



(11) EP 1 621 645 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

01.02.2006 Bulletin 2006/05

(51) Int Cl.: C23C 2/06 (2006.01)

(21) Application number: 04077168.5

(22) Date of filing: 28.07.2004

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR Designated Extension States:

AL HR LT LV MK

(71) Applicant: Corus Staal BV 1970 CA Ijmuiden (NL)

(72) Inventors:

 Maalman, Theodorus Franciscus Jozef 1911 ML Uitgeest (NL) Vlot, Margot Julia
 2318 TG Leiden (NL)

 Bleeker, Robert 1942 EL Beverwijk (NL)

(74) Representative: Kruit, Jan et al Corus Technology BV PO Box 10000 1970 CA IJmuiden (NL)

(54) Steel sheet with hot dip galvanized zinc alloy coating

(57) Steel strip provided with a hot dip galvanized zinc alloy coating layer, in which the coating of the steel strip is carried out in a bath of molten zinc alloy, the zinc alloy in the coating consisting of:

0.3 - 2.3 weight % magnesium; 0.6 - 2.3 weight % aluminium;

optional < 0.2 weight % of one or more additional elements;

unavoidable impurities; the remainder being zinc.

Description

20

25

30

35

40

45

50

55

[0001] The invention relates to a steel strip provided with a hot dip galvanized zinc alloy coating layer and to a process for hot dip galvanising a steel strip with a zinc alloy coating layer, in which the coating of the steel strip is carried out in a bath of molten zinc alloy.

[0002] To provide a steel strip with a zinc coating is well known, especially for automotive and building applications. To get a thin layer of zinc on a steel strip in a cheap way, it is usual to coat the steel strip by hot dip galvanizing, in which the strip is moved through a bath of molten zinc. The molten zinc adheres to the steel, and at the departure of the strip from the bath in most cases the surplus of zinc is removed from the strip to get a thin coating layer, usually using gas knives.

[0003] It is known in the art to add certain chemical elements to the bath to improve the quality of the zinc coating and/or to improve the process of coating the steel strip. As elements usually aluminium and magnesium are chosen.

[0004] European patent 0 594 520 mentions the use of 1 to 3.5 weight % magnesium and 0.5 to 1.5 % aluminium, together with the addition of silicon to a percentage of 0.0010 to 0.0060 in weight %. The silicon has been added in such a small quantity to improve the quality of the zinc coating, which had been found to comprise zones where no zinc had been present (bare spots). The patent mentions a zinc coated steel in which the coating has the composition 2.55 weight % magnesium, 0.93 weight % aluminium, 60 ppm silicon, rest zinc and inevitable impurities.

[0005] It is an object of the invention to provide a zinc alloy coated steel strip having improved properties and a method for producing the same.

[0006] It is another object of the invention to provide a zinc alloy coated steel strip that is cheaper to produce than the known coated steel strip with the same or better properties.

[0007] It is still another object of the invention to provide a zinc alloy coated steel strip having a better corrosion resistance while maintaining or even improving other properties of the coated steel strip.

[0008] It is yet another object of the invention to provide a process that has a lower dross formation in the zinc bath.

[0009] According to the invention, one or more of these objects is reached with a steel strip provided with a hot dip galvanized zinc alloy coating layer, characterized in that the zinc alloy consists of:

0.3 - 2.3 weight % magnesium;

0.6 - 2.3 weight % aluminium;

optional < 0.2 weight % of one or more additional elements;

unavoidable impurities;

the remainder being zinc.

[0010] It has been found that high magnesium levels lead to excessive oxidic dross formation on the zinc bath and to brittle coatings. Therefore, the magnesium level has been limited to a maximum of 2.3 weight %. A minimum of 0.3 weight % magnesium is necessary to have a sufficient high corrosion resistance; magnesium additions improve the corrosion resistance of the coated strip. The magnesium level of 0.3 - 2.3 weight % is high enough to obtain a corrosion protection against red rust that is far higher than the corrosion protection of conventional galvanized strip.

[0011] Aluminium has been added to reduce dross formation on the bath. In combination with magnesium it also improves the corrosion resistance of the coated strip. Aluminium moreover improves the formability of the coated strip material, meaning that the adhesion of the coating on the strip is good when the strip is for instance bended. Since increased aluminium levels will deteriorate the weldability, the aluminium level has been limited to a maximum of 2.3 weight %.

[0012] No silicon has to be added, since it has been found that with the lower magnesium level according to the invention the addition of silicon is not necessary to prevent bare spots. This is advantageous, since it is difficult to keep the silicon content between 10 and 60 ppm when silicon has to be added, especially since silicon is present as an impurity.

[0013] An optional element that could be added in a small amount, less than 0.2 weight %, could be Pb or Sb, Ti, Ca, Mn, Sn, La, Ce, Cr, Ni, Zr or Bi. Pb, Sn, Bi and Sb are usually added to form spangles. These small amounts of an additional element do not alter the properties of the coating nor the bath to any significant extent.

[0014] A further advantage of the zinc alloy coated steel strip according to the invention is that the galling behaviour is better than the galling behaviour of conventional galvanized strip material.

[0015] According to a preferred embodiment, the steel strip has been provided with a hot dip galvanized zinc alloy coating layer in which the zinc alloy contains 1.6 - 2.3 weight % magnesium and 1.6 - 2.3 weight % aluminium. This is a preferred embodiment, because at these values the corrosion protection of the coating is at a maximum, and the corrosion protection is not influenced by small compositional variations. Above 2.3 weight % magnesium and aluminium, the coating becomes rather expensive and coating may become brittle and the surface quality of the coating may decrease.

[0016] On the other hand, another preferred embodiment of the steel strip has been provided with a hot dip galvanized zinc alloy coating layer in which the zinc alloy contains 0.6 - 1.3 weight % aluminium and/or 0.3 - 1.3 weight % magnesium. With these smaller amounts of aluminium and magnesium, no major modifications of the conventional hot dipped gal-

vanising bath and apparatus are needed, whereas magnesium at levels between 0.3 and 1.3 weight % improves the corrosion resistance considerably. Usually, for these amounts of magnesium more than 0.5 weight % of aluminium has to be added to prevent that more oxidic dross is formed on the bath than for conventional baths; dross can lead to defects in the coating. The coatings with these amounts of magnesium and aluminium are optimal for applications with high demands on surface quality and improved corrosion resistance.

[0017] Preferably, the zinc alloy contains 0.8 - 1.2 weight % aluminium and/or 0.8 - 1.2 weight % magnesium. These amounts of magnesium and aluminium are optimal to provide a coating with both a high corrosion resistance, an excellent surface quality, an excellent formability, and a good weldability at limited extra costs as compared to conventional hot dipped galvanising.

[0018] According to a preferred embodiment, the steel strip has been provided with a hot dip galvanized zinc alloy coating layer in which the amount of aluminium in weight % is the same as the amount of magnesium in weight % plus or minus a maximum of 0.3 weight %. It has been found that the dross formed on the bath is suppressed to a considerable level when the amount of aluminium equals or almost equals the amount of magnesium.

[0019] Preferably, the steel strip has been provided with a hot dip galvanized zinc alloy coating layer in which the zinc alloy coating layer has a thickness of 3 - $12~\mu m$. Thin coatings are of course less expensive, but they are also better formable and weldable than thick coatings. The coating thicknesses according to the invention provide enough corrosion protection, even for building and construction purposes, where conventionally hot dipped galvanised coating have a thickness of about $20~\mu m$. For automotive purposes, the coating layer according to the invention can have a thickness of 3 - $10~\mu m$.

[0020] The invention also relates to a process for hot dip galvanising a steel strip with a zinc alloy coating layer, in which the coating of the steel strip is carried out in a bath of molten zinc alloy, wherein the zinc alloy consists of:

0.3 - 2.3 weight % magnesium;

0.5 - 2.3 weight % aluminium;

optional < 0.2 weight % of one or more additional elements;

unavoidable impurities;

the remainder being zinc.

[0021] With this process it is possible to produce the steel strip as discussed above, using the conventional hot dip galvanising equipment. Usually, the amount of aluminium in the coating is slightly higher than the amount of aluminium in the bath. The advantages of the process are mentioned when discussing the steel strip according to the invention.

[0022] According to a preferred process, the zinc alloy bath contains 1.5 - 2.3 weight % magnesium and 1.5 - 2.3 weight % aluminium, as discussed above for the steel strip.

[0023] According to another preferred process, the zinc alloy bath contains 0.6 - 1.3 weight % aluminium and/or 0.3 -1.3 weight % magnesium, as discussed above.

[0024] Preferably, the zinc alloy bath contains 0.7 - 1.2 weight % aluminium and/or 0.7 - 1.2 weight % magnesium, as discussed above.

[0025] According to a preferred embodiment of the process, the temperature of the bath of molten zinc is kept between 380° C and 550° C, preferably between 420° C and 480° C. The melting point of pure zinc is 419° C, and with 3.2% Al and 3.3% Mg the melting temperature is about 337° C, so 380° C is a reasonable lower limit to avoid local solidification. A lower limit of 440° C is absolutely safe to avoid any solidification. Increasing the zinc bath temperature increases the zinc evaporation and leads to dust formation in the galvanising line, giving rise to surface defects. The upper limit should thus be reasonably low, for which 550° C is fair, and preferably 480° C as a technically possible upper limit.

[0026] Preferably the temperature of the steel strip before entering the bath of molten zinc alloy is between 380° C and 850° C, more preferably between the temperature of the bath of molten zinc alloy and 25° C above the bath temperature. The temperature of the steel strip should not be lower than the melting point of the zinc alloy to avoid local solidification of the zinc bath. High steel strip temperatures will lead to higher evaporation of the zinc, resulting in dust formation. High steel strip temperatures can also heat up the zinc bath, requiring continuous cooling of the zinc in the bath, which is expensive. For these reasons a temperature of the steel strip just above the bath temperature is preferred.

[0027] The invention will be elucidated hereinafter, in which some experiments are described and some test results are given.

[0028] First, the test results are given in the following eight tables.

55

10

25

30

35

40

45

Table 1: composition of bath and coating

Ref#	Bath	Bath	Coating	Coating	Coating	Coating
	AI%	Mg%	g/m2	AI%	Mg%	Fe%
1	0,2	0,5	99	0,4	0,5	
2	0,8	0,9		1,0	0,8	0,11
3	1,0	0,9		1,1	0,9	0,18
4	1,0	1,0		1,2	1,0	0,14
5	1,9	1,0		2,0	0,9	0,07
6	1,1	1,1	42	1,3	0,9	0,29
7	1,2	1,2		1,4	1,2	0,15
8	1,5	1,5		1,6	1,4	0,14
9	0,9	1,6		1,1	1,6	0,26
10	1,7	1,7		1,9	1,7	0,10
11	2,5	2,0		2,5	1,8	0,05
12	1,0	2,1	77	1,2	1,8	0,13
13	1,0	2,1	39	1,2	1,8	0,21
14	2,1	2,1		2,2	2,1	0,15
15	1,0	2,5		1,1	2,8	0,06

Table 2: corrosion resistance of flat panel

Ref#	Bath	Bath	Coating	Corrosion flat panel
	AI%	Mg%	thickness (μm)	
1	0,2	0,0	10	0
2	0,5	0,5	4	0
3	0,5	0,5	6	+
4	0,5	0,5	8	++
5	0,5	0,5	10	++
6	0,2	0,5	14	+
7	1,0	0,9	6	++
8	1,0	0,9	7	++
9	1,0	0,9	10	++
10	1,0	0,9	11	++
11	1,0	1,0	6	+
12	1,0	1,0	6	++
13	1,9	1,0	20	+++
14	1,1	1,1	4	+++
15	1,1	1,1	6	+++
16	1,1	1,1	7	+++
17	1,1	1,1	10	++++

Table continued

Ref#	Bath	Bath	Coating	Corrosion flat panel
	AI%	Mg%	thickness (μm)	
18	1,1	1,1	11	++++
19	1,2	1,2	6	++
20	1,5	1,5	6	++++
21	1,7	1,7	6	++++
22	2,5	2,0	25	++++
23	1,0	2,1	5	+
24	1,0	2,1	6	+
25	1,0	2,1	10	+++
26	1,0	2,1	11	+++
27	2,1	2,1	6	++++

Qualification:

0 = no improvement as compared to regular HDG (0.2%Al) of 10 μm in SST

+ = improvement up to a factor 2

++ = improvement up to a factor 4

+++ = improvement up to a factor 8

++++ = improvement more than a factor 8

Table 3: corrosion resistance of deformed panel

Ref#	Bath	Bath	Coating	Corrosion deformed panel
	AI%	Mg%	thickness (μm)	
1	0,2	0,0	10	0
2	1,0	1,0	6	+
3	1,0	1,0	6	++
4	1,0	1,0	3	0
5	1,1	1,1	13	+++
6	1,2	1,2	6	+
7	1,2	1,2	6	++
8	1,5	1,5	4	+
9	1,5	1,5	6	++
10	1,7	1,7	4	++
11	1,7	1,7	6	++
12	2,1	2,1	4	++
13	2,1	2,1	7	++
0 1:0				

Qualification:

0 = no improvement as compared to regular HDG (0.2%Al) of 10 μm in SST

5

10

15

20

25

30

35

40

45

50

Table continued

+ = improvement up to a factor 2

++ = improvement up to a factor 4

+++ = improvement more than a factor 4

Table 4: galling performance

Ref#	Bath	Bath	Coating	Galling perfor	mance
	AI%	Mg%	thickness (μm)	Cylindrical side	Flat side
1	0,2	0,0	7,0	5	4
2	0,2	0,0	7,0	5	4
3	1,0	0,9	6,3	1	1
4	1,0	0,9	5,2	1	1
5	1,2	1,2	5,9	1	1
6	1,2	1,2	5,9	1	1
7	1,5	1,5	5,9	1	1
8	1,5	1,5	5,5	1	1
9	1,7	1,7	5,6	1	1
10	1,7	1,7	6,4	1	1
11	2,1	2,1	7,5	1	1
12	2,1	2,1	5,1	1	1

Qualification:

- 1. Excellent (no deep scratches, homogenous surface)
- 2. Good (a few scratches may occur)
- 3. Moderate (stained or slightly scratched surface)
- 4. Poor (some large scratches)
- 5. Very poor (Heavily scratched/worn surface, material break-out)

Table 5: surface quality

Ref#	Bath	Bath	Coating	Coating
	AI%	Mg%	Surface quality	Formability
1	0,2	0,0	0	0
2	0,5	0,5	+	0
3	0,2	0,5	-	0
4	0,8	0,9	+	0
5	1,0	0,9	+	0
6	1,0	1,0	+	0
7	1,9	1,0	+	
8	1,1	1,1	+	0
9	1,2	1,2	+	0

10

5

15

20

25

30

35

40

45

50

Table continued

Ref#	Bath	Bath	Coating	Coating
	AI%	Mg%	Surface quality	Formability
10	1,5	1,5	+	0
11	2,0	1,6	+	0
12	0,9	1,6	+	0
13	1,7	1,7	+	0
14	2,5	2,0	-	
15	1,0	2,1	+	-
16	2,1	2,1	+	0
17	1,0	2,5	+	-

Qualification: Surface quality

0 = equal to panels from a 0.2%Al-bath produced in the same way

- + = better
- = worse

Qualification: Formability

0 = no cracks present on OT-bend

- = cracks present

Table 6: dross formation

Ref#	Bath	Bath	
	AI%	Mg%	Dross formation
1	0,2	0,0	0
2	0,5	0,5	+
3	0,2	0,5	-
4	0,8	0,9	+
5	1,0	0,9	+
6	1,0	1,0	+
7	1,9	1,0	+
8	1,1	1,1	+
9	1,2	1,2	+
10	1,5	1,5	+
11	2,0	1,6	+
12	0,9	1,6	+
13	1,7	1,7	+
14	2,5	2,0	+
15	1,0	2,1	+
16	2,1	2,1	+

30

5

10

15

20

25

35

40

45

50

Table continued

Ref#	Bath	Bath	
	AI%	Mg%	Dross formation
17	1,0	2,5	-

Qualification:

5

10

15

20

25

30

35

40

45

50

55

- More oxidic dross formation than on a regular (0.2% Al) bath
- 0 Similar amounts of oxidic dross formation than on a regular (0.2%Al) bath
- + Less oxidic dross formation than on a regular (0.2%Al) bath

Table 7: weldability

Ref#	Bath	Bath	Coating	Weldability
	AI%	Mg%	thickness (μm)	
1	0,2	0,0	10	0
2	0,5	0,5	10	0
3	1,0	1,0	10	0

Qualification:

- 0 = similar welding range
- = smaller welding range
- + = larger welding range

Table 8: bath temperature

Ref#	Bath	Bath	Bath	Bath	Coating				
	AI%	Mg%	Temp	SET	thickness (µm)	Surface quality	Formability	Dross formation	Corrosion flat pane
1	1,0	0,9	410	430	6	+	0	+	++
2	1,0	0,9	460	550	7	+	0	+	++
3	1,0	0,9	460	475	6	+	0	+	++
4	1,0	0,9	460	475	6	+	0	+	++
5	1,1	1,1	405	420	11	+	0	+	+++
6	1,1	1,1	460	475	11	+	0	+	+++
7	1,1	1,1	410	480	7	+	0	+	+++
8	1,1	1,1	460	475	6	+	0	+	+++

[0029] The steel used for the experiments is an ultra low carbon steel having the composition (all in weight %): 0.001 C, 0.105 Mn, 0.005 P, 0.004 S, 0.005 Si, 0.028 Al, 0.025 Alzo, 0.0027 N, 0.018 Nb and 0.014 Ti, the remainder being

unavoidable impurities and Fe.

10

40

45

50

55

[0030] The steel panels have been made from cold rolled steel and have a size of 12 by 20 cm and a thickness of 0.7 mm. After degreasing they have been subjected to the following treatment:

- 5 Step 1: in 11 seconds from room temperature to 250° C in an atmosphere of 85.5% N_2 , 2% H_2 , 11% CO_2 and 1.5% CO_3 ;
 - Step 2: in 11 seconds from 250° C to 670° C in the same atmosphere as in step 1;
 - Step 3: in 46 seconds from 670° C to 800° C in an atmosphere of 85% N₂ and 15% H₂;
 - Step 4: in 68 seconds from 800° C to 670° C in the same atmosphere as in step 3;
 - Step 5: in 21 seconds from 670° C to the strip entry temperature (SET), usually 475° C, in the same atmosphere as in step 3;
 - Step 6: dipping in liquid zinc alloy, usually at 460° C for 2 seconds, and wiping the zinc layer on the steel panel with 100% N₂ to regulate the coating weight;
 - Step 7: cooling in 60 seconds to 80° C in 100% N₂.
- [0031] In some experiments the atmosphere in step 1 and 2 has been changed to 85% N₂ and 15% H₂, but no effect on the coating quality has been observed.
 - **[0032]** A Fischer Dualscope according to ISO 2178 has been used to determine the coating thickness at each side of the panel, using the average value of nine points.
- [0033] In table 1, the alloy elements in the zinc bath used for coating the steel panels and the alloy elements in the coating itself are given. Usually, the amount of aluminium in the coating is slightly higher than the amount of aluminium in the bath.
 - **[0034]** In table 2 the corrosion of a flat panel (not deformed) is indicated for a large number of panels. The coating thickness varies. As can be seen, for small amount of Al and Mg the coating has to be thicker to get a better corrosion resistance. For higher amounts of Al and Mg even with a thin layer a very good corrosion resistance can be achieved. A good result can be achieved with 0.8 to 1.2 weight % Al and Mg for higher coating thicknesses; a very good result can be achieved with 1.6 to 2.3 weight % Al and Mg for thin coating layers.
 - **[0035]** The corrosion resistance has been measured using the salt spray test (ASTM-B 117) to get an idea of the corrosion resistance under severe, high chloride containing, wet conditions, which represents some critical corrosive automotive as well as building microclimates.
- 30 [0036] The test has been performed in a corrosion cabinet wherein the temperature is maintained at 35°C, while a water mist containing 5%NaCl solution is continuously sprayed over the samples mounted into racks under an angle of 75°. The side of the sample to be evaluated for its corrosion behaviour is directed towards the salt spray mist. The edges of the samples are taped off to prevent possible, early red rusting at the edges disturbing proper corrosion evaluation at the surface. Once per day the samples are inspected to see if red rust is occurring. First red rust is the main criterion for the corrosion resistance of the product. Reference product is conventional hot dip galvanized steel with a 10 μm zinc coating thickness.
 - **[0037]** Table 3 shows the corrosion resistance of deformed panels. Deformation has been done by an Erichsen 8 mm cup. As can be seen, the corrosion resistance here depends to a large extend on the coating thickness of the zinc alloy layer. However, it is clear that a higher amount of the alloy elements Al and Mg results in a better corrosion resistance of the zinc alloy layer.
 - **[0038]** Table 4 shows the galling performance of the hot dip galvanised steel. All coatings for which the bath contained approximately 1 weight % Al and Mg and more show an excellent galling performance. The galling performance has been measured using the linear friction test (LFT) method. This method uses severe conditions to accelerate galling. The method uses one flat tool and one round tool to develop a highpressure contact with the sample surface. The tool material used was in accordance with DIN 1.3343.
 - **[0039]** For each material/lubrication system, strips of 50mm width and 300mm length were pulled at a speed of 0.33mm/s between the set of tools (one flat, one round) pushed together with a force of 5kN. The strips were drawn through the tools ten times along a testing distance of 55mm. After each stroke the tools were released and the strips returned to the original starting position in preparation for the next stroke. All tests were conducted at 20°C and 50% humidity.
 - **[0040]** Visual analysis of the LFT samples was conducted to assess the extent of galling on the surface of the samples. Three people made an independent assessment of the scarred surface and the median result was recorded. Galling is ranked on a scale of 1 to 5, as defined under table 4.
 - [0041] Table 5 shows the surface quality and formability of a number of panels. The surface quality has been measured by visual inspection of the panels on bare spots, irregularities sticking from the surface (usually caused by dross) and the general appearance or homogeneity of gloss over the panel. As follows from the table, the surface quality is good between approximately 0.5 weight % Al and Mg and 2.1 weight % Al and Mg. With higher amounts of aluminium, the amount of dross in the bath increases, resulting in a lower surface quality. The formability of the coating has been

measured by visual inspection on cracks in the coating after a full bend (0T) of the panel. With higher amounts of magnesium the formability appears to decrease.

[0042] Table 6 shows that the dross formation is less than for a conventional zinc bath when the amount of Al and Mg is between approximately 0.5 and 2.1 weight %. The dross formation has been judged quantatively as compared to the amount of foam and adhering dross measured for four bath compositions: Zn + 0.2 % Al, Zn + 1% Al + 1% Mg, Zn + 1% Al + 2% Mg and Zn + 1% Al + 3% Mg. For these four bath compositions, argon gas has been bubbled for 2.5 hours through the liquid zinc alloy in a vessel to break up the oxide film layer on the surface. After this, the foam on the surface is removed and weighed. The rest of the bath is poured into an empty vessel and the remaining dross adhering on the wall of the original vessel is also removed for weighing. This leads to the following results:

Zinc bath
GI = Zn + 0.2%AI

GI = Zn + 0.2%AI 1.7 1.4 Zn + 1.0%Mg + 1.0%AI 1.1 1.1 Zn + 2.0%Mg + 1.0%AI 1.2 1.3 Zn + 3.0%Mg + 1.0%AI 15 /

Adhering dross on wall (%)*

* Measured as percentage of the total amount of liquid zinc in the vessel.

Foam on surface (%)*

20

30

35

10

15

This measurement was in agreement with the observations during the dipping experiments that clearly showed less dross formation onto the zinc bath for the Zn + 1% A1 + 1% Mg and Zn + 1% Al + 2% Mg composition.

[0043] Table 7 shows that only a few weldability tests have been performed. The weldability appears not to be influenced by the amount of Al and Mg in the zinc bath. A weld growth curve has been made by making welds with increasing welding current with electrodes of 4.6 mm in diameter and a force of 2 kN. The welding range is the difference in current just before splashing and the current to achieve a minimum plug diameter of $3.5\sqrt{t}$, with t the steel thickness. Table 7 shows that 0.5% and 1% Mg and Al-alloyed coated steel have a similar welding range as regular galvanized steel (Ref# 1). **[0044]** Table 8 shows that the influence of the temperature of the bath and the temperature of the strip when it enters the bath is minimal. A temperature of 410° C or 460° C of the bath appears to make no difference, and the same holds for a strip entry temperature of 420° C or 475° C.

[0045] The above results can be summarised as follows: an amount of 0.3 - 2.3 weight % magnesium and 0.6 - 2.3 weight % aluminium in the coating of hot dipped galvanised strip will result in better corrosion resistance than the corrosion resistance of conventional galvanised steel. The corrosion resistance is very good when the amount of both aluminium and magnesium in the coating is between 1.6 and 2.3 weight %, even for thin coating layers. The corrosion resistance is good when the amount of both aluminium and magnesium is between 0.8 and 1.2 weight % for thin coating layers, and very good for thicker coating layers. The amounts of the alloying elements should be not too high to prevent dross formation.

[0046] It will be appreciated that the coatings and the coating method can also be used for strip having a composition different from that used for the above experiments.

40

45

50

Claims

- 1. Steel strip provided with a hot dip galvanized zinc alloy coating layer, characterized in that the zinc alloy consists of:
 - 0.3 2.3 weight % magnesium;
 - 0.6 2.3 weight % aluminium;
 - optional < 0.2 weight % of one or more additional elements;
 - unavoidable impurities;
 - the remainder being zinc.
- 2. Steel strip provided with a hot dip galvanized zinc alloy coating layer according to claim 1, in which the zinc alloy contains 1.6 2.3 weight % magnesium and 1.6 2.3 weight % aluminium.
- 55 3. Steel strip provided with a hot dip galvanized zinc alloy coating layer according to claim 1, in which the zinc alloy contains 0.6 -1.3 weight % aluminium.
 - 4. Steel strip provided with a hot dip galvanized zinc alloy coating layer according to claim 1 or 3, in which the zinc

alloy contains 0.3 - 1.3 weight % magnesium.

5

15

20

35

45

50

55

- **5.** Steel strip provided with a hot dip galvanized zinc alloy coating layer according to claim 1, 3 or 4, in which the zinc alloy contains 0.8 1.2 weight % aluminium.
- **6.** Steel strip provided with a hot dip galvanized zinc alloy coating layer according to claim 1, 3, 4 or 5, in which the zinc alloy contains 0.8 1.2 weight % magnesium.
- 7. Steel strip provided with a hot dip galvanized zinc alloy coating layer according to any one of the preceding claims, in which the amount of aluminium in weight % is the same as the amount of magnesium in weight % plus or minus a maximum of 0.3 weight %.
 - 8. Steel strip provided with a hot dip galvanized zinc alloy coating layer according to any one of the preceding claims, in which the zinc alloy coating layer has a thickness of $3 12 \mu m$, preferably a thickness of $3 10 \mu m$.
 - **9.** Process for hot dip galvanising a steel strip with a zinc alloy coating layer, in which the coating of the steel strip is carried out in a bath of molten zinc alloy, **characterised in that** the zinc alloy consists of:
 - 0.3 2.3 weight % magnesium;
 - 0.5 2.3 weight % aluminium;

optional < 0.2 weight % of one or more additional elements;

unavoidable impurities;

the remainder being zinc.

- **10.** Process according to claim 9, in which the zinc alloy bath contains 1.5 2.3 weight % magnesium and 1.5 2.3 weight % aluminium.
 - 11. Process according to claim 9, in which the zinc alloy bath contains 0.6 1.3 weight % aluminium.
- 30 **12.** Process according to claim 9 or 11, in which the zinc alloy bath contains 0.3 -1.3 weight % magnesium.
 - 13. Process according to claim 9, 11 or 12, in which the zinc alloy bath contains 0.7 1.2 weight % aluminium.
 - 14. Process according to claim 9, 11, 12 or 13, in which the zinc alloy bath contains 0.7 1.2 weight % magnesium.
 - **15.** Process according to any one of the claims 9 14, in which the temperature of the bath of molten zinc is kept between 380° C and 550° C, preferably between 420° C and 480° C.
- 16. Process according to any one of the claims 9 15, in which the temperature of the steel strip before entering the bath of molten zinc alloy is between 380° C and 850° C, preferably between the temperature of the bath of molten zinc alloy and 25° C above the bath temperature.



EUROPEAN SEARCH REPORT

Application Number EP 04 07 7168

Catacas	Citation of document with in	ndication, where appropriate,	Relevant	CLASSIFICATION OF THE
Category	of relevant passa		to claim	APPLICATION (Int.CI.7)
X	EP 0 594 520 A (LOF 27 April 1994 (1994 * column 3, line 50 * column 4, line 22	-04-27)	1-16	C23C2/06
(PATENT ABSTRACTS OF vol. 2003, no. 02, 5 February 2003 (20 & JP 2002 285311 A LTD), 3 October 200 * abstract; example	03-02-05) (SUMITOMO METAL IND 02 (2002-10-03)	1,2,6,9, 10,14,15	
(PATENT ABSTRACTS OF vol. 2003, no. 09, 3 September 2003 (2 & JP 2003 138359 A LTD), 14 May 2003 (* abstract; example	003-09-03) (SUMITOMO METAL IND 2003-05-14)	1-16	
x	PATENT ABSTRACTS OF vol. 2003, no. 12, 5 December 2003 (20 & JP 2004 068075 A 4 March 2004 (2004- * abstract; example	03-12-05) (JFE STEEL KK), 03-04)	1-16	TECHNICAL FIELDS SEARCHED (Int.CI.7)
X	PATENT ABSTRACTS OF vol. 2003, no. 04, 2 April 2003 (2003- & JP 2002 371342 A LTD), 26 December 2 * abstract; example	04-02) (SUMITOMO METAL IND 002 (2002-12-26)	1-16	
	The present search report has I	peen drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	The Hague	8 December 2004	Els	en, D
X : parti Y : parti docu	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anothen to the same category nological background	L : document cited fo	e underlying the in cument, but publis e n the application	vention hed on, or



EUROPEAN SEARCH REPORT

Application Number EP 04 07 7168

	DOCUMENTS CONSIDE	ERED TO BE RELEVA	N I		
Category	Citation of document with in- of relevant passag	dication, where appropriate, jes		elevant claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)
Х	PATENT ABSTRACTS OF vol. 2000, no. 05, 14 September 2000 (& JP 2000 064010 A 29 February 2000 (20 * abstract; example	2000-09-14) (NIPPON STEEL CORP) 000-02-29)	1-1	L6	
X	PATENT ABSTRACTS OF vol. 2003, no. 12, 5 December 2003 (200 & JP 2004 019000 A LTD), 22 January 200 * abstract; example	03-12-05) (SUMITOMO METAL IND 04 (2004-01-22))	.6	
X	GB 2 110 248 A (NIS 15 June 1983 (1983- * page 2, line 30 - 1,4,10-12,15; examp	96-15) line 32; claims	1-1	L 6	
X	DATABASE WPI Section Ch, Week 20 Derwent Publication Class M13, AN 2002- XP002309447 & KR 2002 034 485 A 9 May 2002 (2002-05 * abstract *	s Ltd., London, GB; 672516 (POSCO)	9,1	.0	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
	The present search report has b	een drawn up for all claims			
Place of search The Hague		Date of completion of the search 8 December 2004		Fle	Examiner en, D
X : parti Y : parti docu A : tech O : non	NTEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anoth ment of the same category nological background -written disclosure mediate document	T : theory o E : earlier p. after the er D : docume L : docume	r principle under atent document filing date nt cited in the ap nt cited for other of the same pa	lying the in but publis oplication reasons	ivention hed on, or

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 04 07 7168

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-12-2004

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0594520	A	27-04-1994	FR AT DE DE EP ES	2697031 131214 69300964 69300964 0594520 2082617	T D1 T2 A1	22-04-199 15-12-199 18-01-199 18-07-199 27-04-199 16-03-199
JP 2002285311	Α	03-10-2002	JP	3580261	B2	20-10-200
JP 2003138359	Α	14-05-2003	NONE			
JP 2004068075	Α	04-03-2004	NONE			
JP 2002371342	Α	26-12-2002	NONE			
JP 2000064010	Α	29-02-2000	NONE			
JP 2004019000	Α	22-01-2004	NONE			
GB 2110248	A	15-06-1983	JP JP AU AU CA DE FR KR	58091162 63030984 540419 9022982 1190353 3242625 2537161 8901829	B B2 A A1 A1 A1	31-05-198 21-06-198 15-11-198 26-05-198 16-07-198 26-05-198 08-06-198 25-05-198
KR 2002034485	Α	09-05-2002	NONE			

FORM P0459

© For more details about this annex : see Official Journal of the European Patent Office, No. 12/82