ALUMINUM PLATING PROCESS

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ABSTRACT

Aluminum plating according to which aluminum film formed has no cracks and pin-holes on its surface, a uniform thickness, excellent luster and is strongly bonded to the substrate can be attained by heat treating a substrate covered with aluminum at 400°C the melting point of aluminum for 10 seconds 30 minutes in an inert atmosphere said heat treatment being preceded by or followed by treating of the covered substrate with a surface treating agent comprising active hydrogen-containing compound, oxygen or halogen and thereafter taking out thus treated substrate into the air.

38 Claims, No Drawings
This invention relates to an aluminum plating process and more particularly it concerns a process for effecting excellent aluminum plating on a substrate by contacting a heated substrate with an alkyl aluminum compound to cause thermal decomposition of said alkyl aluminum.

By the term "a substrate covered with aluminum" is meant a substrate which has been covered with aluminum produced by thermal decomposition of an alkyl aluminum compound which is caused by contact of the heated substrate with the alkyl aluminum compound, but which has not yet been taken out into the air.

It has been proposed by K. Ziegler et al. to plate a substrate with aluminum by contacting a heated substrate with a liquid alkyl aluminum compound or with vapor of an alkyl aluminum compound to cause thermal decomposition of said alkyl aluminum. In this respect, see, for example, Japanese Patent No. 234069.

However, such method for plating a substrate with aluminum provides such serious drawbacks as mentioned below.

That is, the aluminum film plated on the substrate has cracks and pin-holes which cause deterioration of the corrosion resistance, the oxidation resistance at a high temperature and the electric characteristics. Furthermore, the thickness of aluminum film is not uniform, luster of the surface is extremely poor and the aluminum film tends to peel off when bended.

As the results of the inventors' intensive research to overcome said drawbacks, it has been found that said drawbacks can completely be eliminated.

One object of this invention is that a substrate covered with aluminum is heat treated at a temperature of not lower than 400°C, but below the melting point of aluminum in an inert atmosphere and thereafter the heated substrate is taken out into the air.

Another object is that a substrate covered with aluminum is contacted with a very small amount of a surface treating agent selected from active hydrogen-containing compounds, oxygen and halogens, then is heat treated at a temperature of not lower than 400°C, but below the melting point of aluminum in an inert atmosphere and thereafter is taken out into the air or that a substrate covered with aluminum is heat treated at a temperature of not lower than 400°C, but below the melting point of aluminum, then is contacted with a very small amount of a surface treating agent selected from active hydrogen-containing compound, oxygen and halogen and thereafter is taken out into the air.

According to the method of this invention, the aluminum film which has no cracks and pin-holes on its surface, has uniform thickness, exhibits excellent surface luster and is bonded strongly to the substrate and is not peeled off therefrom can be obtained.

Other objects will be apparent from the description hereinafter.

Alkyl aluminum compounds used in this invention include any alkyl aluminum compounds capable of depositing aluminum by thermal decomposition. Among them, the following are preferable because they are easily thermally decomposed and are economical. That is, dialkyl aluminum hydride or trialkyl aluminum having alkyl groups of two - 20 carbon atoms such as triethyl aluminum, diethyl aluminum hydride, trinormal propyl aluminum, trisopropyl aluminum, trinormalbutyl aluminum, dinormalbutyl aluminum hydride, triiso-butyl aluminum, disobutyl aluminum hydride, trinormalbenzyl aluminum, trinormalhexyl aluminum, trinormalcylohexyl aluminum, tri-2-ethylhexyl aluminum, di-2-ethylhexyl aluminum hydride, and tridecyl aluminum, or mixtures thereof.

Furthermore, the alkyl aluminum compound may be used together with a compound capable of producing a complex compound with the alkyl aluminum compound such as an alkali metal compound, an ether, a tertiary amine, a quaternary ammonium salt, etc., which are mentioned in U.S. Pat. Nos. 3,154,407 and 3,273,996 to attain plating of aluminum in high purity. In addition, the alkyl aluminum compound may be used in admixture with an inert organic solvent such as hexane, heptane, octane, cyclopentane, cyclohexane, benzene, toluene, xylene, petroleum, paraffins, alkyl benzene, diphenyl, etc.

Substrates to be plated include, for example, metals such as iron, steel, aluminum, copper, brass pottery, glass, organic and inorganic resins, etc.

The substrate is preferably cleaned prior to plating. The substrate is heated to a temperature higher than thermal decomposition temperature of alkyl aluminum compound, preferably of 300° - 600°C and is contacted with plating solution or plating vapor. The substrate may be heated by known heating methods and e.g., resistance heating, induction heating, etc., may be employed depending upon kind or shape of the substrate. The induction heating is preferable for continuous heating of especially thin metal sheet.

As the method for obtaining a substrate covered with aluminum according to this invention, either one of the method according to which a heated substrate is contacted with a liquid alkyl aluminum compound and the method according to which a heated substrate is contacted with vapor of an alkyl aluminum compound may be used. Election of either one of these methods depends upon kind and shape of the substrate to be plated. The substrate may be covered with aluminum by thermal decomposition of an alkyl aluminum compound on a substrate by one time heating or by intermittent two or more hearings. The latter is especially preferable. Further, there is the case that the latter method does not necessitate heat-treating of a substrate covered with aluminum.

The thermal decomposition may be carried out in the presence of a compound capable of accelerating the thermal decomposition such as titanium chloride, tita-nium bromide, vanadium chloride, iron chloride, copper chloride, etc. which are mentioned in U.S. Pat. No. 3,306,732. Addition of said compound is useful especially for plating a substrate of low heat stability.

The thermal decomposition is required to be carried out in an inert atmosphere, but no critical limitation is present in pressure for operation.

The substrate covered with aluminum as mentioned above is then fed to a heat treatment step or is firstly contacted with a very small amount of a surface treating agent selected from the group consisting of active hydrogen-containing compounds, oxygen and halogen, and thereafter fed to the heat treatment step. The heat treatment in this invention is carried out by heating and keeping the substrate at a temperature of not lower than 400°C, but below the melting point of aluminum, preferably of 450° - 600°C.
When the heat treating temperature is lower than 400° C, good surface properties cannot be obtained and furthermore a long period of time is required for heat treatment. For example, with a substrate of iron, a reaction occurs between iron and aluminum and the aluminum film is apt to peel off.

In this invention, the aluminum heat treatment is effected in the presence of an inert gas or a molten salt. Usually, nitrogen, argon and helium are effectively used, but it should be noted that this invention is not limited to the use thereof.

The heat treating time somewhat varies depending upon kind and shape of the substrate, thickness of aluminum film and heating temperature, but generally is 10 seconds - 30 minutes. However, with a substrate of iron, too long treating time causes a reaction between aluminum and iron to deteriorate the plate surface and hence industrially, the substrate is preferably kept for 20 seconds - 15 minutes.

After completion of the heat treatment, the substrate is taken out into the air or firstly is contacted with a small amount of a surface treating agent selected from the group consisting of active hydrogen-containing compound, oxygen and halogen and thereafter taken out into the air.

The contact of the substrate with a surface treating selected from the active hydrogen-containing compound, oxygen and halogen may be carried out before said heat treatment. As mentioned above, the contact of the substrate with a very small amount of a surface treating agent selected from active hydrogen-containing compound, oxygen and halogen before or after the heat treatment results in more excellent aluminum plating than that attained only by heat treatment.

Illustrative of the active hydrogen-containing compounds to be contacted with the substrate covered with aluminum are compounds containing at least one substitutable hydrogen such as water, ammonia primary or secondary amine compounds, e.g., dimethyl amine, monobutyl amine, etc.; sulfides, e.g., hydrogen sulfide, ethyl thioalcohol, dodecyl thioalcohol, etc.; mono- or poly-hydric alcohols, e.g., methanol, ethanol, iso-propylalcohol, butanol, ethylene glycol, propylene glycol, glycerine, etc.; carboxylic acids, e.g., acetic acid, naphthenic acid, stearic acid, adipic acid, maleic acid, phthalic acid, etc.; and inorganic acids, e.g., hydrogen chloride, hydrogen fluoride, hydrogen bromide, nitric acid, etc.

Those active hydrogen-containing compounds are used as a solution which contains 10 - 10,000 ppm, preferably 100 - 1,000 ppm (weight basis) of said compound dissolved in aromatic hydrocarbons such as benzene, toluene, xylene, naphthalene, alkyl benzene, etc., aliphatic hydrocarbons such as pentane, hexane, octane, decene, etc., and mixtures thereof or as an atmosphere of the active hydrogen-containing compound of 0.1 - 20 mmHg, preferably 0.1 - 10 mmHg.

In case of treatment with oxygen, the substrate is contacted with said aromatic or aliphatic hydrocarbon containing 10 - 10,000 ppm, preferably 100 - 1,000 ppm (weight basis) of oxygen or is used as an oxygen atmosphere of 0.01 - 100 mmHg, preferably 0.1 - 80 mmHg.

Furthermore, when halogens such as fluorine, chlorine, bromine, etc. are used, they are used as a halogen atmosphere of 0.01 - 20 mmHg, preferably 0.1 - 10 mmHg or as a solution containing 10 - 2,000 ppm of a halogen dissolved in a suitable solvent such as a paraffin. When the halogen is contacted in a vapor phase, the vapor alone is not contacted, but the vapor is diluted with an inert gas and the treatment is carried out under normal pressure or higher pressure.

Said treatment is carried out at 80° - 300° C, preferably 150° - 200° C.

As mentioned above, the method of this invention provides the following advantages as compared with the conventional method in which the substrate covered with aluminum is taken out without further treatments.

That is, the aluminum film on the substrate has no cracks and pin-holes on its surface, has a uniform thickness, exhibits excellent surface luster and is bonded strongly to the substrate.

The substrate plated with aluminum in accordance with this invention has high corrosion resistance and oxidation resistance at a high temperature and excellent electric characteristics. Furthermore, the substrate plated can be subjected to metal surface treatment, such as known sealing treatment, stabilizaton treatment and anolime finishing. Due to these excellent characteristics the industrial value of this invention is extremely great.

The following Examples are given by way of specifically illustrating this invention and are not intended to be construed as limiting in any case.

**EXAMPLE 1**

A steel sheet of 50 mm × 50 mm × 0.6 mm was washed with water and subsequently with alcohols and then dried. Thus treated steel sheet was used as a specimen.

The whole process steps from the heat treatment of the specimen until taking it out into the air were carried out in argon atmosphere.

Said specimen was heated to 400° C in argon atmosphere and thereafter was dipped in 500 cc of an alkyl aluminum solution which comprises 81 percent by weight of disobutyl aluminum hydride, 11 percent by weight of diethyl aluminum hydride, 5 percent by weight of triisobutyl aluminum, and 3 percent by weight of triethyl aluminum at 20° C.

After lapse of one minute, the specimen was withdrawn from the solution and deposited alkyl aluminum was maintained in argon atmosphere at 100° C and washed away.

Furthermore, the same procedure as mentioned above was repeated once more to effect aluminum plating. Subsequently, the specimen thus plated with aluminum was heated to 450° C in argon atmosphere. After the specimen was kept at that temperature for 5 minutes, it was cooled to room temperature in argon gas and then taken out into the air.

Thus obtained substrate plated with aluminum has a film of 1.1 μ in thickness and has excellent luster of silver white.

Furthermore, an acid resistance test was made by dipping in 500 cc of 25 weight percent aqueous nitric acid solution at 20° C said plated substrate which was covered by solid paraffin in a width of 10 mm around said substrate.

Even after lapse of 30 minutes, no bubbles were generated and no change was observed in the plate surface.
For comparison, the same another specimen which was plated with aluminum in the same manner as mentioned above was taken out into the air without heat treatment.

Thus obtained substrate plated with aluminum has a film of 1.1 μ in thickness and its surface showed silver white. The same acid resistance test was made with this substrate. After lapse of 11 minutes, bubbles were generated and after lapse of 20 minutes the aluminum film on the substrate was nearly peeled off.

From the foregoing results, it will be seen that with the substrates plated with aluminum in the same thickness, the properties of the surface subjected to the heat treatment was extremely superior to those of the surface subjected to no heat treatment.

EXAMPLE 2

The same specimen as in Example 1 and which was cleaned in the same manner as in Example 1 was employed in this Example. The treatment was carried out in argon atmosphere as in Example 1. The specimen was pre-heated to 500° C and was dipped in an alkyl aluminum solution having the same compositions as in Example 1, heated to 200° C.

After lapse of one minute, the specimen was withdrawn and washed with 500 cc of hexane.

Then, the specimen was heated to 500° C in argon atmosphere and kept at that temperature for 5 minutes. Thereafter, it was cooled and taken out into the air. The steel sheet thus plated with aluminum had excellent luster of silver white and had excellent surface properties. The average thickness of the aluminum film was 2.1 μ determined by weight increased.

The specimen was also subjected to the acid resistance test in the same manner as in Example 1. Even after lapse of 30 minutes, no bubbles were generated.

For comparison, the specimen prior to said heat treatment was cooled in argon and then taken out into the air.

The steel sheet thus plated with aluminum had a grey color and little luster. The same acid resistance test as mentioned above was given to the specimen. After lapse of 5 minutes, generation of bubbles was observed.

For further comparison, instead of said heat treatment, the specimen was similarly heated to 300° C in argon atmosphere and kept at that temperature for 5 minutes. Then, it was cooled in argon and taken out into the air. Thus obtained steel sheet plated with aluminum showed grey color and had little luster. The specimen was subjected to the same acid resistance test as mentioned above. After lapse of 7 minutes, generation of bubbles was observed.

From the above results, it will be seen that with the steel sheets plated with aluminum in the same thickness, the luster and properties of the surface treated according to this invention were superior to those of the surface which was not treated in accordance with this invention.

EXAMPLE 3

A substrate covered with aluminum treated in the same manner as in Example 1 until the heat treatment step was contacted with 500 cc of hexane containing 0.01 percent by weight of water at 20° C for one minute and then taken out into the air.

Thus obtained steel sheet plated with aluminum showed excellent luster of silver white and had extremely excellent surface properties.

Said steel sheet was subjected to the same acid resistance test as in Example 1. Even after lapse of 50 minutes, generation of bubbles was not observed.

In said method, instead of water treatment, the steel sheets were treated with 500 cc of hexane containing 0.01 percent by weight of ethanol, 500 cc of hexane containing 0.01 percent by weight of oxygen and argon atmosphere containing chlorine gas of 1 mmHg, respectively and they were taken out into the air. Thus obtained steel sheets plated with aluminum showed excellent luster of silver white and had extremely excellent surface properties.

Each steel sheet was subjected to the same acid resistance test as in Example 1. The same results as in case of the water treatment were obtained.

EXAMPLE 4

A substrate covered with aluminum in the same manner as in Example 1 was contacted with 500 cc of hexane containing 0.01 percent by weight of water at 20° C for one minute. Thereafter, it was heated to 500° C in argon atmosphere for 5 minutes and kept at that temperature. Then, the substrate was cooled to room temperature in argon gas and taken out into the air. Thus obtained steel sheet plated with aluminum showed excellent luster of silver white and had extremely excellent surface properties.

This steel sheet was subjected to the same acid resistance test as in Example 1 to find no generation of bubbles even after lapse of 40 minutes.

In said method, instead of the water treatment, steel sheets were treated with 500 cc of hexane containing 0.01 percent by weight of ethanol, 500 cc of hexane containing 0.01 percent by weight of oxygen and argon atmosphere containing chlorine gas of 1 mmHg, respectively. Thereafter, they were heat treated as mentioned above, cooled and then taken out into the air. They had excellent surface properties as in the case of the water treatment.

Each steel sheet thus treated was subjected to the acid resistance test as in Example 1 to obtain the same results as in case of the water treatment.

What is claimed is:

1. A method for aluminum plating of a substrate by contacting a heated substrate with an alkyl aluminum compound to cause thermal decomposition of said alkyl aluminum compound, an improvement which comprises heat treating said substrate covered with aluminum at a temperature of not lower than 400° C, but below the melting point of aluminum for 10 seconds — 30 minutes in an inert atmosphere, then contacting thus treated substrate with a small amount of a surface treating agent selected from active hydrogen-containing compound, oxygen and halogen, and thereafter taking out the substrate into the air.

2. A substrate plated with aluminum according to the method as claimed in claim 1.

3. A method according to claim 1, wherein the alkyl aluminum compound is selected from diethyl aluminum hydride, trialkyl aluminum having alkyl groups of two—20 carbon atoms and a mixture thereof.

4. A method according to claim 1, wherein the substrate heated to 300°–600° C. was contacted with liquid
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or vapor of the alkyl aluminum compound to plate the substrate with aluminum.

5. A method according to claim 1, wherein the heat treatment was carried out at 450°-600° C. for 20 seconds — 15 minutes.

6. A method according to claim 1, wherein the active-hydrogen containing compound is selected from the group consisting of water, ammonia, primary and secondary amine compounds, sulfides, mono- and polyhydric alcohols, carboxylic acids, and inorganic acids.

7. A method according to claim 6, wherein the primary and secondary amine compounds are selected from the group consisting of dimethyl amine, and monobutyl amine.

8. A method according to claim 6, wherein the sulfide is selected from the group consisting of hydrogen sulfide, ethyl thioalcohol, dodecyl thioalcohol.

9. A method according to claim 6, wherein the mono- and polyhydric alcohols are methanol, ethanol, isopropanol, butanol, ethylene glycol, propylene glycol and glycerine.

10. A method according to claim 6, wherein the carboxylic acid is selected from the group consisting of acetic acid, naphthenic acid, stearic acid, adipic acid, maleic acid and phthalic acid.

11. A method according to claim 6, wherein the inorganic acid is selected from the group consisting of hydrogen chloride, hydrogen fluoride, hydrogen bromide and nitric acid.

12. A method according to claim 1, wherein the halogen is selected from chlorine, fluorine and bromine.

13. A method according to claim 1, wherein the substrate plated with aluminum is contacted with a solution containing active hydrogen-containing compound in an amount of 10 – 10,000 ppm.

14. A method according to claim 1, wherein the substrate plated with aluminum is contacted with an atmosphere of active hydrogen-containing compound of 0.01 – 20 mmHg.

15. A method according to claim 1, wherein the substrate plated with aluminum is contacted with a solution containing 10 – 10,000 ppm of oxygen.

16. A method according to claim 1, wherein the substrate plated with aluminum is contacted with a gas atmosphere containing oxygen of 0.01 – 100 mmHg.

17. A method according to claim 1, wherein the substrate plated with aluminum is contacted with a solution containing 10 – 2,000 ppm of a halogen.

18. A method according to claim 1, wherein the substrate plated with aluminum is contacted with a gas atmosphere containing a halogen of 0.01 – 20 mmHg.

19. A method according to claim 6, wherein the substrate plated with aluminum is contacted with the surface active agent at 0° – 300° C.

20. In a method for aluminum plating a substrate by contacting a heat substrate with an alkyl aluminum compound to cause thermal decomposition of said alkyl aluminum compound, an improvement which comprises contacting said substrate covered with aluminum with a small amount of a surface treating agent selected from active hydrogen-containing compound, oxygen and halogens, then heat treating the substrate at a temperature of not lower than 400° C, but below the melting point of aluminum for 10 seconds — 30 minutes and thereafter taking out thus treated substrate into the air.

21. A method according to claim 20, wherein the alkyl aluminum compound is selected from dialkyl aluminum hydride, trialkyl aluminum having alkyl groups of two–20 carbon atoms and a mixture thereof.

22. A method according to claim 20, wherein the substrate heated to 300°–600° C. was contacted with liquid or vapor of the alkyl aluminum compound to plate the substrate with aluminum.

23. A method according to claim 20, wherein the heat treatment was carried out at 450°–600° C. for 20 seconds — 15 minutes.

24. A method according to claim 20, wherein the active-hydrogen containing compound is selected from the group consisting of water, ammonia, primary and secondary amine compounds, sulfides, mono- and polyhydric alcohols, carboxylic acids, and inorganic acids.

25. A method according to claim 24, wherein the primary and secondary amine compounds are selected from the group consisting of dimethyl amine, and monobutyl amine.

26. A method according to claim 24, wherein the sulfide is selected from the group consisting of hydrogen sulfide, ethyl thioalcohol, dodecyl thioalcohol.

27. A method according to claim 24, wherein the mono- and polyhydric alcohols are methanol, ethanol, isopropanol, butanol, ethylene glycol, propylene glycol and glycerine.

28. A method according to claim 24, wherein the carboxylic acid is selected from the group consisting of acetic acid, naphthenic acid, stearic acid, adipic acid, maleic acid and phthalic acid.

29. A method according to claim 24, wherein the inorganic acid is selected from the group consisting of hydrogen chloride, hydrogen fluoride, hydrogen bromide and nitric acid.

30. A method according to claim 24, wherein the halogen is selected from chlorine, fluorine and bromine.

31. A method according to claim 20, wherein the substrate plated with aluminum is contacted with a solution containing active hydrogen-containing compound of 0.01 – 20 mmHg.

32. A method according to claim 20, wherein the substrate plated with aluminum is contacted with an atmosphere of active hydrogen-containing compound of 0.01 – 20 mmHg.

33. A method according to claim 20, wherein the substrate plated with aluminum is contacted with a solution containing 10 – 10,000 ppm of oxygen.

34. A method according to claim 20, wherein the substrate plated with aluminum is contacted with a gas atmosphere containing oxygen of 0.01 – 100 mmHg.

35. A method according to claim 20, wherein the substrate plated with aluminum is contacted with a solution containing 10 – 2,000 ppm of halogen.

36. A method according to claim 30, wherein the substrate plated with aluminum is contacted with a gas atmosphere containing a halogen of 0.01 – 20 mmHg.

37. A method according to claim 20, wherein the substrate plated with aluminum is contacted with the surface active agent at 0° – 300° C.

38. A substrate plated with aluminum according to the method as claimed in claim 20.