A hot dip zinc-aluminum alloy coating process is disclosed, which comprises the step coating a steel or iron materials by adding into a coating bath comprising 0.10 to 10 % by weight of aluminum, 1.5 to 10 % by weight of copper and the remainder consisting essentially of zinc by a direct immersion method which is simple and economical. The process enables the preparation of a highly corrosion-resistant hot dip zinc-aluminum alloy-coated material having a thick coated layer having a thickness of 30 μm or more and also having a good appearance.
FIELD OF THE INVENTION

The present invention relates to a hot dip zinc-aluminum alloy coating process on a steel or iron materials as the base. More particularly, this invention relates to a hot dip zinc-aluminum alloy coating process obtained by forming a thick coated layer having a good appearance and high corrosion resistance.

BACKGROUND OF THE INVENTION

Zinc-aluminum alloy coating is recently attracting attention because it offers higher corrosion resistance as compared with zinc coating, and has come to be used extensively in outdoor applications such as building materials, support lines for electric or telephone, and metal parts over-head fittings and fasteners for transmission lines or electric powerlines. This coating is regarded as an anti-corrosive measure for steel materials to be used in severe corrosive environments including the marine, sea coast regions, and hot-spring areas and for steel materials required to be maintenance-free.

In the general process for zinc-aluminum alloy coating, a steel material as a base is degreased or annealed and subjected to pickling or reduction thereby to clean the surface, and the cleaned steel material is then immersed in or passed through a molten zinc-aluminum alloy bath either after flux treatment is conducted or while the reducing atmosphere is maintained. Techniques for immersing the bases in molten zinc-aluminum alloy baths can be roughly divided into the following two groups; (1) the direct immersion method in which the base is immersed directly in a molten zinc-aluminum alloy bath, and (2) the indirect immersion method in which the base is first subjected to zinc coating (by either hot dipping or electroplating) or to metal coating and is then immersed in a molten zinc-aluminum alloy bath.

The thickness of a coated layer formed by galvanizing or zinc-aluminum alloy coating is usually in proportion to corrosion resistance. That is, the larger the thickness of a coated layer, the higher the corrosion resistance. Hence, even though the corrosion resistance of a zinc-aluminum alloy coated layer is three times that of a zinc coated layer of the same thickness, the alloy coated layer comes to have the same corrosion resistance as the zinc coated layer if the thickness of the former is only 1/3rd of that of the latter. Accordingly, in order to enable the zinc-aluminum alloy coated layer to exhibit high corrosion resistance, the zinc-aluminum alloy coated layer is required to have the same thickness as the zinc coated layer. In hot dip galvanizing or hot dip zinc-aluminum alloy coating, the factors which determine coating thickness are the wet adhesion and viscosity of the coating bath, the thickness of an intermetallic compound layer (alloy layer) such as Fe-Zn, Fe-Al, or Fe-Al-Zn formed at the steel-coated layer interface, the drawing-up speed of the coated steel leaving the molten zinc or zinc-aluminum alloy bath, wiping conditions of molten coated layer, and cooling conditions.

In general, it is difficult in hot dip galvanizing or zinc-aluminum alloy coating to change the wet adhesion and viscosity of the molten zinc or zinc-aluminum bath because these are determined almost unconditionally by bath composition and temperature. Further, although the thickness of a coated layer can be increased to some degree by heightening the drawing-up speed of the coated steel leaving the molten zinc or zinc-aluminum alloy bath (e.g., increasing the line speed), a vibration may be caused, resulting in difficulties in obtaining uniformity of thickness. The drawing-up speed can be changed with ease in the case of continuous coating of a continuous material such as steel sheet or steel wire, but cannot be changed easily in batch type coating. With respect to wiping and cooling conditions, since the thickness of the coated layer has been determined to a great extent when the steel has left the coating bath, control of these conditions is conducted as an auxiliary technique for reducing or maintaining the coating thickness. Therefore, the coating thickness as a whole is generally being controlled by adjusting the thickness of an alloy layer formed at the interface between the steel and the coated layer.

For example, an Fe-Zn alloy layer is formed at the interface in galvanizing. The thickness of this alloy layer is determined mostly by the kind of steel (i.e., steel composition), the bath temperature, and the time period over which the steel material is immersed in the bath (i.e., dipping time). The alloy layer thickness can be increased by either heightening the bath temperature or lengthening the immersion time (dipping time). It is, therefore, possible in hot dip galvanizing to easily obtain a thick coated layer of 30 μm or more. In the case where hot dip galvanizing is used in applications where processability is required, such as galvanized steel sheet, it is necessary to restrain the growth of an Fe-Zn alloy layer. For this purpose, aluminum is added in the galvanizing bath in an amount of about from 0.1 to 0.5% by weight thereby to regulate the thickness in the range of from 10 to 30 μm by taking advantage of the aluminum's function of inhibiting an Fe-Zn alloy-forming reaction.

On the other hand, in zinc-aluminum alloy coating, the behavior of the alloy layer varies greatly depending on the concentration of Al in the bath. In the case of an aluminum concentration of about from 3
to 7% by weight which is ordinarily used frequently, the growth of an Fe-Zn alloy layer is restrained due to the aforementioned aluminum’s function of inhibiting an Fe-Zn alloy-forming reaction to give a thin coated layer having a thickness below 30 μm, under such most common conditions that the bath temperature is from 430 to 460 °C which is relatively low and the immersion time (dipping time) is 3 minutes or less which also is relatively short. If this coating method is modified by raising the bath temperature to higher than 460 °C or lengthening the immersion time (dipping time), the result is the rapid growth of an Fe-Al alloy layer and the thus-formed layer, if it is thick, has poor appearances such as gray spot, rough surface, and peeling and is of no commercial value.

In the case of an aluminum concentration of from 7 to 60% by weight, the bath also gives a deposit having no commercial value due to the abnormal growth of an Fe-Al alloy layer. The Fe-Al alloy layer growth can be inhibited by silicon addition into the bath in an amount of from 3 to 5% by weight based on the amount of the aluminum contained in the bath. This inhibiting effect of silicon is produced also at an aluminum concentration of from 3 to 7% by weight. However, because of this inhibiting effect, an Fe-Al alloy layer grows little and a thin coated layer having a thickness below 30 μm results.

It has so far been attempted to add a slight amount, i.e., 1% by weight or less, of nickel to a galvanizing bath for the purpose of controlling the growth of an Fe-Zn alloy layer. However, except the addition of silicon, almost no reports have been made on expedients for controlling the growth of an Fe-Al alloy layer in zinc-aluminum alloy coating. Further, although there is a report on the addition of copper in an amount as slight as 1% by weight or less in zinc-aluminum alloy coating for the purpose of improving corrosion resistance, control of the growth of an Fe-Al alloy layer cannot be attained when copper is added in such a small amount.

As described above, it has been difficult in zinc-aluminum alloy coating to obtain a thick coated layer having a thickness of 30 μm or more and a good appearance by a direct immersion method. Accordingly, when a thick zinc-aluminum alloy coated layer having a thickness of 30 μm or more is to be obtained, the only means for this has conventionally been to adopt an indirect immersion method in which zinc coating is first conducted to develop an Fe-Zn alloy layer and, after a desired thickness has been ensured, the resulting material is immersed in a zinc-aluminum alloy bath to replace part of the zinc in the coated layer with a zinc-aluminum alloy (substitution) or to cause diffusion of aluminum, thereby forming a coated layer consisting of a Zn-Fe-Al ternary alloy layer and a zinc-aluminum alloy layer. However, the indirect immersion method necessitates more than one bath and the process is complicated. For example, it is necessary to take a measure to cope with changes of the aluminum concentration in the zinc-aluminum alloy bath and with fluctuations of the bath level. It is also necessary to take a measure to avoid inclusion of aluminum into the zinc bath. Because of the above, there is a strong desire for a technique for obtaining, by a simple and economical direct immersion method, a zinc-aluminum alloy coated layer having a thickness of 30 μm or more and also having a good appearance and high commercial value.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for preparing a highly corrosion-resistant hot dip zinc-aluminum alloy-coated material obtained by a direct immersion method which is simple and economical and by which a zinc-aluminum alloy coated layer having a thickness of 30 μm or more and also having a good appearance and high commercial value can be obtained by hot dipping and the drawbacks of the currently-employed indirect immersion methods are overcome, such zinc-aluminum alloy coated layer being unable to be obtained by any conventional direct immersion method.

The above object of the present invention has been attained by a hot dip zinc-aluminum alloy coating process which comprises the step of coating a steel by adding into a molten coating bath comprising 0.10 to 10 % by weight of aluminum, 1.5 to 10 % by weight of copper and the remainder consisting essentially of zinc.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photomicrograph showing a copper-free thin normal coated layer at a magnification of 400 diameters.

Fig. 2 is a photomicrograph showing a copper-free thick abnormal coated layer at a magnification of 400 diameters.

Fig. 3 is a photomicrograph showing a copper-containing thick normal coated layer according to the present invention at a magnification of 400 diameters.
The present invention having such a constitution has been accomplished as a result of intensive studies in which various additive elements were added into a bath comprising a zinc-aluminum alloy containing from 0.10 to 10% by weight of aluminum with the remainder consisting of zinc exclusive of unavoidable impurities in order to obtain a zinc-aluminum alloy coated layer having a thickness of 30 µm or more by a direct immersion method using the bath, and in which the effect of the addition of these elements on coated layer's thickness and on alloy-forming reactions occurring at the steel base interface were investigated. It has been found from the studies that addition of copper into the above-described bath in an amount of from 1.5 to 10% by weight is extremely effective in obtaining a thick coated layer having a uniform thickness of 30 µm or more and a good appearance.

If the amount of copper is below 1.5% by weight, the growth of an Fe-Al alloy layer cannot be controlled because the copper produces no effects, resulting in a thin coated layer having a thickness below 30 µm or in a defective thick coated layer in which an Fe-Al alloy layer has grown abnormally. On the other hand, copper amounts exceeding 10% by weight are uneconomical in that because the alloy comes to have a heightened melting point, the bath should be kept at a higher temperature, leading to higher cost.

The material to be coated in the process of the present invention is not particularly limited as long as it is a steel material commonly used as a material in zinc-aluminum alloy coating. However, since coated layer's thickness varies depending on the kind of steel, it is necessary to fix beforehand coating conditions suited for the kind of the particular steel. The steel material may be pretreated by a known method. In the case where the coating is to be conducted in the atmospheric condition, flux treatment is necessary. The flux for use in this case should be one for use in zinc-aluminum alloy coating, such as that shown in JP-B-64-5110. (The term "JP-B" as used herein means an "examined Japanese patent publication"). If a flux for ordinary zinc coating is used, the flux-treated steel material shows poor wettability during coating and may remain uncoated.

The coating bath is not particularly limited as long as it has the composition as specified above, and any method may be used for preparing the bath. For example, zinc may be mixed with aluminum and copper. Alternatively, a zinc-aluminum alloy may be used with either copper or a zinc-copper alloy. To the coating bath, other element generally added in zinc-aluminum alloy coating, i.e., magnesium, sodium, a mish metal, lanthanum, or cerium, may be further added. The bath temperature desirably is in the range of from a temperature 20 °C higher than the melting point of the coating material to one 50 °C higher than that, although the preferred bath temperature cannot be specified unconditionally because the melting point of the coating bath composition varies. The immersion time (dipping time) may be the same as that in ordinary hot dipping. Since coated layer's thickness is determined by a combination of bath temperature and immersion time (dipping time), it is necessary to fix beforehand the bath temperature and immersion time (dipping time) so as to give the desired coated layer's thickness. Further, drawing-up and cooling after coating may be conducted by a known method.

The reasons why the range of the aluminum concentration in the bath should be from 0.10 to 10% by weight in the present invention are as follows. That is, at an aluminum concentration of less than 0.10% by weight, the alloy layer formed at the interface between the coated layer and the steel material usually consists of an Fe-Zn intermetallic compound (whose phases are represented by ξ and η phases), whereas an alloy layer consisting of an Fe-Al intermetallic compound is formed when the aluminum concentration is above 0.10% by weight. Based on this, since the growth of Fe-Al alloy layer is controlled in the present invention, the lower limit of aluminum concentration has been fixed at 0.1% by weight. On the other hand, if the aluminum concentration exceeds 10% by weight, the bath comes to have a higher melting point and the coating should be conducted at a higher temperature, resulting in a lessened practical utilization value, although the Fe-Al alloy layer-controlling effect of copper is observed. Based on this, the upper limit of aluminum concentration has been fixed at 10% by weight. It is, however, possible to apply the present invention even at an Al concentration of more than 10% by weight.

It should be noted that the bath temperature and immersion time (dipping time) used in the Example of the present invention were selected based on the kind, shape, number, and industrial value of the materials to be coated, so that higher temperature or a reduction or prolongation of the immersion time (dipping time) is a factor which is suitably varied according to the kind, shape, and number of the materials to be coated. Thus, bath temperature and immersion time (dipping time) are not conditions which limit the scope of the present invention.

Besides hot dip coating, there are many opportunities of using a pot, jig, or stirrer material made of iron or stainless steel in processes where a zinc-aluminum alloy is used such as smelting, dissolution, mixing, alloy production, casting, e.g., die casting, and utilization in molds. In this case, since copper has been
added according to the present invention, this copper has an additional effect of inhibiting to an extent both the dissolution of the iron or steel material into the molten zinc-aluminum alloy bath and a corrosion reaction of the material.

According to the present invention as described above, a zinc-aluminum alloy coated layer which is free from non-uniformity or any appearance defect and retains good coated layer quality such as corrosion resistance can be obtained using a single coating bath (direct immersion method) as in hot dip galvanizing, by only performing compositional control of the coating bath and fixing the bath temperature and the immersion time (dipping time) at constant values, without the necessity of conducting a high level of operation or a special operation. Furthermore, since a uniform and thick zinc-aluminum coated layer is thus obtained according to the present invention, high corrosion resistance can be obtained stably due to the increase in thickness in addition to the effect of aluminum.

The present invention will be explained below in more detail with reference to the following Example, but the invention is not construed as being limited thereto.

**EXAMPLE**

As materials to be coated, use was made of a rolled steel (SS 400 in JIS) for use as general-purpose structural material which had dimensions of 50W x 100L x 3.2T mm and a low-carbon SPCC cold rolled steel sheet having a thickness of 0.3 mm. These steel specimens were subjected to the steps of alkaline degreasing (20 wt% aqueous solution of sodium orthosilicate, 80 °C, 10 minutes), rinsing, pickling (10 wt% aqueous solution of hydrochloric acid, room temperature, 20 minutes), rinsing, flux treatment (the 30 wt% flux aqueous solution for Zn-Al coating which is described in JP-B-64-5110, 90 °C, 1 minute), and drying in this order as a pretreatment.

Using coating baths having the compositions shown in the table given later, coating was then conducted in the atmospheric condition under the following conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath temperature</td>
<td>430-500 °C</td>
</tr>
<tr>
<td>Immersion time</td>
<td>0.5-5 min</td>
</tr>
<tr>
<td>Drawing-up speed</td>
<td>5-10 m/min</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>10-20 °C/sec</td>
</tr>
</tbody>
</table>

After the coating, the thickness of each coated layer was measured with a magnetic thickness tester and by microscopic examination of a section of the coated layer. Further, the appearance of each coated layer was evaluated with the naked eye in three grades as follows.

A : good (no gray spot or no rough surface)
B : partly having gray spot or rough surface
C : defective with gray spot over the whole surface

Moreover, a salt spray test was conducted in accordance with JIS Z 2371 to measure the time required for each steel to appear a red rust, thereby to examine the corrosion resistance of the coated layer. The results thus obtained are also summarized in Table 1.
The results in the table show that stable and thick zinc-aluminum alloy layer is obtained by the copper addition and the coated layer simultaneously exhibits high corrosion resistance.

### Table 1

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Bath composition (wt%)</th>
<th>Temperature (°C)</th>
<th>Immersion time (min)</th>
<th>Drawing speed (m/min)</th>
<th>Cooling rate (°C/sec)</th>
<th>Coating thickness (μm)</th>
<th>At least 30 μm coating thickness</th>
<th>Appearance</th>
<th>Time to red rust appearing in salt spray test (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>5.2</td>
<td>470</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>129</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 2</td>
<td>5.2</td>
<td>460</td>
<td>3</td>
<td>5</td>
<td>15</td>
<td>81</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 3</td>
<td>5.2</td>
<td>480</td>
<td>1</td>
<td>7</td>
<td>20</td>
<td>60</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 4</td>
<td>5.2</td>
<td>480</td>
<td>2</td>
<td>7</td>
<td>10</td>
<td>93</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 5</td>
<td>0.14</td>
<td>460</td>
<td>3</td>
<td>10</td>
<td>15</td>
<td>85</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 6</td>
<td>9.2</td>
<td>490</td>
<td>1</td>
<td>10</td>
<td>20</td>
<td>99</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 7</td>
<td>5.2</td>
<td>490</td>
<td>1</td>
<td>5</td>
<td>15</td>
<td>78</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Example 8</td>
<td>5.2</td>
<td>490</td>
<td>2</td>
<td>5</td>
<td>15</td>
<td>133</td>
<td>yes</td>
<td>A</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>5.0</td>
<td>460</td>
<td>1</td>
<td>5</td>
<td>10</td>
<td>17</td>
<td>no</td>
<td>A</td>
<td>850</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>5.0</td>
<td>free</td>
<td>3</td>
<td>7</td>
<td>15</td>
<td>15</td>
<td>no</td>
<td>A</td>
<td>770</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>5.3</td>
<td>free</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>100-183</td>
<td>yes (abnormal thick coating)</td>
<td>C</td>
<td>&gt;1500</td>
</tr>
</tbody>
</table>
Claims

1. A hot dip zinc-aluminum alloy coating process on a steel or iron materials using a bath comprising the step of coating a steel or iron materials by adding into a coating bath comprising 0.10 to 10 % by weight of aluminum, 1.5 to 10 % by weight of copper and the remainder consisting essentially of zinc.

2. The hot dip zinc-aluminum alloy coating process as in claim 1, wherein said the coated layer has a thickness of 30 μm or more.
## EUROPEAN SEARCH REPORT

**Application Number**

EP 92 12 1339

**DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cls.)</th>
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<tbody>
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<td>DE-A-2 146 376 (A/S FREDERICIA GALVANISERINGSANSTALT) * page 5, line 11 - line 14; claim 1 *</td>
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**TECHNICAL FIELDS SEARCHED (Int. Cls.)**

C23C

The present search report has been drawn up for all claims.

**Place of search**

THE HAGUE

**Date of completion of the search**

04 AUGUST 1993

**Examiner**

ELSEN D.B.

**CATEGORY OF CITED DOCUMENTS**

- X: particularly relevant if taken alone
- Y: particularly relevant if combined with another document of the same category
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
- #: member of the same patent family, corresponding document