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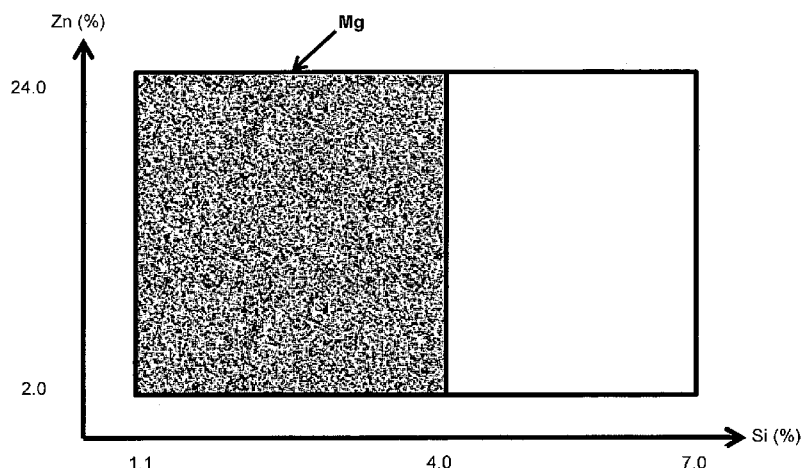
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(54) Title: METHOD FOR THE MANUFACTURE OF A HARDENED PART WHICH DOES NOT HAVE LME ISSUES

Figure 1



(57) Abstract: The present invention relates to a method for the manufacture of a hardened part comprising the following steps: A) the provision of a steel sheet pre-coated with a metallic coating comprising from 2.0 to 24.0% by weight of zinc, from 1.1 to 7.0% by weight of silicon, optionally from 1.1 to 8.0% by weight of magnesium when the amount of silicon is between 1.1 and 4.0%, 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, wherein the ratio Al/Zn is above 2.9, 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 martensitic-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%.



Method for the manufacture of a hardened part which does not have LME issues

The present invention relates to a method for the manufacture of a
5 hardened part starting from a steel sheet coated with a metallic coating. The invention is particularly well suited for the manufacture of automotive vehicles.

Zinc based coatings are generally used because they allows for a protection against corrosion thanks to barrier protection and cathodic protection. The barrier effect is obtained by the application of a metallic coating on steel
10 surface. Thus, the metallic coating prevents the contact between steel and corrosive atmosphere. The barrier effect is independent from the nature of coating and substrate. On the contrary, sacrificial cathodic protection is based on the fact that zinc is a metal less noble than steel. Thus, if corrosion occurs, zinc is consumed preferentially to steel. Cathodic protection is essential in areas where
15 steel is directly exposed to corrosive atmosphere, like cut edges where surrounding zinc will be consumed before steel.

However, when heating steps are performed on such zinc coated steel sheets, for example press hardening or welding, cracks are observed in steel which spread from the coating. Indeed, occasionally, there is a reduction of metal
20 mechanical properties due to the presence of cracks in coated steel sheet after heating steps. These cracks appear with the following conditions: high temperature; contact with a liquid metal having a low melting point (such as zinc) in addition to stress; heterogeneous diffusion of molten metal with substrate grain bulk and boundary. The designation for such phenomenon is liquid metal embrittlement (LME), also called liquid metal assisted cracking (LMAC).
25

The patent application US2013/0206824 discloses a method for producing a steel component with a metallic anti-corrosion coating from a steel sheet comprising at least 0.4% by weight Mn. The sheet steel product is annealed in a continuous furnace under an annealing atmosphere containing up to 25% by
30 volume H₂, 0.1% to 10% by volume NH₃, H₂O, N₂, and process-related impurities as the remainder, at a dew point between -50°C and -5°C at a temperature of 400 to 1100°C for 5 to 600s. The annealed steel sheet has a 5 to 200 µm thick nitration

layer with a particle size finer than the particle size of the inner core layer. Once coated with a metallic protective layer, a blank is separated from the annealed steel sheet, heated to an austenitising temperature of 780 to 950°C, hot-formed, and cooled so that a hardened structure forms.

5 At high temperature, the nitration layer allows for a minimization of risk of embrittlement in a sheet steel produced even when the sheet steel product is provided with a metallic coating. The metallic coating, which can be applied to the steel substrate, is based on Zn, Al, Zn—Al, Zn—Mg, Zn—Ni, Zn—Fe, Al—Mg, Al—Si, Zn—Al—Mg or Zn—Al—Mg—Si.

10 However, from an industrial point of view, because of the presence of ammoniac gas during the nitriding treatment, lines have to be redesigned. Indeed, this step has to be done in a hermetic box to prevent the leakage of this gas. this hermetic box difficult to produce results in an increase of productivity costs. Moreover, it is difficult to find a material which can handle the corrosive ammoniac.
15 Additionally, the nitriding treatment is added to the method for producing the coated part. Thus, the duration of this method is elongated resulting in a loss of productivity. Finally, the nitration layer inhibits the wettability of zinc coatings when hot-dip galvanization is realized.

20 The object of the invention is to provide a method for the manufacture of a hardened part which does not have LME issues. It aims to make available, in particular, an easy to implement method in order to obtain a part which does not have LME issues generated by the hot-forming.

25 This object is achieved by providing a method for the manufacture of a hardened part according to claim 1. The method can also comprise characteristics of claims 2 to 23.

 The invention also covers a part according to claim 25. The part can also comprise characteristics of claims 24 and 30.

 The invention also covers the use of such part for the manufacture of an automotive vehicle according to claim 31.

30 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:

Figure 1 illustrates a schematic representation of the composition according to the invention comprising from 2.0 to 24.0% of zinc, from 1.1 to 7.0% by weight of silicon and optionally magnesium when the amount of silicon is between 1.1 and 4.0%.

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: $0.03\% \leq C \leq 0.50\%$; $0.3\% \leq Mn \leq 3.0\%$; $0.05\% \leq Si \leq 0.8\%$; $0.015\% \leq Ti \leq 0.2\%$; $0.005\% \leq Al \leq 0.1\%$; $0\% \leq Cr \leq 2.50\%$; $0\% \leq S \leq 0.05\%$; $0\% \leq P \leq 0.1\%$; $0\% \leq B \leq 0.010\%$; $0\% \leq Ni \leq 2.5\%$; $0\% \leq Mo \leq 0.7\%$; $0\% \leq Nb \leq 0.15\%$; $0\% \leq N \leq 0.015\%$; $0\% \leq Cu \leq 0.15\%$; $0\% \leq Ca \leq 0.01\%$; $0\% \leq W \leq 0.35\%$, the balance being iron and unavoidable impurities from the manufacture of steel.

For example, the steel sheet is 22MnB5 with the following composition: $0.20\% \leq C \leq 0.25\%$; $0.15\% \leq Si \leq 0.35\%$; $1.10\% \leq Mn \leq 1.40\%$; $0\% \leq Cr \leq 0.30\%$; $0\% \leq Mo \leq 0.35\%$; $0\% \leq P \leq 0.025\%$; $0\% \leq S \leq 0.005\%$; $0.020\% \leq Ti \leq 0.060\%$; $0.020\% \leq Al \leq 0.060\%$; $0.002\% \leq B \leq 0.004\%$, the balance being iron and unavoidable impurities from the manufacture of steel.

The steel sheet can be Usibor®2000 with the following composition: $0.24\% \leq C \leq 0.38\%$; $0.40\% \leq Mn \leq 3\%$; $0.10\% \leq Si \leq 0.70\%$; $0.015\% \leq Al \leq 0.070\%$; $0\% \leq Cr \leq 2\%$; $0.25\% \leq Ni \leq 2\%$; $0.020\% \leq Ti \leq 0.10\%$; $0\% \leq Nb \leq 0.060\%$; $0.0005\% \leq B \leq 0.0040\%$; $0.003\% \leq N \leq 0.010\%$; $0.0001\% \leq S \leq 0.005\%$; $0.0001\% \leq P \leq 0.025\%$; 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: $0.05\% \leq Mo \leq 0.65\%$; $0.001\% \leq W \leq 0.30\%$; $0.0005\% \leq Ca \leq 0.005\%$, the balance being iron and unavoidable impurities from the manufacture of steel.

For example, the steel sheet is Ductibor®500 with the following composition: $0.040\% \leq C \leq 0.100\%$; $0.80\% \leq Mn \leq 2.00\%$; $0\% \leq Si \leq 0.30\%$; $0\% \leq S \leq 0.005\%$; $0\% \leq P \leq 0.030\%$; $0.010\% \leq Al \leq 0.070\%$; $0.015\% \leq Nb \leq 0.100\%$;

$0.030\% \leq \text{Ti} \leq 0.080\%$; $0\% \leq \text{N} \leq 0.009\%$; $0\% \leq \text{Cu} \leq 0.100\%$; $0\% \leq \text{Ni} \leq 0.100\%$; $0\% \leq \text{Cr} \leq 0.100\%$; $0\% \leq \text{Mo} \leq 0.100\%$; $0\% \leq \text{Ca} \leq 0.006\%$, 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 3.0mm.

The invention relates to a method for the manufacture of a hardened part which does not have LME issue. Firstly, this method comprises the provision of steel sheet pre-coated with a metallic coating comprising from 2.0 to 24.0% by weight of zinc, from 1.1 to 7.0% by weight of silicon, optionally from 1.1 to 8.0% by weight of magnesium when the amount of silicon is between 1.1 and 4.0%, 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, wherein the ratio Al/Zn is above 2.9.

The coating composition is illustrated Figure 1. According to the invention, the coating comprises optionally from 1.1 to 8.0% by weight of magnesium when the amount of silicon is between 1.1 and 4.0%. The optional presence of magnesium is represented in grey in this Figure.

Without willing to be bound by any theory, it seems that if these conditions are not met, LME issue appears because Zn-rich phases are in too high amount and liquid zinc can diffuse towards the steel / coating interface and create macro-cracks in the steel.

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.

Preferably, the ratio Al/Zn is between 5 and 9. Without willing to be bound by any theory, it has been found that when the ratio Al/Zn is not between 5 and 9,

there is a risk that the decrease of LME issue is less important because zinc is no longer in solid solution in the aluminum matrix and Zn-rich phases start to form.

Preferably, the ratio Zn/Si is between 2.9 and 8. Without willing to be bound by any theory, it has been found that when the ratio Zn/Si is not between 2.9 and 8, there is a risk that the decrease of LME issue is less important because the proportion of Zn-rich phases is a little too high in the coating.

Advantageously, the coating comprises from 2.0 to 5.0%, preferably 2.1 to 4.9% by weight of silicon. In another preferred embodiment, the coating comprises from 1.5 to 3.5% by weight of silicon. In another preferred embodiment, the coating comprises from 4.5 to 5.5% by weight of silicon.

Preferably, the coating comprises from 5.0 to 19.0%, preferably 5.0 to 15.0%, advantageously from 10.0 to 15.0% by weight of zinc.

Advantageously, when the amount of silicon is between 1.1 and 4.0% by weight, the coating can comprise from 0.5 to 3.0%, preferably from 1.0 to 2.9% by weight of magnesium. In another preferred embodiment, the coating comprises from 3.1 to 8.0%, preferably from 4.0 to 8% by weight of magnesium.

Advantageously, the coating comprises above 71%, preferably 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
5 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.

10 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
15 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
20 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
25 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
30 less than or equal to 10%.

Thus, a hardened part without LME according to the invention is obtained.

Preferably, the microstructure of the coating of the part comprises an interdiffusion layer Fe+Fe₃Al, AlFe intermetallic phases containing dissolved Si

and Zn, binary Zn-Al and Si-rich phases. When magnesium is present in the coating, the microstructure comprises also Zn_2Mg phase and/or Mg_2Si phase.

In a preferred embodiment, the part is a press hardened steel part having a variable thickness, i.e. the press hardened steel part of the invention can have a thickness which is not uniform but which can vary. Indeed, it is possible to achieve the desired mechanical resistance level in the zones which are the most subjected to external stresses, and to save weight in the other zones of the press hardened part, thus contributing to the vehicle weight reduction. In particular, the parts with non-uniform thickness can be produced by continuous flexible rolling, i.e. by a process wherein the sheet thickness obtained after rolling is variable in the rolling direction, in relationship with the load which has been applied through the rollers to the sheet during the rolling process.

Thus, within the conditions of the invention, it is possible to manufacture advantageously vehicle parts with varying thickness in order to obtain for example a tailored rolled blank. Specifically, the part can be a front rail, a seat cross member, a side sill member, a dash panel cross member, a front floor reinforcement, a rear floor cross member, a rear rail, a B-pillar, a door ring or a shotgun.

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.

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

Examples

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

8

= 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%.

All coatings were deposited by hot-dip galvanization process.

5

Example 1: Cracking resistance test:

This test is used to determine the presence of cracks obtainable after the hot-forming during the press hardening process.

Trials 1 to 10 were prepared and subjected to the Cracking resistance test.

10

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 parts having an omega shape. Then, parts were cooled to obtain a hardening by martensitic transformation.

15

Finally, the deformed section of parts was cut. Then, the presence of cracks was analyzed by SEM (Scanning Electron Microscopy). 0 means excellent, in other words, there is no cracks at all; 1 means that there are microcracks having a deep between 0 and 50µm and 2 means very bad, in other words, there are macrocracks having a deep above 50µm. Results are shown in the following Table

20 1:

Trials	Coating						Thickness (µm)	thermal treatment at 900°C	
	Al	Si	Zn	Mg	Al/Zn	Zn/Si		Dwell time = 5 minutes	Dwell time = 10 minutes
1	81	9	10	-	8.1	1.1	27	2	2
2	77	9	10	4	7.7	1.1	27	2	1
3	73	9	10	8	7.3	1.1	27	2	2
4	76	9	15	-	5.1	1.7	27	2	2
5	79	5	15	1	5.3	3.0	27	2	2
6	78	5	15	2	5.2	3.0	27	2	2
7*	80	5	15	-	5.3	3.0	27	0	0
8*	83	2	15	-	5.6	7.5	27	0	0
9*	86	2	10	2	8.6	5.0	27	0	0
10*	88	2	10	-	8.8	5.0	27	0	0

*: examples according to the invention.

All Trials according to the invention (Trials 7 to 10) show excellent behavior during hot-stamping. Indeed, no crack appears with the parts according to the present invention in contrary to Trials 1 to 6.

Example 2: Tool degradation test:

This test is used to determine the presence of scratch and coating smearing in the press tool after the hot-stamping.

Thus, the press tool was analyzed by naked eyes after the hot-stamping of Trials 1, 2, 4 and 7 to 10 prepared in Example 1. 0 means excellent, in other words, there is no tool degradation and no coating smearing in the press tool; 1 means that there are scratches and slight coating smearing in the press tool and 2 means very bad, in other words, there are heavy scratches and important coating smearing in the press tool. Results are shown in the following Table 2:

Trials	Coating						Covering rate after a thermal treatment at 900°C (%)	
	Al	Si	Zn	Mg	Al/Zn	Zn/Si	Dwell time = 5 minutes	Dwell time = 10 minutes
11	81	9	10	-	9.1	1.1	1	1
12	77	9	10	4	7.7	1.1	2	2
13	76	9	15	-	5.1	1.7	2	1
14*	80	5	15	-	5.3	3.0	0	0
15*	83	2	15	-	5.5	7.5	0	0
16*	86	2	10	2	8.6	5.0	0	0
17*	88	2	10	-	8.6	5.0	0	0

*: examples according to the invention.

Trials 14 to 17 according to the invention have an excellent behavior in a press tool in contrary to Trials 11 to 13.

CLAIMS

1. A method for the manufacture of a hardened part comprising the following steps:

5 A) the provision of a steel sheet pre-coated with a metallic coating comprising from 2.0 to 24.0% by weight of zinc, from 1.1 to 7.0% by weight of silicon, optionally from 1.1 to 8.0% by weight of magnesium when the amount of silicon is between 1.1 and 4.0%, and optionally additional elements chosen from Pb, Ni, Zr, or Hf, the content by weight of each additional element
10 being less than 0.3% by weight, the balance being aluminum and unavoidable impurities and residuals elements, wherein the ratio Al/Zn is above 2.9,

B) the cutting of the coated steel sheet to obtain a blank,

15 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,

20 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%.

2. A method according to claim 1, wherein the ratio Al/Zn is between 5 and 9.

25 3. A method according to claim 1 or 2, wherein the ratio Zn/Si is between 2.9 and 8.

4. A method according to anyone of claims 1 to 3, wherein the coating comprises from 2.0 to 5.0 % by weight of silicon.

5. A method according to claim 4, wherein the coating comprises from 2.1 to 4.9 % by weight of silicon.
6. A method according to anyone of claims 1 to 3, wherein the coating comprises from 1.5 to 3.5 % by weight of silicon.
7. A method according to anyone of claims 1 to 3, wherein the coating comprises from 4.5 to 5.5 % by weight of silicon.
8. A method according to anyone of claims 1 to 7, wherein the coating comprises from 5.0 to 19.0% by weight of zinc.
9. A method according to claim 8, wherein the coating comprises from 5.0 to 15.0% by weight of zinc.
- 10.A method according to claim 9, wherein the coating comprises from 10.0 to 15.0% by weight of zinc.
- 11.A method according to anyone of claims 1 to 10, wherein the coating comprises from 0.5 to 3.0% by weight of magnesium.
- 12.A method according to claim 11, wherein the coating comprises from 1.0 to 2.9% by weight of magnesium.
- 13.A method according to anyone of claims 1 to 10, wherein the coating comprises from 3.1 to 8.0% by weight of magnesium.
- 14.A method according to claim 13, wherein the coating comprises from 4.0 to 8.0% by weight of magnesium.

15.A method according to anyone of claims 1 to 14, wherein the coating comprises above 71% by weight of aluminum.

16.A method according to anyone of claims 1 to 15, wherein the coating
5 comprises above 76% by weight of aluminum.

17.A method according to anyone of claims 1 to 16, wherein the thickness of the coating is between 5 and 50 μ m

18.A method according to claim 17, wherein the thickness is between 10 and 35 μ m.
10

19.A method according to claim 18, wherein the thickness between 12 and 18 μ m.

20.A method according to claim 18, wherein the thickness between 26 and 31 μ m.
15

21.A method according to anyone of claims 1 to 20, 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.

22.A method according to anyone of claims 1 to 21, wherein step C) is performed during a dwell time between 1 to 12 minutes in an inert atmosphere or an atmosphere comprising air.
20

23.A method according to anyone of claims 1 to 22, wherein during step E) the hot-forming of the blank at a temperature between 600 and 830°C.
25

24.Part coated with a metallic coating obtainable from the method according to anyone of claim 1 to 23.
30

25. Part according to claim 24, wherein the microstructure of the metallic coating comprises an interdiffusion layer $\text{Fe}+\text{Fe}_3\text{Al}$, AlFe intermetallic phases containing dissolved Si and Zn, binary Zn-Al and Si-rich phases.

5 26. Part according to anyone of claim 24 or 25, wherein the microstructure of the metallic coating comprises Zn_2Mg phase or Mg_2Si phase or both.

27. Part according to anyone of claims 24 to 26, being a press hardened steel part having a variable thickness.

10

28. Part according to claim 27, wherein said variable thickness is produced by a continuous flexible rolling process.

29. Part according to anyone of claims 24 to 28, being a tailored rolled blank.

15

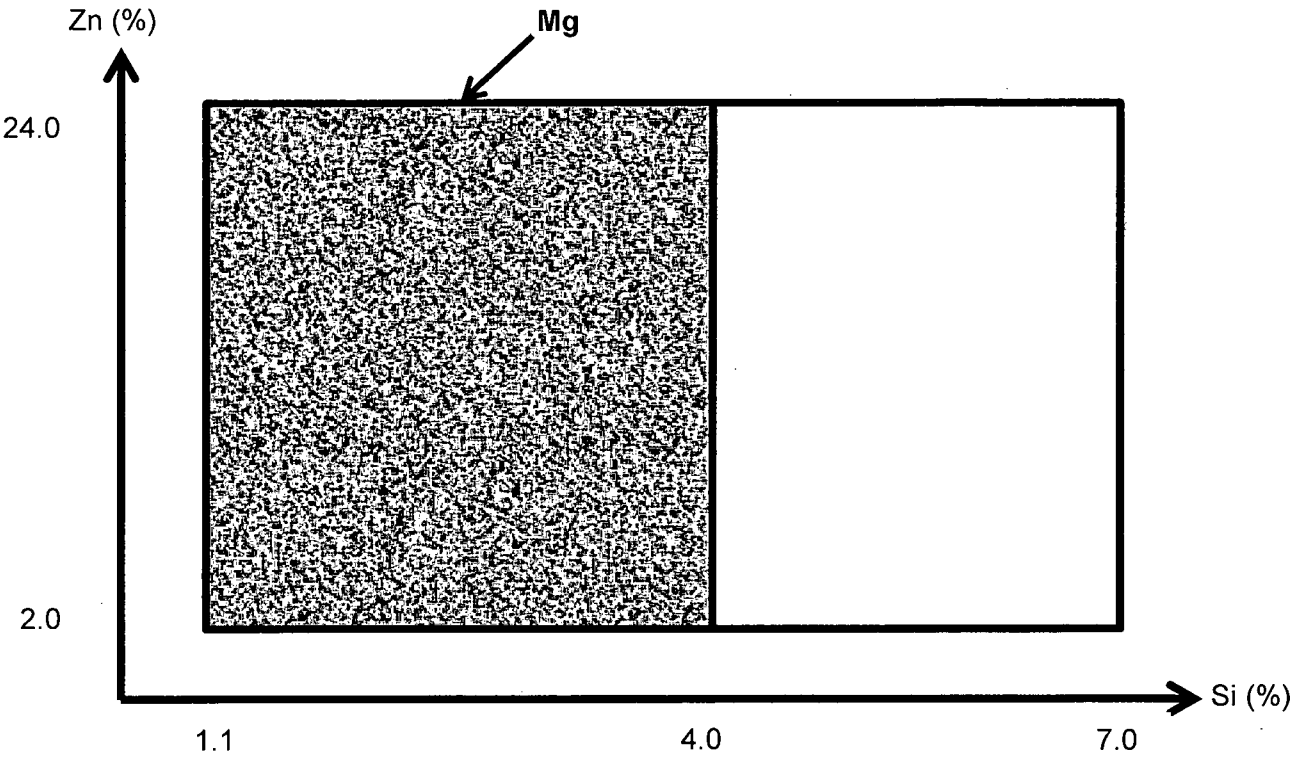
30. Part according to anyone of claims 24 to 29, being a front rail, a seat cross member, a side sill member, a dash panel cross member, a front floor reinforcement, a rear floor cross member, a rear rail, a B-pillar, a door ring or a shotgun.

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31. Use of a part according to anyone of claims 24 to 30, or obtainable according to the method of anyone of claims 1 to 23, for the manufacture of automotive vehicle.

25

Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/000983

A. CLASSIFICATION OF SUBJECT MATTER

INV. C21D1/673 B32B15/01 C23C2/12 C23C2/26 C23C2/28
C22C21/10

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)

C21D B32B C23C C22C

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.
Y	WO 2010/085983 A1 (ARCELORMITTAL INVESTIGACION Y [ES]; AUDI AG [DE]; VOLKSWAGEN AG [DE];) 5 August 2010 (2010-08-05) page 5, line 25 - page 6, line 22; claims 1-15; figures 1-6	1-31
Y	US 2010/221572 A1 (LAURENT JEAN-PIERRE [FR] ET AL) 2 September 2010 (2010-09-02) claims 1-13; examples 1,2	1-31
Y	JP H10 176238 A (SUMITOMO METAL IND) 30 June 1998 (1998-06-30) abstract; example 14; table 2	1-31
	----- -/-	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

7 September 2016

Date of mailing of the international search report

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP H11 279735 A (NISSHIN STEEL CO LTD) 12 October 1999 (1999-10-12) abstract; examples 32-36,39-43,46-50; table 1 -----	1-31
Y	JP 2010 070784 A (JFE STEEL CORP) 2 April 2010 (2010-04-02) abstract; examples 11-14; table 1 -----	1-31
A	US 2011/274945 A1 (SHIMODA NOBUYUKI [JP] ET AL) 10 November 2011 (2011-11-10) claims 1-7; example 74 -----	1-31
A	DE 20 2012 000616 U1 (BENTELER AUTOMOBILTECHNIK GMBH [DE]) 29 February 2012 (2012-02-29) paragraphs [0027], [0028], [0044]; figures 6a,b -----	1-31
A	WO 2014/059475 A1 (BLUESCOPE STEEL LTD [AU]) 24 April 2014 (2014-04-24) page 10, lines 7-12; claim 35 -----	1-31
A	JP 2005 290418 A (JFE STEEL KK; JFE GALVANIZING & COATING CO) 20 October 2005 (2005-10-20) abstract; table 4 -----	1-31
A	HAUGER A ET AL: "FLEXIBLES WALZEN VON TAILER ROLLED BLANKS//FLEXIBLE ROLLING OF TAILOR ROLLED BLANKS", STAHL UND EISEN, VERLAG STAHLEISEN, DUSSELDORF, DE, vol. 126, no. 5, 1 January 2006 (2006-01-01), pages 21-23, XP001245875, ISSN: 0340-4803 abstract; figures 1-3 -----	1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/000983

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010085983 A1	05-08-2010	BR PI1007895 A2 CA 2751062 A1 CN 102300707 A JP 5551184 B2 JP 2012516939 A KR 20110113763 A MA 33095 B1 RU 2011136436 A UA 97934 C2 US 2012085467 A1 WO 2010085983 A1 WO 2010086186 A1 ZA 201105023 B	16-02-2016 05-08-2010 28-12-2011 16-07-2014 26-07-2012 18-10-2011 01-03-2012 10-03-2013 26-03-2012 12-04-2012 05-08-2010 05-08-2010 28-03-2012
US 2010221572 A1	02-09-2010	AR 065764 A1 AT 556152 T BR PI0809006 A2 CA 2680623 A1 CN 101631880 A EP 2137327 A1 ES 2387229 T3 JP 5726419 B2 JP 2010521584 A KR 20090128414 A KR 20150048913 A MA 31235 B1 RU 2009137930 A UA 99127 C2 US 2010221572 A1 US 2014216612 A1 WO 2008110670 A1 WO 2008132303 A1 ZA 200905998 B	01-07-2009 15-05-2012 16-09-2014 06-11-2008 20-01-2010 30-12-2009 18-09-2012 03-06-2015 24-06-2010 15-12-2009 07-05-2015 01-03-2010 20-04-2011 25-07-2012 02-09-2010 07-08-2014 18-09-2008 06-11-2008 28-04-2010
JP H10176238 A	30-06-1998	JP 3267178 B2 JP H10176238 A	18-03-2002 30-06-1998
JP H11279735 A	12-10-1999	NONE	
JP 2010070784 A	02-04-2010	JP 5600868 B2 JP 2010070784 A	08-10-2014 02-04-2010
US 2011274945 A1	10-11-2011	AU 2010205171 A1 BR PI1007387 A2 CA 2749695 A1 CN 102292464 A CN 103805930 A EP 2388353 A1 ES 2524071 T3 JP 4644314 B2 KR 20110088573 A MY 155139 A NZ 594317 A TW 201035376 A US 2011274945 A1 WO 2010082678 A1 ZA 201105166 B	11-08-2011 16-02-2016 22-07-2010 21-12-2011 21-05-2014 23-11-2011 04-12-2014 02-03-2011 03-08-2011 15-09-2015 25-01-2013 01-10-2010 10-11-2011 22-07-2010 28-03-2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/000983

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 202012000616 U1	29-02-2012	NONE	

WO 2014059475 A1	24-04-2014	AU 2013332257 A1	09-04-2015
		US 2016168658 A1	16-06-2016
		WO 2014059475 A1	24-04-2014

JP 2005290418 A	20-10-2005	NONE	
