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(54) Title: A METHOD FOR THE MANUFACTURE OF A PHOSPHATABLE PART STARTING FROM A STEEL SHEET COATED WITH A METALLIC COATING BASED ON ALUMINIUM

(57) Abstract: The present invention relates to a method for the manufacture of a hardened part coated with a phosphatable coating comprising the following steps: A) the provision of a steel sheet pre-coated with a metallic coating comprising from 4.0 to 20.0% by weight of zinc, from 1.0 to 3.5% by weight of silicon, optionally from 1.0 to 4.0% by weight of magnesium, and optionally additional elements chosen from Pb, Ni, Zr, or Hf, the content by weight of each additional element being less than 0.3% by weight, the balance being aluminum and unavoidable impurities and residuals elements, B) the cutting of the coated steel sheet to obtain a blank, C) the thermal treatment of the blank at a temperature between 840 and 950°C to obtain a fully austenitic microstructure in the steel, D) the transfer of the blank into a press tool, E) the hot-forming of the blank to obtain a part, F) the cooling of the part obtained at step E) in order to obtain a microstructure in steel being martensitic or martensite-bainitic or made of at least 75% of equiaxed ferrite, from 5 to 20% of martensite and bainite in amount less than or equal to 10%.

A method for the manufacture of a phosphatable part starting from a steel sheet coated with a metallic coating based on aluminum

The present invention relates to a method for the manufacture of hardened parts starting from a steel sheet coated with a coating based on aluminum. The part has good characteristics with respect to the phosphating, and therefore exhibits good paint adhesion and good corrosion resistance. The invention is particularly well suited for the manufacture of automotive vehicles.

Hardened parts can be coated with an aluminum-based coating having a good corrosion resistance and thermal properties. Usually, the method for manufacture of these parts comprise the provision of the steel sheet, the cut of the sheet to obtain a blank, the thermal treatment of the blank, the hot-stamping followed by a cooling in order to obtain a hardening by martensitic transformation or martensite-bainitic transformation.

Generally, a paint film is applied on hardened parts, notably an e-coating layer. Previously, a phosphating is often performed. Thus, phosphate crystals are formed on the part surface to be coated, increasing the paint adhesion, and in particular the e-coating layer.

Hardened parts coated with a metallic alloy based on aluminum are not phosphatable, i.e. there is a little or no phosphate crystals formed on the surface of the coating. Thus, the application of the paint film is directly achieved without phosphating step beforehand. The microroughness of the parts surface coated with an alloy based on aluminum allows for paint adhesion. However, in some cases, the paint is not evenly distributed on the part surface resulting in red rust areas.

The patent application US2012/0085466 discloses a method for producing a steel component provided with a metallic coating comprising the following production steps:

- a) coating a steel flat product, produced from an alloyed heat-treated steel, with an Al coating comprising at least 85% wt. Al and optionally up to 15% wt. Si;
- b) coating the steel flat product provided with the Al coating with a Zn coating comprising at least 85% wt. Zn;

c) coating the steel flat product, provided with the Al coating and the Zn coating lying on it, with a top layer comprising a main constituent of at least one metal salt of phosphoric acid or diphosphoric acid;

5 d) heat-treating the steel flat product at a heat-treating temperature which is at least 750° C.;

e) heating the steel flat product to a hot-forming temperature;

f) hot-forming the steel component made from the heated steel flat product; and

10 g) forming a finish-formed steel component by cooling the hot-formed steel component at a cooling rate which is sufficient to form a tempered or martensitic structure.

The hot-formed steel component comprises a base layer comprising at least 30% wt. Al, at least 20% wt. Fe, at least 3% wt. Si and at most 30% wt. Zn; the intermediate layer comprising at least 60% wt. Zn, at least 5% wt. Al, up to 10% wt. F; and up to 10% wt. Si and the top layer comprising at least 8% wt. Zn, as well
15 as ZnO, P and Al, wherein the P content is at most 1% wt. and the main constituent of the top layer is ZnO. The top layer allows for paint adhesion.

However, this process requires the deposition of three layers to form a metallic coating. The Al coating can be deposited by hot-dip galvanization. The Zn coating can be deposited by hot-dip galvanization, physical vapour deposition
20 process or electrolytic galvanizing. The top layer can be deposited by spray coating, dip-coating, vapor deposition or by means of a gel/sol mist.

Consequently, the duration of this method is very long resulting in a loss of productivity and in an increase of productivity costs. Additionally, this patent application discloses that in practice, the top layer predominantly consist of
25 diphosphates and zinc oxide and/or aluminum oxide. Aluminum oxide, also called alumina, is not phosphatable. Finally, this patent application is silent about the coverage rate of phosphate crystals on the coated hot-formed steel.

The object of the invention is to provide an easy to implement method for the manufacture of a phosphatable hardened part, and consequently having a
30 good paint adhesion, starting from a coated steel sheet. In particular, it aims to make available a hardened part which can be phosphated in order to obtain a high coverage rate of phosphate crystals on the part surface, i.e. a rate superior or equal to 80%.

This object is achieved by providing a method for the manufacture of a phosphatable hardened part according to claim 1. The method can also comprise characteristics of claims 2 to 15.

5 The second object is achieved by providing a coated steel sheet according to claim 16.

The third object is achieved by providing a part according to claim 17. The hardened part can also comprise characteristic of claims 18 to 23.

The fourth object is achieved by providing the use of such part for the manufacture of an automotive vehicle according to claim 24.

10 Other characteristics and advantages of the invention will become apparent from the following detailed description of the invention.

To illustrate the invention, various embodiments and trials of non-limiting examples will be described, particularly with reference to the following Figure:

15 Figure 1 illustrates one corrosion cycle corresponding to 168 hours of the norm VDA 233-102.

The following terms will be defined:

- "coverage rate of phosphate crystals" is defined by a percentage. 0% means that the surface of the part is not covered at all by phosphate crystals, 100% means that the surface of the part is totally covered by phosphate crystals".

20 The designation "steel" or "steel sheet" means a steel sheet for press hardening process having a composition allowing the part to achieve a higher tensile strength above or equal to 500 MPa, preferably above or equal to 1000 MPa, advantageously above or equal to 1500 MPa. The weight composition of steel sheet is preferably as follows: $0.03\% \leq C \leq 0.50\%$; $0.3\% \leq Mn \leq 3.0\%$;
25 $0.05\% \leq Si \leq 0.8\%$; $0.015\% \leq Ti \leq 0.2\%$; $0.005\% \leq Al \leq 0.1\%$; $0\% \leq Cr \leq 2.50\%$;
 $0\% \leq S \leq 0.05\%$; $0\% \leq P \leq 0.1\%$; $0\% \leq B \leq 0.010\%$; $0\% \leq Ni \leq 2.5\%$; $0\% \leq Mo \leq 0.7\%$;
 $0\% \leq Nb \leq 0.15\%$; $0\% \leq N \leq 0.015\%$; $0\% \leq Cu \leq 0.15\%$; $0\% \leq Ca \leq 0.01\%$; $0\% \leq W \leq 0.35\%$, the balance being iron and unavoidable impurities from the manufacture of steel.

30 For example, the steel sheet is 22MnB5 with the following composition: $0.20\% \leq C \leq 0.25\%$; $0.15\% \leq Si \leq 0.35\%$; $1.10\% \leq Mn \leq 1.40\%$; $0\% \leq Cr \leq 0.30\%$;
 $0\% \leq Mo \leq 0.35\%$; $0\% \leq P \leq 0.025\%$; $0\% \leq S \leq 0.005\%$; $0.020\% \leq Ti \leq 0.060\%$;

0.020% ≤ Al ≤ 0.060%; 0.002% ≤ B ≤ 0.004%, the balance being iron and unavoidable impurities from the manufacture of steel.

The steel sheet can be Usibor®2000 with the following composition: 0.24% ≤ C ≤ 0.38%; 0.40% ≤ Mn ≤ 3%; 0.10% ≤ Si ≤ 0.70%; 0.015% ≤ Al ≤ 0.070%; 0 %
5 ≤ Cr ≤ 2%; 0.25% ≤ Ni ≤ 2%; 0.020% ≤ Ti ≤ 0.10%; 0% ≤ Nb ≤ 0.060%; 0.0005% ≤ B ≤ 0.0040%; 0.003% ≤ N ≤ 0.010%; 0.0001% ≤ S ≤ 0.005%; 0.0001% ≤ P ≤ 0.025%; it being understood that the contents of titanium and nitrogen satisfy Ti/N > 3.42; and that the contents of carbon, manganese, chromium and silicon satisfy:

$$2,6C + \frac{Mn}{5,3} + \frac{Cr}{13} + \frac{Si}{15} \geq 1,1\%$$

the composition optionally comprising one or more of the following: 0.05% ≤ Mo ≤
10 0.65%; 0.001% ≤ W ≤ 0.30%; 0.0005% ≤ Ca ≤ 0.005%, the balance being iron and unavoidable impurities from the manufacture of steel.

For example, the steel sheet is Ductibor®500 with the following composition: 0.040% ≤ C ≤ 0.100%; 0.80% ≤ Mn ≤ 2.00%; 0% ≤ Si ≤ 0.30%; 0% ≤ S ≤ 0.005%; 0% ≤ P ≤ 0.030%; 0.010% ≤ Al ≤ 0.070%; 0.015% ≤ Nb ≤ 0.100%;
15 0.030% ≤ Ti ≤ 0.080%; 0% ≤ N ≤ 0.009%; 0% ≤ Cu ≤ 0.100%; 0% ≤ Ni ≤ 0.100%; 0% ≤ Cr ≤ 0.100%; 0% ≤ Mo ≤ 0.100%; 0% ≤ Ca ≤ 0.006%, the balance being iron and unavoidable impurities from the manufacture of steel.

Steel sheet can be obtained by hot rolling and optionally cold rolling depending on the desired thickness, which can be for example between 0.7 and
20 3.0mm.

The invention relates to a method for the manufacture of a hardened part coated with a phosphatable coating. Firstly, the method comprises the provision of a steel sheet pre-coated with a metallic coating comprising from 4.0 to 20.0% by weight of zinc, from 1.0 to 3.5% by weight of silicon, optionally from 1.0 to 4.0% by
25 weight of magnesium, and optionally additional elements chosen from Pb, Ni, Zr, or Hf, the content by weight of each additional element being less than 0.3% by weight, the balance being aluminum and unavoidable impurities and residuals elements.

Without willing to be bound by any theory, it seems that if these conditions
30 are not met, in particular if the amount of silicon is above 3.5%, there is a risk that the zinc is localized in aluminum matrix or an intermetallic compound Zn-Al is

formed. Thus, zinc cannot rise to the surface of the coated steel sheet. Alumina layer, which is not phosphatable, is formed on the surface of the coated steel sheet.

In most cases, when coverage rate of phosphate crystals is low, there is a risk of poor paint adhesion. However, in some cases, although the coverage rate of phosphate crystals is low, the paint adhesion is good but the corrosion resistance after painting is poor. Indeed, the microroughness of the coated parts surface coated allows for paint adhesion. But, the paint is not evenly distributed on the part surface. In this case, phosphate crystals cannot play the role of binder between the paint and the coating. Consequently, in a corrosive environment, water infiltrates easily under paint resulting in red rust areas.

Preferably, the metallic coating does not comprise elements selected among Cr, Mn, Ti, Ce, La, Nd, Pr, Ca, Bi, In, Sn and Sb or their combinations. In another preferred embodiment, the metallic coating does not comprise any of the following compounds: Cr, Mn, Ti, Ce, La, Nd, Pr, Ca, Bi, In, Sn and Sb. Indeed, without willing to be bound by any theory, it seems that when these compounds are present in the coating, there is a risk that the properties of the coating, such as electrochemical potential, are altered, because of their possible interactions with the essential elements of the coatings.

Advantageously, the coating comprises from 1.5 to 3.5% by weight of silicon, preferably from 1.5 to 2.5% by weight of silicon. In another preferred embodiment, the coating comprises from 2.1 to 3.5% by weight of silicon.

Preferably, the coating comprises from 10.0 to 15.0% by weight of zinc.

In a preferred embodiment, the ratio Zn/Si in the coating is between 5 and 7.5.

Without willing to be bound by any theory, it has been found that when the ratio Zn/Si is not between 5 and 7.5, there is a risk that the coverage rate of phosphate crystals decreases because of a too high content of Al and Fe at the coating surface.

Advantageously, the coating comprises from 1.1 to 3.0% by weight of magnesium.

Advantageously, the coating comprises above 76% by weight of aluminum.

The coating can be deposited by any methods known to the man skilled in the art, for example hot-dip galvanization process, electrogalvanization process, physical vapour deposition such as jet vapor deposition or sputtering magnetron. Preferably, the coating is deposited by hot-dip galvanization process. In this process, the steel sheet obtained by rolling is dipped in a molten metal bath.

The bath comprises zinc, silicon, aluminum and optionally magnesium. It can comprise additional elements chosen from Pb, Ni, Zr, or Hf, the content by weight of each additional element being less than 0.3% by weight. These additional elements can improve among others ductibility, coating adhesion on the steel sheet.

The bath can also contain unavoidable impurities and residuals elements from feeding ingots or from the passage of the steel sheet in the molten bath. Residual element can be iron with a content up to 3.0% by weight.

The thickness of the coating is usually between 5 and 50 μm , preferably between 10 and 35 μm , advantageously between 12 and 18 μm or between 26 to 31 μm . The bath temperature is usually between 580 and 660°C.

After the deposition of the coating, the steel sheet is usually wiped with nozzles ejecting gas on both sides of the coated steel sheet. The coated steel sheet is then cooled. Preferably, the cooling rate is above or equal to 15°C.s⁻¹ between the beginning of the solidification and the end of the solidification. Advantageously, the cooling rate between the beginning and the end of the solidification is superior or equal to 20°C.s⁻¹.

Then, a skin-pass can be realized and allows work hardening the coated steel sheet and giving it a roughness facilitating the subsequent shaping. A degreasing and a surface treatment can be applied in order to improve for example adhesive bonding or corrosion resistance.

Then, the coated steel sheet is cut to obtain a blank. A thermal treatment is applied to the blank in a furnace under non protective atmosphere at an austenitization temperature T_m usually between 840 and 950°C, preferably 880 to 930°C. Advantageously, said blank is maintained during a dwell time t_m between 1 to 12 minutes, preferably between 3 to 9 minutes. During the thermal treatment before the hot-forming, the coating forms an alloy layer having a high resistance to corrosion, abrasion, wear and fatigue.

After the thermal treatment, the blank is then transferred to a hot-forming tool and hot-formed at a temperature between 600 and 830°C. The hot-forming comprises the hot-stamping and the roll-forming. Preferably, the blank is hot-stamped. The part is then cooled in the hot-forming tool or after the transfer to a specific cooling tool.

The cooling rate is controlled depending on the steel composition, in such a way that the final microstructure after the hot-forming comprises mostly martensite, preferably contains martensite, or martensite and bainite, or is made of at least 75% of equiaxed ferrite, from 5 to 20% of martensite and bainite in amount less than or equal to 10%.

Thus, a phosphatable hardened part according to the invention is obtained.

Preferably, the microstructure of the coating of the part comprises an intermetallic layer Fe_3Al , an interdiffusion layer Fe-Si-Al , a low quantity of silicon distributed in the coating and a ZnO layer at the surface of the coating. When magnesium is present in the coating, the microstructure comprises also Zn_2Mg phase and/or Mg_2Si phase. Advantageously, the microstructure does not comprise metallic zinc.

For automotive application, after phosphating step, the part is dipped in an e-coating bath. Usually, the thickness of the phosphate layer is between 1 and 2 μm and the thickness of the e-coating layer is between 15 and 25 μm , preferably inferior or equal to 20 μm . The cataphoresis layer ensures an additional protection against corrosion.

After the e-coating step, other paint layers can be deposited, for example, a primer coat of paint, a basecoat layer and a top coat layer.

Before applying the e-coating on the part, the part is previously degreased and phosphated so as to ensure the adhesion of the cataphoresis. After the phosphating, a high coverage rate of phosphate crystals on the surface of the part is obtained. The coverage rate of phosphate crystals on the surface of the part is above or equal to 80%, preferably above or equal to 90%, advantageously above or equal to 99%.

The invention will now be explained in trials carried out for information only. They are not limiting.

Examples

- 5 For all samples, steel sheets used are 22MnB5. The composition of the steel is as follows: C = 0.2252% ; Mn = 1.1735% ; P = 0.0126% , S = 0.0009% ; N = 0.0037% ; Si = 0.2534% ; Cu = 0.0187% ; Ni = 0.0197% ; Cr = 0.180% ; Sn = 0.004% ; Al = 0.0371% ; Nb = 0.008% ; Ti = 0.0382% ; B = 0.0028 % ; Mo = 0.0017% ; As = 0.0023% et V = 0.0284%.
- 10 All coatings were deposited by hot-dip galvanization process.

Example 1: Phosphating test:

Phosphatability test is used to determine the adhesion of phosphate crystals on hardened parts by assessing the coverage rate on the part surface.

- 15 Trials 1 to 9 were prepared and subjected to the phosphating test.

To this end, coated trials were cut in order to obtain a blank. Blanks were then heated at a temperature of 900°C during a dwell time varying between 5 and 10 minutes. Blanks were transferred into a press tool and hot-stamped in order to obtain a part. Finally, the part was cooled to obtain a hardening by martensitic transformation.

20

- A degreasing was then realized. It was followed by a phosphating step realized by dipping into a bath comprising a solution of Gardobond® 24 TA, Gardobond® Add H7141, Gardobond® H7102, Gardobond® Add H7257, Gardobond® Add H7101, Gardobond® Add H7155 during 3 minutes at 50°C.
- 25 Parts were then wiped with water and dried with hot air. The parts surface were observed by SEM. Results are shown in the following Table 1:

Trials	Coating					Thickness (µm)	Covering rate after a thermal treatment at 900°C (%)	
	Al	Si	Zn	Mg	Zn/Si		Dwell time = 5 minutes	Dwell time = 10 minutes
1	91	9	-	-	-	27	0	0
2	81	9	10	-	1.1	27	<5	<10
3	76	9	15	-	1.7	27	0	20
4	71	9	20	-	2.2	27	<10	<10
5	80	5	15	-	3.0	27	50	70
6	78	5	15	2	3.0	27	50	50
7*	88	2	10	-	5	27	95	95
8*	83	2	15	-	7.5	27	>99	>99
9*	81	2	15	2	7.5	27	ND	90

*: examples according to the invention, ND: not done.

The above results show that Trials 7 to 9 have a high coverage rate of phosphate crystals on hardened part.

Example 2: Paint adhesion test:

This test is used to determine the paint adhesion of the hardened parts.

An e-coating layer of 20µm is deposited on Trials 1 to 5 and 7 to 9 prepared in Example 1. To this end, all trials were dipped into a bath comprising an aqueous solution comprising Pigment paste® W9712-N6 and Resin blend® W7911-N6 of PPG Industries during 180 seconds at 30°C. A 200V current was applied. Then, the panel was wiped and cured in the oven at 180°C during 35 minutes.

Then, painted parts are dipped into a sealed box comprising demineralized water during 10 days at a temperature of 50°C. After the dipping, a grid is realized with a cutter. The paint is ripped with a scotch.

The removed paint is assessed by naked eyes: 0 means excellent, in other words, there is a little or no paint removed and 5 means very bad, in other words, there are lots of paint removed. Results are shown in the following Table 2:

Trials	Coating					Paint adhesion after a thermal treatment at 900°C (%)	
	Al	Si	Zn	Mg	Zn/Si	Dwell time = 5 minutes	Dwell time = 10 minutes
10	91	9	-	-	-	0	0
11	81	9	10	-	1.1	5	5
12	76	9	15	-	1.7	5	5
13	71	9	20	-	2.2	5	5
14	80	5	15	-	3.0	0	0
15*	88	2	10	-	5.0	0	0
16*	83	2	15	-	7.5	0	0
17*	81	2	15	2	7.5	2	0

*: examples according to the invention.

Trials 15 to 17 according to the present invention show good paint adhesion, as trials 10 and 14.

5

Example 3: Delamination test:

This test is used to determine the corrosion after painting of the hardened parts.

10 An e-coating layer of 20µm is deposited on Trials 1 to 5, 7 and 9 prepared at Example 1. To this end, all trials were dipped into a bath comprising an aqueous solution comprising Pigment paste® W9712-N6 and Resin blend® W7911-N6 of PPG Industries during 180 seconds at 30°C. A 200V current was applied. Then, the panel was wiped and cured in the oven at 180°C during 35 minutes.

Then, scratches were realized on the e-coating layer with a cutter.

15 Finally, a test, consisting in submitting panels to corrosion cycles according to the norm VDA 233-102, was realized. Trials were put in a chamber wherein an aqueous solution of sodium chloride of 1% by weight was vaporized on trials with a rate of flow of 3mL.h⁻¹. The temperature varied from 50 to -15°C and the humidity rate varied from 50 to 100%. Figure 1 illustrates one cycle corresponding
20 to 168 hours, i.e. one week.

The presence of delamination was observed by naked eyes: 0 means excellent, in other words, there is no delamination and 5 means very bad, in other words, there are lots of delamination. Results are shown in the following Table 3:

Trials	Coating					2 corrosion cycles	5 corrosion cycles			
						thermal treatment at 900°C				
	Al	Si	Zn	Mg	Zn/Si	Dwell time = 5 minutes	Dwell time = 10 minutes	Dwell time = 5 minutes	Dwell time = 10 minutes	
18	91	9	-	-	-	0.5	1	4.5	5	
19	81	9	10	-	1.1	5	0.5	ND	ND	
20	76	9	15	-	1.7	5	1	5	5	
21	71	9	20	-	2.2	4.5	4.5	ND	ND	
22	80	5	15	-	3.0	2	2	4.5	4	
23*	88	2	10	-	5.0	1	1	2.5	3	
24*	81	2	15	2	7.5	0.5	0.5	2	2	

*: examples according to the invention, ND: not done.

Trials according to the invention (Trials 23 and 24) lead to a little delamination
5 after 2 and 5 weeks of corrosion cycle, in contrary to Trials 18 to 22.

CLAIMS

1. A method for the manufacture of a hardened part coated with a phosphatable coating comprising the following steps:
 - 5 A) the provision of a steel sheet pre-coated with a metallic coating comprising from 4.0 to 20.0% by weight of zinc, from 1.0 to 3.5% by weight of silicon, optionally from 1.0 to 4.0% by weight of magnesium, and optionally additional elements chosen from Pb, Ni, Zr, or Hf, the content by weight of each additional element being less than 0.3% by weight, the balance being
10 aluminum and unavoidable impurities and residuals elements,
 - B) the cutting of the coated steel sheet to obtain a blank,
 - C) the thermal treatment of the blank at a temperature between 840 and 950°C to obtain a fully austenitic microstructure in the steel,
 - D) the transfer of the blank into a press tool,
 - 15 E) the hot-forming of the blank to obtain a part,
 - F) the cooling of the part obtained at step E) in order to obtain a microstructure in steel being martensitic or martensite-bainitic or made of at least 75% of equiaxed ferrite, from 5 to 20% of martensite and bainite in amount less than or equal to 10%.
- 20 2. A method according to claim 1, wherein the coating comprises from 1.5 to 3.5% by weight of silicon.
3. A method according to claim 2, wherein the coating comprises from 1.5 to
25 2.5% by weight of silicon.
4. A method according to claim 2, wherein the coating comprises from 2.1 to 3.5% by weight of silicon.
- 30 5. A method according to anyone of claims 1 to 4, wherein the coating comprises from 10.0 to 15.0% by weight of zinc.

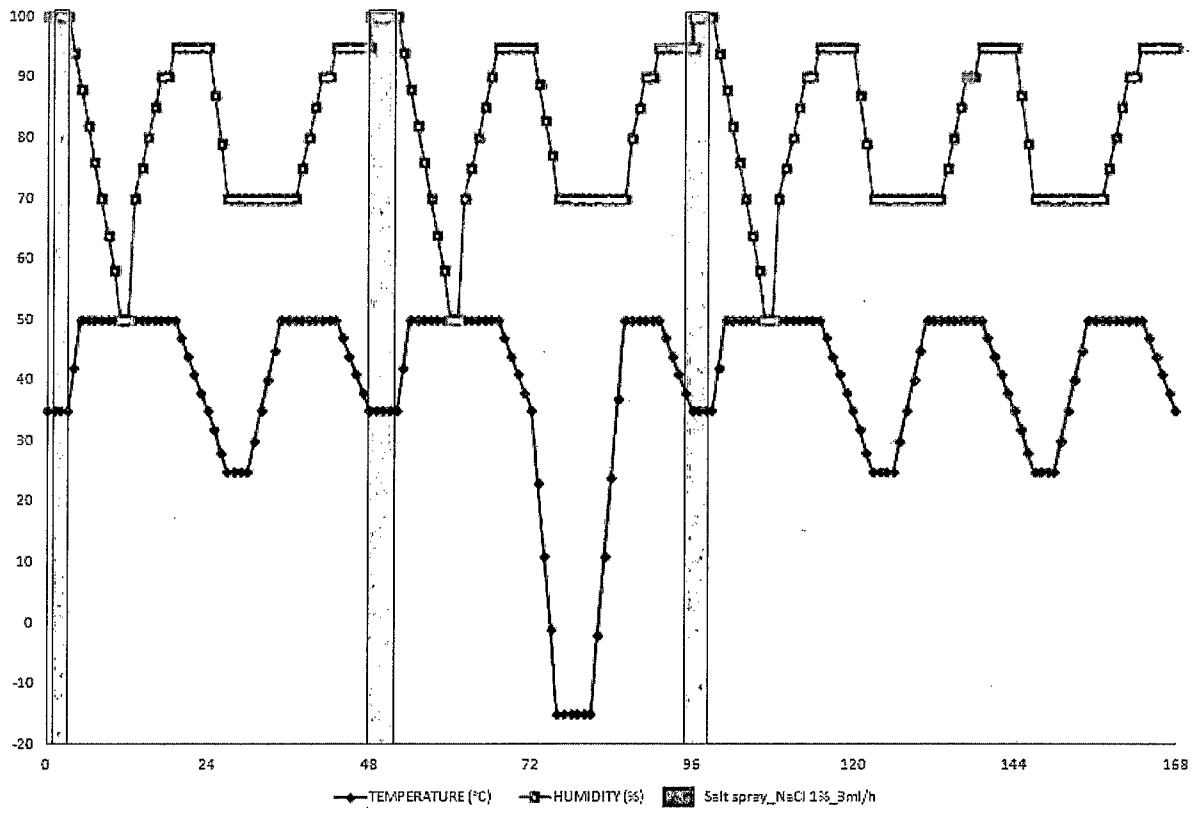
6. A method according to anyone of claims 1 to 5, wherein the coating of the steel sheet is such that the ratio Zn/Si is between 5 and 7.5.
- 5 7. A method according to anyone of claims 1 to 6, wherein the pre-coating of the steel sheet comprises from 1.1 to 3.0% by weight of magnesium.
8. A method according to anyone of claims 1 to 7, wherein the coating comprises above 76% by weight of aluminum.
- 10 9. A method according to anyone of claims 1 to 8, wherein the thickness of the metallic pre-coating is between 5 and 50 μ m
- 15 10. A method according to claim 9, wherein the thickness of the metallic pre-coating is between 10 and 35 μ m.
11. A method according to claim 10, wherein the thickness between 12 and 18 μ m.
12. A method according to claim 10, wherein the thickness between 26 and 31 μ m.
- 20 13. A method according to anyone of claims 1 to 12, wherein the coating does not comprise elements selected among Cr, Mn, Ti, Ce, La, Nd, Pr, Ca, Bi, In, Sn and Sb or their combinations.
- 25 14. A method according to anyone of claims 1 to 13, wherein step C) is performed during a dwell time between 1 to 12 minutes in an inert atmosphere or an atmosphere comprising air.
- 30 15. A method according to anyone of claims 1 to 14, wherein during step E) the hot-forming of the blank is performed at a temperature between 600 and 830°C.

16. A steel sheet coated with a metallic alloy comprising aluminum, from 35 to 60% by weight of iron, silicon, zinc, and optionally magnesium obtained by the thermal treatment at a temperature between 840 and 950°C of said steel sheet pre-coated with a metallic coating comprising from 4.0 to 20.0% by weight of zinc, from 1.0 to 3.5% by weight of silicon, optionally from 1.0 to 4.0% by weight of magnesium, and optionally additional elements chosen from Pb, Ni, Zr, or Hf, the content by weight of each additional element being less than 0.3% by weight, the balance being aluminum and unavoidable impurities and residuals elements, and wherein the microstructure of steel is fully austenitic.
17. Part coated with a metallic coating obtainable according to the method of anyone of claims 1 to 15, comprising a ZnO layer on the metallic coating and a phosphate crystals layer on the ZnO layer obtained after an additional phosphating step G).
18. Part according to claim 17, wherein the coverage rate of phosphate crystals on the part surface is equal or above 90%.
19. Part according to claim 18, wherein the coverage rate of phosphate crystals on the part surface is equal or above 99%.
20. Part according to anyone of claims 17 to 19, comprising in addition an e-coating layer on the phosphate crystals layer.
21. Part according to anyone of claims 17 to 20, wherein the metallic coating comprises an intermetallic layer Fe₃Al, an interdiffusion layer Fe-Si-Al, a low quantity of silicon distributed in the coating.
22. Part according to anyone of claims 17 to 21, wherein the microstructure comprises Zn₂Mg phase or Mg₂Si phase or both.
23. Part according to anyone of claims 17 to 22, wherein, the microstructure does not comprise metallic zinc.

24. Use of a part according to anyone of claims 17 to 23, or obtainable according to the method of anyone of claims 1 to 15, for the manufacture of automotive vehicle.

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Figure 1



INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2015/001285

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C2/12 C23C2/06 C23C2/28 C21D1/673
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C C21D C21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/085466 A1 (LUPP BARBARA [DE] ET AL) 12 April 2012 (2012-04-12) cited in the application	16-24
A	paragraphs [0017] - [0028], [0031] - [0036], [0039], [0041] - [0048], [0055] - [0062], [0066], [0070] - [0076], [0082]; figure 1	1-15
X	----- EP 2 695 963 A1 (NIPPON STEEL & SUMITOMO METAL CORP [JP]) 12 February 2014 (2014-02-12)	16,17, 20,21, 23,24
A	paragraphs [0016], [0018], [0022], [0026] - [0034], [0043] - [0054], [0081] - [0082]; example 4 ----- -/--	1-15,18, 19,22

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 April 2016

Date of mailing of the international search report

02/05/2016

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2015/001285

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 839 049 A1 (ARCELORMITTAL INVESTIGACIÓN Y DESARROLLO SL [ES]) 25 February 2015 (2015-02-25)	16,17, 20-24
A	the whole document	1-15,18, 19

X	DE 20 2012 000616 U1 (BENTELER AUTOMOBILTECHNIK GMBH [DE]) 29 February 2012 (2012-02-29)	16,17, 21,24
A	paragraphs [0026] - [0028], [0047]; figures 8a,8b	1-15, 18-20, 22,23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/001285

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2012085466	A1	12-04-2012	DE 102009007909 A1	12-08-2010
			EP 2393953 A1	14-12-2011
			US 2012085466 A1	12-04-2012
			WO 2010089273 A1	12-08-2010

EP 2695963	A1	12-02-2014	CA 2831305 A1	11-10-2012
			CN 103492605 A	01-01-2014
			EP 2695963 A1	12-02-2014
			JP 5614496 B2	29-10-2014
			KR 20130132623 A	04-12-2013
			KR 20160015388 A	12-02-2016
			RU 2013148805 A	10-05-2015
			US 2014030544 A1	30-01-2014
			US 2015191813 A1	09-07-2015
			WO 2012137687 A1	11-10-2012

EP 2839049	A1	25-02-2015	AU 2012377741 A1	04-12-2014
			CA 2870532 A1	24-10-2013
			CN 104302802 A	21-01-2015
			EA 201401136 A1	31-03-2015
			EP 2839049 A1	25-02-2015
			JP 2015520797 A	23-07-2015
			KR 20150008114 A	21-01-2015
			US 2015284861 A1	08-10-2015
			WO 2013156688 A1	24-10-2013

DE 202012000616	U1	29-02-2012	NONE	
