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(54) **Process for preparing hot-dip zinc-plated steel sheets**

(57) In a process for preparing a hot-dip zinc plated steel sheet, the improvement which comprises using a plating bath consisting essentially of 0.35 - 3.0 % Al, 0.15 - 1.0 % Mg and not more than 0.015 % Pb, the remainder being Zn and incidental impurities. The plating bath *per se* is also claimed. Plated sheets thus obtained are superior to those obtained using a conventional plating bath both in corrosion resistance and in surface appearance without sacrificing workability.

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SPECIFICATION

Process for preparing hot-dip zinc-plated steel sheets

This invention relates to a process for preparing hot-dip zinc-plated steel sheets which have excellent corrosion resistance and excellent coatability.

In recent years, use of hot-dip zinc-plated steel sheets has become more diversified and sophisticated. Whereas these steel sheets have conventionally been used for roofs and walls, they are now used as materials for automobiles, as precoated materials for coloured sheets, etc. In these uses the steel sheets are subjected to severe plastic working such as bending, deep drawing, etc. and the finished products must have excellent surface properties and appearance. There is thus increasing demand for products which are far better than the conventional ones not only in the formability of the substrate sheet but also in the formability of the alloyed layer, as well as in the corrosion resistance of the alloyed layer of the formed parts.

In order to improve the corrosion resistance of hot-dip zinc-plated steel sheets, two methods have hitherto been resorted to. One is to increase the thickness of plated zinc layer and the other is to improve the quality of the plated zinc layer itself by incorporating other elements in the plating bath.

The former will enhance the protective effect of the zinc layer for the iron substrate, but a thick layer is susceptible to cracking when the plated sheet is worked, and flaking of the plated layer and deterioration in the surface appearance may result. Therefore, this method is practically unacceptable.

Regarding the latter method, U.S. Patent No. 4,027,478 proposes use of a zinc bath containing 0.2 - 17% Al, 0.003 - 0.15% Mg and 0.02 - 0.15% Pb. Use of this zinc bath gives considerably improved corrosion resistance. However, a close study revealed that the resulting corrosion resistance is not entirely sufficient and that this method does not give sheets with satisfactory coatability. We now believe the reason for this to be that the balance among the added elements such as Al, Mg and Pb is not completely satisfactory. More specifically the Pb content is rather too high and the Mg content is insufficient relative to the Pb content.

In order to improve the surface appearance and mechanical properties of zinc plated steel sheets, it is also generally practiced to cool the plated sheet by spraying water mist immediately before the plated zinc solidifies after plating so as to minimize the size of the zinc crystal grains, or to smooth the surface of the sheet by stretcher leveling and temper rolling in combination. However, rapid cooling of the plated layer or mechanical smoothing increases the number of activated points at which corrosion may be initiated. Therefore, these methods are not desirable from the viewpoint of corrosion resistance, and especially excessive temper rolling should be avoided.

Further, when use of zinc-plated steel sheets for precoated sheets or automobile materials is considered, a thinner plated layer is preferred because these materials have to be subjected to shaping and welding and thinly plated sheets are advantageous in this respect. Therefore, a steel sheet with a thinner plated layer and high corrosion resistance is desired. Nowadays, the thickness of plated layers is controlled by gas-wiping under high speed operation (160 - 200 m/min). Under such high speed operation, the amount of plated zinc is in the range of 45-60 g/m^2 per side (the amount of plated zinc will be indicated per surface hereinafter) with the conventional plating bath (0.15 - 0.18 % Al). This is far from the target of 30 g/m^2 or less, which is desirable from the standpoint of working of the plated sheets. The measure generally employed in order to reduce the amount of plated zinc is to slow the plating speed by 20 - 30% below the standard speed to increase gas wiping effect. However, this lowers the productivity and therefore is not desirable in an industrial process.

We have now studied the above problem and found that changes in the plating both greatly assist a solution to the problem.

According to this invention, there is provided a zinc plating bath consisting essentially of 0.35 - 3.0 % Al, 0.15 - 1.0 % Mg and having a Pb content of not more than 0.015 %, the remainder being Zn and incidental impurities.

Further, there is provided, in a process for preparing a hot-dip zinc-plated sheet, the improvement which comprises using a plating bath consisting essentially of 0.35 - 3.0 % Al, 0.15 - 1.0 % Mg and a Pb content of not more than 0.015 %, the remainder being Zn and incidental impurities.

In a preferred embodiment, the amount of zinc plated on the sheets is not more than 30 g/m^2 per side. Also the plated sheets are preferably heated so as to form alloyed layers.

A preferred bath composition is from 0.35 - 2.0 % Al, 0.15 - 0.8 % Mg and not more than 0.01 % Pb, the balance being Zn and incidental impurities.

A more preferred bath composition contains 0.35 - 1.0 % Al, 0.15 - 0.5 % Mg and a Pb content of not more than 0.007 %.

By incidental impurities is meant impurities contained in commercially available zinc, that is, not more than 0.01 % Cd, not more than 0.01 % Sn and not more than 1.0 % Fe.

This invention has the following advantages.

1. Products may be obtained with a corrosion resistance more than three times that of products produced with a conventional plating bath containing from 0.15 - 0.18 % Al.

2. Smooth plated sheets with minimized spangles may be obtained without particularly rapid cooling after the sheets have passed through the plating bath.

3. Products having excellent surface appearance and mechanical properties may be obtained by

subjecting the sheets to a light temper rolling (around 1% reduction) after plating.

4. As a result of increasing the Al content in the bath from 2.5 - 20 times, the fluidity of the bath is increased and the wiping effect in gas wiping is enhanced under the same gas wiping condition at the same temperature and thus products with a thinner plated layer may be obtained.

Each component of the bath composition and the concentration thereof may be explained as follows:

1. Aluminum

As the Al content in the hot-dip zinc-plating bath is increased, the fluidity of the bath at the same temperature increases remarkably over that of a conventional plating bath. When the Al content is increased from 0.15 % as in the conventional bath to 0.3 % or more, the fluidity of the plating bath is increased by 1.5 - 2.0 % or so. The lower limit of the Al content of the bath in this invention is defined as 0.35 %. The upper limit is defined as 3.0 %, since we have found that if the Al content exceeds this value, the Zn-Al eutectic structure becomes noticeable and local cells are formed between the eutectic phase and the zinc phase and this induces deterioration in corrosion resistance.

2. Magnesium

Mg is one of the elements added for the purpose of increasing corrosion resistance. The corrosion resistance of the formed alloyed layer markedly improved when about 0.15 % or more Mg is present. As the Mg content increases, the corrosion resistance increases accordingly, but if it exceeds 1.0 %, deterioration in the surface appearance of the alloyed layer by formation of wrinkles, and oxidation of the surface gradually becomes pronounced, and at the same time oxidation (formation of dross) on the surface of the plating bath is promoted, which results in wasting of the plating bath. The allowable upper limit of the Mg content in our invention is 1.0 %.

3. Lead

Pb has almost no solid-solubility in Zn at ordinary temperature and therefore, it usually precipitates within the crystal grains or at the grain boundaries, as minute particles which form local cells. This is one of the causes of deterioration in corrosion resistance. We prefer therefore that the Pb content be as low as possible. It has been confirmed, as the result of close investigation, that when the Pb content is not more than 0.015 %, microscopically almost no precipitation of Pb in grains and at grain boundaries of the alloyed layer is found, practically no intergranular corrosion is found; and almost no crystal spangles of Zn can be observed by the naked eye. Thus the Pb content in our invention is defined as not more than 0.015 %.

By using the Zn plating bath of the above-mentioned composition, Zn-plated steel plates with a very thin plated layer (not more than 30 g/m^2) and having excellent appearance and corrosion resistance can be obtained under the conventional operation conditions.

It should also be noted that although the thinness of the plated layer is one of the characteristics of this invention, the amount of the plated Zn can be varied by changing the conditions of gas wiping. Therefore, thicker plated layers can also be obtained.

Now the invention is explained in detail by way of working non-limiting Examples.

Example 1

Using a Zn plating bath, the composition of which is shown in Table 1, non-annealed rimmed steel sheets 0.4 mm in thickness and 300 mm in width were plated with Zn with a conventional gas reduction plating apparatus under the following conditions.

Pre-treatment:

Temperature of sheets at the outlet of the non-oxidizing furnace: 590-600°C

Reduction furnace gas: H_2 75%, N_2 25%

Temperature of the gas at the outlet of the reduction furnace: 700-720°C

Bath temperature: 460°C ± 5°C

Thickness of plated layer: 120 g/m^2 per side

After-treatment:

Temper rolling: not employed

After-treatment with chromic acid: not employed

The methods for testing of characteristics of the obtained products and for evaluation of the test results were as follows:

Size of spangles: Observation by naked eye

Adherence of plated layer: Plated sheets were lock-formed and a cellophane adhesive tape was applied on the worked portion, whereafter flaking of the plated layer was observed when the cellophane tape was peeled off. No flaking is rated as 'good'.

Existence of Pb in grains and at grain boundaries:

Determined by means of a scanning electron microscope and rated as 'large', 'medium', 'small' and 'minute'.

Corrosion resistance:

(1) Time (hour) until generation of red rust was observed in the salt water spray test (ASTM B117-73) was measured.

(2) Corrosion weight loss (g/m^2) was determined 200 hours after the salt water (ASTM B117-73).

TABLE 1

	Sample No.	Composition of plating bath % Al	Pb	Mg	Cooling	Spangle Size	Adhesion of Plated Layer	Existence of Pb in grains and at grain boundaries	Salt-Spray Test: Time required for generation of red rust	Corrosion Weight Loss g/m² (200 hours)
Samples of this invention	1	0.35	0.005	0.25	Spontaneous	Minute	Good	Slight	1050	18.0
	2	0.40	0.014	0.50	Spontaneous	Small	Good	Slight-Small	1500	20.5
	3	0.40	0.006	0.80	Spontaneous	Minute	Good	Slight	1940	19.4
	4	0.81	0.010	0.25	Spontaneous	Small	Good	Slight-Small	1000	29.4
	5	0.70	0.004	0.45	Spontaneous	Minute	Good	Slight	1400	21.3
	6	0.82	0.006	0.90	Spontaneous	Minute	Good	Slight	2050	18.7
	7	1.50	0.005	0.25	Spontaneous	Minute	Good	Slight	1000	20.4
	8	2.0	0.010	0.50	Spontaneous	Small	Good	Slight-Small	1400	20.8
	9	3.0	0.006	0.80	Spontaneous	Minute	Good	Slight	1800	19.9
Comparative Samples	10	0.18	0.15	-	Water cooling	Small	Good	Large	150	red rust generated
	11	0.18	0.15	0.25	Spontaneous	Medium	Good	Large	800	38.5
	12	0.31	0.16	0.04	Spontaneous	Large	Good	Large	170	red rust generated
	13	0.25	0.10	0.12	Spontaneous	Medium-Large	Good	Large	480	89.7
	14	1.50	0.02	0.05	Spontaneous	Medium	Good	Medium	650	48.5
	15	3.52	0.14	-	Spontaneous	Medium	Good	Large	300	120.5

The test results are summarized in Table 1 together with the bath composition. The characteristics of the products of the process of this invention and those of the conventional process (comparative samples) are explained in comparison.

1. Spangle size:

The products of the process of this invention exhibited very minute spangles despite the fact that the plated sheets were allowed to spontaneously cool by themselves. The rating 'minute' in the table means that spangles were almost unrecognizable by naked eye and the surface appearance was very smooth. In contrast, apparent 'medium' and 'large' spangles could be observed by the naked eye in all the comparative samples in which the plated sheets were cooled spontaneously. The spangles were 'small' only in sample No. 10 in which the sheets were forcibly cooled (water cooling). It is noted that water cooling makes the spangles minute in all the comparative samples, although inferior in homogeneity. When water cooling was not employed, apparent spangles were observed and the surfaces were considerably rough. Therefore rather high level temper rolling was necessary in order to smooth the surfaces.

2. Adherence of plated layer

Although there was no problem in either the products of the comparative samples or those of this invention in the adherence of the plated layer per se, occurrence of cracking in the plated layer at the bent portion was very rare in the products of the process of this invention, while in the comparative samples considerable noticeable cracking in the plated layer within the crystal grains and at the grain boundaries were detected. The products of the process of this invention were much superior to the comparative samples.

3. Existence of Pb in grains and at grain boundaries

As a result of restricting the Pb content to not more than 0.015 %, existence of Pb in grains and at boundaries was very slight and could not be clearly discerned in the scanning electron microscopic photographs. In contrast, in the comparative samples in which the Pb content was high, existence of Pb in grains and at grain boundaries was clearly observed, in all the samples except No. 4.

4. Corrosion resistance

In all the products of the process of this invention, more than 1000 hours passed before red rust was generated, and the corrosion weight loss was less than 30 g/m^2. On the other hand, red rust was generated within 800 hours in the rather better sample No. 11 and within 200 hours in the inferior samples No. 10 and 12. The corrosion eight loss of the comparative samples were 2 - 6 times as great as that of the products of the process of this invention.

Example 2

Using a hot-dip zinc plating bath of the composition shown in Table 2, very thinly plated zinc-plated steel sheets were prepared with the same apparatus as used in Example 1 under the following conditions.

Substrate sheets: 0.4 mm thick rimmed steel sheets
Pre-treatment: the same as in Example 1
Thickness of plated layer (condition of gas wiping)
  Gas pressure: 0.35 kg/cm^2
  Position of nozzle: 150 mm from the bath surface
  Distance between strip and nozzle tip: 6 mm
After-treatment:
  Temper rolling: not employed
  After treatment with chromic acid: not employed

The test results are summarized in Table 2 together with the bath composition. The characteristics of the products of the process of this invention and those of the conventional process (comparative samples) are explained in comparison.

TABLE 2

	Sample No.	Bath Composition % Al	Mg	Pb	Amount of plated zinc (per side) g/m²	Salt Spray Test: Time before red rust is generated (hours)	Salt Spray Test: Time before red rust covers 30% of surface area (hours)
Samples of this invention	16	0.45	0.25	0.005	9.6	140	520
	17	0.45	0.50	0.004	10.0	270	840
	18	1.00	0.29	0.009	9.2	180	580
Comparative Samples	19	0.18	tr	0.15	22.8	50	100
	20	0.18	0.25	0.14	24.2	200	450

1. Amount of plated zinc

It is apparent from the table that the amount of plated zinc is around 10 g/m^2 per side in the products of this invention, meaning that it is very thin plating, while the amount of the plated zinc is about twice that in the comparative samples. This means that the process of this invention is very effective in controlling the thickness of the plated layer by gas wiping.

2. Corrosion resistance

As the plated layer is very thin in the process of this invention, the corrosion resistance of the products was a matter of concern. However, it was confirmed that considerably higher corrosion resistance was acquired as seen in the table. That is, the time required for generation of red rust was 270 hours in Samples No. 17, 140 hours and 180 hours respective in Nos. 16 and 18. The time before the generated red rust spread to about 30% of the tested area was 840 hours, 520 hours and 580 hours respectively in Nos. 17, 16 and 18. That is, development of corrosion was considerably slow and good corrosion resistance was recognized. On the other hand, the amount of plated zinc in the comparative samples was about twice that of the samples of the process of this invention, and yet the area covered by red rust exceeded 30 % in 100 hours in No. 19 and exceeded 30 % in 450 hours even in No. 20, which had a thick plated layer. This fact means that the process of this invention is superior to the conventional process even in the corrosion resistance of the products.

It has been also confirmed that alloyed zinc plated steel sheets which are obtained by heat-treating the plated sheets made in accordance with the process of this invention are provided with far better corrosion resistance than the products produced by using the conventional plating bath.

Also it has been confirmed that single side zinc-plated steel sheets for automobiles produced on the trial base by using a plating inhibitor are excellent in both corrosion resistance and workability.

The zinc-plated steel sheets produced by the process of this invention are expected to find use as pre-coated sheets for coloured sheets, automobile materials, materials for household electric appliances as well as in industrial fields which will be developed from now on, in addition to the conventional use as materials for roofs and walls. The invention of this application will be highly evaluated in its industrial application.

CLAIMS

1. In a process for preparing a hot-dip zinc plated steel sheet, the improvement which comprises using a plating bath consisting essentially of 0.35 - 3.0 % Al, 0.15 - 1.0 % Mg and not more than 0.015 % Pb, the remainder being Zn and incidental impurities.

2. A process as claimed in claim 1 wherein the amount of zinc plated on the sheet is not more than 30 g/m^2 per side.

3. A process as claimed in claim 1 or claim 2 wherein only one side of the sheet is plated.

4. A process as claimed in any one of the preceding claims wherein the Al content is 0.35 - 2.0 %, the Mg content is 0.15 - 0.8 % and the Pb content is not more than 0.01 %.

5. A process as claimed in claim 4 wherein the Al content is 0.35 - 1.0 %. The Mg content is 0.15 - 0.5 % and the Pb content is not more than 0.007 %.

6. A process as claimed in any one of the preceding claims wherein the plated sheet is heated so as to form alloyed layers.

7. A process as claimed in claim 1 substantially as herein described.

8. A process as claimed in claim 1 substantially as herein described with reference to the Examples.

9. A hot-dip zinc-plated steel sheet which has been prepared by the process claimed in any one of the preceding claims.

10. A hot-dip zinc plating bath consisting essentially of 0.35 - 3.0 % Al, 0.15 - 1.0 % Mg and not more than 0.015 % Pb, the remainder being Zn and incidental impurities.

11. A hot-dip zinc plating bath as claimed in claim 10 wherein the Al content is 0.35 - 2.0 %, the Mg content is 0.15 - 0.8 % and the Pb content is not more than 0.01 %.

12. A hot-dip zinc plating bath as claimed in claim 11 wherein the Al content is 0.35 - 1.0 %, the Mg content is 0.15-0.5 % and the Pb content is not more than 0.007 %.

13. A hot dip zinc plating bath as claimed in claim 10 substantially as herein described.

14. A hot dip zinc plating bath as claimed in claim 10 substantially as herein described with reference to the Examples.

15. Each and every novel method, process, product and apparatus herein described.

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