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3,505,042

METHOD OF HOT DIP COATING WITH A ZINC BASE ALLOY CONTAINING MAGNESIUM AND THE RESULTING PRODUCT

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19 Claims

ABSTRACT OF THE DISCLOSURE

A method of hot dip coating a ferrous metal surface with a magnesium-containing zinc base alloy to impart thereto improved surface properties in which a ferrous metal surface in a reduced oxide state is coated in a hot dip zinc base alloy coating bath containing between about 1.5 and 5 percent by weight magnesium and which preferably contains at least 0.05 percent by weight aluminum with the balance comprised essentially of zinc.

A ferrous metal sheet hot dip coated with a zinc base alloy containing between about 3 and 5 percent by weight magnesium exhibits very good corrosion resistance against aqueous sodium chloride solutions and good adherence and formability properties.

This application is a continuation-in-part application of U.S. application Ser. No. 396,707, filed Sept. 15, 1964.

The present invention relates generally to an improved method of providing a hot dip zinc base alloy protective coating on a ferrous metal and to a ferrous metal article having an improved protective hot dip zinc base alloy coating.

Zinc hot dip coatings have long been used to protect ferrous metal bases against attack by corrosion. Various alloying metals have been added to a molten zinc bath comprised mainly of zinc to improve the properties of the metal coating or the coating process. The alloying metals added to the zinc bath are generally used in an amount ranging upwardly from a fraction of one percent and serve to improve the corrosion resistance or the appearance of the coatings or reduce the amount of intermetallic compounds formed. Among the metals which have heretofore been added to a molten zinc coating bath are lead, tin, aluminum, cadmium, antimony, and magnesium.

It has heretofore been reported, for example, that the magnesium concentration in a molten zinc bath which is required to produce a coating having optimum corrosion resistance is from about .04 percent to 0.5 percent by weight magnesium. It has also been reported that the use of magnesium at a concentration substantially above about .05 percent by weight magnesium creates serious operating difficulties in a molten zinc bath. For example, it has been reported that a hot dip zinc bath containing in excess of about 0.1 percent by weight magnesium results in excess losses due to high flux consumption and large ash build-up on the surface of the bath. (See the paper by John A. Heath, "A New Frontier in Hot-Dip Galvanizing: A Magnesium Containing Coating,"

delivered to the American Hot Dip Galvanizing Association, Mar. 24, 1961.)

Hot dip zinc base alloy coatings containing up to about 1 percent magnesium have been prepared for testing purposes and found to be less formable than conventional zinc coatings and to severely crack and scale off when subjected to a conventional bend test. Moreover, the addition of magnesium up to about 1 percent by weight to a zinc coating bath was found to have no substantial favorable influence on the corrosion resistance of the resulting zinc alloy coating when exposed to damp air and only a slight favorable improvement in the corrosion resistance when exposed to industrial atmosphere (see Stahl & Eisen, vol. 84, 1964, No. 12, pages 713-8).

It was also reported by the prior art that when attempts were made to hot dip coat a metal with a zinc base alloy coating containing in excess of 1 percent by weight magnesium, it was not possible to form adherent hot dip coatings with such alloys, and it was necessary to limit the hot dip zinc base alloy coatings containing magnesium to those having a magnesium concentration not exceeding about 1 percent by weight magnesium (see Corrosion, vol. 6, pp. 195-200, June 1950). Accordingly, there remains a great need for an improved method of applying a hot dip zinc base alloy protective coating and for providing a hot dip zinc base alloy coating having improved surface properties, such as improved corrosion resistance, good adherence and, good ductility properties.

It is therefore an object of the present invention to provide an improved method of coating a ferrous metal base to produce a protective zinc base alloy coating having improved corrosion resistance with good ductility and adherence properties.

It is still another object of the present invention to provide an improved method of hot dip coating a ferrous metal base with a zinc base alloy containing substantially in excess of one percent by weight magnesium.

It is a further object of the present invention to provide an improved ferrous metal article having a hot dip zinc base alloy coating with a high magnesium content which exhibits substantially improved corrosion resistance and good adherence and ductility properties.

Other objects of this invention will be apparent to those skilled in the art from the detailed description and claims to follow.

It has unexpectedly been discovered that a protective zinc base alloy coating having markedly improved corrosion resistance along with good adherence and ductility properties can be provided on a ferrous metal surface by applying a hot dip zinc base alloy coating having a metallic magnesium content appreciably in excess of the amounts previously considered usable. For example, an adherent hot dip coating exhibiting an increase in corrosion resistance of at least about 400 percent over conventional zinc coatings of similar weight without loss of adherence or ductility has been obtained by applying in accordance with the present invention a hot dip zinc base alloy coating containing about 3 percent by weight magnesium. The following Table I illustrates the significant improvement obtained where a relatively thin zinc base alloy coating which contains magnesium within the range of concentrations of the

present invention and compares therewith a coating of similar thickness made from a standard zinc spelter on a conventional continuous hot dip galvanizing line:

TABLE I

Kinds of bath	Average coating thickness (oz./ft. ²)	Time to failure in 5% salt fog (hrs.)
Normal zinc spelter.....	.53	336
3% Mg-Zn spelter.....	.50	2028

The following Table IA presents corrosion data for hot dip zinc alloy coatings containing from 1 percent to 5 percent by weight magnesium with 0.5 percent by weight aluminum included to reduce top skimming losses in the coating bath and the balance being essentially zinc. Each of the zinc base alloy coatings was applied to a ferrous sheet metal panel as herein described and was tested by immersion in a 1 percent aqueous sodium chloride solution at 180° F. for a 96 hour test period. The corrosion rate data are expressed in "Inches Penetration per Year" (IPY):

TABLE IA

Coating composition:	IPY in 1% NaCl
0.5% Al, 1% Mg, bal. Zn046
0.5% Al, 2% Mg, bal. Zn038
0.5% Al, 3% Mg, bal. Zn004
0.5% Al, 4% Mg, bal. Zn004
0.5% Al, 5% Mg, bal. Zn003

While the corrosion resistance to aqueous salt solution increases somewhat as the magnesium concentration in the zinc base alloy is increased from 1 percent to 2 percent by weight magnesium, it will be evident from Table IA that a very substantial and unexpected improvement in the corrosion resistance of a ferrous metal base is obtained when the magnesium concentration is increased above 2 percent to the level of about 3% to 5% by weight magnesium.

Other unexpected and very significant improvements are present in the zinc base alloy coatings of the present invention when the magnesium content is at the preferred level of about 3 percent by weight magnesium (i.e. between about 2.7 percent and 3.6 percent by weight magnesium), such as the very good adherence and ductility properties of the coating. The good ductility properties (i.e. formability) of the zinc alloy coating containing about 3 percent magnesium, which is about the eutectic mixture for zinc and magnesium, was entirely unexpected because it was observed that the eutectic mixture of magnesium and zinc when in block form before application as a thin hot dip coating was very brittle and would shatter when a mass thereof was dropped. However, the hot dip coatings of the present invention when applied in any of the conventional hot dip coating weights exhibit good ductility and can be formed and bent without damaging the coating.

From the phase diagram for metallic zinc and magnesium mixtures ("Constitution of Binary Alloys" published by McGraw-Hill Book Co., Inc. 1958, p. 928), it is evident that the eutectic mixture containing about 3 percent magnesium and 97 percent zinc on a weight basis has a relatively low melting point of about 367° C. (692° F.). Thus, it is possible, by using a zinc base alloy bath containing about 3 percent magnesium to operate at a temperature substantially below the usual operating temperature of a conventional galvanizing bath. More particularly, with the eutectic mixture of about 3 percent magnesium and about 97 percent zinc on a weight basis, it is possible to operate the alloy coating bath at a temperature of about 750° F. which is about 100° F. below the usual operating temperature of a conventional continuous galvanizing bath.

It will also be evidenced from the phase diagram for zinc-magnesium mixtures that the magnesium-zinc alloys containing between about 1.5 percent magnesium and

about 5 percent magnesium have melting points below 800° F. and below the normal operating temperature of a conventional continuous zinc galvanizing bath, and coating with such alloys are within the scope of the present invention. However, since magnesium-zinc alloy mixtures containing about 3 percent by weight magnesium (i.e. between 2.7 percent and about 3.6 percent magnesium by weight) have a lower melting point than those having less than 2.7 percent magnesium and greater than 3.6 percent magnesium, the latter more limited range of magnesium-zinc alloys containing about between 2.7 and 3.6 percent (i.e. about 3%) by weight magnesium are preferred in the present invention.

As a result of being able to operate the zinc base alloy hot dip coating baths of the present invention at a significantly lower temperature than is possible with conventional galvanizing baths, particularly when about 3 percent by weight magnesium is used in the hot dip coating baths, a smaller amount of intermetallic compound is formed at the interface between the zinc alloy coating and the ferrous metal when no other additives are included in the bath, and a hot dip coating having improved formability properties is thereby obtained. The data in the following Table II show the amount of intermetallic compounds formed when applying a hot dip coating from coating baths having the indicated composition on a weight basis and at the temperatures specified:

TABLE II

Hot-dip bath compositions	Bath temperatures (° F.)	Thickness of intermetallic layer (mils)
Pure zinc.....	860	.50
3% Mg+Zn.....	750	Below .04
3% Mg+Zn.....	780	.10
3% Mg+Zn.....	820	.20
3% Mg+Zn.....	850	.30
3% Mg+Zn+.2% Al.....	750	Below .04
3% Mg+Zn+.2% Al.....	800	Below .04
3% Mg+Zn+.2% Al.....	850	Below .04

From Table II it is evident that when the lower operating temperature of 750° F. is used with a 3 percent magnesium-zinc alloy coating bath of the present invention a very thin intermetallic layer is obtained even without the addition of aluminum. The data of Table II further indicate that the inclusion of 0.2% by weight aluminum in the magnesium-zinc alloy coating bath of the present invention does not appear to have a significant effect on the amount of intermetallic compounds formed when the alloy hot dip coating bath is operated at a temperature of 750° F. If, however, the hot dip coating bath is operated at temperatures substantially above 750° F. the inclusion of aluminum does have a very beneficial effect by inhibiting the formation of intermetallic compounds. The addition of small amounts of aluminum, in the range of 0.15-0.20 percent by weight, has thus been found to effectively retard iron-zinc alloy growth at the higher bath temperatures of a magnesium-zinc hot dip coating bath.

Because it is possible to operate the hot dip coating baths of the present invention at a lower temperature than heretofore, additional savings are possible due to the reduction in the oxidation of magnesium on the surface of the hot dip coating bath (i.e. top skimming losses). The data of Table II show the results of static tests carried out in a stainless steel pot at operating temperatures of 750° F. and 850° F., respectively:

TABLE III

Bath composition	Bath temperatures (° F.)	Static tests (hrs.)	Amount of top skimming formed (grams)
3% Mg+Zn.....	850	4	145
3% Mg+Zn.....	750	8	15

Further tests have shown that in order to minimize magnesium losses in the high magnesium-zinc coating bath due to surface oxidation of magnesium, particularly when operating in an unprotected non-oxidizing atmosphere and

at a bath temperature above 750° F., it is advisable to include in the hot dip alloy coating baths of the present invention a small amount of aluminum ranging between about 0.05 and 0.5 percent on a weight basis and preferably at a level of about 0.2 percent by weight aluminum. Larger amounts of aluminum can be used in the coating baths, such as 1.0 percent by weight, and such amounts do not interfere with the present invention. While the use of aluminum at even substantially higher levels does not interfere with the present invention, such amounts are not required to prevent the formation of an objectionable intermetallic compound layer or to reduce surface oxidation losses.

Further important improvements in the hot dip coating process of the present invention which have overcome the difficulties encountered in the prior art attempt to hot dip coat steel with a zinc base alloy containing in excess of 1 percent by weight magnesium and which now makes it possible to hot dip coat with zinc-magnesium alloys containing substantially in excess of 1 percent magnesium, comprise contacting the ferrous metal surface with the high magnesium containing zinc base hot dip alloy coating only when the metal surface is clean and substantially free of surface oxides and other material containing oxygen, such as fluxes. It is also important to avoid as much as possible oxidizing the hot dip coating as the coated metal is withdrawn from the hot dip coating bath. Both of these operating conditions can be achieved by conducting the hot dip coating operation entirely within an enclosed chamber or zone containing a non-oxidizing or reducing atmosphere, such as an atmosphere of dry 10 percent hydrogen and 90 percent nitrogen.

Where it is not feasible to conduct the entire hot dip coating operation within an enclosed chamber or enclose the entire alloy coating bath in a controlled atmosphere having a low oxidizing potential, the desired operating conditions can be achieved by introducing the clean oxide-free metal base into the coating bath through a tube or snout in which a non-oxidizing or reducing atmosphere is maintained, and thereafter withdrawing the coated metal base from the bath through a chamber or zone having a low oxidizing potential atmosphere from which most of the oxygen of the air is excluded and maintaining the alloy coating in the substantially non-oxidized condition until the temperature falls below the melting point of the alloy (i.e. coating solidifies). A zone having a low oxidizing potential of the above type can be provided by applying (i.e. blowing) nitrogen gas or other non-oxidizing gas onto the coated surface just as the metal is withdrawn from the coating bath so that the surface of the alloy coating immediately on leaving the coating bath is surrounded or blanketed by an atmosphere having a substantially reduced oxygen content which has a low oxidizing potential for the magnesium in the alloy bath and coating and which preferably has no oxidizing action upon the alloy coating and bath.

metal article having the improved alloy coating of the present invention is not rapidly cooled immediately after withdrawal from the hot dip bath, the surface tends to be irregular and somewhat pitted. These surface defects are substantially reduced by applying a cooling fluid, and preferably a gas which is non-reactive with the coating, such as cool gaseous nitrogen, to the surface of the alloy coating as soon as the article is withdrawn from the coating bath.

In order to further illustrate the present invention the following specific examples are given, without, however, limiting the invention to the particular materials and conditions used.

Example No. 1

A series of 4" x 8" steel test panels were obtained from 20 gauge full hard steel sheets which has a thickness of .034" and chemical compositions of about .04 percent carbon, .29 percent to .35 percent manganese, .01 percent to .011 percent phosphorus, .019 percent to .020 percent sulphur and .04 percent copper, with the balance essentially iron. All the panels were precleaned by the oxidation method according to the following procedures: (1) vapor degreased with trichloro-ethylene for 15 minutes at 170° F., and (2) oxidized in a furnace at 1650° F. for 30 seconds. The oxidized panels were then transferred into the "dry box" which contained the laboratory galvanizing equipment. The atmosphere inside the "dry box" contained 10 percent hydrogen with the balance nitrogen. The dew point inside the dry box was always kept below -15° F. during the dipping operation. The cleaned panel was preheated at 1800° F. for 3 minutes in the reducing atmosphere of the dry box during which surface oxides were reduced, and then cooled to the bath temperature for dipping.

An alloy containing 3 percent by weight magnesium metal and 97 percent conventional zinc spelter was melted in a graphite pot at a temperature of about 750° F. A test series was run with the 3 percent Mg-Zn alloy in which the molten bath temperature was varied from 750° F. to 850° F. The time of immersion was maintained at about 5 seconds. The effect of the lower bath temperature on the thickness of the intermetallic layer can be seen from the following data:

TABLE IV

Bath temperature (°F.):	Thickness of intermetallic layer (mils)
750	0.04
780	.10
800	.15
820	.20-.25
850	.25-.30

The standard 5 percent salt fog test performance results of the zinc alloy coatings applied in the foregoing manner are shown in the following Table V:

TABLE V

[5% salt fog test performance of 3% Mg-Zn alloy coated steel]

Test Series	Percent Al in alloy	No. of panels	Coating thickness range (mils)	Alloy coating time to red rust		Normal galvanized time to red rust (avg. hrs.)
				Range (hrs.)	Avg.	
1		4	.76-1.00	1,968-2,616	2,322	264
2		5	.90-1.00	2,184-2,496	2,300	336
3		6	.90-1.60	1,992-3,000	2,700	288
4	.20	4	.74-1.20	1,848-3,000	2,610	288
Avg.					2,483	294

It has also been found advisable to rapidly cool the magnesium containing zinc alloy hot dip coating of the present invention as the coated article is withdrawn from the coating bath in order to obtain a smoother and more attractive surface on the coated article. When the ferrous

It can be seen from the 5% salt fog test results in Series 1 and 2 of Table V that for a coating thickness ranging between .76 and 1.00 mils, the average performance of the 3% Mg-Zn alloy coated panels was about 2300 hours as compared to about 300 hours for

the normal galvanized steel control panels of the same thickness. The alloy coatings of the present invention exhibit almost eight times the corrosion resistance of normal galvanized coatings. When the average coating thicknesses were greater than 1.0 mil, the 5% salt fog test performances averaged about 2655 hours. From the data of Series 3 and 4, aluminum appear to have no effect on the 5% salt fog test performance results. In Test Series No. 3, for example, the average performance of the coatings produced from the aluminum-free bath was 2700 hours while in Series 4 the test performance of the coatings produced from the 3% Mg-Zn alloy containing .2 percent aluminum was 2610 hours. The latter alloy coating also exhibited satisfactory adhesion and formability of the coating produced from molten baths maintained at between about 750° F. and 850° F. Also, the painting characteristics of the 3 percent magnesium-zinc alloy coatings are comparable to that of galvanized steel and are considered satisfactory.

Example No. 2

A standard steel hot mill band having a thickness of about 0.080 inch is cold reduced on a five-stand tandem mill to form a steel strip having a thickness of about 0.0236 inch thick (24 gauge). The full hard 0.0236 inch strip thus formed having a Rockwell hardness (30 T-scale) of about 80 is cleaned by passing through a continuous cleaning line, followed by conventional box annealing heat treatment to restore the ductility lost when the strip was cold reduced. The annealed strip is then temper rolled to provide a suitable surface for continuous hot dip coating.

The annealed endless steel strip after cleaning as in Example 1 and after being enclosed in a zone having a dry reducing atmosphere of the type used in Example 1 is then immersed in a molten magnesium-zinc alloy bath having the following composition:

	Percent by weight
Magnesium -----	2.77
Aluminum -----	0.20
Iron -----	0.01
Lead -----	0.013
Zinc -----	97.007

with the alloy bath maintained at a temperature of 750° F. and with the steel strip traveling at a line speed of about 28 feet per minute, the enclosed strip was fed into the alloy bath at an angle of about 70° to the horizontal. The strip was allowed to remain in the alloy bath about 5 seconds (and not more than 10 seconds), and was continuously withdrawn from the bath at an angle of about 90° to the horizontal through coating rolls. The coating rolls were flame covered to retard oxide pick-up from the bath. As the alloy coated strip was withdrawn from the bath, the molten alloy coating was rapidly cooled by blowing thereover nitrogen gas at 15 p.s.i. and at a temperature below 100° F. and preferably at about 50° F. An alloy coating was obtained having a thickness on each side of the strip between about 0.9 mil and 1.3 mils. The latter alloy coating exhibited the improved properties of the coating of Example 1.

Example No. 3

An annealed endless steel strip processed as in Example 2 was immersed in a molten bath having a temperature of 750° F. in the same manner as in Example 2, with the bath having following composition:

	Percent by weight
Magnesium -----	2.97
Iron -----	.07
Lead -----	.013
Aluminum -----	.12
Zinc -----	96.827

The resulting alloy coated strip has the same properties as the strip of Example 2.

Example No. 4

An annealed endless steel strip processed as in Example 2 was immersed in a molten zinc base alloy hot dip coating bath having a temperature of 800° F. in the same manner as in Example 2, with the bath having the following composition:

	Percent by weight
Magnesium -----	3.56
Iron -----	.07
Lead -----	.013
Aluminum -----	.50
Zinc -----	95.857

The resulting alloy coating has the same properties as the coatings in Example 1 and Example 2. The top skimming losses were small, despite the higher bath temperature.

Others may practice the invention in any of the numerous ways which are suggested to one skilled in the art by this disclosure, and all such practice of invention are considered to be a part hereof which fall within the scope of the appended claims.

We claim:

1. A method of hot dip alloy coating a ferrous metal surface which comprises; immersing a ferrous metal article having a surface thereof substantially free of oxides and substances which contain oxygen into a molten zinc base alloy hot dip coating bath consisting essentially of zinc and containing as an alloying element between about 1.5% and 5% by weight magnesium and withdrawing said article from said bath to form on said surface an adherent protective hot dip zinc base alloy coating.

2. A method as in claim 1, wherein said surface immediately before immersion in said bath is maintained in contact with a reducing gas which reduces any oxides on said surface to a non-oxidized state before immersion in said bath.

3. A method as in claim 1, wherein said bath contains between about 2.7 and 3.6 percent by weight magnesium and is maintained at a temperature from just above the melting point of said bath up to temperature of about 800° F.

4. A method as in claim 3, wherein said bath temperature is maintained at about 750° F.

5. A method as in claim 1, wherein said coating bath consists essentially of zinc, magnesium and contains as a further alloying element about 0.05% to 1.0% by weight aluminum.

6. A method as in claim 1, comprising blanketing said alloy coating as said article is withdrawn from said coating bath with a protective gaseous atmosphere which is substantially non-oxidizing to said alloy coating.

7. A method as in claim 1, wherein said alloy coating is blanketed with a protective gaseous atmosphere by blowing onto said coating as said article is withdrawn from said bath a gas which prevents appreciable surface oxidation of said alloy coating before said coating solidifies.

8. A method as in claim 1, wherein said coating bath in at least the are where said article enters said bath and said article immediately before being immersed in said bath are enclosed within a zone containing a protective gaseous atmosphere which is non-oxidizing to said bath and said article and which prevents contact therewith by the normally oxidizing ambient atmosphere.

9. A method as in claim 8, wherein a gas which is substantially non-oxidizing relative to said alloy coating is maintained in contact with said alloy coating as said article is withdrawn from said bath.

10. A method as in claim 1, wherein said bath is enclosed within a zone having an atmosphere which is non-oxidizing with respect to said alloy bath.

11. A method as in claim 1, wherein said hot dip coating bath in at least the area where said article is withdrawn from said bath and said alloy coating as said article is withdrawn from said bath are maintained in contact with an atmosphere which is non-oxidizing with-
5 respect to said alloy coating bath and said alloy coating.

12. A method as in claim 6, wherein said atmosphere has a temperature below about 100° F.

13. An article comprising a ferrous metal sheet having on a surface thereof a corrosion resistant hot dip zinc base alloy coating containing between about 3 percent and 5 percent by weight magnesium with the balance
10 comprised essentially of zinc.

14. An article as in claim 13, wherein said hot dip alloy coating consists essentially of zinc, magnesium and
15 further contains aluminum in an amount between about 0.15 percent and 0.5 percent by weight.

15. An article comprising a ferrous metal sheet having on a surface thereof a corrosion resistance hot dip zinc base alloy coating consisting essentially of zinc and containing as alloying elements between about 1.5 percent and 5 percent by weight magnesium and between about 0.05 percent and 1.0 percent by weight aluminum, and
20 said coating having good adherence and formability properties.

16. An article as in claim 15, wherein said hot dip zinc

base alloy coating contains between about 2.7 percent and 3.6 percent by weight magnesium.

17. An article as in claim 16, wherein said hot dip zinc base alloy coating contains about 0.2 percent by weight aluminum.

18. An article as in claim 17, wherein said ferrous metal sheet is an endless steel strip.

19. An article as in claim 15, wherein said aluminum is present in an amount between about 0.15 percent and
0.5 percent by weight.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,505,042 Dated April 7, 1970

Inventor(s) Sievert et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

col. 1, line 56, "0.5 per cent" should read -.05-; Col. 5, line 19, "dig" should read --dip--; Col. 8, line 63, "at least the are" should read --at least the area--.

SIGNED AND
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(SEAL)

Attest:

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