. The zinc-iron alloy layer plated on the steel 16 is examined to have a smooth and gorgeous surface without burning. When the steel is successively forwarded to effect the electroplating of the zinc-iron alloy, no iron ion was oxidized on the anode from Fe^{2+} to Fe^{3+}. Even if Fe^{3+} is contaminated in the plating bath 12, the zinc, the iron ion and the pH does not become unbalanced because Fe^{3+} is reduced on the gas diffusion electrode 1 to Fe^{2+}. Accordingly, the circulation of the plating solution of the plating bath 12 to the electrolytic reduction apparatus equipped with the ion exchange membrane is unnecessary, and the plating solution of the plating bath 12 can be effectively used without being discharged. No change of the thickness of the zinc-iron alloy layer plated on the steel 16 is generated, and no partial roughness on the surface is found.

Since the gas diffusion electrodes 1 functioning as an anode are supported in the reinforcing frame 4 so as to elevate the mechanical strength, the electrodes are not flapped nor bent even when the steel 16 moves in the small plating bath 12 at a speed as high as 200 m/min. Since the protection member 5 may be formed on the front surface of the reinforcing frame 4, the moving steel 16 is not in contact with the gas diffusion electrode 1 so that the scratches and sparks are not produced.

The invention will now be illustrated by Examples which, however, are to be considered a merely exemplary of practice of the invention, and not as delimitive thereof.

Example

A gas diffusion electrode 1 having a length of 100 mm and a width of 100 mm was formed by a gas diffusion layer 2 of which a thickness was 500 μ m and a reaction layer 3 of which a thickness was 100 μ m attached together, the gas diffusion layer 2 consisting of hydrophobic carbon black of which an average particle size was 420 Å and polytetrafluoroethylene of which an average particle size was 0.3 μ m, and the reaction layer 3 consisting of hydrophilic carbon black of which an average particle size was 420 Å carrying a platinum catalyst of 0.56mg/cm^2, hydrophobic carbon black of which an average particle size was 420 Å and polytetrafluoroethylene of which an average particle size was 0.3 μ m. Ten gas diffusion electrodes 1 were installed and supported in an electroconductive reinforcing frame 4 made of titanium. A protection member 5 was equipped on the front surface of the reinforcing frame 4 at the reaction layer 3 side of the gas diffusion electrode 1.

As shown in Fig. 2, a gas diffusion electrode apparatus 9 was disposed in an electrolytic cell 10, and a chloride bath 12 consisting of 50g/liter-$FeCl_2 \cdot nH_2O$, 245g/liter-$ZnCl_2$, 1.5g/liter-$NaPH_2O_2$ (pH=3.0) was filled in the cell 11 formed in the reaction layer 3 side of the gas diffusion electrode 1. A hydrogen gas was successively introduced into the cell 13 in the gas diffusion layer 2 side of the gas diffusion electrode 1. At the same time, the current was flown to the respective gas diffusion electrodes 1 through the reinforcing frame 4. Under this circumstance, a steel 16 as a cathode material was passed through the plating bath 12 of the cell 11 at the rate of 200m/min., at a current density of 150 A/dm^2 and a bath voltage of 8.6 V so that the steel 16 was electroplated with the zinc-iron alloy layer having a thickness of 4 μ m.

Since the gas diffusion electrode 1 was employed as an anode supplying the hydrogen gas to the gas diffusion layer 2 side of the gas diffusion electrode 1 so as to make the anode reaction of the chloride plating bath 12 to the hydrogen oxidation reaction, no chlorine gas was evolved on the anode. The zinc-iron alloy layer plated on the steel 16 was examined to have a smooth and gorgeous surface without burning. When the steel was successively forwarded to effect the electroplating of the zinc-iron alloy, no iron ion was oxidized on the anode from Fe^{2+} to Fe^{3+}. Even if Fe^{3+} was contaminated in the plating bath 12, the zinc, the iron ion and the pH did not become unbalanced because Fe^{3+} was reduced on the gas diffusion electrode 1 to Fe^{2+}. Accordingly, the circulation of the plating solution of the plating bath 12 to the electrolytic reduction apparatus equipped with the ion exchange membrane was unnecessary, and the plating solution of the plating bath 12 could be effectively employed without being discharged. No change of the thickness of the zinc-iron alloy layer plated on the steel 16 was generated, and no partial roughness on the surface was found.

Since the gas diffusion electrodes 1 functioning as an anode were supported in the reinforcing frame 4 so as to elevate the mechanical strength, the electrodes were not flapped nor bent even when the steel 16 moved in the small plating bath 12 at a speed as high as 200 m/min. Since the protection member 5 was formed on the front surface of the reinforcing frame 4, the moving steel 16 was not in contact with the gas permeable electrode 1 so that the scratches and sparks were not produced.

Similar results were obtained when a sulfate bath was used in place of the chlorine bath.

Although the present invention has been described in its preferred Example, it is understood that the invention is not restricted thereto, and various changes and the modifications may be made in the present invention by those skilled in the art without departing from the spirit and scope of the present invention.

Claims

1. A process for electroplating a zinc alloy which comprises disposing in an electrolytic cell a gas diffusion electrode apparatus comprising a plurality of gas diffusion electrodes which function as an anode and are formed by a gas diffusion layer and a reaction layer being attached together, and an electroconductive reinforcing frame to which the gas diffusion electrodes are supported ; forming a zinc alloy plating bath on the reaction layer side of the electrolytic cell which functions as anode chamber ; supplying electricity to the gas diffusion electrodes through the reinforcing frame while supplying a hydrogen gas to the electrolytic cell of the gas diffusion layer side ; and electroplating a steel with the zinc alloy by passing the steel as a cathode material through the zinc alloy bath.

2. A gas diffusion electrode apparatus which comprises a plurality of gas diffusion electrodes supported in an electroconductive reinforcing frame; the gas diffusion electrode comprising a gas diffusion layer formed by hydrophobic carbon black and fluorine resin, and a reaction layer formed by hydrophilic carbon black supported with a catalyst or catalyst particles and hydrophobic carbon black and fluorine resin, attached together.

Fig. 1 a

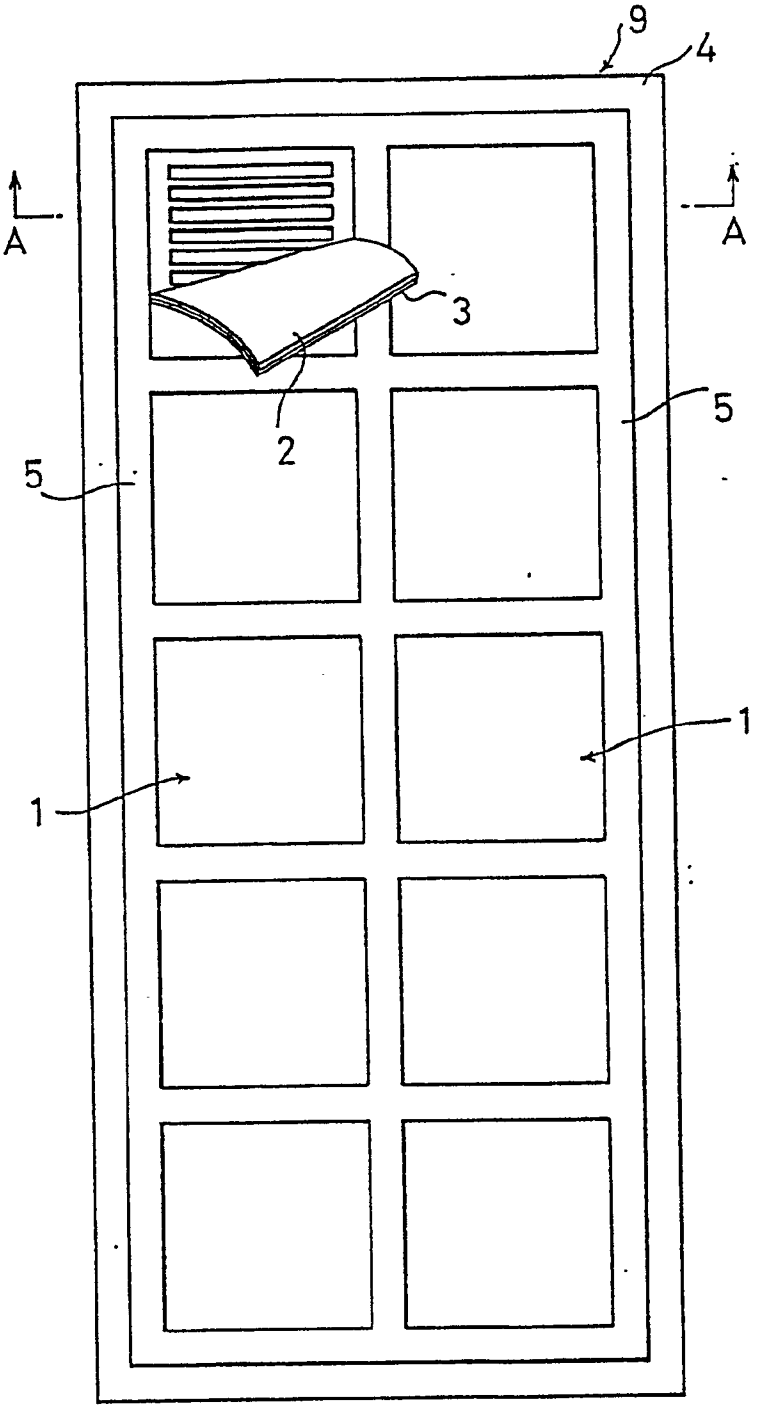


Fig. 1 b

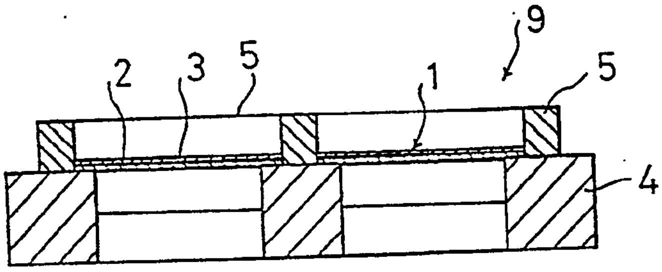


Fig. 2