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(54) COATED STEEL STRIP OR SHEET HAVING ADVANTAGEOUS PROPERTIES

VORBESCHICHTETER STAHLSTREIFEN ODER -BLECH MIT VORTEILHAFTEN EIGENSCHAFTEN

FEUILLE OU BANDE D'ACIER REVÊTUE PRÉSENTANT DES PROPRIÉTÉS AVANTAGEUSES

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Description

[0001] The invention relates to a strip or sheet of cold formable cold rolled steel coated with a zinc alloy layer containing aluminium and magnesium. The invention also relates to a method for producing such a steel strip or sheet, to a method

[0002] Steel strip and sheet coated with a zinc or zinc alloy layer are well known and often used in the automotive industry. In recent years zinc alloy coatings containing aluminium and magnesium are often used in view of their improved corrosion and galling resistance in comparison to galvanized or galvanized coatings. These zinc alloy layers often contain 0.3 - 5 weight% Al and 0.3 - 5 weight% Mg, the remainder being zinc and unavoidable impurities, and optionally at most 0.2 weight % in total of one or more additional elements selected from the group consisting of Pb, Sb, Ti, Ca, Mn, Sn, La, Ce, Cr, Ni, Zr, Bi, Si and Fe.

[0003] This aluminium and magnesium containing zinc coated steel however has the drawback that the adhesive bonding thereof is less than the adhesive bonding of normal hot dip zinc coated steel. Also the spot weldability of hot dip coatings is often less than that of electrogalvanized steel. Moreover, the aluminium and magnesium containing zinc coatings have a somewhat higher coefficient of friction than normal zinc coatings.

[0004] It is an object of the invention to provide a steel strip or sheet coated with a zinc alloy layer containing aluminium and magnesium with a good adhesive bonding.

[0005] It is another object of the invention to provide a steel strip or sheet coated with a zinc alloy layer containing aluminium and magnesium with a good spot weldability.

[0006] It is a further object of the invention to provide a steel strip or sheet coated with a zinc alloy layer containing aluminium and magnesium having an improved coefficient of friction.

[0007] It is moreover an object of the invention to provide a method for producing such a steel strip or sheet coated with a zinc alloy layer containing aluminium and magnesium.

[0008] It is also an object of the invention to provide a method for producing a part from such a steel strip or sheet according to the invention.

[0009] Furthermore it is an object of the invention to provide a product produced from a part made from the steel strip or sheet according to the invention and at least one other part, having good joining properties between the parts.

[0010] According to a first aspect of the invention, one or more of these objects is reached with a strip or sheet of cold formable cold rolled steel coated with a zinc alloy layer, having the features of claim 1.

[0011] The inventors have surprisingly found that with the siloxane or polysiloxane layer as specified above, the joining behaviour of the zinc alloy coated steel is better than the joining behaviour without such a layer, especially the adhesive bonding behaviour, but also the spot weldability. The strength and failure mode of adhesive bonded joints of the zinc alloy coated steel provided with a siloxane or polysiloxane layer is better than that of the zinc alloy coated steel without such a siloxane or polysiloxane layer. Furthermore the friction of the zinc alloy coated steel is reduced with at least 10 % with the application of the siloxane or polysiloxane layer, which is advantageous for for instance deep drawing operations. The galling behaviour of the zinc alloy coated steel with the siloxane or polysiloxane layer is at least as good as that of the material without such a layer. Phosphate coverage of the zinc alloy coated steel that has been coated with a siloxane or polysiloxane layer is as good as phosphate coverage of zinc alloy coated steel without siloxane or polysiloxane layer.

[0012] Use of siloxane or polysiloxane to improve adhesive bonding of aluminium parts is known, but it is not known to use siloxane or polysiloxane for improving the adhesive bonding of zinc or zinc alloy coated steel parts. Siloxane or polysiloxane on zinc coated steels is well known to improve corrosion resistance and lacquer adhesion, but for automotive purposes this has not been an option because of spot welding and phosphate forming limitations. US 5,433,976 discloses a cold rolled steel strip coated with siloxane. Moreover, WO 2008/102009 A1 discloses a hot dip galvanized cold rolled steel strip coated with a zinc alloy coating layer comprising magnesium and aluminium. According to an earlier filed, not pre-published patent application with filing number PCT/EP2012/002416 a siloxane or polysiloxane layer is used on a hot formable zinc or zinc alloy coated steel strip, sheet or blank resulting in a reduction of the oxidation of the zinc layer and a reduction of zinc losses during the hot forming process. The siloxane or polysiloxane according to the older patent application is thus used for a different type of steel and for a different process. The present invention in contrast relates to cold formable cold rolled steel, not being a steel for hot forming at a temperature of 600° C or above.

[0013] According to a preferred embodiment, the cold rolled steel has a composition in weight% of:

$$0.001 < C < 0.15$$

$$0.01 < Mn < 2.0$$

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$$0.001 < Si < 0.5$$

5

$$Cr < 1.0$$

$$Al < 0.5$$

10

$$Mo < 0.2$$

15

$$Ti < 0.2$$

$$P < 0.12$$

20

$$N < 0.15$$

$$S < 0.05$$

25

$$B < 0.01$$

the remainder being Fe and unavoidable impurities. Steel types having a composition within these ranges are generally used for cold forming operations.

30 **[0014]** Preferably, the steel strip or sheet has a tensile strength of at most 600 MPa, such as an Interstitial Free steel (IF-steel), a bakehardenable steel or a dual phase steel (DP steel). This type of steel is frequently used in the automotive industry for parts that are bonded to other parts.

[0015] According to a preferred embodiment, the zinc alloy layer on the steel has a thickness of 20 - 140 g/m² on each side. These zinc alloy thicknesses are generally used in the automotive industry on steel.

35 **[0016]** The siloxane or polysiloxane layer has a layer thickness corresponding with 1 - 8 mg/m² Si, preferably a thickness of 1 - 5 mg/m² Si. It has been found that with these thicknesses the advantages are retained, while it is preferred to use thin layers from an economic perspective.

40 **[0017]** According to a preferred embodiment the siloxane or polysiloxane layer has been formed from a bis-tri(m)ethoxysilylalkane, preferably a bis-triethoxysilylethane (BTSE), and preferably in combination with another silane such as γ -aminopropyltriethoxysilane (γ APS), bis-aminosilane (BAS), bis-diaminosilane (BDAS), vinyltriacetoxysilane (VTAS), γ -ureidopropyltrimethoxysilane (γ UPS) and/or bis-trimethoxysilylpropylurea (BUPS). These silane chemicals can be used as a water based solution that is relatively easy to apply on a zinc alloy coated steel strip or sheet. In water the silane chemicals will hydrolyze to form silanols.

45 **[0018]** According to a preferred embodiment the zinc alloy layer contains 1.0 - 3.5 weight% Al and 1.0 - 3.5 weight% Mg, preferably 1.4 - 2.2 weight% Al and 1.4 - 2.2 weight% Mg. These amounts of Al and Mg in the zinc layer usually provide a corrosion protection that is suitable for automotive purposes. Higher amounts make the zinc alloy comparatively expensive and less easy to weld.

[0019] The siloxane or polysiloxane layer is covered by an oil. Zinc or zinc alloy coated strip is usually provide with a thin layer of oil before it is supplied to the automotive industry.

50 **[0020]** According to a second aspect of the invention a method for producing a strip or sheet according to the first aspect of the invention is provided in accordance with claim 9.

[0021] In this way it is relatively easy to apply the siloxane or polysiloxane layer to the zinc alloy coated steel strip or sheet in an environmentally friendly way.

55 **[0022]** Preferably the silane/silanol containing water based solution contains a fluoride, preferably hydrogen fluoride, fluorosilicic acid, fluorozirconic acid and/or fluorotitanic acid. Such fluorides are added to improve the adhesion of the siloxane or polysiloxane layer to the zinc alloy layer on the steel strip or sheet.

[0023] According to a third aspect of the invention a method for producing a part from a zinc alloy coated cold rolled steel strip or sheet with a siloxane or polysiloxane layer according to the first aspect of the invention is provided, wherein

- a blank is cut from the strip or sheet
- the blank is placed in a forming tool such as a press
- the blank is cold formed into a part.

5 **[0024]** Using this method, the friction of the blank against the forming tool is reduced due to the presence of the siloxane or polysiloxane layer. This is an advantage for all steels that are cold formed using a forming tool, also for the use of high strength steels which suffer from poor deep drawing properties.

[0025] According to a fourth aspect of the invention there is provided a product produced from a part made from the strip or sheet according to the first aspect of the invention and one or more other parts, wherein the part made from the strip or sheet is joined to at least one of the other parts using spot welding and/or a sealant or adhesive. The joining is improved due to the siloxane or polysiloxane layer.

10 **[0026]** Preferably one or more other parts are made from a strip or sheet according to the first aspect of the invention. These parts provide a product that has good joining properties, provided by the siloxane or polysiloxane layer that has been provided on the zinc alloy coated steel strip or sheet. An additional advantage is the improved cold forming property of the blanks cut from the steel strip or sheet due to the improved coefficient of friction.

15 **[0027]** According to a preferred embodiment the product is provided with a phosphate layer, and subsequently with a paint layer. For automotive purposes, where the product is part of a car, the car is usually alkaline cleaned and phosphated to provide a good adhesion for the application of a paint layer. A good adhesion will only be obtained when the zinc alloy coating is not hampered by remaining surface contaminants, because the zinc alloy layer must give a good electrochemical reaction with the phosphate solution to result in a fine crystalline, pore-free phosphate layer. It has been found that the applied siloxane or polysiloxane layer does not hinder the forming of a good phosphate layer.

20 **[0028]** The invention will be elucidated with reference to the following non-limiting examples.

Figure 1 shows the friction behaviour of zinc alloy coated steels with and without a siloxane or polysiloxane layer.

25 Figure 2 shows the paint delamination of painted zinc alloy steel with and without a siloxane or polysiloxane layer.

[0029] Experiments have been performed wherein a zinc alloy coated steel sheet has been coated with a siloxane or polysiloxane layer in two different thicknesses. Samples of the thus coated sheets have been tested and compared with zinc alloy coated sheet without a siloxane or polysiloxane layer.

30 **[0030]** For the experiments two types of steel sheet have been used. Steel grade 1 was a cold rolled boron steel having a gauge of 0.7 mm. Steel grade 2 was a cold rolled formable steel having a gauge of 0.7 mm.

[0031] The ZnAlMg coating on both steel types was applied on a continuous hot dip galvanising production line where the coating thickness was regulated by nitrogen wiping to about 70 mg/m² per side (approximately 10 μm per side). The composition of the coating was approximately 1.6 weight% Al and 1.6 weight% Mg, with a small amount of Fe by reaction of the aluminium with the steel strip during hot dip galvanising (about 0.005 - 0.02 weight% Fe), the remainder being zinc with inevitable impurities. The coated steel was temper rolled with about 0.8% elongation, with Electro Discharge Texturing (EDT) roughness.

35 **[0032]** A water based solution containing both bis-triethoxysilyl ethane (BTSE) and aminopropyltriethoxysilane (APS) has been applied on the ZnAlMg coated steel with a chem. coater to provide a (poly)siloxane layer having a thickness of 2 and 12 mg/m² Si respectively after drying and/or curing. In the remainder of the description, both siloxane layer are polysiloxane layer will be referred to as 'siloxane layer'.

[0033] The specimens for the lap shear test were prepared according to the StahlEisen SEP 1160 Teil 5 procedure:

- Size of steel coupons: 100 mm x 25 mm
- Cleaning: US degreased in heptane for 10 minutes
- Oil application (if applied): 2 g/m² MULTIDRAW PL61 of Zeller&Gmelin (standard automotive Prelube)
- Overlap: 10 mm
- Adhesive thickness: 0.2 to 0.3 mm, controlled using glass beads
- Excess adhesive removed before curing
- Cure: 15 minutes at 180°C object temperature
- Test length: 110 mm
- Test speed: 10 mm/min.

45 **[0034]** The adhesive used was Betamate 1496V of DOW Chemical. Some samples were not re-oiled after cleaning to evaluate the interaction with the oil separately. In general, the oil will be absorbed by the adhesive, making it slightly less strong.

50 **[0035]** The strength upon failure of the bond is given in Table 1. This strength depends heavily on the steel grade and its gauge, and can only be compared to a similar reference sample. The bond can break in the adhesive (cohesive

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failure), which is the preferred failure mode. It can also break between the adhesive and the metallic coating (adhesive failure), which is less favourable. Often, the broken bond shows a combination of both failure modes, and the amount of each is estimated visually (in % of the overlap area).

[0036] Results (see Table 1) show that both strength and failure mode of the ZnAlMg coated steel with a thin (2 mg/m² Si) siloxane layer are better than ZnAlMg coated steel without siloxane (ref1 versus #1 and ref3 versus #2 and ref4 versus #3). The best failure mode is achieved for oiled conditions.

[0037] At thickness of the siloxane layer with Si >10 mg/m² there is no improvement, on the contrary (see ref2 versus #1), although now some cohesive failure is obtained.

Table 1: adhesive properties

	Steel grade	Silane (mg/m ²)	Oil (prelube)	Strength bond (kN) of	Standard Deviation (kN)	% cohesive	% adhesive
ref1	1	0	no	8,1	0,6	0	100
ref2	1	12	no	7,2	1,1	10	90
#1		2	no	9,7	0,2	30	70
ref3	2	0	no	4,4	0,1	0	100
ref4	2	0	yes	4,2	0,1	0	100
#2	2	2	no	4,8	0,1	60	40
#3	2	2	yes	4,7	0,1	70	30
<u>#1 and #2 are not according to the invention.</u>							

[0038] The friction and galling of siloxane (2 mg/m² Si) coated ZnAlMg coated steel (steel grade 2) has also been evaluated in a Linear Friction Test.

[0039] The test uses one flat tool and one round tool to develop a high-pressure contact with the sample surfaces. The tool material used was DIN 1.3343. 1 g/m² of Multidraw PL61 of Zeller & Gmelin prelube oil was applied on the samples.

[0040] For each material/lubrication system, strips of 50 mm width and 300 mm length were pulled at a speed 20 mm/min between a set of tools pushed together with a normal force of 5 kN. The strips were drawn through the tools six times (passes) 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 performed in triplicate.

[0041] Figure 1 shows the number of passes on the horizontal axis and the friction coefficient on the vertical axis. The continuous line shows the results of the tests with a siloxane coating, the interrupted line shows the results without siloxane coating. The results in Figure 1 show that the thin siloxane layer reduces friction, which means a better drawing behaviour. Galling behaviour of ZnAlMg coated steel, which is normally good and much better than of hot dip zinc coated steel, electro galvanized steel and galvanized steel, is even better now.

[0042] Samples having a size of 100x200 mm were phosphated according to automotive standards, with a standard automotive alkaline cleaner, activation and phosphate of Chemetall. The amount of resulting phosphate was determined (by weighing) and the crystal size and homogeneity was checked (by secondary electron microscopy).

[0043] The results can be found in Table 2. All results are good and the presence of the thin layer of siloxane does not have a negative impact on the phosphate-ability, except for the phosphate-ability of steel grade 1 provided with a siloxane layer having a thickness of 12 mg/m².

Table 2: Phosphating

	Steel grade type	Silane (mg/m ²)	Phosphate type (Chemetall)	Amount phosphate (g/m ²)	of Phosphate crystal size and homogeneity
ref1	1	0	Spray phosphate GB R2830E3 with 100 -200 ppm F	3,3	OK
ref2	1	12	Spray phosphate GB R2830E3 with 100 -200 ppm F	2,4	Not OK

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(continued)

	Steel grade type	Silane (mg/m ²)	Phosphate type (Chemetall)	Amount phosphate (g/m ²)	of Phosphate crystal size and homogeneity	
5	#1	1	2	Spray phosphate GB R2830E3 with	3,5	OK
				100 - 200 ppm F		
10	ref3	2	0	Dip phosphated with GB R2600	2,6	OK
	#2	2	2	Dip phosphated with GB R2600	2,3	OK

[0044] For testing the spot welding behaviour, the welding range was determined according to StahlEisen SEP 1220 Teil 2 for a sample without siloxane and in duplicate for a sample with a thin layer of siloxane (2 mg/m² Si) on steel grade 2. A standard prelube (1 g/m² Quaker N6130) was applied on all samples.

[0045] The welding range is the range between the current (I_{min}) necessary to achieve the minimum welding nugget and the maximum current (I_{max}) before splashing occurs during welding. A larger welding range is a strong indication for a better electrode life, the number of welds before an electrode needs to be replaced to achieve a good weld.

[0046] The minimum and maximum welding currents and the welding range are given in Table 3. The welding range of the ZnAlMg coating with the silane (#2 and #3) is larger than the welding range on the same samples without the silane (ref3).

Table 3: Welding range

	Steel grade	Silane (mg/m ²)	I _{min} (kA)	I _{max} (kA)	Range (kA)
ref3	2	0	8,4	10,1	1,7
#2	2	2	6,8	10,5	3,7
#3	2	2	8,1	10,6	2,5

[0047] The phosphated samples (ref3 and #2 from Table 2) were additionally E-coated with 20-25 μm Cathoguard 500 from BASF for the following tests:

For a corrosion test scribes were made on (duplicate) panels with a Van Laar pencil, down to the steel. The panels were subjected to 10 weeks of an accelerated cyclic corrosion test according to VDA 621-415. The paint delamination was evaluated according to Volvo STD 1029.

[0048] For an E-coat adhesion test panels were scribed by a cross hatch pattern (6 vertical, 6 horizontal, Gitterschnitt) and an Andreas Cross (into the steel). These panels were put first 120 hours in a humidity test according to GMW 14829 and checked for delamination along the scribes. After that, they were put for 300 hours in a water immersion test (ISO 13523-9). Evaluation was done according to ISO 4628 - 3: 2003 (E).

[0049] The corrosion results can be found in Figure 2. On the vertical axis, the delamination of the E-coat after the corrosion test is given in millimetres. The samples with siloxane layer are denominated A, the samples without siloxane layer are denominated B. The visible delamination is indicated in the white stave, the visible plus non-visible delamination is indicated by the dark stave. The variance in delamination is indicated in the figure. As can be seen, the difference in corrosion resistance of the ZnAlMg coated steel with and without the siloxane layer is small.

[0050] The E-coat adhesion was good after the humidity test (no delamination). The results after the water immersion test are given in Table 4. The results of the siloxane treated sample and the reference were almost the same.

Table 4: E-coat adhesion after the water immersion test

	Cross hatch		Andreas cross	
	Size	Quantity	Size	Quantity
With siloxane	3	5	3	3
Without siloxane	3-4	5	3	4

Claims

1. Strip or sheet of cold formable cold rolled steel coated with a zinc alloy layer, wherein the zinc alloy layer contains 0.3 - 5 weight% Al and 0.3 - 5 weight% Mg, the remainder being zinc and unavoidable impurities and optionally at most 0.2 weight % in total of one or more additional elements selected from the group consisting of Pb, Sb, Ti, Ca, Mn, Sn, La, Ce, Cr, Ni, Zr, Bi, Si and Fe, wherein the zinc alloy layer is coated with a siloxane or polysiloxane layer, the siloxane or polysiloxane layer having a layer thickness corresponding with 1-8 mg/m² Si, and wherein the siloxane or polysiloxane layer is covered by an oil.

2. Strip or sheet according to claim 1, wherein the cold rolled steel has a composition in weight% of:

$$0.001 < C < 0.15$$

$$0.01 < Mn < 2.0$$

$$0.001 < Si < 0.5$$

$$Cr < 1.0$$

$$Al < 0.5$$

$$Mo < 0.2$$

$$Ti < 0.2$$

$$P < 0.12$$

$$N < 0.15$$

$$S < 0.05$$

$$B < 0.01$$

the remainder being Fe and unavoidable impurities.

3. Strip or sheet according to claim 1 or 2, wherein the steel has a tensile strength of at most 600 MPa, such as an Interstitial Free steel (IF-steel), a bakehardenable steel or a dual phase steel (DP steel).

4. Strip or sheet according to claim 1, 2 or 3, wherein the zinc alloy layer on the steel has a thickness of 20 - 140 g/m² on each side.

5. Strip or sheet according to anyone of the preceding claims, wherein the siloxane or polysiloxane layer has a layer thickness corresponding with 1 - 5 mg/m² Si.

6. Strip or sheet according to any one of the preceding claims, where the siloxane or polysiloxane layer has been formed from a bis-tri(m)ethoxysilylalkane, preferably a bis-triethoxysilylethane (BTSE), and preferably in combination with another silane such as γ -aminopropyltriethoxysilane (γ APS), bis-aminosilane (BAS), bis-diaminosilane (BDAS),

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vinyltriacetoxysilane (VTAS), γ -ureidopropyltrimethoxysilane (γ UPS) and/or bis-trimethoxysilylpropylurea (BUPS).

7. Strip or sheet according to any one of the preceding claims, wherein the zinc alloy layer contains 1.0 - 3.5 weight% Al and 1.0 - 3.5 weight% Mg, preferably 1.4 - 2.2 weight% Al and 1.4 - 2.2 weight% Mg.

8. Method for producing a strip or sheet according to any one of the preceding claims, wherein the siloxane or polysiloxane layer is formed by providing the zinc alloy layer with a silane/silanol containing water based solution applied by dipping and/or spraying with additional squeezing, or by rolling, followed by drying and/or curing.

9. Method according to claim 8, wherein the silane/silanol containing water based solution contains a fluoride, preferably hydrogen fluoride, fluorosilicic acid, fluorozirconic acid and/or fluorotitanic acid.

10. Method for producing a part from a strip or sheet according to any one of the claims 1-7, wherein

- a blank is cut from the strip or sheet
- the blank is placed in a forming tool such as a press
- the blank is cold formed into a part.

11. Product produced from a part made from the strip or sheet according to any one of the claims 1 - 7 and one or more other parts, wherein the part made from the strip or sheet is joined to at least one of the other parts using spot welding and/or a sealant or adhesive.

12. Product according to claim 11, wherein one or more other parts are made from a strip or sheet according to the invention as well.

13. Product according to claim 11 or 12, wherein the product is provided with a phosphate layer, and subsequently with a paint layer.

Patentansprüche

1. Band oder Blech aus kaltverformbarem kaltgewalztem Stahl, das oder der mit einer Zinklegierungsschicht beschichtet ist, wobei die Zinklegierungsschicht 0,3 - 5 Gew.-% Al und 0,3 - 5 Gew.-% Mg enthält, wobei der Rest Zink und unvermeidbare Unreinheiten und optional höchstens 0,2 Gew.-% insgesamt von einem oder mehreren zusätzlichen Elementen, die ausgewählt sind aus der Gruppe bestehend aus Pb, Sb, Ti, Ca, Mn, Sn, La, Ce, Cr, Ni, Zr, Bi, Si und Fe, sind, wobei die Zinklegierungsschicht mit einer Siloxan- oder Polysiloxanschicht beschichtet ist, wobei die Siloxan- oder Polysiloxanschicht eine Schichtdicke entsprechend 1-8 mg/m² Si aufweist, und wobei die Siloxan- oder Polysiloxanschicht durch ein Öl abgedeckt ist.

2. Band oder Blech nach Anspruch 1, wobei der kaltgewalzte Stahl eine Zusammensetzung in Gew.-% wie folgt aufweist:

$$0,001 < C < 0,15$$

$$0,01 < Mn < 2,0$$

$$0,001 < Si < 0,5$$

$$Cr < 1,0$$

$$Al < 0,5$$

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$$\text{Mo} < 0,2$$

5

$$\text{Ti} < 0,2$$

$$\text{P} < 0,12$$

10

$$\text{N} < 0,15$$

$$\text{S} < 0,05$$

15

$$\text{B} < 0,01$$

wobei der Rest Fe und unvermeidbare Unreinheiten sind.

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3. Band oder Blech nach Anspruch 1 oder 2, wobei der Stahl eine Zugfestigkeit von höchstens 600 MPa aufweist, wie ein Interstitiell Freier Stahl (IF-Stahl), ein Bake-Hardening-Stahl oder ein Dualphasenstahl (DP-Stahl).

25

4. Band oder Blech nach Anspruch 1, 2 oder 3, wobei die Zinklegierungsschicht auf dem Stahl eine Dicke von 20 - 140 g/m² auf jeder Seite aufweist.

5. Band oder Blech nach einem der vorhergehenden Ansprüche, wobei die Siloxan- oder Polysiloxanschicht eine Schichtdicke entsprechend 1-5 mg/m² Si aufweist.

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6. Band oder Blech nach einem der vorhergehenden Ansprüche, wo die Siloxan- oder Polysiloxanschicht aus einen Bis-tri(m)ethoxysilylalkan, vorzugsweise einem Bistriethoxysilylethan (BTSE), und vorzugsweise in Kombination mit einem weiteren Silan, wie γ -Aminopropyltriethoxysilan (γ APS), Bis-aminosilan (BAS), Bis-diaminosilan (BDAS), Vinyltriacetoxysilan (VTAS), γ -Ureidopropyl-trimethoxysilan (γ UPS) und/oder Bis-trimethoxysilylpropylurea (BUPS), gebildet worden ist.

35

7. Band oder Blech nach einem der vorhergehenden Ansprüche, wobei die Zinklegierungsschicht 1,0 - 3,5 Gew.-% Al und 1,0 - 3,5 Gew.-% Mg, vorzugsweise 1,4 - 2,2 Gew.-% Al und 1,4 - 2,2 Gew.-% Mg enthält.

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8. Verfahren zum Herstellen eines Bandes oder Blechs nach einem der vorhergehenden Ansprüche, wobei die Siloxan- oder Polysiloxanschicht gebildet wird durch Versehen der Zinklegierungsschicht mit einer Silane/Silanol enthaltenden wasserbasierten Lösung, die durch Eintauchen und/oder Sprühen mit zusätzlichem Pressen, oder durch Walzen, gefolgt von Trocknen und/oder Aushärten aufgetragen wird.

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9. Verfahren nach Anspruch 8, wobei die Silan/Silanol enthaltende wasserbasierte Lösung ein Fluorid, vorzugsweise Wasserstofffluorid, eine Fluorkieselsäure, Fluorzirkonsäure und/oder Fluortitansäure enthält.

10. Verfahren zum Fertigen eines Teils aus einem Band oder Blech nach einem der Ansprüche 1-7, wobei

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- eine Platine aus dem Band oder Blech geschnitten wird
- die Platine in einem Umformwerkzeug, wie eine Presse, platziert wird
- die Platine zu einem Teil kaltumgeformt wird.

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11. Produkt, das aus einem Teil, das aus dem Band oder Blech nach einem der Ansprüche 1 - 7 hergestellt ist, und einem oder mehreren anderen Teilen gefertigt ist, wobei das Teil, das aus dem Band oder Blech hergestellt ist, mit mindestens einem von den anderen Teilen unter Verwendung von Punktschweißen und/oder einem Dichtungsmittel oder Klebstoff verbunden ist.

12. Produkt nach Anspruch 11, wobei ein oder mehrere Teile aus einem Band oder Blech nach einem der Ansprüche

1-7 hergestellt ist.

13. Produkt nach Anspruch 11 oder 12, wobei das Produkt mit einer Phosphatschicht und anschließend mit einer Farbschicht versehen ist.

5

Revendications

1. Bande ou feuille d'acier laminé à froid, formable à froid, revêtue d'une couche d'alliage de zinc, la couche d'alliage de zinc contenant 0,3 - 5 % en poids d'Al et 0,3 - 5 % en poids de Mg, le reste étant le zinc et les impuretés inévitables, et optionnellement un maximum de 0,2 % en poids en tout d'un ou plusieurs éléments additionnels sélectionnés dans le groupe constitué de Pb, Sb, Ti, Ca, Mn, Sn, La, Ce, Cr, Ni, Zr, Bi, Si et Fe, la couche d'alliage de zinc étant revêtue d'une couche de siloxane ou de polysiloxane, la couche de siloxane ou de polysiloxane ayant une épaisseur de couche correspondant à 1-8 mg/m² Si, et dans laquelle la couche de siloxane ou de polysiloxane est couverte d'une huile.

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2. Bande ou feuille selon la revendication 1, dans laquelle l'acier laminé à froid a une composition en % de poids de :

20

$$0,001 < C < 0,15$$

$$0,01 < Mn < 2,0$$

25

$$0,001 < Si < 0,5$$

30

$$Cr < 1,0$$

$$Al < 0,5$$

35

$$Mo < 0,2$$

$$Ti < 0,2$$

40

$$P < 0,12$$

$$N < 0,15$$

45

$$S < 0,05$$

50

$$B < 0,01$$

le reste étant Fe et les impuretés inévitables.

3. Bande ou feuille selon la revendication 1 ou 2, dans laquelle l'acier a une résistance maximale à la traction de 600 MPa, tel qu'un acier sans interstitiels (IFS), un acier durcissable à la cuisson ou un acier biphasé (acier DP).

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4. Bande ou feuille selon la revendication 1, 2 ou 3, dans laquelle la couche d'alliage de zinc sur l'acier a une épaisseur de 20 - 140 g/m² de chaque côté.

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5. Bande ou feuille selon l'une quelconque des revendications précédentes, dans laquelle la couche de siloxane ou de polysiloxane a une épaisseur de couche correspondant à 1 - 5 mg/m² Si.
- 5 6. Bande ou feuille selon l'une quelconque des revendications précédentes, où la couche de siloxane ou de polysiloxane a été formée à partir d'un bis-tri(m)éthoxysilylalkane, de préférence un bis-triéthoxysilyléthane (BTSE), et de préférence en combinaison avec un autre silane tel que : γ -aminopropyltriéthoxysilane (γ APS), bis-aminosilane (BAS), bisdiaminosilane (BDAS), vinyltriacétoxysilane (VTAS), γ -ureidopropyl-triméthoxysilane (γ UPS) et/ou bis-triméthoxysilylpropylurée (BUPS).
- 10 7. Bande ou feuille selon l'une quelconque des revendications précédentes, dans laquelle la couche d'alliage de zinc contient 1,0 - 3,5 % en poids d'Al et 1,0 - 3,5 % en poids de Mg, de préférence 1,4 - 2,2 % en poids d'Al et 1,4 - 2,2 % en poids de Mg.
- 15 8. Procédé de production d'une bande ou feuille selon l'une quelconque des revendications précédentes, dans lequel la couche de siloxane ou de polysiloxane est formée en fournissant à la couche d'alliage de zinc une solution à base d'eau contenant du silane/silanol appliquée par immersion et/ou pulvérisation avec compression additionnelle, ou par laminage suivi de séchage et/ou durcissement.
- 20 9. Procédé selon la revendication 8, dans lequel la solution à base d'eau contenant du silane/silanol contient un fluorure, de préférence : fluorure d'hydrogène, acide fluorosilicique, acide fluorozirconique et/ou acide fluorotitanique.
- 25 10. Procédé pour produire une pièce à partir d'une bande ou feuille selon l'une quelconque des revendications 1-7, dans lequel
- un flan est découpé dans la bande ou la feuille
 - le flan est placé dans un outil de formage, tel qu'une presse
 - le flan est formé à froid pour devenir une pièce.
- 30 11. Produit réalisé à partir d'une pièce fabriquée à partir de la bande ou feuille selon l'une quelconque des revendications 1-7 et d'une ou plusieurs autres pièces, dans lequel la pièce réalisée à partir de la bande ou de la feuille est jointe à au moins une des autres pièces au moyen d'un soudage par points et/ou d'un mastic ou d'un adhésif.
- 35 12. Produit selon la revendication 11, dans lequel une ou plusieurs autres pièces sont fabriquées à partir d'une bande ou feuille selon l'une quelconque des revendications 1-7.
- 40 13. Produit selon la revendication 11 ou 12, le produit recevant une couche de phosphate, puis une couche de peinture.
- 45
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- 55

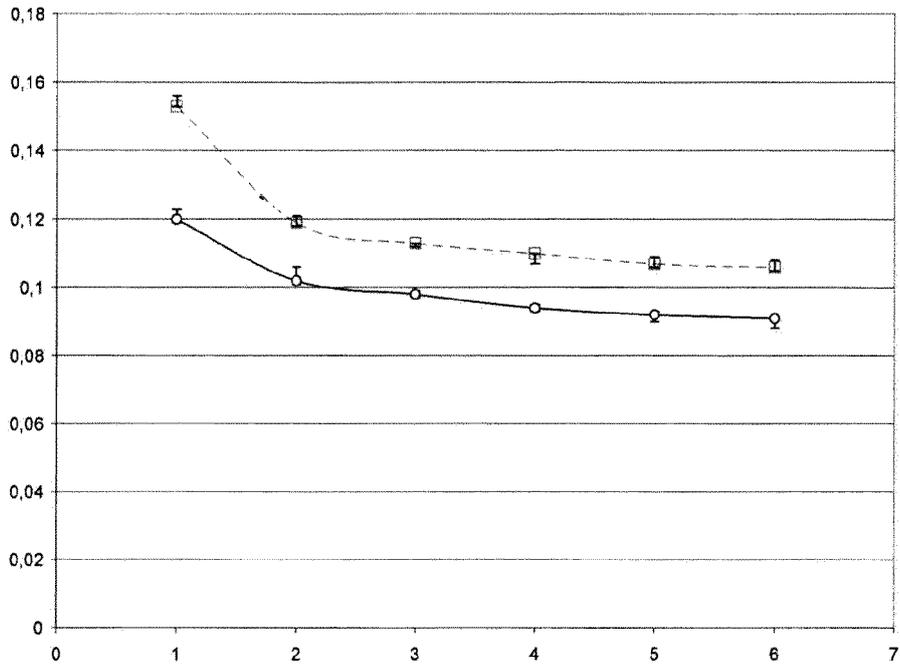


Figure 1

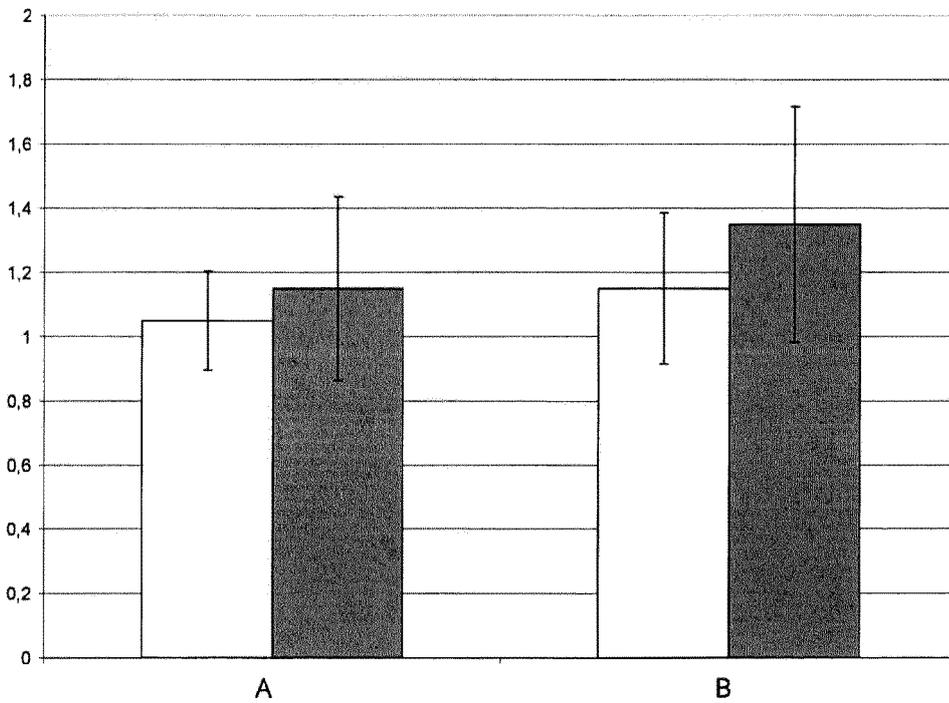


Figure 2

REFERENCES CITED IN THE DESCRIPTION

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