The invention relates to a steel substrate coated with a zinc alloy containing aluminium and magnesium. According to the invention the zinc alloy coating consists of (in weight%): 0.5 - 3.8 Al, 0.5 - 3.0 Mg, 0.01 - 0.5 in total of Bi and/or Pb and/or Sn and/or Sb, optional < 0.2 in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, unavoidable impurities, the remainder being zinc. The invention also relates to a method for producing such a steel substrate coating with the zinc alloy coating according to the invention.
STEEL SUBSTRATE WITH ZINC ALLOY COATING

The invention relates to a steel substrate with a zinc alloy coating. Over the past decade zinc alloy coatings containing aluminium and magnesium have been developed, most of which contain between 0.5 and 4.0 weight% aluminium and magnesium. Such zinc alloy coatings show a corrosion resistance that is much higher than the traditional galvanised or galvannealed coatings. Most steel companies are now marketing such so called ZnAlMg coatings because they provide an improved corrosion resistance to the customer. Such coatings are also of interest because they can be used with a coating thickness that is thinner than traditionally used while still providing an improved corrosion resistance, thereby saving in the use of zinc. Such ZnAlMg coatings are also frequently used for organic coated steel substrates, both for use inside buildings and for exterior use.

It has been found however that when a strip, sheet or blank coated with a ZnAlMg coating is deformed and tension forces are applied to the ZnAlMg coating, a crack pattern arises due increased hardness. When an organic top coat is present on the ZnAlMg coating, this organic top coat cannot withstand the high deformation forces if wide crack openings are formed in the ZnAlMg coating, and thus the topcoat also cracks. The result is that cracks run from the surface of the coating through the organic and metallic coating down to the base steel substrate. Though these cracks will not result in corrosion of the steel substrate due to the cathodic protection by the zinc alloy coating, such cracks negatively influence the surface quality of the organic coated steel substrate, and in the cracks some white rust can be formed, deteriorating the visual aspect of the organic coated steel.

It is an object of the invention to provide a steel substrate with a zinc alloy coating that during bending behaves such that the visual aspect of an organic coating on the zinc alloy coating is not impaired.

It is another object of the invention to provide a steel substrate with a zinc alloy coating of which the zinc alloy coating itself has a high quality visual appearance.

It is another object of the invention to provide a process for producing such a steel substrate.

According to the invention one or more of these aspects are reached with a steel substrate coated with a zinc alloy containing aluminium and magnesium, wherein the zinc alloy coating consists of (in weight%):

0.5 - 3.8 Al,
0.5 - 3.0 Mg,
0.01 - 0.5 in total of Bi and/or Pb and/or Sn and/or Sb,
optional < 0.2 in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr,
unavoidable impurities,
the remainder being zinc.

The inventors have found that due to the addition of 0.01 - 0.5 weight% Bi, Pb,
Sn or Sb, or a combination thereof, the crack pattern after bending of the ZnAlMg
coating is changed. Instead of numerous wide cracks, now a pattern with a very high
density of fine cracks is formed. These fine cracks result in a higher surface quality of
the zinc alloy coated steel substrate. When an organic coating is present on top of the
ZnAlMg coating, the organic coating can take up the local forces at the fine crack
openings and therefore remain intact. Thus, the surface quality of the steel substrate
with organic topcoat remains unimpaired.

It is known to optionally add Bi, Pb, Sn, Sb, Si, Ti, Ca, Mn, La, Ce, Cr, Ni or Zr in
small amounts, up to 0.2 weight% in total. These optional elements do not influence
the corrosion resistance, and therefore they are usually not added since they make
the coated steel substrate more costly. Additional elements are usually only added to
prevent dross forming in the bath with molten zinc alloy for hot dip galvanising, or to
form spangles in the coating layer. The additional elements are thus kept as low as
possible, usually below 0.01 weight%.

The inventors have now found that by adding more of Bi, Pb, Sn or Sb, or a
combination thereof, the crystal structure of the ZnAlMg coating is influenced. Since
the zinc alloy coating contains Al and Mg, the zinc alloy coating exhibits a solidification
path during its cooling down after galvanisation in a bath with molten zinc alloy. During
solidification, nucleation of the zinc takes place at the steel interface. Subsequently,
zinc dendrites start to grow from the nuclei into the slightly supercooled liquid layer of
zinc alloy. During the growth stage the dendrites grow initially sideways parallel to the
interface, and at a later stage thickening of the dendrites occur. At a lower
temperature a binary phase consisting of zinc and MgZn2 starts to solidify and this
binary phase solidifies in between the zinc dendrites. The last liquid, enriched in Mg
and Al, solidifies at 336° C. This ternary phase consists of three distinct compounds: a
zinc, an aluminium and a MgZn2 phase. Both the binary and the ternary phase have a
lamella structure, but the structure of the ternary phase is coarser.

The addition of Bi, Pb, Sn or Sb to the coating bath increases the growth
velocity of the zinc dendrites. The principle is not yet fully understood, but the
inventors are of the opinion that Bi (or Pb, Sn or Sb) segregates in the liquid zinc alloy
ahead of the growing dendrites, lowering the surface tension and thereby allowing the
growth velocity of the zinc dendrites to increase. The theory is that the growth velocity of the zinc dendrites now is so high, that only the dendrites with a favourable growth direction develop, and the development of dendrites with a non-favourable growth direction is suppressed. On the primary dendrites the secondary and ternary dendrites grow very rapidly, developing a very fine dendritic network.

When tension forces are applied to the zinc alloy coating, for instance by bending the steel substrate, the zinc alloy starts to crack. Once nucleated the cracks grow preferentially further through the binary and ternary phases. Due to the fine phase distribution of the binary and ternary phases in the Bi (or Pb, Sn or Sb) containing coating, more cracks per area originate.

According to a preferred embodiment the zinc alloy layer has a thickness of 2 - 30 µm, preferably a thickness of 3 - 25 µm, more preferably thickness of 4 - 20 µm, most preferably a thickness of 7 - 15 µm. These are the thicknesses (on each side) that are most commonly used for galvanised steel both without and with a top layer.

Preferably the zinc alloy coating contains 0.01 - 0.4 weight% in total of Bi and/or Pb and/or Sn and/or Sb, more preferably 0.02 - 0.3 weight% in total of Bi and/or Pb and/or Sn and/or Sb, most preferably 0.04 - 0.2 weight% in total of Bi and/or Pb and/or Sn and/or Sb. Though the upper limit of 0.5 weight% Bi (or Pb or Sn or Sb) can be used, a lower limit can be used in practice. For instance above 0.3 weight% Bi the solidification sequence is changed, and aluminium is the first phase to solidify. Above 0.3 weight% Bi formation of Mg3Bi2 particle occurs.

According to a preferred embodiment the zinc alloy coating contains 0.01 - 0.4 weight% Bi, preferably 0.02 - 0.3 weight% Bi, more preferably 0.04 - 0.2 weight% Bi. Bismuth has been found to be an element that can be very well used with out Pb, Sn or Sb. Preferably only small amounts are used, which gives the desired effect.

According to another preferred embodiment the zinc alloy coating contains 0.1 - 0.4 weight% Pb, preferably 0.1 - 0.3 weight% Pb, more preferably 0.1 - 0.2 weight% Pb. Lead has been found to also give the desired effect without Bi, Sn or Sb, but slightly more of this element is needed.

Preferably the zinc alloy coating optional contains < 0.1 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, preferably < 0.04 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, more preferably < 0.02 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, most preferably < 0.01 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr. These elements are optional, but are usually not added because they make the zinc alloy coating more costly. However, they can be added to prevent dross forming, but then in very small amounts.
According to a preferred embodiment the zinc alloy coating contains 1.0 - 2.5 weight% Al and 1.0 - 2.5 weight% Mg, preferably 1.0 - 2.0 weight% Al and 1.0 - 2.0 weight% Mg, most preferably 1.4 - 1.9 weight% Al and 1.4 - 1.9 weight% Mg. It has been found that preferably the amount of Al and Mg is neither too high nor too low, to get a balance between corrosion properties that are good enough and cost of the alloying elements that are not too high.

According to a first preferred embodiment the steel substrate is a steel strip having a length of 100 - 4000 m, a width of 500 - 3000 mm and a thickness of 0.5 - 4.0 mm. This is the type of strip that is usually produced from a slab through hot rolling and cold rolling, which once provided with a zinc alloy coating can be used in a number of industries, such as in the building industry for external and internal building uses, household appliances, and automotive after providing it with a top coating.

Preferably the steel substrate is a low carbon steel, consisting essentially of iron, preferably with a carbon content from about 0.001 weight% to about 0.15 weight% carbon, and other elements like Mn, P, S, Al, N, Ti, Mo, Nb, to obtain a desired alloying effect.

Low carbon steel strip is used for most applications, especially in the building industry.

More preferably the zinc alloy coated steel substrate is provided with a conversion coating either phosphate-based or chrome-based or silicon-based, to promote the adhesion of the single or multiple organic top layers. In this way the zinc alloy coated steel substrate can be directly used in the building industry.

According to a second preferred embodiment the steel substrate is a three-dimensional object such as a tube or work piece.

According to a second aspect of the invention is provided a process for producing a steel substrate provided with a zinc alloy coating according to the first aspect of the invention, wherein the steel substrate is hot dip galvanised using a bath of molten zinc alloy consisting of (in weight%):

- 0.5 - 3.8 Al,
- 0.5 - 3.0 Mg,
- 0.01 - 0.5 in total of Bi and/or Pb and/or Sn and/or Sb,
- optional < 0.2 in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr,
- unavoidable impurities,
- the remainder being zinc,

the bath of molten zinc alloy having a bath temperature between 340 and 550° C.

By hot dip coating a steel strip using the process as described herein, a zinc
alloy coated steel strip is provided having the advantageous effect that only fine cracks are formed during deformation, due to the addition of Bi and/or Pb and/or Sn and/or Sb.

According to a preferred embodiment the bath temperature is between 370 and 550° C, preferably between 380 and 500° C. The bath temperature varies with the composition. Start of solidification is 335° C for a very rich composition, but 410° C for a lean composition. The composition of the zinc alloy thus determines the temperature of the bath and the strip.

Preferably the temperature of the steel substrate before entering the bath of molten zinc alloy is at most 30° C above the bath temperature. The temperature of the steel strip should not be lower than the melting point of the zinc alloy to prevent local solidification of the zinc bath. High steel strip temperatures will lead to higher evaporation of the zinc, causing dust forming. High strip temperatures could also heat up the zinc bath, leading to the necessity to cool the zinc bath, which is expensive. Therefore the strip temperature should be just above the temperature of the bath.

According to a preferred embodiment the steel substrate is a steel strip entering the bath of molten zinc alloy having a speed higher than 15 metres per minute, preferably having a speed higher than 30 metres per minute. A high strip speed reduces or even prevents sagging of the zinc alloy during solidification thereof.

The invention will be elucidated with the following examples.

All experiments are performed in a Hot Dip Simulator using standard process settings as used for zinc alloy coatings containing 1.6 weight% Al and 1.6 weight% Mg, the remainder being zinc.

The substrate used was a low carbon steel with a sample size of 200 x 120 mm and a thickness of 0.7 mm, having a composition of Interstitial-Free steel (IF steel). The bath temperature was 440 °C.

As reference test a zinc alloy coating was used containing only 1.6 weight% Al and 1.6 weight% Mg. After coating with a thickness of 8-12 μm at the test side and cooling down to room temperature, the sample was bent according to the 0T bend test (EN 13523-7). A SEM image was obtained of the bent portion, showing cracks having a width of up to 30 μm.

The zinc alloy coating according to the invention was tested as follows.

In a first experiment an amount of 0.1 weight% Bi was added to the standard alloy containing 1.6 weight% Al and 1.6 weight% Mg, the remainder being zinc. The same processing as for the reference test was used to coat a sample of low carbon steel. After the same bending test a SEM image showed cracks having a width of at
most 15 μm.

In a second experiment an amount of 0.2 weight% Pb was added to the standard alloy containing 1.6 weight% Al and 1.6 weight% Mg, the remainder being zinc. The same processing as for the reference test was used to coat a sample of low carbon steel. After the same bending test a SEM image showed cracks having a width of at most 15 μm.
CLAIMS

1. Steel substrate coated with a zinc alloy containing aluminium and magnesium, wherein the zinc alloy coating consists of (in weight%):
   - 0.5 - 3.8 Al,
   - 0.5 - 3.0 Mg,
   - 0.01 - 0.5 in total of Bi and/or Pb and/or Sn and/or Sb,
   - optional < 0.2 in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr,
   - unavoidable impurities,
   - the remainder being zinc.

2. Steel substrate according to claim 1, wherein the zinc alloy layer has a thickness of 2 - 30 \( \mu \text{m} \), preferably a thickness of 3 - 25 \( \mu \text{m} \), more preferably thickness of 4 - 20 \( \mu \text{m} \), most preferably a thickness of 7 - 15 \( \mu \text{m} \).

3. Steel substrate according to claim 1 or 2, wherein the zinc alloy coating contains 0.01 - 0.4 weight% in total of Bi and/or Pb and/or Sn and/or Sb, preferably 0.02 - 0.3 weight% in total of Bi and/or Pb and/or Sn and/or Sb, more preferably 0.04 - 0.2 weight% in total of Bi and/or Pb and/or Sn and/or Sb.

4. Steel substrate according to any one of the preceding claims, wherein the zinc alloy coating contains 0.01 - 0.4 weight% Bi, preferably 0.02 - 0.3 weight% Bi, more preferably 0.04 - 0.2 weight% Bi.

5. Steel substrate according to one of claims 1 - 4, wherein the zinc alloy coating contains 0.1 - 0.4 weight% Pb, preferably 0.1 - 0.3 weight% Pb, more preferably 0.1 - 0.2 weight% Pb.

6. Steel substrate according to any one of the preceding claims, wherein the zinc alloy coating optional contains < 0.1 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, preferably < 0.04 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, more preferably < 0.02 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr, most preferably < 0.01 weight% in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr.

7. Steel substrate according to any one of the preceding claims, wherein the zinc
alloy coating contains 1.0 - 2.5 weight% Al and 1.0 - 2.5 weight% Mg, preferably 1.0 - 2.0 weight% Al and 1.0 - 2.0 weight% Mg, most preferably 1.4 - 1.9 weight% Al and 1.4 - 1.9 weight% Mg.

8. Steel substrate according to any one of the preceding claims, wherein the steel substrate is a steel strip having a length of 100 - 4000 m, a width of 500 - 3000 mm and a thickness of 0.5 - 4.0 mm.

9. Steel substrate according to claim 8, wherein the steel substrate is a low carbon steel, preferably with a carbon content from about 0.001 weight% to about 0.15 weight% carbon, and other elements like Mn, P, S, Al, N, Ti, Mo, Nb, to obtain a desired alloying effect.

10. Steel substrate according to any one of the preceding claims, wherein the zinc alloy coated steel substrate is provided with a conversion coating either phosphate-based or chrome-based or silicon-based, to promote the adhesion of the single or multiple organic top layers.

11. Steel substrate according to one of the claims 1 - 7, wherein the steel substrate is a three-dimensional object such as a tube or work piece.

12. Process for producing a steel substrate providing with a zinc alloy coating according to any one of the preceding claims 1 - 11, wherein the steel substrate is hot dip galvanised using a bath of molten zinc alloy consisting of (in weight%):

- 0.5 - 3.8 Al,
- 0.5 - 3.0 Mg,
- 0.01 - 0.5 in total of Bi and/or Pb and/or Sn and/or Sb,
- optional < 0.2 in total of Si, Ti, Ca, Mn, La, Ce, Cr, Ni and/or Zr,
- unavoidable impurities,
- the remainder being zinc,
- the bath of molten zinc alloy having a bath temperature between 340 and 550°C.

13. Process according to claim 12 wherein the bath temperature is between 370 and 550°C, preferably between 380 and 500°C.

14. Process according to claim 12 or 13, wherein the temperature of the steel
substrate before entering the bath of molten zinc alloy is at most 30° C above the bath temperature.

15. Process according to claim 12, 13 or 14, wherein the steel substrate is a steel strip entering the bath of molten zinc alloy having a speed higher than 15 metres per minute, preferably having a speed higher than 30 metres per minute.
**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C23C 2/06  C22C 18/04

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  C22C

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>EP 1 621 645 A1 (CORUS STAAL BV [NL]) 1 February 2006 (2006-02-01) paragraphs [0009], [0013], [0019] - [0020], [0025] - [0026]; claims 1,8,9,15,16</td>
<td>1-15</td>
</tr>
<tr>
<td>X</td>
<td>JP 558 189363 A (NISSHIN STEEL CO LTD) 5 November 1983 (1983-11-05) translated patent abstract; table 1</td>
<td>1-15</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
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**Date of the actual completion of the international search**

4 November 2014

**Date of mailing of the international search report**

12/11/2014

Name and mailing address of the ISA:

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NL - 2280 HV Rijswijk
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Authorized officer

Nikolaou, Ioannis
<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CN 101 027 421 A (CORUS STAAL BV [NL]) 29 August 2007 (2007-08-29) the whole document</td>
<td>1-15</td>
</tr>
<tr>
<td>A</td>
<td>EP 0 594 520 Al (LORRAINE LAMINAGE [FR]) 27 April 1994 (1994-04-27) the whole document</td>
<td>1-15</td>
</tr>
<tr>
<td>A</td>
<td>JP 2002 371342 A (SUMITOMO METAL IND) 26 December 2002 (2002-12-26) the whole document</td>
<td>1-15</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
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<tr>
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<td>-------------------------</td>
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<tr>
<td>EP 1621645</td>
<td>01-02-2006</td>
<td>NONE</td>
</tr>
<tr>
<td>JP S58189363</td>
<td>05-11-1983</td>
<td>NONE</td>
</tr>
<tr>
<td>US 2011017362</td>
<td>27-01-2011</td>
<td>CN 101849029 A</td>
</tr>
<tr>
<td>EP 2055799</td>
<td>06-05-2009</td>
<td></td>
</tr>
<tr>
<td>JP 2011503352</td>
<td>27-01-2011</td>
<td></td>
</tr>
<tr>
<td>US 2011017362</td>
<td>27-01-2011</td>
<td></td>
</tr>
<tr>
<td>WO 2009059950</td>
<td>14-05-2009</td>
<td></td>
</tr>
<tr>
<td>AU 758643</td>
<td>27-03-2003</td>
<td></td>
</tr>
<tr>
<td>AU 1803000</td>
<td>12-12-2000</td>
<td></td>
</tr>
<tr>
<td>CA 2374757</td>
<td>30-11-2000</td>
<td></td>
</tr>
<tr>
<td>CN 1342211</td>
<td>27-03-2002</td>
<td></td>
</tr>
<tr>
<td>DE 69936071</td>
<td>24-01-2008</td>
<td></td>
</tr>
<tr>
<td>EP 1199376</td>
<td>24-04-2002</td>
<td></td>
</tr>
<tr>
<td>ES 2283142</td>
<td>16-10-2007</td>
<td></td>
</tr>
<tr>
<td>HK 1044968</td>
<td>06-05-2005</td>
<td></td>
</tr>
<tr>
<td>PT 1199376</td>
<td>23-07-2007</td>
<td></td>
</tr>
<tr>
<td>TW 1236968</td>
<td>01-08-2005</td>
<td></td>
</tr>
<tr>
<td>US 6465114</td>
<td>15-10-2002</td>
<td></td>
</tr>
<tr>
<td>WO 0071773</td>
<td>30-11-2000</td>
<td></td>
</tr>
<tr>
<td>CN 101027421</td>
<td>29-08-2007</td>
<td>CN 101027421 A</td>
</tr>
<tr>
<td>UA 84778</td>
<td>25-11-2008</td>
<td></td>
</tr>
<tr>
<td>DE 69300964</td>
<td>18-01-1996</td>
<td></td>
</tr>
<tr>
<td>DE 69300964</td>
<td>18-07-1996</td>
<td></td>
</tr>
<tr>
<td>EP 0594520</td>
<td>27-04-1994</td>
<td></td>
</tr>
<tr>
<td>ES 2082617</td>
<td>16-03-1996</td>
<td></td>
</tr>
<tr>
<td>FR 2697031</td>
<td>22-04-1994</td>
<td></td>
</tr>
<tr>
<td>JP 2002371342</td>
<td>26-12-2002</td>
<td></td>
</tr>
</tbody>
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