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(54) Title: A METHOD FOR THE MANUFACTURE OF A COATED STEEL SHEET

(57) Abstract: The present invention relates a method for the manufacture of a coated steel sheet.

A method for the manufacture of a coated steel sheet

The present invention relates to a method for the manufacture of a coated steel sheet. The invention is particularly well suited for the manufacture of automotive vehicles.

Zinc based coatings are generally used because they allow 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 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 which is more active metal as compared to steel. Thus, if corrosion occurs, zinc is consumed preferentially to steel. Cathodic protection is essential in areas where 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 hot press hardening or welding, cracks are observed in steel which spread from the steel/coating interface. Indeed, occasionally, there is a reduction of metal mechanical properties due to the presence of cracks in coated steel sheet after the above operation. 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 presence of an external stress; heterogeneous diffusion of molten metal with substrate grain and grain boundaries. The designation for such phenomenon is known as liquid metal embrittlement (LME) and also called liquid metal assisted cracking (LMAC).

Thus, the object of the invention is to provide a steel sheet coated with a metallic coating 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 after the forming and/or the welding.

This object is achieved by providing a steel sheet according to claim 1. The steel sheet can also comprise any characteristics of claims 2 to 12.

Another object is achieved by providing a method according to claim 13. The method can also comprise any characteristics of claims 14 to 17.

Another object is achieved by providing a spot welded joint according to claim 18. The spot welded joint can also comprise characteristics of claims 19 to 22.

Finally, another object is achieved by providing the use of the steel sheet or the assembly according to claim 23.

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

The designation "steel" or "steel sheet" means a steel sheet, a coil, a plate having a composition allowing the part to achieve a tensile strength up to 2500 MPa and more preferably up to 2000MPa. For example, the tensile strength is above or equal to 500 MPa, preferably above or equal to 980 MPa, advantageously above or equal to 1180 MPa and even above or equal 1470 MPa.

The invention relates to a steel sheet coated with a coating comprising from 10 to 40% of nickel, the balance being zinc, such steel sheet having a microstructure comprising from 1 to 50% of residual austenite, from 1 to 60% of martensite and optionally at least one element chosen from: bainite, ferrite, cementite and pearlite, and the following chemical composition in weight:

$0.10 < C < 0.50\%$,

$1.0 < Mn < 5.0\%$,

$0.7 < Si < 3.0\%$,

$0.05 < Al < 1.0\%$

$0.75 < (Si+Al) < 3.0\ \%$

and on a purely optional basis, one or more elements such as

$Nb \leq 0.5\ \%$,

$B \leq 0.005\%$,

$Cr \leq 1.0\%$,

$Mo \leq 0.50\%$,

$Ni \leq 1.0\%$,

$Ti \leq 0.5\%$,

the remainder of the composition making up of iron and inevitable impurities resulting from the elaboration. In this case, the martensite can be tempered or untempered.

Without willing to be bound by any theory, it seems that the specific steel sheet coated with a coating comprising zinc and nickel according to the present prevents liquid zinc penetration into steel during any heating steps being for example a welding. Thus, by applying the method according to the present invention, it is possible to obtain zinc-nickel intermetallic compounds during above heating step. These intermetallic compounds have high melting temperature and remain solid during above heating step and thus prevents LME.

Preferably, the coating comprises from 10 to 30%, more preferably from 10 to 20% and advantageously from 11 to 15 wt.% by weight of nickel.

In a preferred embodiment, the coating consists of zinc and nickel.

Advantageously, the coating is directly in contact with the steel sheet.

Preferably, the coating has a thickness between 5 to 15µm and more preferably between 5 to 10µm.

In a preferred embodiment, the steel sheet has a microstructure comprising from 5 to 25 % of residual austenite.

Preferably, the steel sheet has a microstructure comprising from 1 to 60% and more preferably between 10 to 60% of tempered martensite.

Advantageously, the steel sheet has a microstructure comprising from 10 to 40% of bainite, such bainite comprising from 10 to 20% of lower bainite, from 0 to 15% of upper bainite and from 0 to 5% of carbide free bainite.

Preferably, the steel sheet has a microstructure comprising from 1 to 25% of ferrite.

Preferably, the steel sheet has a microstructure comprising from 1 to 15% untempered martensite.

According to the present invention, the method for the manufacture of the coated steel sheet comprises the following steps:

A. The provision of an annealed steel sheet having the chemical composition according to the present invention, such steel sheet being annealed at a temperature between 600 to 1200°C and

B. the coating of the steel sheet obtained in step A) with a coating comprising from 1 to 40% of nickel, the balance being zinc.

Preferably, in step A), the steel sheet is annealed in a continuous annealing. For example, the continuous annealing comprises a heating, a soaking and a cooling step. It can further comprise a pre-heating step.

Advantageously, the thermal treatment is performed in an atmosphere comprising from 1 to 30% of H_2 at a dew point between -10 and -60°C. For example, the atmosphere comprises from 1 to 10% of H_2 at a dew point between -10°C and -60°C.

Preferably, the coating in step B) is deposited by vacuum deposition or electro-plating method. Advantageously, the coating is deposited by electro-plating method.

After the manufacture of a steel sheet, in order to produce some parts of a vehicle, it is known to assembly by welding two metal sheets. Thus, a spot welded joint is formed during the welding of at least two metal sheets, said spot being the link between the at least two metal sheets.

To produce a spot welded joint according to the invention, the welding is performed with an effective intensity is between 3kA and 15kA and the force applied on the electrodes is between 150 and 850 daN with said electrode active face diameter being between 4 and 10mm.

Thus, a spot welded joint of at least two metal sheets, comprising the at least one coated steel sheet according to the present invention, is obtained, such said joint containing less than 2 cracks having a size above 100µm and wherein the longest crack has a length below 250µm.

Preferably, the second metal sheet is a steel sheet or an aluminum sheet. More preferably, the second metal sheet is a steel sheet according to the present invention.

In another embodiment, the spot welded joint comprises a third metal sheet being a steel sheet or an aluminum sheet. For example, the third metal sheet is a steel sheet according to the present invention.

The steel sheet or the spot welded joint according to the present invention can be used for the manufacture of parts for automotive vehicle.

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

Example

For all samples, steel sheets used have the following composition in weight percent: - Steel sheet 1: C=0.37%, Mn=1.9%, Si=1.9%, Cr=0.35% and Mo=0.1% and

- Steel sheet 2: C= 0.18%, Mn= 2.7% and Si= 1.8%.

Trials 1 to 4 were prepared by performing an annealing in a continuous annealing in an atmosphere comprising 5% of H_2 and 95% of N_2 at a dew point of -60°C. The steel 1 and steel 2 sheets were respectively heated at a temperature of 900°C and 820°C. Then, Trials 1 and 2 sheets were coated with a coating comprising 13% of nickel, the balance being zinc. The coating was deposited by electro-deposition method.

For comparison purpose in Trials 3 and 4, pure zinc was electro-deposited on the sheet sheets 1 and 2 heat treated under above mentioned condition.

LME resistance of the above Trials were evaluated using resistance spot welding method. To this end, for each Trial, two coated steel sheets were welded together by resistance spot welding. The type of the electrode was ISO Type B with a diameter of 16mm; the force of the electrode was of 5kN and the flow rate of water of was 1.5g/min. The details of welding cycle is shown in Table 1.

Table 1. Welding schedule

Weld time	Pulses	Pulse (cy)	Cool time (cy)	Hold time (cy)
Cycle	2	12	2	10

The number of cracks above 100µm was then evaluated using an optical microscope as well as SEM (Scanning Electron Microscopy) as follows as reported in Table 2:

Table 2. LME crack details after spot welding (2 layer stack-up condition)

Trials	coating	Sheet Steel	Thickness (µm)	Number of cracks (> 100µm) per spot weld	Maximum crack length (µm)
Trial 1*	Zn-Ni	1	7	0	0
Trial 2*	Zn-Ni	2	7	0	0
Trial 3	Zn	1	7	3	760
Trial 4	Zn	2	7	2	250

*: according to the present invention.

Trials 1 and 2 according to the present invention show an excellent resistance to LME compared to Trials 3 and 4.

The LME crack resistance behavior was also evaluated using 3 layer stack-up condition. For each Trial, three coated steel sheets were welded together by resistance spot welding. The number of cracks 100µm was then evaluated using an optical microscope as reported in Table 3.

Table 3. LME crack details after spot welding (3 layer stack-up condition)

Trials	Sheet Steel	Number of cracks per spot weld (>100 µm)	Maximum crack length (µm)
Trial 1*	1	1	150
Trial 2*	2	0	200
Trial 3	1	7	850
Trial 4	2	3	350

*: according to the present invention.

Trials 1 and 2 according to the present invention show an excellent resistance to LME compared to Trial 3 and 4.

Claims

1. A steel sheet coated with a coating comprising from 10 to 40% of nickel, the balance being zinc, such steel sheet having a microstructure comprising from 1 to 50% of residual austenite, from 1 to 60% of martensite and optionally at least one element chosen from: bainite, ferrite, cementite and pearlite, and the following chemical composition in weight:

$0.10 < C < 0.50\%$,

$1.0 < Mn < 5.0\%$,

$0.7 < Si < 3.0\%$,

$0.05 < Al < 1.0\%$

$0.75 < (Si+Al) < 3.0\ \%$

and on a purely optional basis, one or more elements such as

$Nb \leq 0.5\ \%$,

$B \leq 0.005\%$,

$Cr \leq 1.0\%$,

$Mo \leq 0.50\%$,

$Ni \leq 1.0\%$,

$Ti \leq 0.5\%$,

the remainder of the composition making up of iron and inevitable impurities resulting from the elaboration.

2. Steel sheet according to claim 1, wherein the coating comprising from 10 to 30% by weight of nickel.

3. Steel sheet according to claim 2, wherein the coating comprising from 10 to 20% by weight of nickel.

4. Steel sheet according to claim 3, wherein the coating consists of zinc and nickel.

5. Steel sheet according to anyone of claims 1 to 4, wherein the coating is directly in contact with the steel sheet.

6. Steel sheet according to anyone of claims 1 to 5, wherein the coating has a thickness between 5 to 15µm.

7. Steel sheet according to claim 6, wherein the coating has a thickness between 5 to 10µm.

8. Steel sheet according to anyone of claims 1 to 7, wherein the steel sheet microstructure comprises from 5 to 25 % of residual austenite.

9. Steel sheet according to anyone of claims 1 to 8, the steel sheet microstructure comprises from 1 to 60% of tempered martensite.

10. Steel sheet according to anyone of claims 1 to 9, wherein the steel sheet microstructure comprises from 10 to 40% of bainite.

11. Steel sheet according to anyone of claims 1 to 10, wherein the steel sheet microstructure comprises from 1 to 25% of ferrite.

12. Steel sheet according to anyone of claims 1 to 11, wherein the steel sheet microstructure comprises from 1 to 15% of untempered martensite.

13. Method for the manufacture of a coated steel sheet comprising the following step:

A. The provision of an annealed steel sheet having the chemical composition according to anyone of claims 1 to 7, such steel sheet being annealed at a temperature between 600 to 1200°C and

B. the coating of the steel sheet obtained in step A) with a coating comprising from 1 to 40% of nickel, the balance being zinc.

14. Method according to claim 13, wherein in step A), the steel sheet is annealed in a continuous annealing.

15. Method according to claim 13 or 14 , wherein in step A), the annealing is performed in an atmosphere comprising from 1 to 30% of H_2 at a dew point between -10 and -60°C.

16. Method according to anyone of claims 13 to 15, the coating in step B) is deposited by vacuum deposition or electro-plating method. .

17. Method according to claim 16, wherein the coating is deposited by electro-plating method.

18. Spot welded joint of at least two metal sheets comprising at least a steel sheet according to anyone of claims 1 to 12 or obtainable from the method according to anyone of claims 13 to 17, said joint containing less than 2 cracks having a size above 100µm and wherein the longest crack has a length below 250µm.

19. Spot welded joint according to claim 18, wherein the second metal sheet is a steel sheet or an aluminum sheet.

20. Spot welded joint according to claim 19, wherein the second metal sheet is a steel sheet according to anyone of claims 1 to 12 or obtainable from the method according to claims 13 to 17.

21. Spot welded joint according to anyone of claims 18 to 20 comprising a third metal sheet being a steel sheet or an aluminum sheet.

22. Spot welded joint according to of claim 21, wherein said joint contains no cracks having a size above 100µm.

23. Use of a coated steel sheet according to anyone of claims 1 to 12 or a spot welded point according to anyone of claims 18 to 22, for the manufacture of part for automotive vehicle.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C2/02 C23C2/06 C23C2/40 C25D3/12 C25D3/22
C23C14/16
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 C25D

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, INSPEC, IBM-TDB, 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	JP 2004 124187 A (SUMITOMO METAL IND) 22 April 2004 (2004-04-22) paragraphs [0006], [0043] - [0044]; examples F17, F49, F50	1-23
X	US 2014/370330 A1 (SATO HIRONORI [JP]) 18 December 2014 (2014-12-18) paragraphs [0005] - [0007], [0157] - [0168]	1-23
X	EP 3 088 557 A1 (POSCO [KR]) 2 November 2016 (2016-11-02) paragraphs [0025] - [0040]; table 1	1-23

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

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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