FIG. 1

Temp. 160°C

Current Efficiency (%)

HCl Gas Pass Volume cc/min/Liter Bath

FIG. 2

Anode/Cathode

○ 1:1

□ 1:1

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FIG. 3

Current Efficiency (%) vs. Bath Temperature °C

Bath Temperature °C

FIG. 4

Current Efficiency (%) vs. Mol % AlCl₃

Mol % AlCl₃

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METHOD OF ELECTROPLATING ALUMINUM IN A BATH OF MOLTEN SALTS

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ABSTRACT OF THE DISCLOSURE

In a method of electroplating aluminum in a bath of fused salts, aluminum ions of low valence formed in the bath during a plating operation are oxidized into trivalent aluminum ions to prevent the bath from degrading. The oxidation can be effected concurrently with the normal electroplating operation or during interruption there-of.

RELATED APPLICATIONS


FIELD OF THE INVENTION

This invention relates to a method of electroplating aluminum in a bath of molten salts. Aluminum ions of a low atomic valence formed in the bath during the plating operation are oxidized to form trivalent aluminum ions to perform the plating operation while increasing the current efficiency and preventing precipitation of coarse crystals of the dendritic structure, thus providing excellent and dense aluminum platings.

BACKGROUND OF THE INVENTION

Heretofore, in the electroplating of aluminum in a bath of fused salts, many efforts have been made to maintain high electrolytic efficiency, to prevent deterioration of the bath, and to prevent deposition of dendritic products. However, as is well known in the art, prevention of the deterioration of the bath is extremely difficult and the tendency of depositing flaky or powdery aluminum of poor adhesiveness increases gradually, thus greatly reducing the current efficiency of electrolysis.

We have already proposed to supply hydrogen ions into the bath for the purpose of eliminating these problems. Continuous introduction of hydrogen chloride gas into the bath as the source of hydrogen ions has been found to be considerably effective. For example, FIG. 1 shows the relation between the HCl gas pass volume and current efficiency under the conditions of a one-liter bath containing a mixture comprising 58 mol percent of AlCl₃ and 42 mol percent of NaCl, 10 minutes of HCl gas pass time, a temperature of 160°C, and a bath voltage of 500 mv. This method, however, has not always been satisfactory in that degradation occurred owing to strong corrosive action of the hydrogen chloride gas, operating costs were increased, and homogeneous plating of a thickness of more than 30 microns was difficult to achieve even when the bath was stirred.

It is therefore an object of this invention to provide a novel method of aluminum plating which can eliminate the difficulties described above, particularly preventing deterioration of the bath over long periods of time, and to provide plated products of excellent quality.

SUMMARY OF THE INVENTION

In accordance with the present invention, the plating operation is improved by oxidizing unstable aluminum ions of low valence. Although such a method of electrolytic oxidation has been used in the electrolysis of aqueous solutions, it has not been utilized in the electrolysis of fused salts.

When an electroplating operation of aluminum in a fused salt bath is operated continuously, an aluminum anode or aluminum which has been deposited on a steel plate will be dissolved in the bath to form a metal mist or aluminum ions of low valence which gradually increase. This degrades the bath with the result that the deposited aluminum will assume a flaky or powdery form having poor adhesion to the steel plate. Accordingly, such plated aluminum can be readily peeled off by washing the steel plate with water, thus exposing underlying metal.

SPECIFIC EMBODIMENTS OF THE INVENTION

According to the plating method of the present invention the tendency of forming such aluminum ions of low valence in the bath is greatly reduced by utilizing oxidation. If any of such ions are formed, they are immediately oxidized so that the aluminum deposited on the cathode forms a flat, strong and dense coating.

The presence of low valence aluminum and the oxidation thereof are based on the following experimental results. Electroplating is conducted at a temperature of 160°C in a fused salt bath of conventional composition, wherein Pt-AI electrodes are positioned to determine the variation of the voltage between said electrodes. The measured voltage indicates 1100 mv. initially and gradually decreases to 1000 mv., when low valence aluminum is formed and deteriorates the bath composition. At this moment, therefore, a Pt-anode is inserted into the bath with DC current flow and said bath compositions are oxidized twice for 10 minutes, respectively. As a result, the voltage increases to 1890 mv. due to the fact that low valence aluminum is oxidized to trivalent aluminum.

According to a first feature of this invention, in addition to a conventional electrolytic device, a platinum wire anode and an aluminum cathode are immersed in the bath, and these electrodes are connected to a DC source to oxidize a metal mist or aluminum ions of low valence.

According to a second feature of this invention, the surface area of the aluminum anode electrode is decreased to increase the voltage near the anode electrode thereby imparting the ability of electrolytic oxidation to the aluminum electrode itself.

The following table shows test results under conditions wherein the ratio of anode area to cathode area is in the range of 1:2 to 1:11.

| Table 1                  | 1:1 | 1:2 | 1:4 | 1:11
|--------------------------|-----|-----|-----|-----
| Bath voltage (mv.)       |     |     |     |     
|                          | 620 | 530 | 530 | 1,000
|             | 60 | 56 | 60 | 60

Table 1

1 Rough surface.
2 Compact smooth surface.

The voltage measured at every 1.5 cm. from the anode to the cathode is shown in FIG. 2. The results shown in FIG. 2 are based on the conditions where either bar or plate anode and steel cathode are used, keeping cathode current density at approximately 2 a./dm.², and HCl gas...
is blown through the electroplating bath at a rate of 80 cc./min. per liter of the bath. This graph demonstrates that the voltage near the anode increases remarkably in the case where the ratio of anode area to cathode area is 1:11.

According to a third feature, in addition to a conventional electrolytic plating, a selected plating bath for electrolytic oxidation is immersed in the bath and an alternating current is superimposed between an article to be plated and this platinum electrode.

The following specific examples are given by way of illustration, and are not to be construed as limiting in any way the scope and spirit of the invention.

**EXAMPLES**

A cylindrical glass beaker is used for a plating cell and is heated from the bottom thereof so as to keep the temperature of fused salt at 150° C. The beaker is covered with a lid made of heat resistant electric insulator with holes to hold electrodes. The plating bath composition gradually deteriorates upon contact with the atmosphere. To insure long use, therefore, the bath surface is covered with N₂ gas, HCl gas, Ar gas or the like to prevent direct contact with the atmosphere. Steel plates to be plated are rinsed and dried beforehand after conventional cleaning and plating. The bath contains anhydrous AlCl₃ and dry NaCl and KCl without moisture.

Experiments are made in accordance with the following procedure. The bath contains a mixture comprising 54 to 62 mol percent of anhydrous AlCl₃, 25 to 46 mol percent of NaCl and 0 to 21 mol percent of KCl. Approximately one liter of the above mixture is poured into the plating cell, in which an Al anode and a steel cathode to be plated are picked. A slender glass tube is positioned in the plating bath to afford fine bubbles of HCl. The metal to be plated is cleaned by conventional methods. Electroplating is conducted for up to 10 minutes to 5 hours at a bath temperature of 150 to 160°C, and at a plating current density of approximately 2.0 to 2.4 A/dm² for the cathode area. When a Pt-Al electrode is used to oxidize the aluminum ion, 2 to 7 V. of direct current are passed to the one liter bath, and when alternating current is passed to a Pt-Fe electrode, alternating current of 50 cycles and 1.3 to 9.2 V. and 4 to 11 A. are flowed to the same.

After plating, the cathode is taken out of the bath and washed with water. The thickness of the resulting plating layer is measured so that current efficiency can be calculated. The conditions during plating are carefully observed. The temperature of the plating bath ranges from 150°C to 160°C in accordance with the experimental results shown in FIG. 3. The electroplating in FIG. 3 is conducted in the plating bath under the conditions where plating voltage is 500 mv. and HCl gas blown is 40 cc./min./l.1 bath. The main bath composition comprises 54 to 62 mol percent of AlCl₃ and the balance is NaCl and KCl.

**FIG. 4 shows variant current efficiencies according to AlCl₃ content of the bath, under the cathode current densities of 2.1 A./dm², 2.9 A./dm² and 3.7 A./dm².**

**Example 1**

One liter of fused salts consisting of 60 mol percent of aluminum chloride, 25 mol percent of sodium chloride and 15 mol percent of potassium chloride was maintained at a temperature of 160°C, and a steel plate 100 mm. long, 50 mm. wide and 0.2 mm. thick was immersed in this bath as the cathode. Two aluminum plates having the same dimensions as the steel plate were disposed on each side of the steel plate as anodes and a direct current of 2 A./dm² was passed between both electrodes to effect electrolytic plating. During repeated use the bath degraded gradually, and on the 10th plating finally dendritic aluminum was deposited which could be readily peeled off from the plate by washing.

When hydrogen chloride gas was passed through the degraded bath at a rate of 50 cc./min. and a platinum plate anode 100 mm. x 80 mm. x 0.1 mm. and an aluminum wire (diameter of 1 mm.) acting as the cathode electrode, were immersed in the bath and a DC potential of 2 volts was applied across these electrodes for 20 minutes. At first a relatively large current of 2 A. was noted, but the current decreased gradually to 70 ma. after 20 minutes.

At this stage, the flow of hydrogen chloride gas and current through the platinum plate was stopped. Thereafter, electrolytic plating was resumed with a conventional electrolytic plating device; no deposition of the dendritic structure was found; rather, a highly adhesive dense aluminum coating was found on the steel plate.

In the absence of oxidation by the platinum plate, even when about 10 times the quantity of hydrogen chloride gas was introduced, we got far inferior plating to that obtained by this invention.

Even after the above described oxidation process was applied and the bath was supposed to be improved, when plating operations were repeated without current through the platinum plate for the purpose of oxidation, the bath was found to degrade gradually. In this example, the 20th steel plate showed unsatisfactory plating.

However, when plating operations were repeated while passing current through the platinum plate, no unsatisfactory plating was formed after many operations.

**Example 2**

Five liters of fused salts consisting of 62 mol percent of aluminum chloride and 38 mol percent of sodium chloride were maintained at a temperature of 150°C. A steel plate, 170 mm. long, 100 mm. wide and 0.6 mm. thick, and acting as the cathode, and two aluminum rods, 3 mm. diameter and 25 cm. long, and acting as the anode electrodes, were immersed in the fused bath. While passing hydrogen chloride gas through the bath at a rate of 80 to 100 cc./min., electrolytic plating was carried out at a current density of 2 A./dm² for 5 hours.

Again, deposition of dendritic aluminum was not noted and a flat and dense coating was produced having a surprisingly large thickness of 70 microns.

Such a thick plating cannot be attained when an aluminum anode of a large surface area is used in accordance with prior practice. Under ordinary plating conditions, a plating layer of only 10 microns can be obtained.

**Example 3**

Five liters of fused salts consisting of 62 mol percent of aluminum chloride, and 38 mol percent of sodium chloride were maintained at a temperature of 160°C. A steel plate 200 mm. long, 100 mm. wide and 0.2 mm. thick was immersed in the bath to act as the cathode electrode. Aluminum plates 100 mm. wide, 1 mm. thick and 200 mm. long each, were immersed in the bath on both sides of the steel plate to act as anode electrodes. Further, a platinum wire having a diameter of 0.5 mm. and a length of 2000 mm. was coiled about the steel plate without contacting it, and an alternating current of about 50 cycles, 3 volts, 6 a., was applied between this coil of platinum wire and the steel plate. While passing hydrogen chloride gas through the bath at a rate of 80 to 100 cc./min., a direct current (2 A./dm²) was passed through said steel plate (cathode electrode) and aluminum plates (anode electrodes) for 30 minutes to effect electrolytic plating. The quantity of the plating was excellent and a uniform and dense coating was obtained.

When the electrolytic operation was performed without passing alternating current between the platinum coil and the steel plate, deposition of fine, flaky aluminum was noted after three steel sheets of the above dimensions were successively plated. However, by passing alternating current the bath gradually recovered, thus providing an excellent aluminum coating. It was also noted that the same
result could be obtained by merely dipping a straight platinum wire instead of forming it into a coil.

Example 4

5 liters of the mixture comprising 62 mol percent of AlCl₃ and 38 mol percent of NaCl are poured into the electroplating bath and are heated to a temperature of approximately 160° C. Ti-alloy (6 Al—4 v. Ti-alloy) of 150 mm. length, 100 mm. width and 1 mm. thickness is used as a plate material and washed in a nitric acid, hydrogen fluoride mixture and then washed in and dried. This material is charged with alternating current of 50 cycles and 2 a./dm.² for 5 minutes, and is plated under a direct current of 2 a./dm.² for 20 minutes. Consequently, a plating layer of aluminum of approximately 5 microns is formed.

The examples set forth above can be summarized as follows:

According to Example 1, oxidizing means comprising the platinum plate anode oxidizes the metal mist or aluminum ions of low valence formed in the fused bath thus forming homogeneous coatings on the steel plate.

According to Example 2, the surface area of the aluminum anode itself is reduced to increase the anodic voltage and current density near the anode thus providing the function of electrolytic oxidation for the aluminum anode itself.

Whereas, according to Example 3, alternating current and direct current are superimposed through the article to be plated so as to act for one period as the cathode and the next period as the anode. During the periods in which the article acts as the anode, electrolytic oxidation is realized.

Thus, this invention is characterized by providing an electrolytic plating of aluminum after aluminum ions of low valence have been oxidized or while they are being oxidized.

Although in each of Examples 1–3 illustrated hereinabove, hydrogen chloride gas is blown into the bath during the plating operation, it should be understood that this is to effectively regenerate the bath and hence to prevent deterioration thereof and that blowing of said gas is an advantageous factor of this invention. As shown by Example 4, hydrogen chloride gas can be omitted. The present techniques are applicable not only to steel but also any other kind of metal under the above conditions as shown in FIG. 4. The essential matter of this invention lies in the feature that aluminum is separated out of the fused salt.

As can be noted from foregoing description it is evident that this invention provides a novel method of electroplating aluminum with fused salts which can form, under stabilized operating conditions, flat and dense aluminum coatings which adhere strongly to the base metal and which can withstand severe mechanical working or handling. Moreover, the useful life of the bath is prolonged.

It will be clear to those skilled in the art that this invention is not limited to specific base metals, particular configurations, dimensions, current or voltage values described above. In addition to batch processes shown above, the invention is also applicable to continuous processes.

What is claimed is:

1. A method of electroplating aluminum in a bath of fused salt in which aluminum is positioned as an anode and the material to be plated as a cathode, comprising applying direct current to additional electrodes positioned in said bath, one additional electrode being an anode of platinum and another additional electrode being a cathode of aluminum, to oxidize low valency aluminum ions produced in the bath.

2. The method of claim 1, wherein the material is a metal.

3. The method of claim 1, wherein the metal is steel.

4. The method of electroplating aluminum according to claim 1, wherein said application of direct current is carried out concurrently with the normal electroplating step.

5. A method of electroplating aluminum in a bath of fused salt with aluminum as anode and material to be plated as cathode, comprising applying alternating current to an additionally inserted electrode of platinum and said material to be plated in order to oxidize low valency aluminum ion produced in the bath.

6. The method of claim 5, wherein the material is a metal.

7. The method of claim 5, wherein the material is steel.

8. A method of electroplating aluminum in a bath of fused salt with aluminum as anode and material to be plated as cathode, comprising maintaining a ratio of surface area of said anode to said cathode in the range of 1:2 to 1:1 to increase the voltage of said anode.

9. The method of claim 8, wherein the material is a metal.

10. The method of claim 8, wherein the material is steel.

References Cited

UNITED STATES PATENTS
2,807,575 9/1957 Chariton et al. ........... 204—39

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204—67, 231