

[54] **METHOD OF PLATING
ALUMINUM-CHROMIUM ALLOYS**

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[51] Int. Cl. C23b 5/32

[58] **Field of Search** 204/39

[56] **References Cited**
UNITED STATES PATENTS

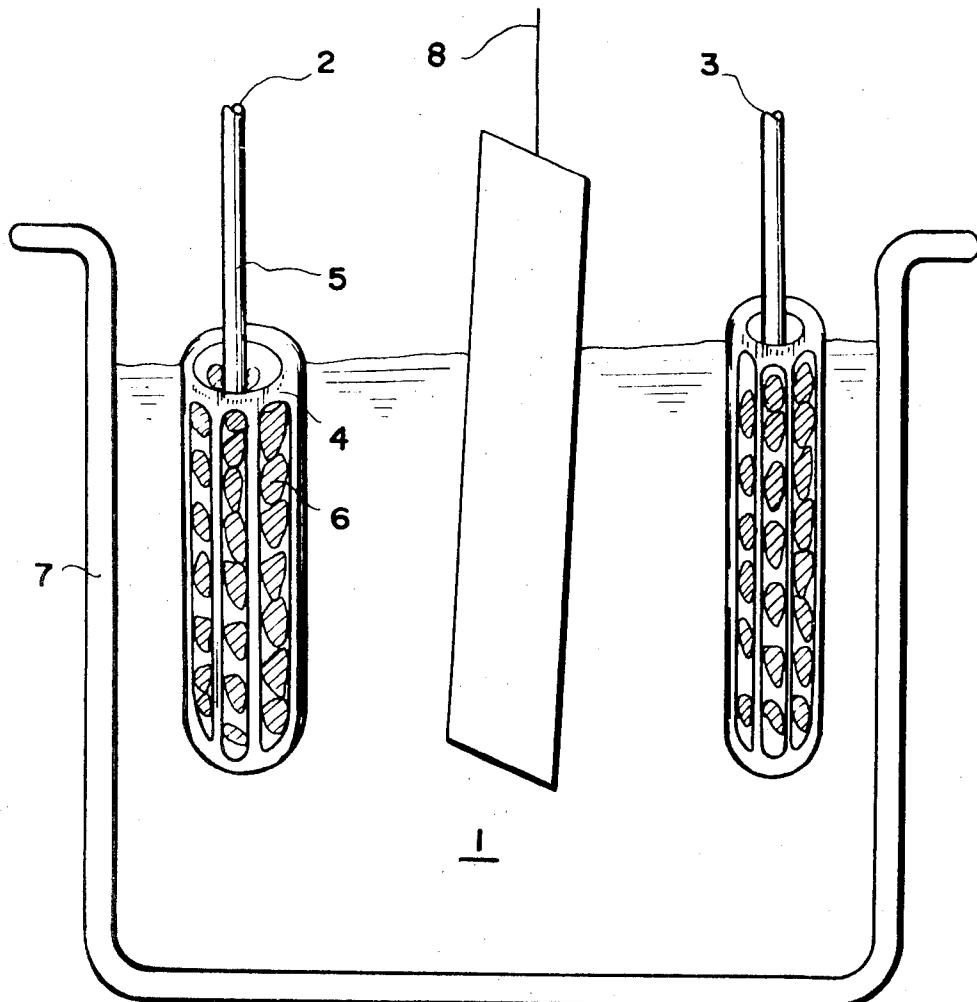
3,480,521 11/1969 Miyata et al. 204/39
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[57] **ABSTRACT**

In a method of electroplating an aluminum-chromium coating on a surface of a metal article by using a molten aluminum salt bath, containing chromium. An aluminum-chromium alloy coating is electrodeposited from said bath.

6 Claims, 3 Drawing Figures

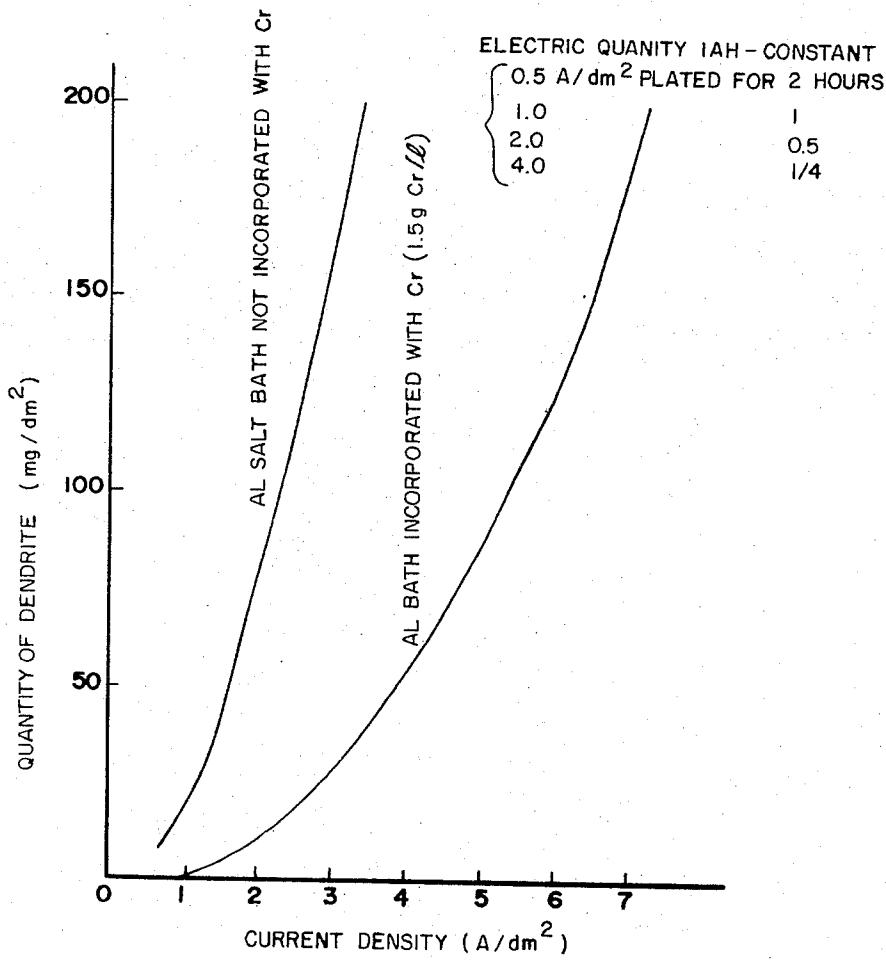


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FIG. 1

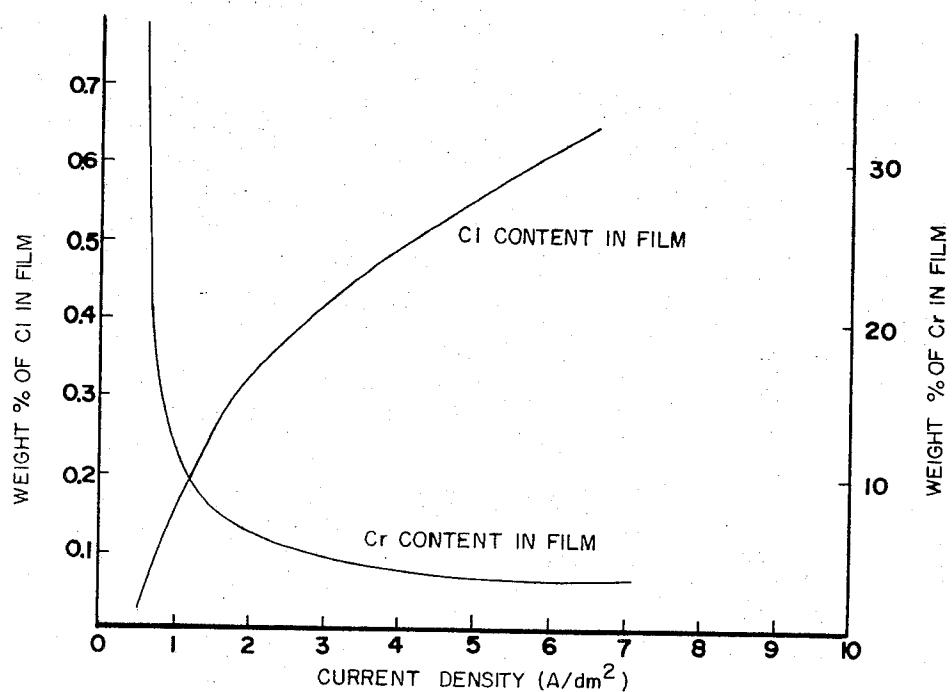


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FIG. 2

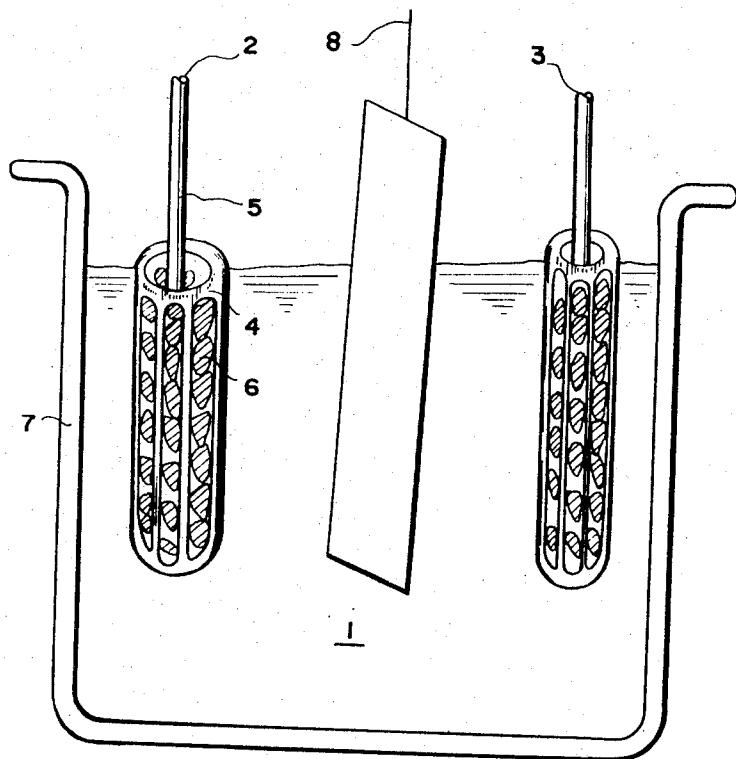


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FIG. 3



METHOD OF PLATING ALUMINUM-CHROMIUM ALLOYS

BACKGROUND OF THE INVENTION

This invention relates to a method of electroplating an aluminum-chromium alloy on a metal substrate and an article prepared by the novel method.

It is well known in the art to plate aluminum on the surface of a substrate of metal such as steel, steel alloys, titanium or the like for the purpose of preventing corrosion of the substrate. Generally, aluminum is plated by vacuum vapour deposition, hot dipping or electrolytically with molten salt bath. With the vacuum vapour deposition method, however, it is difficult to adjust the plating conditions so that it is difficult to produce a uniform plating. With the hot dipping method, the thickness of the plated layer tends to increase and there is a tendency to form a brittle alloy layer between the aluminum and the substrate. Moreover, this brittle alloy layer adversely effects the workability of the plated metal article.

The molten salt bath electroplating method is also disadvantageous in that chlorine is entrapped in the plated layer, thereby decreasing the corrosion resistance not only of the plated layer but also of the metal substrate and increasing the brittleness of the metal substrate. Moreover, molten salt bath electrodeposition often forms a plated layer of dendritic structure whereby it is difficult to obtain homogeneous plated layers having excellent corrosion resistance.

A number of proposals have been made to eliminate these difficulties.

For example, U.S. Pat. Nos. 3,167,403 and 3,268,422 disclose a method wherein 0.2-5% of manganese is incorporated into a molten aluminum salt bath to plate an Al-Mn alloy containing 10 to 70% manganese. However, the manganese in the plated layer obtained by this method acts to decrease flexibility and workability of plated metal articles, this tendency increasing with the amount of the manganese incorporated.

U.S. Pat. No. 3,567,409 discloses a coated sheet steel, the coating consisting essentially of 15 to 50 weight percent of one selected from the group consisting of chromium and titanium, and the balance of aluminum, and a method of manufacturing the coated sheet steels by vacuum vapour deposition technique. However, in the specification of this patent nothing is mentioned about the workability of the coated sheet steels and various problems inherent in the vapour deposition technique.

It has also been proposed to use a molten salt bath containing a small quantity of iron in U.S. Pat. No. 3,259,557. However, the purpose of incorporating a small quantity of iron is to stabilize the bath and not to form an alloy plating.

SUMMARY OF THE INVENTION

According to this invention, there is provided a new and improved method of forming an Al-Cr alloy coat or deposit on a metal substrate by using a molten aluminum salt bath containing chromium ions, and metal articles plated with the alloy.

An object of this invention is to provide a novel method of electroplating capable of decreasing the amount of chlorine contained in the plated aluminum

layer which is formed by the molten chloride salt bath method.

Another object of this invention is to provide a method of electroplating capable of preventing the deterioration of the molten salt bath.

Still another object of this invention is to provide a metal article plated with an Al-Cr alloy film of excellent adhesiveness and in which the aluminum alloy is prevented from depositing in dendritic form.

10 A further object of this invention is to provide a metal article provided with a homogeneous coating having excellent corrosion resistance properties.

15 A still further object of this invention is to provide a plated metal article having higher flexibility and workability than prior art plated metal articles.

These and other objects can be attained by incorporating a suitable amount of chromium in the molten aluminum salt bath.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIG. 1 is a graph showing the relationship between cathode current density and the quantity of the deposit in the form of dendrite;

25 FIG. 2 is a graph showing the relationship between cathode current density and the contents of chlorine and chromium in the plated coatings and

30 FIG. 3 is a schematic representation of apparatus utilized for electrolytically supplying chromium to a molten aluminum salt plating bath.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The metal substrate utilized in this invention is a 35 moulded or shaped article which may be a single metal or an alloy. However, the type and composition of the metal and the configuration of the article are immaterial to the invention. But the invention is especially suitable for metal substrates of titanium, titanium alloys, steel or alloy steels. Steel is the most commonly used metal for the substrate and the substrate is shaped to have a desired configuration before or after plating. In the latter case, the plated metal substrate is required to have excellent workability. To this end, it is advantageous to use an Al-Cr alloy of a composition in which the chromium percentage lies in a range of from 2.0 to 11.0, by weight.

Titanium and titanium alloys are used in applications 50 wherein anti-corrosion properties and fatigue resistant properties are essential under severe operating conditions. Since the presence of chlorine in the coating adversely affects the foregoing properties and since the plated alloy coating prepared by the method of this invention contains only an extremely small quantity of chlorine, the invention is especially suitable for plating metal articles of titanium or titanium alloys. Usually, since the substrates of titanium or titanium alloys are not worked after plating, the workability of the coated article is not important. For this reason, it is not necessary to limit to any particular value the weight ratio of aluminum to chromium in the plated alloy coating. Practically, however, it is advantageous to use a chromium percentage of from 1.0 to 27.0, by weight.

60 The metal substrate may take any configurations such as strips, plates, wires, bolts, nuts or may be of very complicated ones as in the case of electric machines and apparatus.

Any source of chromium ions may be used for incorporating chromium into the molten salt bath, but it is advantageous to use granules of metallic chromium or an auxiliary electrode of chromium or chromium-aluminum mother alloy anode.

The temperature of the bath was maintained at 160° C, the cathode current density was 2.0 A/dm² and the plating time was 30 minutes. Chromium ion was added by dissolving granules of metallic chromium in the molten bath.

Table 1

No. of the Sample	Content of Cr (weight%) in the plated coating	Content of chlorine in the plated coating (wt.%)	Salt Spray Test 200 hours	Flexibility 180° bend	Appearance	Thickness of the coating	Content of Cr (g/l) in the plating bath	
1	Al	0	0.8 - 1.5	thin white rust	good	white mat	10 μ	0
2		0.3	0.75	very thin white rust	do.	pale gray mat	do.	0.5
3		2.0	0.60	no change	do.	do.	do.	1.0
4		6.0	0.35	do.	do.	do.	do.	1.5
5		8.0	0.32	do.	do.	do.	do.	2.0
6		11.0	0.244	do.	do.	do.	do.	3.5
7		18.0	0.19	do.	do.	pale gray partly luster	do.	4.5
8		27.0	0.09	do.	coating was peeled off	about 50% luster	do.	5.5
9		31.0	0.07	do.	do.	60-70% luster	do.	8.0

The molten salt bath may be any bath usually employed as the aluminum electro-plating bath, for example a bath consisting of aluminum chloride, sodium chloride and potassium chloride.

When oxygen gas is dissolved (absorbed) in the molten salt electrolyte for electroplating aluminum, even in an extremely small quantity, it was found that the characteristic of the coating plated with the electrolyte degrades greatly. For this reason, it is usual to cover the surface of the electrolyte with inert gas such as argon, nitrogen or carbon dioxide or to contain the electrolyte in a sealed vessel for the purpose of preventing oxygen from dissolving into the electrolyte. However, the oxygen in the atmosphere will become entrained in the inert gas or leaks thereinto or the oxygen adhering to the surface of the article to be plated is brought into the electrolyte thereby degrading the same.

According to this invention, chromium ion exists in the electrolyte and that chromium at once takes oxygen out of the electrolyte by easily being oxidized to assure excellent plating.

Since the chromium oxide formed in the electrolyte in this manner is in the form of fine colloidal particles in the nascent state, the chromium oxide functions in the same manner as a brightener commonly added to the electroplating solution, thereby manifesting a remarkable effect of preventing the deposition of dendrite which otherwise is formed on the plated surface in electrolytic aluminum plating.

The following examples are given for illustration but not limitation.

EXAMPLE 1

Examples of the novel method of alloy plating and characteristics of the resulting plated coatings are shown in the following table 1. The metal substrates employed in these examples were cold rolled steel plates, each having a thickness of 0.2 mm, a width of 50 mm, a length of 100 mm, and the molten salt bath used for the plating had following composition.

AlCl ₃	60 mol%	1285g/l
NaCl	25 mol%	238g/l
KCl	15 mol%	180g/l

EXAMPLE 2

25 A steel bolt was used as a metal substrate and the surface thereof was plated with the novel aluminum-chromium alloy.

In this example, 1,285g of aluminum chloride, 238g of sodium chloride, and 180g of potassium chloride 30 were put in a cylindrical hard glass beaker having a capacity of 1 litre, and the mixture was heated at a temperature of 160° C to prepare an ordinary molten salt bath for electroplating aluminum. 1.5g of granules of metallic chromium was incorporated into the bath and 35 the bath was let standstill for 24 hours. Then the metallic chromium was dissolved completely. An aluminum rod (a diameter of 10 mm and a length of 50 mm) as an anode, and an aluminum plate (15 mm \times 70 mm) for supplying cathode current to steel bolts to be plated 40 were dipped in the bath. 5 bolts (6 mm ϕ \times 34 mm length) were made to roll on the cathode and a DC current of 1.9A was passed for 30 minutes. By this operation each bolt was covered with an Al-Cr coating having a thickness of 9 microns and containing 6% of chromium.

To determine the heat resistant and corrosion resistant characteristics of the resulting bolts, after treating with a commercial chromate solution the bolts were heated in the atmosphere in an electric furnace at a 50 temperature of 700° F (370° C) for 2 hours and then at a temperature of 1,000° F (540° C) for 2 hours according to the test specification of AMS No. 2416 (Aerospace Material Specification, U.S.A.). After cooling the products (bolts) of this invention, the surface was slightly blackened but the plated layers did not show any defects such as cracks, blisters or peeling. Then, the bolts were cooled to room temperature and thereafter subjected to a salt spray test (JIS-Z2371 or ASTM, B117-49T). It was found that the bolts did not 60 show any tendency of corrosion after 100 hours as provided by the AMS-2416 and no corrosion even after 200 hours. This means that these bolts have excellent corrosion resistant properties even after the heat resistance tests. As a control, steel bolts of the same were 65 electroplated with aluminum alone to a thickness of 10 microns. The resulting bolts were red rusted after the tests.

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EXAMPLE 3

In the same manner as in examples 1 and 2, 1,285g of aluminum chloride, 238g of sodium chloride and 180g of potassium chloride were put into one litre cylindrical beaker of hard glass and heated up to 160°C and melted. With this plating bath, aluminum chloride sublimes from the liquid surface so that when the beaker is closed by a lid of hard glass, sublimed aluminum chloride was deposited on the inner surface of the lid. After the bath was left alone for 16 hours the deposited aluminum chloride amounted to 128g. A plating bath was prepared under the same conditions and 1.5g of granules of metallic chromium were added and dissolved in the plating bath. In this case it was found that the sublimation of the aluminum chloride was greatly decreased so that only 20g of aluminum chloride was deposited on the inner surface of the lid after 16 hours. This shows that the addition of the chromium into the plating bath is effective to prevent sublimation of aluminum chloride, the essential ingredient of the plating bath, and is advantageous in the maintenance of the molten aluminum salt plating bath.

EXAMPLE 4

Using both types of the molten plating baths described in example 3, the conventional aluminum plating bath, and a bath containing with 1.5g of granules of metallic chromium, cold rolled steel plates, each having a thickness of 0.2 mm, a width of 50 mm, and a length of 100 mm, were electroplated with current densities of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0 and 7.0 A/dm², respectively. The characteristics of the plated films were measured and the results were plotted as shown in FIGS. 1 and 2. As shown in FIG. 1, where the electroplating was carried out at a constant electric quantity (1 Ampere hour), the tendency to deposit the dendritic structure of poor adhesiveness increased as the current density increased. However, the quantity of the dendritic deposits is greatly decreased by the addition of the chromium into the plating bath. Thus, it was confirmed that the plating bath containing chromium enables electroplating at higher efficiencies at much higher current densities than the plating bath not containing chromium.

EXAMPLE 5

This example illustrates a method of electrolytically incorporating chromium into the molten aluminum salt plating bath. FIG. 3 shows apparatus employed in this method. A molten aluminum salt plating bath 1 consisting of 1,285g of aluminum chloride, 235g of sodium chloride and 180g of potassium chloride was put into a glass vessel 7 having a diameter of 120 mm and a height of 120 mm, and chromium source electrodes 2 and 3 were immersed in the bath.

Each chromium source electrode comprised a glass cage 4 having an inner diameter of 12 mm and a length of 100 mm, an aluminum rod 5 having a diameter of 5 mm and a length of 150 mm and inserted in the cage 4, and 20g. of small pieces of metallic chromium packed between the cage 4 and the aluminum rod 5.

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To supply chromium ion to the plating bath, chromium source electrodes 2 and 3 were connected to the positive line of a DC source and a cold rolled steel plate 8 having a thickness of 0.2 mm, a width of 50 mm and a length of 100 mm was connected to the negative line. Then, the small pieces of chromium were electrolytically dissolved into the plating bath. After 2A of DC was passed through the chromium anodes, a desired quantity of chromium has been added, and the chromium source electrodes 2 and 3 and the steel plate 8 were removed from the plating bath. Thereafter, two aluminum rod anodes (6 mm^φ) and steel sheet (50 mm × 100 mm) plated were dipped in the bath to electroplate, and electroplating was carried out for 15 minutes with a current of 2A.

Table 2 below shows the relationship between the time in which current was passed through the chromium electrodes and the quantity of chromium contained in the bath and the plated film which was formed on the metal article immediately after incorporation of chromium.

Table 2

25	Time of dissolving chromium (minutes)	The content of chromium in the bath (mg/l)	The percentage of chromium in the plated film
	10	384	1.5
	20	811	4.4
	45	—	6.3
	65	—	11.8

EXAMPLE 6

In this example an aluminum-chromium alloy anode electrode was used to supplement the supply of chromium ion in the plating bath.

After incorporating 1.5 g/l chromium into the plating bath by using the chromium source electrodes as described in example 5, the chromium source electrodes were removed from the plating bath. Then two aluminum rods of 5 mm diameter each were dipped in the plating bath as the anodes and a cold rolled steel plate having a length of 100 mm, a width of 50 mm and a thickness of 0.2 mm was placed between the anodes as the cathode. The electrolytic plating was carried out for 30 minutes with a current of 2A. The resulting plated aluminum alloy film was contained 4.9% of chromium. However, as the plating operation was repeated under the same plating condition, the content of chromium in the plating bath and plated film gradually decreased and it was found that the content of chromium in the fifth plated film was 2.3%.

After supplementing the supply of chromium ion in this plating bath by utilizing the chromium source electrodes, electroplating was repeated several times by utilizing two sheets of aluminum-chromium alloy plates as the anode electrodes, each alloy plate containing 5% of chromium and having a length of 100 mm, a width of 20 mm and a thickness of 14 mm. The same plating condition mentioned above was used. At first the content of chromium in the plating bath was 1.5 g/l and firstly plated aluminum alloy film contained 4.2% of chromium.

When the plating operation was repeated under the same conditions, the content of chromium in the fourth plated film was 4.1% and the content of chromium in the plating bath was 1.4 g/l. Even in the eighth plated

film, the content of chromium was 3.6% and the content of chromium in the bath was 1.1 g/l.

In this manner where an aluminum-5% chromium alloy is used as the anode, the chromium consumed in the plating bath is supplemented thereby always forming plated aluminum film containing a constant quantity of chromium.

EXAMPLE 7

In this example, an aluminum coating containing chromium was electro-plated on the surface of a substrate of a titanium alloy. Electroplating was performed by dissolving 1.5g of metallic chromium in a one liter plating bath consisting of 1,285g of aluminum chloride, 235g of sodium chloride and 180g of potassium chloride while blowing hydrogen chloride gas through the bath. The Ti-6A -4V alloy bolts having a diameter of 6 mm and a length of 30 mm were plated.

Four bolts were made to roll on a cathode bed (15 mm width \times 70 mm length) and were electroplated using an aluminum rod and by DC of 1.5A for 30 minutes.

After electroplating, the bolts were cleansed with water agitated by ultrasonic waves, dried thoroughly and subjected to a glass bead peening treatment. These films contained 5% of chromium.

EXAMPLE 8

In this example, an aluminum coating containing chromium was electroplated on the surface of a titanium plate in accordance with the method of this invention.

7.5g of metallic chromium was dissolved in a 5 liters aluminum fused salt plating bath consisting of 6,500g of aluminum chloride, 1,128g of sodium chloride and 864g of potassium chloride while blowing hydrogen chloride gas through the bath. Consequently chromium content in this bath was 1.5 g/l.

The titanium plate had a length of 300 mm, a width of 100 mm and a thickness of 0.2 mm, degreased with acetone, and pickled with a 10:1 nitric-hydrofluoric acid for 30 seconds. After drying thoroughly in the air, the pretreated titanium plate was dipped in the plating bath to a depth of 180 mm then electroplated by a plating current of 7.2A by using the plate as the cathode and two aluminum rods, each having a diameter of 5 mm and a length of 180 mm as the anode electrodes. Plating for 30 minutes formed a plated film having a thickness of 10 microns and high adhesiveness. The film contained 5.6% of chromium.

EXAMPLE 9

In this example, an aluminum coating containing chromium was electroplated on the surface of an aluminum plate.

1.5g of metallic chromium was dissolved in a one liter aluminum fused salt plating bath consisting of 1,300g of aluminum chloride, and 400g of sodium chloride while blowing hydrogen chloride gas through the bath.

The aluminum plate was commercial aluminum having a purity of 99.7%, a length of 50 mm, a width of 10 mm and a thickness of 3 mm.

The aluminum plate was degreased with acetone and then dipped in a 3% aqueous solution of hydrofluoric acid for several seconds. After thoroughly drying in the air, the resulting aluminum plate was dipped in the plating bath and plated for one and one half hours by pass-

ing a plating current of 0.2A by using two aluminum rod anodes, each having a diameter of 5 mm and a length of 10 cm, and placed on the opposite side of the plate. A highly adhesive plated film having a thickness of 30 microns was formed. The content of chromium in the plated film was 4.8%.

EXAMPLE 10

In this example the surface of a stainless steel plate 10 was electroplated with an aluminum coating containing chromium according to the method of this invention.

1.5g of metallic chromium was dissolved in a 1 liter aluminum fused salt bath consisting of 1,285g of aluminum chloride, 235g of sodium chloride and 180g of potassium chloride, and the resulting bath was used for the plating operation. The plated stainless steel plate had a length of 60 mm, a width of 20 mm and a thickness of 3 mm. The plate was degreased with acetone, dipped in 3% aqueous solution of hydrofluoric acid and then washed thoroughly with water. The plate was dried thoroughly and then dipped in the plating bath. Two aluminum rods, each having a diameter of 5 mm and a length of 10 cm were used as the anode electrode. The plating operation was carried out for 30 minutes with a plating current of 0.48A to obtain a highly adhesive Al-Cr alloy film having a thickness of 10 microns. The film contained 4.0% of chromium.

EXAMPLE 11

30 In this example, the surface of an alloy steel was electroplated with an aluminum film containing chromium in accordance with the method of this invention and then the aluminum film was anodized.

0.8g of metallic chromium was dissolved in a 2 liters 35 fused aluminum salt bath consisting of 2,600g of aluminum chloride, 470g of sodium chloride and 360g of potassium chloride. The chemical composition of the plated alloyed steel test piece was: C—0.4%, Mn—0.7%, P—0.035%, S—0.04%, Si—0.30%, Ni—1.70%, Cr—0.80% and Mo—0.3%. The test piece 40 had a length of 100 mm, a width of 25 mm and a thickness of 1 mm.

The test piece was cleaned by blasting No. 120 emery powder with compressed air under pressure of 4 kg/cm² 45 and pickled with 10% hydrochloric acid containing 2% of an inhibitor and then washed with water. After drying, this alloy steel test piece was dipped in the plating bath and plated with a current of 1A; using two aluminum rods each having a diameter of 5 mm and a length 50 of 120 mm as the anode electrode. After electroplating for 1.5 hours a highly adhesive aluminum alloy coating having a thickness of 30 microns was formed. The film contained 1% of chromium. After peening with 80—120 μ glass beads, the film was subjected to anodic oxidation under the following conditions.

60	Solution for anodizing Temperature Current	15% (by volume) sulfuric acid 15°C DC, 15 mA/cm ²
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Then the plated aluminum coat containing chromium was subjected to anodic oxidation under the above described conditions by utilizing the aluminum coat as the anode and an aluminum plate as the cathode. The voltage was increased to 23 volts so that it was possible to continue the anodic oxidation treatment for 30 min-

utes. The cross-section was inspected by a microscope and it was found that a dense oxide layer having a thickness of 10 microns was formed.

What is claimed is:

1. A method of electroplating a chromium-containing aluminum coating on the surface of a metal article by immersing said metal article in a molten aluminum salt bath comprising aluminum chloride and containing at least one alkali metal chloride and chromium ions in an amount of 1 to 5.5 g/l and electrodepositing a coating of an aluminum-chromium alloy onto the surface of said metal article.

2. The method according to claim 1 wherein said molten aluminum salt bath contains chromium ions in an amount of 1 to 3.5 g/l.

5 3. The method according to claim 2 wherein said chromium ions are anodically dissolved into said molten salt bath from a source selected from the group

consisting of (i) granules of metallic chromium and an

auxiliary electrode of chromium, and (ii) Cr-Al

mother alloy.

10 4. The method according to claim 2 wherein said metal article is iron or an iron alloy.

5. The method according to claim 2 wherein said metal article is titanium or a titanium alloy.

15 6. The method according to claim 2 wherein said molten salt bath comprises aluminum chloride, sodium chloride and potassium chloride.

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