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• **YAMAMOTO, Shunsuke****Tokyo 100-0011 (JP)**(54) **METHOD FOR MANUFACTURING HIGH-STRENGTH, HOT-DIP GALVANIZED STEEL SHEET**

(57) There is provided a method for producing a high-strength hot-dip galvanized steel sheet, which can prevent deterioration of the appearance quality of the steel sheet, can provide a steel sheet having excellent LME cracking resistance and ductility, and can reduce deterioration of the delayed fracture resistance of the steel sheet caused by hydrogen embrittlement.

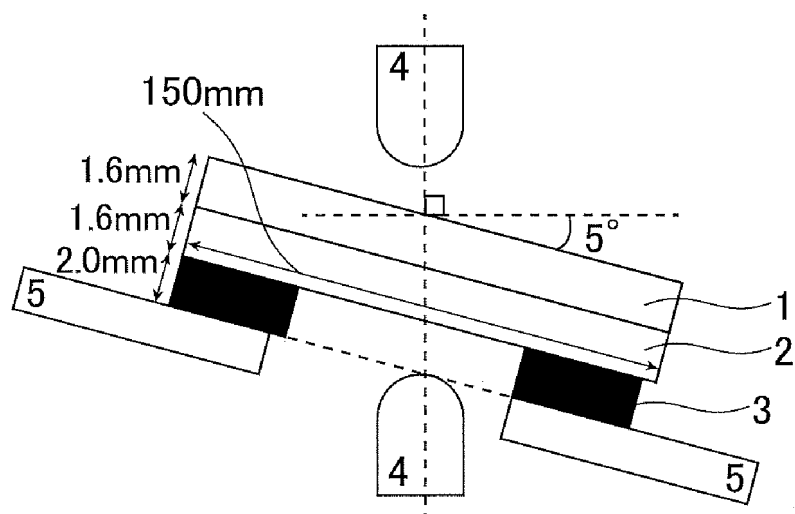
According to the method for producing a high-strength hot-dip galvanized steel sheet, in a direct-fired furnace, in an early stage, a steel sheet is heated to a temperature of not less than 400°C and not more than 670°C in an atmosphere containing 1000 ppm by volume or more of O₂ and 1000 ppm by volume or more of H₂O, and in a later stage, the steel sheet is heated to a

temperature of not less than 600°C and not more than 700°C in an atmosphere containing 500 ppm by volume or less of O₂, and

in an annealing furnace including a radiant tube-type heating and holding furnace, the steel sheet is held at a temperature of not less than 650°C and not more than 900°C for at least 90 seconds in an atmosphere which satisfies the following conditions: the H₂O concentration is not less than 5000 ppm by volume and not more than 40000 ppm volume, the H₂ concentration is not less than 2% by volume and not more than 20% by volume, and the logarithm of the ratio of the partial pressure of H₂O (P_{H₂O}) to the partial pressure of H₂ (P_{H₂}), i.e. log(P_{H₂O}/P_{H₂}), is not less than -1.1 and not more than 0.5.

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FIG. 1



Description

Technical Field

- 5 **[0001]** The present invention relates to a method for producing a hot-dip galvanized steel sheet having excellent resistance to resistance-welding cracking and excellent delayed fracture resistance.

Background Art

- 10 **[0002]** In recent years, from the standpoint of global environment protection, there has been a strong demand for improvement in fuel efficiency in automobiles. Further, from the standpoint of ensuring the safety of occupants in the event of a collision, there is a strong demand for improved safety of automobiles. In order to meet these demands, it is necessary to achieve both a reduction in the weight and an increase in the strength of automotive bodies. Therefore, for hot-dip galvanized steel sheets for use as a material for automotive parts, active developments are being made to increase the strength, thereby achieving thinner automotive parts. Most automotive parts are each produced by subjecting a steel sheet to a forming process. Such a steel sheet is therefore required to have excellent formability in addition to high strength.

- 15 **[0003]** There are various methods to increase the strength of a hot-dip galvanized steel sheet. Utilization of martensite by the addition of C and solid solution strengthening by the addition of Si are examples of methods which can increase the strength of a hot-dip galvanized steel sheet without significantly impairing its formability. On the other hand, in the production of an automotive part, press-formed parts are often assembled by resistance welding (spot welding). When a steel sheet contains a large amount of C and Si, zinc in a coated layer melts and diffuses into crystal grain boundaries during resistance welding while a residual stress is produced around a welding portion. This may cause liquid metal embrittlement (LME), resulting in the occurrence of intergranular cracking (LME cracking) in the steel sheet. Especially when welding is performed with welding electrodes at an angle to the steel sheet, an increased residual stress may be produced, leading to cracking. A residual stress produced in a steel sheet is considered to increase with increase in the strength of the steel sheet. Thus, there is a fear of the occurrence of LME cracking associated with the increase in the strength of a steel sheet.

- 20 **[0004]** It is also known that as the strength of a steel material increases, delayed fracture due to hydrogen embrittlement is more likely to occur. This tendency is strong particularly in a high-strength steel having a tensile strength of 1180 MPa or more. Delayed fracture refers to a phenomenon where when a high-strength steel material is held under a static load stress (load stress lower than tensile strength), brittle fracture suddenly occurs, without any substantial apparent plastic deformation, upon the elapse of a period of time. Such delayed fracture is caused by corrosion that occurs due to the use environment of a steel sheet, and often caused by hydrogen that has entered the steel sheet. In particular, hydrogen, which has entered a steel sheet during an annealing process in a continuous galvanizing line (CGL), deteriorates the mechanical properties of the steel sheet and causes brittle fracture of the sheet especially when it has a tensile strength exceeding 980 PMA.

- 25 **[0005]** Thus, there is a need for a high-strength steel sheet which has excellent resistance to resistance-welding cracking (hereinafter also referred to simply as "LME cracking resistance") and reduces the deterioration of mechanical properties caused by hydrogen in the steel.

- 30 **[0006]** Patent Literature 1 discloses a method for improving bare spot defects that may occur in a Si-added steel. The method involves heating a Si-added steel sheet to 700°C or higher in an atmosphere containing O₂ to oxidize the surface of the steel sheet, and reducing an oxide in a surface layer of the steel sheet in an H₂-containing atmosphere having a dew point of 5°C or more. However, the amount of oxidation of the steel sheet is large when it is heated to 700°C or more in an atmosphere containing O₂. This may cause adhesion of an oxide to the steel sheet in a furnace during reduction annealing, resulting in a deterioration of the appearance quality of the steel sheet.

- 35 **[0007]** Patent Literature 2 discloses a method which involves heating a Si-added steel sheet to a temperature of not less than 600°C and not more than 850°C in an atmosphere containing O₂ to oxidize the surface of the steel sheet, and reducing an oxide in a surface layer of the steel sheet in an atmosphere having a dew point of 5°C or more and containing H₂O and H₂ in an amount of not less than 500 ppm by volume and not more than 5000 ppm by volume. Patent Literature 3 discloses a method which involves oxidizing the surface of a Si-added steel sheet by increasing the air ratio in a direct-fired furnace (DFF), and reducing an oxide in a surface layer of the steel sheet in an atmosphere where log (P_{H₂O}/P_{H₂}) is not less than -3.4 and not more than -1.1. These methods can adjust the amount of oxidation of a steel sheet, and can therefore ensure good appearance quality of the steel sheet. However, a large amount of hydrogen, which has entered the steel during annealing, remains in the steel sheet, resulting in a failure to achieve sufficient LME cracking resistance and delayed fracture resistance.

Citation List

Patent Literature

[0008]

PTL 1: Japanese Patent No. 5652219

PTL 2: Japanese Patent No. 6052270

PTL 3: Japanese Patent No. 6172297

Summary of Invention

Technical Problem

[0009] It is an object of the present invention to provide a method for producing a high-strength hot-dip galvanized steel sheet, which can prevent deterioration of the appearance quality of the steel sheet due to adhesion of an oxide to the steel sheet in a furnace during reduction annealing, which may occur when the amount of oxidation of the steel sheet is excessive. Further, the method can provide a high-strength hot-dip galvanized steel sheet having excellent LME cracking resistance and ductility, and can reduce deterioration of the delayed fracture resistance of the steel sheet caused by hydrogen embrittlement.

Solution to Problem

[0010] The present inventors found that the appearance quality of a steel sheet can be ensured by optimizing the O_2 concentration and the temperature during oxidation of the steel sheet according to the Si concentration and the Mn concentration of the steel sheet and thus avoiding excessive oxidation. The present inventors also found that by optimizing the H_2O concentration, the H_2 concentration, and $\log (P_{H_2O}/P_{H_2})$ during reduction annealing, it becomes possible to provide a steel sheet having excellent resistance to resistance-welding cracking while reducing the deterioration of delayed fracture resistance caused by hydrogen embrittlement, leading to completion of the present invention.

[0011] The present invention was accomplished based on such findings. Thus, the present invention is summarized as follows:

[1] A method for producing a high-strength hot-dip galvanized steel sheet, comprising: a hot rolling step of hot-rolling a slab containing, in % by mass, C: not less than 0.05% and not more than 0.30%, Si: not less than 0.45% and not more than 2.0%, and Mn: not less than 1.0% and not more than 4.0%, and coiling the hot-rolled sheet at a temperature equal to or lower than a temperature T_C ($^{\circ}C$) calculated from the following equation (1), followed by pickling; a cold rolling step of cold-rolling the hot-rolled sheet obtained in the hot rolling step; a step of continuously annealing the cold-rolled steel sheet, obtained in the cold rolling step, in a direct-fired furnace and in an annealing furnace comprising a radiant tube-type heating and holding furnace; and a step of hot-dip galvanizing the annealed steel sheet,

wherein in the direct-fired furnace, in an early stage, the steel sheet is heated to a temperature of not less than $400^{\circ}C$ and not more than $670^{\circ}C$ in an atmosphere containing 1000 ppm by volume or more of O_2 and 1000 ppm by volume or more of H_2O , and in a later stage, the steel sheet is heated to a temperature of not less than $600^{\circ}C$ and not more than $700^{\circ}C$ in an atmosphere containing 500 ppm by volume or less of O_2 , and

wherein in the annealing furnace comprising the radiant tube-type heating and holding furnace, the steel sheet is held at a temperature of not less than $650^{\circ}C$ and not more than $900^{\circ}C$ for at least 90 seconds in an atmosphere which satisfies the following conditions: the H_2O concentration is not less than 5000 ppm by volume and not more than 40000 ppm volume, the H_2 concentration is not less than 2% by volume and not more than 20% by volume, and the logarithm of the ratio of the partial pressure of H_2O (P_{H_2O}) to the partial pressure of H_2 (P_{H_2}), i.e. $\log (P_{H_2O}/P_{H_2})$, is not less than -1.1 and not more than 0.5:

$$T_C = -30 ([Si] + [Mn]) + 775 \quad (1)$$

where $[Si]$ is the Si content (mass %) of the steel sheet, and $[Mn]$ is the Mn content (mass %) of the steel sheet.

[2] The method for producing a high-strength hot-dip galvanized steel sheet as set forth in [1], wherein the steel sheet after the hot-dip galvanization is subjected to an alloying treatment.

[3] The method for producing a high-strength hot-dip galvanized steel sheet as set forth in [1] or [2], further comprising a cooling and heating step of cooling the steel sheet, which has undergone the heating and holding in the radiant tube-

type heating and holding furnace, from the final holding temperature during the annealing to a temperature of 150 to 350°C at an average cooling rate of at least 10°C/sec, and then heating the steel sheet to a temperature of 350 to 600°C and holding it at that temperature for 10 to 600 seconds.

[4] The method for producing a high-strength hot-dip galvanized steel sheet as set forth in any one of [1] to [3], wherein the logarithm of the ratio of the partial pressure of H₂O (P_{H2O}) to the partial pressure of H₂ (P_{H2}), i.e. $\log(P_{H2O}/P_{H2})$, is not less than -0.99 and not more than 0.5.

[5] The method for producing a high-strength hot-dip galvanized steel sheet as set forth in any one of [1] to [4], wherein the logarithm of the ratio of the partial pressure of H₂O (P_{H2O}) to the partial pressure of H₂ (P_{H2}), i.e. $\log(P_{H2O}/P_{H2})$, is not less than -0.9 and not more than 0.5.

[6] The method for producing a high-strength hot-dip galvanized steel sheet as set forth in any one of [1] to [5], wherein the logarithm of the ratio of the partial pressure of H₂O (P_{H2O}) to the partial pressure of H₂ (P_{H2}), i.e. $\log(P_{H2O}/P_{H2})$, is not less than -0.7 and not more than 0.5.

Advantageous Effects of Invention

[0012] According to the present invention, it is possible to provide a high-strength steel sheet which has excellent resistance to resistance-welding cracking in a welding portion and good appearance quality, and contains a sufficiently reduced amount of hydrogen which causes deterioration of the delayed fracture resistance of the steel sheet.

Brief Description of Drawings

[0013]

[FIG. 1] FIG. 1 is a diagram illustrating the structure of a test material for evaluating LME cracking resistance.

[FIG. 2] The upper diagram of FIG. 2 is a plan view of a sheet assembly with a welding portion, and the lower diagram is a diagram showing a thickness-direction cross section of the sheet assembly with a welding portion after it is cut at the cutting position shown in the upper diagram.

Description of Embodiments

[0014] Embodiments of the present invention will now be described.

[0015] In the following description, the unit of the content of each element in the chemical composition of a Si-containing slab and the unit of the content of each element in the chemical composition of a coated layer are "% by mass", and will be expressed simply as "%" unless otherwise specified. As used herein, a numerical range expressed as "X to Y" includes X and Y as the lower limit and the upper limit. A steel sheet having "high strength" herein refers to a steel sheet whose tensile strength TS, measured in accordance with JIS Z 2241(2011), is 590 MPa or more.

[0016] The chemical composition of a Si-containing slab will be described first.

<Components of Slab>

Si: not less than 0.45% and not more than 2.0%

[0017] Si has a significant effect of increasing the strength of steel through solid solution (high solid solution strengthening ability) without materially impairing the formability, and therefore is an effective element for achieving an increase in the strength of a steel sheet. On the other hand, Si has an adverse effect on the resistance to resistance-welding cracking in a welding portion. When Si is added to achieve an increase in the strength of a steel sheet, it is necessary to add Si in an amount of 0.45% or more. If the Si content is less than 0.45%, Si poses no significant problem in the resistance to resistance-welding cracking in a welding portion; therefore, there is no significant need for the application of the present invention. On the other hand, if the Si content exceeds 3.0%, the hot rollability and the cold rollability will be greatly reduced, which will adversely affect the productivity and cause a reduction in the ductility of a steel sheet itself. Therefore, Si is added in an amount in the range of not less than 0.45% and not more than 3.0%.

[0018] The amount of Si is preferably 0.7% or more, more preferably 0.9% or more. Further, the amount of Si is preferably 2.5% or less, more preferably 2.0% or less.

C: 0.30% or less

[0019] C improves the formability of a steel sheet through the formation of martensite or the like as a steel microstructure. When C is contained, the amount of C is preferably made 0.8% or less, more preferably 0.30% or less in order to achieve

good weldability and LME cracking resistance. The lower limit of the amount of C is not particularly limited; however, in order to achieve good formability, the amount of C is preferably made 0.03% or more, more preferably 0.05% or more.

Mn: 1.0% or more and 4.0% or less

[0020] Mn is an element which increases the strength of steel by solid solution strengthening, improves hardenability, and promotes the formation of retained austenite, bainite, and martensite. Such an effect is produced by inclusion of Mn in an amount of 1.0% or more. On the other hand, when the amount of Mn is 4.0% or less, the above effects can be achieved without causing an increase in cost. Therefore, the amount of Mn is preferably made not less than 1.0%, and is preferably made not more than 4.0%. The amount of Mn is more preferably made 1.8% or more. Further, the amount of Mn is more preferably made 3.3% or less.

[0021] There is no limitation on the contents of the following components; their preferred contents are as follows.

P: 0.1% or less (not including 0%)

[0022] The use of a low content of P can prevent a reduction in weldability and, in addition, can prevent segregation of P at grain boundaries, thereby preventing deterioration of ductility, bendability, and toughness. The addition of a large amount of P promotes ferrite transformation, leading to an increase in the size of crystal grains. Therefore, the amount of P is preferably made 0.1% or less. While the lower limit of the amount of P is not particularly limited, the amount is more than 0% due to constraints of production technology, and is generally 0.001% or more.

S: 0.03% or less (not including 0%)

[0023] The amount of S is preferably made 0.03% or less, more preferably 0.02% or less. The use of a low amount of S can prevent a reduction in weldability, and can prevent a reduction in ductility during hot rolling, thereby preventing hot cracking and significantly improving the surface quality of a steel sheet. Furthermore, the use of a low amount of S can prevent a reduction in the ductility, bendability, and stretch flangeability of the steel sheet due to the formation of a coarse sulfide by S as an impurity element. These problems are noticeable when the amount of S is more than 0.03%. Thus, the S content is preferably made as low as possible. While the lower limit of the amount of S is not particularly limited, the amount is more than 0% due to constraints of production technology, and is generally 0.001% or more.

Al: 0.1% or less (not including 0%)

[0024] Al is thermodynamically most easily oxidizable; Al is oxidized before Si and Mn are oxidized. Thus, Al has the effect of suppressing the oxidation of Si and Mn in the outermost layer of a steel sheet, and promoting the oxidation of Si and Mn inside the steel sheet. This effect is achieved when the amount of Al is 0.01% or more. On the other hand, the use of Al in an amount of more than 0.1% leads to an increase in cost. Therefore, when Al is added, the amount of Al is preferably made 0.1% or less. While the lower limit of the amount of Al is not particularly limited, the amount is more than 0%, and is generally 0.001% or more.

N: 0.010% or less (not including 0%)

[0025] The content of N is preferably made 0.010% or less. By making the N content 0.010% or less, N can be prevented from forming a coarse nitride with Ti, Nb, or V at a high temperature. This can prevent a deterioration in the effect of increasing the strength of a steel sheet achieved by the addition of Ti, Nb, or V. Further, by making the N content 0.010% or less, it is possible to prevent a reduction in the toughness. Moreover, by making the N content 0.010% or less, it is possible to prevent the occurrence of slab cracking and surface flaws during hot rolling. The N content is preferably 0.005% or less, more preferably 0.003% or less, and still more preferably 0.002% or less. While the lower limit of the amount of N is not particularly limited, the amount is more than 0% due to constraints of production technology, and is generally 0.0005% or more.

[0026] The chemical composition may further optionally comprise one, two or more selected from the group consisting of B: 0.005% or less, Ti: 0.2% or less, Cr: 1.0% or less, Cu: 1.0% or less, Ni: 1.0% or less, Mo: 1.0% or less, Nb: 0.20% or less, V: 0.5% or less, Sb: 0.200% or less, Ta: 0.1% or less, W: 0.5% or less, Zr: 0.1% or less, Sn: 0.20% or less, Ca: 0.005% or less, Mg: 0.005% or less, and REM (Rare Earth Metal): 0.005% or less.

B: 0.005% or less

[0027] B is an effective element for improving the hardenability of steel. In order to improve the hardenability, the amount

of B is preferably made 0.0003% or more, more preferably 0.0005% or more. However, if B is added excessively, the formability will be poor. Therefore, the amount of B is preferably made 0.005% or less.

Ti: 0.2% or less

[0028] Ti is effective for precipitation strengthening of steel. While the lower limit of the amount of Ti is not particularly limited, the amount is preferably made 0.005% or more in order to achieve the effect of adjusting the strength. However, if Ti is added excessively, a hard phase will be too large and the formability will be poor. Therefore, when Ti is added, the amount of Ti is preferably made 0.2% or less, more preferably 0.05% or less.

Cr: 1.0% or less

[0029] The amount of Cr is preferably made 0.005% or more. By making the amount of Cr 0.005% or more, it is possible to improve the hardenability, thereby improving the balance between strength and ductility. When Cr is added, the amount of Cr is preferably made 1.0% or less from the viewpoint of avoiding an increase in cost.

Cu: 1.0% or less

[0030] The amount of Cu is preferably made 0.005% or more. By making the amount of Cu 0.005% or more, the formation of a retained γ phase can be promoted. When Cu is added, the amount of Cu is preferably made 1.0% or less from the viewpoint of avoiding an increase in cost.

Ni: 1.0% or less

[0031] The amount of Ni is preferably made 0.005% or more. By making the amount of Ni 0.005% or more, the formation of a retained γ phase can be promoted. When Ni is added, the amount of Ni is preferably made 1.0% or less from the viewpoint of avoiding an increase in cost.

Mo: 1.0% or less

[0032] The amount of Mo is preferably made 0.005% or more. By making the amount of Mo 0.005% or more, the effect of adjusting the strength can be achieved. The amount of Mo is more preferably made 0.05% or more. When Mo is added, the amount of Mo is preferably made 1.0% or less from the viewpoint of avoiding an increase in cost.

Nb: 0.20% or less

[0033] The inclusion of Nb in an amount of 0.005% or more can achieve the effect of increasing the strength. When Nb is contained, the amount of Nb is preferably made 0.20% or less from the viewpoint of avoiding an increase in cost.

V: 0.5% or less

[0034] The inclusion of V in an amount of 0.005% or more can achieve the effect of increasing the strength. When V is contained, the amount of V is preferably made 0.5% or less from the viewpoint of avoiding an increase in cost.

Sb: 0.200% or less

[0035] Sb can be contained from the viewpoint of inhibiting nitridation, oxidation, or decarburization that occurs in an area ranging from the surface of a steel sheet to a depth of tens of micrometers due to oxidation. Sb inhibits nitridation and oxidation at the surface of the steel sheet, thereby preventing a decrease in the amount of martensite formed in the surface of the steel sheet, and improving the fatigue properties and surface quality of the steel sheet. In order to achieve such an effect, the amount of Sb is preferably made 0.001% or more. On the other hand, in order to achieve good toughness, the amount of Sb is preferably made 0.200% or less.

Ta: 0.1% or less

[0036] The inclusion of Ta in an amount of 0.001% or more can achieve the effect of increasing the strength. When Ta is contained, the amount of Ta is preferably made 0.1% or less from the viewpoint of avoiding an increase in cost.

W: 0.5% or less

[0037] The inclusion of W in an amount of 0.005% or more can achieve the effect of increasing the strength. When W is contained, the amount of W is preferably made 0.5% or less from the viewpoint of avoiding an increase in cost.

Zr: 0.1% or less

[0038] The inclusion of Zr in an amount of 0.0005% or more can achieve the effect of increasing the strength. When Zr is contained, the amount of Zr is preferably made 0.1% or less from the viewpoint of avoiding an increase in cost.

Sn: 0.20% or less

[0039] Sn is an effective element for inhibiting denitrification, deboration, or the like, thereby preventing a reduction in the strength of steel. In order to achieve such an effect, the amount of Sn is preferably made 0.002% or more. On the other hand, in order to achieve good impact resistance, the amount of Sn is preferably made 0.20% or less.

Ca: 0.005% or less

[0040] The inclusion of Ca in an amount of 0.0005% or more can control the shape of a sulfide, thereby improving the ductility and the toughness. The amount of Ca is preferably made 0.005% or less from the viewpoint of achieving good ductility.

Mg: 0.005% or less

[0041] The inclusion of Mg in an amount of 0.0005% or more can control the shape of a sulfide, thereby improving the ductility and the toughness. When Mg is contained, the amount of Mg is preferably made 0.005% or less from the viewpoint of avoiding an increase in cost.

REM: 0.005% or less

[0042] The inclusion of REM in an amount of 0.0005% or more can control the shape of a sulfide, thereby improving the ductility and the toughness. When REM is contained, the amount of REM is preferably made 0.005% or less from the viewpoint of achieving good ductility.

[0043] In the Si-containing slab of this embodiment, the balance of the chemical composition consists of Fe and incidental impurities. As used herein, a Si-containing steel sheet may be either a cold-rolled steel sheet or a hot-rolled steel sheet.

<Hot Rolling>

[0044] The hot rolling step is a step of hot-rolling the above-described slab, and coiling the hot-rolled steel sheet at a temperature equal to or lower than a temperature T_C (°C) calculated from the below-described equation (1), followed by pickling.

[0045] The technical significance of the hot rolling step will now be described. In the usual hot rolling step, after rolling is completed and the steel sheet is coiled, oxygen diffuses into the steel sheet from oxide scale while the steel sheet is cooled. Accordingly, internal oxides of Si and Mn are formed inside the surface of the steel sheet. The internal oxides of Si and Mn, formed after rolling, are non-uniform. Upon later hot-dip galvanization performed in a CGL, the non-uniform internal oxides cause poor appearance such as uneven adhesion of a coating, uneven alloying after an alloying treatment, etc. Therefore, in hot rolling, it is important to suppress the formation of internal oxidation. In order to suppress the formation of the internal oxides of Si and Mn, it is effective to lower the coiling temperature during coiling after rolling. Further, in the case of using steel having a high content of Si and Mn which form oxides, it is necessary to further lower the coiling temperature.

[0046] A further investigation revealed that the internal oxidation of Si and Mn can be made more uniform by controlling the amount of internal oxidation (the total amount of an internal Si oxide and an internal Mn oxide formed in a surface portion of a hot-rolled steel sheet, located immediately beneath scale and ranging from the sheet surface to a depth of 10 μm . The amount of internal oxidation is expressed as the amount of oxygen at a position corresponding to the longitudinal and width-direction center of the coil after rolling) at the longitudinal and width-direction center of the coil to 0.10 g/m² or less. Therefore, upon later hot-dip galvanization, uneven adhesion of a coating and uneven appearance after an alloying treatment can be further prevented. Further, as a result of an experiment in which steels having varying contents of Si and Mn were subjected to hot rolling, and the amount of internal oxidation at the longitudinal and width-direction center of each

coil after cooling was determined, it was found that the total amount of an internal Si oxide and an internal Mn oxide, formed in a hot rolling step, can be controlled to 0.10 g/m² or less by performing coiling at a temperature equal to or lower than a temperature T_C (°C) calculated from the following equation (1).

$$T_C = -30([Si] + [Mn]) + 775 \quad (1)$$

where T_C is the coiling temperature after rolling, and [Si] and [Mn] are the Si content and the Mn content of the steel, respectively. T_C is preferably 400°C or higher.

[0047] The heating temperature before hot rolling and the finishing temperature upon hot rolling are not particularly limited; however, from the viewpoint of microstructural control, it is preferred to heat the slab at 1100 to 1300°C, and to complete finish rolling at 800 to 1000°C.

[0048] In the present invention, after the above-described rolling, pickling is performed to remove scale. A method for pickling is not particularly limited; any conventional method may be used.

<Cold Rolling Step>

[0049] The cold rolling step is a step of cold-rolling the hot-rolled sheet obtained in the hot rolling step. Conditions for the cold rolling are not particularly limited. For example, the cooled hot-rolled sheet may be cold-rolled at a predetermined rolling reduction ratio in the range of 30 to 80%.

<Annealing Step>

[0050] The annealing step of the present invention consists of a step of oxidizing the cold-rolled steel sheet, obtained in the cold rolling step, using a direct-fired furnace having two or more separate zones, and a step of reducing the oxidized steel sheet using a radiant tube-type heating and holding furnace.

[0051] The direct-fired furnace (oxidation annealing step for the steel sheet) will be described first.

[0052] In order to achieve high strength and high formability of steel, it is effective to add C, Si, and Mn to the steel. However, when a steel sheet to which these elements have been added is used, oxides of Si and Mn are formed at the surface of the steel sheet during the annealing step (oxidation treatment + reduction annealing) performed prior to hot-dip galvanization, which makes it difficult to ensure coatability. The oxidation of Si and Mn at the surface of the steel sheet is effectively prevented by causing these elements to be oxidized within the steel sheet. However, as described above, it is essential to the present invention that the formation of internal oxidation after hot rolling be suppressed from the viewpoint of uneven adhesion of a coating and uneven alloying. Even when internal oxides are thus formed in a small amount after hot rolling, Si and Mn can be oxidized within the steel sheet during the annealing step by strictly controlling the annealing conditions (oxidation conditions + reduction annealing conditions) before hot-dip galvanization. This can improve coatability and increase the reactivity between a coating and the steel sheet, thereby improving the adhesion of the coating. In the annealing step, an oxidation treatment is performed to oxidize Si and Mn within the steel sheet and to thereby prevent oxidation at the surface of the steel sheet. In particular, it is necessary to obtain iron oxide in at least a certain amount in the oxidation treatment. Thereafter, the steel sheet is subjected to reduction annealing and hot-dip galvanization. If necessary, it is effective to perform an alloying treatment of the galvanized steel sheet.

[0053] In order to obtain a sufficient amount of iron oxide, it is necessary to control the heating atmosphere and the heating temperature. The atmosphere is controlled by controlling the air ratio in the direct-fired furnace. The direct-fired furnace is configured to heat a steel sheet by applying a burner flame, produced by burning a mixture of air and a fuel such as coke oven gas (COG) which is a byproduct gas in a steel mill, directly to the surface of the steel sheet. When the air ratio is increased to increase the proportion of air to the fuel, unreacted oxygen remains in the flame, and the oxygen can promote oxidation of the steel sheet. Besides coke oven gas, it is possible to use natural gas, hydrogen gas, ammonia gas, or the like as a fuel in the direct-fired furnace. CO, CO₂, H₂O, NO_x, etc. are generated as oxidation products upon combustion of such a fuel. N₂ in the combustion air is also present in the atmosphere.

[0054] On the other hand, if the steel sheet is oxidized excessively, a phenomenon called pickup occurs where oxides are detached from the steel sheet and attached to a roll in the subsequent reduction annealing step. If pickup occurs on a roll, the appearance of the galvanized steel sheet will be greatly impaired. Therefore, the step of oxidizing the steel sheet using the direct-fired furnace needs to be performed in two or more separate zones where the steel sheet is heated in two or more different atmospheres. An early-stage heating zone and a later-stage heating zone will now be described.

Early-Stage Heating Zone

Heating the steel sheet to 400°C to 670°C in an atmosphere containing 1000 vol. ppm or more of O₂ and 1000 vol. ppm or more of H₂O

[0055] In the early-stage heating zone, the air ratio is adjusted to create an atmosphere containing 1000 ppm by volume or more of O₂ and 1000 ppm by volume or more of H₂O, and the cold-rolled steel sheet is heated. When the O₂ concentration is 1000 ppm by volume or less or the H₂O concentration is 1000 ppm by volume or less, the oxidation of the steel sheet will be insufficient. On the other hand, when the O₂ concentration is less than 1000 ppm by volume and the H₂O concentration is less than 1000 ppm by volume, the O₂ concentration and the H₂O concentration do not have a significant influence on the oxidation of the steel sheet, while the temperature of the steel sheet has a significant influence thereon. Therefore, no particular limitation is placed on the upper limits of the O₂ concentration and the H₂O concentration. Preferably, from the viewpoint of equipment deterioration, the O₂ concentration is 10000 ppm by volume or less, and the H₂O concentration is 10000 ppm by volume or less. The steel sheet is heated to a temperature in the range of not less than 400°C and not more than 670°C. If the temperature of the steel sheet is less than 400°C, the oxidation of the steel sheet will be insufficient, whereas if the temperature of the steel sheet exceeds 670°C, the oxidation of the steel sheet will be excessive, resulting in the above-described pickup on a roll. Therefore, it is essential to the present invention that the steel sheet be heated to a temperature in the range of not less than 400°C and not more than 670°C.

Later-Stage Heating Zone

Heating the steel sheet to 600°C to 700°C in an atmosphere containing 500 vol. ppm or less of O₂

[0056] The later stage of heating is an important factor in the present invention for preventing the above-described roll pickup and obtaining a beautiful surface appearance free of roll marks or the like. In order to prevent the occurrence of the pickup phenomenon, it is important to reduce a portion (surface layer) of the surface of the steel sheet that has been oxidized. To perform such a reduction treatment, in the later-stage heating zone, the air ratio is adjusted so that the O₂ concentration of the atmosphere becomes 500 ppm by volume or less, and the steel sheet that has passed through the early-stage heating zone is heated. If the O₂ concentration exceeds 500 ppm by volume, the steel sheet will be oxidized excessively, resulting in the occurrence of the above-described pickup on a roll. The steel sheet is heated to a temperature in the range of not less than 600°C and not more than 700°C. If the temperature of the steel sheet is less than 600°C, the portion (surface layer) of the surface of the steel sheet will not be sufficiently reduced. If the temperature of the steel sheet exceeds 700°C, the portion (surface layer) of the surface of the steel sheet may not be reduced and oxidation may be promoted, resulting in the occurrence of the above-described pickup on a roll. Therefore, it is essential to the present invention that the steel sheet be heated to a temperature in the range of not less than 600°C and not more than 700°C.

[0057] The radiant tube-type heating and holding furnace (reduction annealing step for the steel sheet) will now be described.

[0058] As described above, addition of C, Si, and Mn to steel is effective to achieve high-strength, high-formability steel. However, when a steel sheet containing, in particular, a large amount of C and Si is used, zinc in a coated layer may melt and diffuse into grain boundaries. This may cause LME, resulting in the occurrence of intergranular cracking (LME cracking) in the steel sheet. Further, it is known that as the strength of a steel material increases, delayed fracture due to hydrogen embrittlement is more likely to occur. Such delayed fracture is caused by corrosion that occurs due to the use environment of a steel sheet, and often caused by hydrogen that has entered the steel sheet. In particular, hydrogen, which has entered a steel sheet during an annealing process in a CGL, causes a deterioration of the delayed fracture resistance of the steel sheet especially when it has a tensile strength exceeding 980 PMA.

[0059] In order to solve these problems, it is important to control the atmosphere of reduction annealing in the annealing process (oxidation treatment + reduction annealing) performed prior to hot-dip galvanization. Although the mechanism is not fully understood, it appears that control of the atmosphere of reduction annealing reduces the amounts of solute Si and solute Mn around internal oxidation layers of Si and Mn formed. Further, C is oxidized by H₂O in the atmosphere and released as CO gas in the furnace, whereby the C concentration in a surface layer of the steel sheet decreases. Consequently, a region deficient in solute C and solute Si, which may cause LME cracking, is formed in the surface layer. Thus, LME cracking is less likely to occur. In addition, internal oxides of Si and Mn exist in a surface layer of the steel sheet. Upon alloying of a coated layer and the steel substrate, such internal oxides of Si and Mn in the surface layer of the steel sheet will diffuse into the coated layer. This promotes removal of hydrogen, which has entered the steel sheet, from the sheet after production, so that good delayed fracture resistance can be achieved.

[0060] Radiant-tube type heating and holding can be used for the reduction annealing. By controlling the H₂O concentration of the atmosphere to be not less than 5000 ppm by volume and not more than 40000 ppm by volume, LME cracking can be prevented and dehydrogenation can be promoted. If the H₂O concentration is less than 5000 ppm by

volume, the LME cracking resistance and the dehydrogenation promoting effect may be insufficient. On the other hand, if the H_2O concentration exceeds 40000 ppm by volume, there is a fear of equipment damage. Therefore, the H_2O concentration is preferably 40000 ppm by volume or less. The difference between the H_2O concentration at the top of the interior space of the furnace and that at the bottom of the interior space of the furnace needs to be 2000 ppm by volume or less. If the difference in H_2O concentration exceeds 2000 ppm by volume, Si and Mn in the steel will be oxidized externally without being oxidized internally, which may impair the coatability and form bare spot defects. Further, it is possible that an internal oxidation layer may not be formed sufficiently, resulting in insufficient LME cracking resistance and an insufficient dehydrogenation promoting effect.

[0061] The H_2 concentration during reduction annealing also greatly influences the formation of an internal oxidation layer. The H_2 concentration needs to be not less than 2% by volume and not more than 20% by volume. Further, the ratio of the partial pressure of H_2O ($P_{\text{H}_2\text{O}}$) to the partial pressure of H_2 (P_{H_2}) needs to satisfy the below-described relation (2). If the H_2 concentration is less than 2% by volume, reduction of the oxidized steel sheet may sometimes be insufficient, resulting in the formation of bare spot defects and reduced adhesion of a coating upon hot-dip galvanization. On the other hand, if the hydrogen concentration exceeds 20% by volume, a large amount of hydrogen will remain in the steel sheet. Even when dehydrogenation is promoted, a considerable amount of hydrogen will remain in the steel, resulting in a failure to achieve good delayed fracture resistance. The formation of an internal oxidation layer is influenced by the ratio of the partial pressure of H_2O ($P_{\text{H}_2\text{O}}$) to the partial pressure of H_2 (P_{H_2}). In order to achieve good LME cracking resistance and dehydrogenation promoting effect, $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ needs to be not less than -1.1 and not more than 0.5. If $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ is less than -1.1, it is possible that an internal oxidation layer may not be formed sufficiently, resulting in a failure to achieve good LME cracking resistance and dehydrogenation promoting effect. On the other hand, if $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ exceeds 0.5, there is a fear of equipment damage. Therefore, $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ is preferably 0.5 or less.

[0062] Further, it has been found that increasing $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ is effective also for the bendability required for the formability of a high-strength steel sheet. Although the mechanism is not fully understood, this is considered to be due to an improvement in formability achieved by the decrease in the amount of hydrogen in the steel sheet, and to a change in the strain dispersion ability caused by the presence of a surface layer having relatively good formability, which is due to the presence of an internal oxidation layer. Thus, the bendability is also improved by making $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ -1.1 or more. The bendability is further improved by making $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ -0.99 or more. $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ may be made -0.90 or more, or -0.7 or more so that the bendability can be still further improved. In either case, the upper limit of $\log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ is preferably 0.5 or less.

[0063] Besides H_2O and H_2 , the reduction annealing atmosphere preferably contains N_2 from the viewpoint of cost. In addition, NO_x , SO_x , CO , CO_2 , etc. can exist in the atmosphere.

[0064] The reduction annealing temperature needs to be not less than 650°C and not more than 900°C. If the temperature is less than 650°C, the formation of an internal oxidation layer, which is necessary to improve the LME cracking resistance and to promote dehydrogenation, may be insufficient. If the temperature exceeds 900°C, there is a fear of damage to the furnace body of the annealing furnace; therefore, the temperature should preferably be 900°C or lower.

[0065] The above-described reducing atmosphere conditions may be satisfied by part or the whole of the atmosphere in the furnace. When the above-described reducing atmosphere conditions are satisfied by part of the atmosphere, it is necessary to perform the annealing in the specified atmosphere for at least 90 seconds. As long as the annealing is performed in the specified atmosphere for at least 90 seconds, the reduction annealing atmosphere need not be wholly controlled in the above-described manner throughout the furnace.

<Cooling and Heating Step>

[0066] The cooling and heating step is a step of cooling the steel sheet, which has undergone the reduction annealing, from the final holding temperature in the reduction annealing to a cooling end temperature of 150 to 350°C at an average cooling rate of at least 10°C/sec, and then heating the steel sheet to a reheating temperature of 350 to 600°C and holding it at that temperature for 10 to 600 seconds. The cooling and heating step can further improve the mechanical properties. The cooling and heating step is not an essential step of the present invention, and may be performed as necessary.

[0067] If the cooling rate during cooling from the final holding temperature in the reduction annealing is less than 10°C/sec, pearlite will be formed, resulting in a reduction in "TS × EL" and in flangeability. Therefore, the cooling rate during cooling from the final holding temperature in the reduction annealing is preferably at least 10°C/sec. The final holding temperature in the reduction annealing herein refers to the temperature when at least one of the annealing temperature, the hydrogen concentration, the dew point, and the holding time in the reduction annealing has come to fall outside the range described above.

[0068] If the cooling end temperature is more than 600°C, the temperature of a galvanizing bath increases in the subsequent hot-dip galvanizing step, which may promote the formation of dross that impairs the surface appearance quality. Therefore, the cooling end temperature is preferably 600°C or less. The mechanical properties can be improved by making the cooling end temperature 350°C or less. If the cooling end temperature is lower than 150°C, most of austenite is

transformed into martensite during cooling, and the amount of non-transformed austenite decreases. Therefore, the cooling end temperature is preferably in the range of 150 to 350°C. Any cooling method, such as gas jet cooling, mist cooling, water cooling, or metal quenching, may be used as long as the intended cooling rate and the intended cooling stop temperature (cooling end temperature) can be achieved.

[0069] In some cases, after cooling the steel sheet to the cooling end temperature, the steel sheet may be heated to the reheating temperature and held at that temperature for at least 10 seconds. By holding the steel sheet for at least 10 seconds, martensite that has been formed during cooling is tempered and becomes tempered martensite, resulting in improved flangeability. Further, non-transformed austenite that has not been transformed into martensite during cooling may be stabilized, and a sufficient amount of retained austenite may be finally obtained, leading to improved ductility.

[0070] In the case of reheating the steel sheet, if the reheating temperature exceeds 600°C, non-transformed austenite that exists upon stoppage of cooling will be transformed into pearlite, resulting in a failure to finally obtain retained austenite at an area ratio of 3% or more. If the holding time upon reheating is less than 10 seconds, the stabilization of austenite will be insufficient, while if the holding time exceeds 600 seconds, the non-transformed austenite that exists upon stoppage of cooling will be transformed into bainite, resulting in a failure to finally obtain a sufficient amount of retained austenite.

Therefore, in the case of reheating, the reheating temperature is made in the range of 350 to 600°C, and the holding time in that temperature range is made 10 to 600 seconds.

<Hot-Dip Galvanization Step>

[0071] After performing hot-dip galvanization of the steel sheet, it may be subjected to an alloying treatment. The hot-dip galvanization step is a step of hot-dip galvanizing the annealed steel sheet after the annealing step in a hot-dip galvanizing bath containing 0.12 to 0.22% by mass of Al.

[0072] In the present invention, the Al concentration in the galvanizing bath is made 0.12 to 0.22% by mass. If the Al concentration is less than 0.12% by mass, an Fe-Zn alloy phase will be formed during galvanization, which may lead to poor adhesion of a coating and uneven appearance. If the Al concentration exceeds 0.22% by mass, a thick Fe-Al alloy phase will be formed at the coating and steel substrate interface during galvanization, resulting in poor weldability. Further, because of the large amount of Al in the bath, a large amount of Al oxide film will be formed on the surface of the galvanized steel sheet, which may impair not only the weldability but the appearance as well.

[0073] In the case of carrying out an alloying treatment, the Al concentration in the galvanizing bath is preferably 0.12 to 0.17% by mass. If the Al concentration is less than 0.12% by mass, an Fe-Zn alloy phase will be formed during galvanization, which may lead to poor adhesion of a coating and uneven appearance. If the Al concentration exceeds 0.17% by mass, a thick Fe-Al alloy phase may be formed at the coating and steel substrate interface during galvanization. The Fe-Al alloy phase will be an obstacle to an Fe-Zn alloying reaction, resulting in a high alloying temperature and poor mechanical properties.

[0074] There is no limitation on other conditions in the hot-dip galvanization. For example, galvanization is performed by immersing the steel sheet at a sheet temperature of 440 to 550°C in the hot-dip galvanizing bath generally at a temperature in the range of 440 to 500°C. The amount of coating can be adjusted, e.g., by gas wiping.

<Alloying Step>

[0075] The alloying step is a step of alloying the steel sheet after the hot-dip galvanization step at a temperature in the range of 450 to 550°C for 10 to 60 seconds.

[0076] While the alloying degree (i.e., Fe concentration of the coated layer) after the alloying treatment is not particularly limited, it is preferably 7 to 15% by mass. If the alloying degree is less than 7% by mass, an η phase will remain, leading to poor press formability. If the alloying degree exceeds 15% by mass, the adhesion of the coating will be poor.

EXAMPLES

[0077] Molten steels, having the chemical compositions shown in Table 1, were each continuously cast into a slab.

[0078] After heating the slab at 1200°C, it was hot-rolled to a thickness of 2.6 mm at a finishing temperature of 890°C, coiled at the coiling temperature shown in Table 2, cooled, and then pickled to remove black scale, thereby obtaining a hot-rolled sheet. The amount of internal oxidation of Si and/or Mn at the longitudinal and width-direction center of the coil was measured by the below-described method.

[Table 1]

Steel symbol	C	Si	Mn	P	S	N	Al	B	Ti	Cr	Mo	Cu	Ni	Nb	Sb	
A	0.18	0.41	1.53	0.01	0.002	0.004	0.038	0.001	0.01	-	-	-	-	-	-	Ref. Example
B	0.11	0.45	2.52	0.02	0.001	0.003	0.032	0.001	0.01	0.59	-	-	-	0.04	-	Example
C	0.09	0.62	2.72	0.01	0.002	0.005	0.035	0.001	0.01	-	-	-	-	0.02	-	Example
D	0.15	0.93	2.13	0.03	0.002	0.004	0.034	-	-	-	-	-	-	-	-	Example
E	0.18	1.03	3.09	0.01	0.002	0.006	0.037	0.001	0.01	-	-	-	-	0.01	0.007	Example
F	0.12	1.18	1.86	0.01	0.001	0.004	0.031	0.001	0.01	-	-	-	-	0.01	0.012	Example
G	0.24	1.42	1.29	0.01	0.001	0.003	0.033	0.001	0.01	-	-	-	-	-	-	Example
H	0.13	1.38	1.97	0.02	0.001	0.007	0.034	0.001	0.01	-	-	-	-	-	-	Example
I	0.12	1.45	1.54	0.01	0.001	0.003	0.037	0.001	0.01	-	-	-	-	-	-	Example
J	0.17	1.50	2.33	0.02	0.001	0.004	0.035	-	-	-	0.11	-	-	-	-	Example
K	0.19	1.53	2.74	0.03	0.001	0.004	0.038	0.001	0.01	-	-	0.12	-	-	-	Example
L	0.15	1.62	1.31	0.01	0.002	0.005	0.034	0.001	0.01	-	-	-	0.14	-	-	Example
M	0.17	1.65	2.52	0.01	0.002	0.004	0.035	0.001	0.01	-	-	-	-	-	-	Example

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[Table 2]

	No.	Steel types	Tc (°C)	Hot rolling Coiling temp. (°C)	Cold rolling	Direct-fired furnace				Radiant tube-type heating and holding furnace				Cooling step				Hot-dip galvanization	Alloying	Category		
						Early-stage heating			Later-stage heating	Max. temp. of steel sheet (°C)	Holding time (s)	H ₂ O conc. (vol. ppm)	H ₂ conc. (vol. %)	log(P _{H₂O} /P _{H₂})	Cooling rate (°C/s) *1	Cooling stop temp. (°C)	Reheating temp. (°C)				Holding time (s)	
						Max. temp. of steel sheet (°C)	O ₂ conc. (vol. ppm)	H ₂ O conc. (vol. ppm)	Max. temp. of steel sheet (°C)													O ₂ conc. (vol. ppm)
5	1	K	648	650	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	2	K	648	600	done	700	3000	1500	750	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	3	K	648	600	done	380	3000	1500	500	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	4	K	648	600	done	630	800	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	5	K	648	600	done	630	3000	800	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
10	6	K	648	600	done	630	3000	1500	720	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	7	K	648	600	done	530	3000	1500	580	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	8	K	648	600	done	630	3000	1500	680	550	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	9	K	648	600	done	630	3000	1500	680	300	920	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	10	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
15	11	K	648	600	done	630	3000	1500	680	300	800	80	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	12	K	648	600	done	630	3000	1500	680	300	800	120	4500	10	-1.35	15	550	-	10	done	done	Comp. Ex.
	13	K	648	600	done	630	3000	1500	680	300	800	120	45000	10	-0.35	15	550	-	10	done	done	Comp. Ex.
	14	K	648	600	done	630	3000	1500	680	300	800	120	20000	21	-1.02	15	550	-	10	done	done	Comp. Ex.
	15	K	648	600	done	630	3000	1500	680	300	800	120	20000	1	0.12	15	550	-	10	done	done	Comp. Ex.
20	16	K	648	600	done	630	3000	1500	680	300	800	120	45000	1	0.65	15	550	-	10	done	done	Comp. Ex.
	17	K	648	600	done	630	3000	1500	680	300	800	120	7000	11	-1.20	15	550	-	10	done	done	Comp. Ex.
	18	K	648	640	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	19	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	20	K	648	550	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
25	21	K	648	500	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	22	K	648	600	done	660	3000	1500	700	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	23	K	648	600	done	600	3000	1500	670	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	24	K	648	600	done	500	3000	1500	630	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	25	K	648	600	done	400	3000	1500	600	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
30	26	K	648	600	done	630	10000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	27	K	648	600	done	630	5000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	28	K	648	600	done	630	2000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	29	K	648	600	done	630	1500	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	30	K	648	600	done	630	1000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
35	31	K	648	600	done	630	3000	10000	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	32	K	648	600	done	630	3000	5000	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	33	K	648	600	done	630	3000	2000	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	34	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	35	K	648	600	done	630	3000	1000	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
40	36	K	648	600	done	630	3000	1500	680	500	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	37	K	648	600	done	630	3000	1500	680	100	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	38	K	648	600	done	630	3000	1500	680	20	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	39	K	648	600	done	630	3000	1500	680	300	900	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	40	K	648	600	done	630	3000	1500	680	300	700	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
45	41	K	648	600	done	630	3000	1500	680	300	650	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	42	K	648	600	done	630	3000	1500	680	300	800	###	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	43	K	648	600	done	630	3000	1500	680	300	800	600	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	44	K	648	600	done	630	3000	1500	680	300	800	300	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	45	K	648	600	done	630	3000	1500	680	300	800	90	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
50	46	K	648	600	done	630	3000	1500	680	300	800	120	40000	2	0.30	15	550	-	10	done	done	Inventive Ex.
	47	K	648	600	done	630	3000	1500	680	300	800	120	30000	5	-0.22	15	550	-	10	done	done	Inventive Ex.
	48	K	648	600	done	630	3000	1500	680	300	800	120	10000	10	-1.00	15	550	-	10	done	done	Inventive Ex.
	49	K	648	600	done	630	3000	1500	680	300	800	120	25000	20	-0.90	15	550	-	10	done	done	Inventive Ex.
	50	K	648	600	done	630	3000	1500	680	300	800	120	5000	6	-1.08	15	550	-	10	done	done	Inventive Ex.
55	51	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	13	300	500	15	done	done	Inventive Ex.
	52	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	13	200	500	15	done	done	Inventive Ex.
	53	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	54	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	no	Inventive Ex.
	55	K	648	600	done	630	3000	1500	680	300	800	120	20000	10	-0.70	13	200	500	15	done	no	Inventive Ex.
	56	B	685	690	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	57	B	685	670	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	58	C	676	680	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	59	C	676	660	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive Ex.
	60	D	683	690	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Comp. Ex.
	61	D	683	670	done	630	3000	1500	680	300	800	120	20000	10	-0.70	15	550	-	10	done	done	Inventive

<Internal Oxidation Amount After Hot Rolling>

[0079] The amount of internal oxidation was measured by an "impulse furnace melting-infrared absorption method". The concentration of oxygen in the steel was measured before and after polishing a 10 mm × 70 mm area in a surface layer portion (at the center (width-direction and longitudinal center) of the coil) by 10 μm on both sides of the hot-rolled sheet. Further, from the difference between the measured values, the amount of oxygen, existing in a 10-μm region from the steel sheet surface, per unit area of one surface was determined as the amount of internal oxidation of Si and/or Mn (g/m²). The fact that the internal oxide, formed in the surface layer portion of the hot-rolled sheet, is an oxide of Si and/or Mn was confirmed by SEM observation and by elemental analysis using an EDS (energy dispersive X-ray spectroscope) after embedding the hot-rolled sheet into a resin and polishing a cross-section. The measured amounts of internal oxidation are shown in Table 3.

[0080] Next, the steel sheet was cold-rolled to obtain a cold-rolled sheet having a thickness of 1.2 mm. The cold-rolled sheet was then subjected to annealing and hot-dip galvanization in a CGL. Early-stage heating was performed under the conditions shown in Table 2 in a direct-fired furnace having a nozzle mix burner. Later-stage heating was then performed under the conditions shown in Table 2 in a direct-fired furnace having a premix burner. The oxidation start temperature was 300°C. The oxidation start temperature does not significantly affect the coating appearance; therefore, it is possible to create an oxidizing atmosphere at a temperature of less than 400°C. Reduction annealing was performed in a radiant tube-type heating and holding furnace under the conditions shown in Table 2, followed by cooling. Subsequently, hot-dip galvanization was performed using a zinc bath at 460°C, containing 0.135% of Al, as shown in Table 2, followed by gas wiping to adjust the coating weight to about 50 g/m². An alloying treatment was performed in some cases.

[0081] For each of the high-strength hot-dip galvanized steel sheets thus obtained, the appearance was evaluated and the tensile property was measured. Further, the LME cracking resistance, the dehydrogenation behavior, and damage to the furnace body were evaluated. The following measurement methods and evaluation methods were used.

<Appearance>

[0082] The appearance of each steel sheet was visually observed. A steel sheet was evaluated as "◎" when it was free of appearance defects such as bare spot portions, roll marks due to the pickup phenomenon, or uneven alloying, evaluated as "o" when it had slight appearance defects, but was acceptable as a product, and evaluated as "×" when it had clear uneven alloying, bare spot portions, or roll marks. The appearance of a steel sheet was judged to be good when the above evaluation was "◎" or "o".

<Tensile Property>

[0083] A tensile test was conducted in accordance with JIS Z 2241 using a JIS No. 5 test specimen with the rolling direction as the tensile direction. A test specimen was judged to be good when TS (MPa) × EL (%) was 8000 (MPa·%) or more.

<LME Cracking Resistance>

[0084] A test specimen was cut from each hot-dip galvanized steel sheet to a size of 150 mm in the longer direction and 50 mm in the shorter direction, with the longer direction being a direction (TD) perpendicular to the rolling direction, and the shorter direction coinciding with the rolling direction. The test specimen was superimposed on a hot-dip galvanized steel sheet for testing (thickness 1.2 mm, TS: 980 MPa grade) with a coating weight of 50 g/m² per one surface, which had the same size as the test specimen, to form a sheet assembly. The sheet assembly was assembled such that the hot-dip galvanized layer of the test specimen met the surface of the hot-dip galvanized layer of the commercially available hot-dip galvanized steel sheet. As shown in FIG. 1(A), the sheet assembly was fixed to a fixing base, via 2.0 mm-thick spacers, in an inclined position at an angle of 5°, which is the maximum inclination expected for the shape of some part. The spacers were a pair of steel sheets, each having a size of 50 mm in the longer direction × 45 mm in the shorter direction × 2.0 mm in thickness, and were disposed such that the long-direction end surfaces of each of the pair of steel sheets were aligned with the short-direction end surfaces of the sheet assembly. Therefore, the distance between the pair of steel sheets, constituting the spacers, is 60 mm. The fixing base is a single plate with a hole in the center.

[0085] Next, using a servo motor pressurized single-phase AC (50 Hz) resistance welding machine, the sheet assembly was subjected to resistance welding with a pressure of 3.5 kN and a holding time of 0.10 seconds or 0.16 seconds while pressing and bending the sheet assembly by means of a pair of electrodes (tip diameter: 6 mm). The welding was performed under such welding current and welding time conditions that would make the weld nugget diameter 5.9 mm (i.e., welding current and welding time were adjusted for each sheet assembly so that the nugget diameter would be 5.9 mm), thereby obtaining a sheet assembly with the welding portion. During the welding, the pair of electrodes pressed the sheet

assembly from above and below in the vertical direction, and the lower electrode pressed the test specimen through the hole of the fixing base. During the pressing of the sheet assembly, the lower electrode of the pair of electrodes and the fixing base were fixed such that the lower electrode contacts a plane extending from the contact plane between each spacer and the fixing base, while the upper electrode was allowed to move. Further, the upper electrode was brought into contact with the center of the hot-dip galvanized steel sheet for testing. The holding time refers to the time from the end of the application of a welding current to the start of opening of the electrodes. The nugget diameter refers to the distance between the ends 10 of the nugget in the longer direction of the sheet assembly, as shown in FIG. 2.

[0086] Next, as shown in FIG. 2, the sheet assembly with the welding portion was cut along a plane including the welding portion (nugget). The cross-section of the welding portion was observed by an optical microscope (200x), and the resistance to resistance-welding cracking in the welding portion was evaluated according to the following criteria. The upper diagram of FIG. 2 is a plan view of the sheet assembly with the welding portion, showing the cutting position. The lower diagram of FIG. 2 is a diagram showing the thickness-direction cross-section of the sheet assembly after cutting, schematically illustrating a crack formed in the test specimen. If a crack is formed in the hot-dip galvanized steel sheet for testing, a stress in the test specimen is dispersed, and therefore an appropriate evaluation is not possible. Therefore, data 15 obtained without the formation of a crack in the hot-dip galvanized steel sheet for testing was used as data for examples.

[0087] When the below-described evaluation was "o" or "◎", the resistance to resistance-welding cracking in the welding portion was judged to be good and excellent, respectively, while it was judged to be poor when the evaluation was "×".

[0088]

◎: No crack having a length of 0.1 mm or more was observed when the holding time was 0.10 seconds.

◦: A crack(s) having a length of 0.1 mm or more was observed when the holding time was 0.10 seconds, whereas no crack having a length of 0.1 mm or more was observed when the holding time was 0.16 seconds.

[0089] ×: A crack(s) having a length of 0.1 mm or more was observed when the holding time was 0.16 seconds.

<Dehydrogenation Behavior>

[0090] A rectangular test specimen having a long-axis length of 30 mm and a short-axis length of 5 mm was taken from the center of the width of each hot-dip galvanized steel sheet. The coated layer of the test specimen was removed by a Leutor, and immediately thereafter the test specimen was subjected to a hydrogen analysis using a thermal desorption analyzer under the conditions of an analysis start temperature of 25°C, an analysis end temperature of 300°C, and a heating rate of 200°C/hr to measure the amount of released hydrogen (mass ppm/min), which is the amount of hydrogen released from the surface of the test specimen, at each temperature. The total amount of released hydrogen from the analysis start temperature to 300°C was calculated as the amount of diffusible hydrogen in steel. A test specimen was evaluated as "◎" when the amount of diffusible hydrogen in steel was 0.10 ppm by mass or less, and evaluated as "o" when the amount of diffusible hydrogen in steel was 0.30 ppm by mass or less. Further, based on the empirical fact that the delayed fracture resistance of a steel sheet is often poor when the amount of diffusible hydrogen in steel exceeds 0.30 ppm by mass, a test specimen having such an amount of diffusible hydrogen was evaluated as "×". The dehydrogenation behavior was judged to be excellent when the above evaluation was "◎" or "o".

<Damage to Furnace Body>

[0091] Damage to the furnace body was evaluated by visual inspection to check whether discoloration occurred in the steel shell (SUS310S) inside the annealing furnace. A steel sheet which caused no discoloration of the steel shell was evaluated as "o", and judged to be non-damaging to the furnace body. A steel sheet which caused appreciable discoloration of the steel shell was evaluated as "×", and judged to be damaging to the furnace body.

<Method for Evaluating Bendability>

[0092] A 25 mm × 100 mm rectangular test specimen was cut from each galvanized steel sheet such that the short sides of the specimen were parallel to the rolling direction. The test specimen was then subjected to a 90° V-bend test in which the test specimen was bent such that the ridge formed extended in the rolling direction. The streak speed was 50 mm/min, and the specimen was pressed against a die for 5 seconds under a load of 10 tons. The test was performed while varying the radius of curvature R at the tip of a V-shaped punch in 0.5 steps. An area around the ridge of the specimen was observed through a 20x lens to check for the presence or absence of a crack(s). R/t was calculated from the minimum R at which no crack was formed and the thickness (t mm, rounded to the nearest hundredth) of the test specimen, and used as an index of bendability. A smaller R/t value indicates better bendability. A test specimen having an R/t value of less than 1.0 was

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evaluated as "⊙+", a test specimen having an R/t value of less than 1.5 was evaluated as "⊙", a test specimen having an R/t value of less than 2.0 was evaluated as "o", a test specimen having an R/t value of less than 4.0 was evaluated as "Δ", and a test specimen having an R/t value of 4.0 or more evaluated as "×".

[0093] The results obtained above, together with the production conditions, are shown in Table 3.

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[Table 3]

No.	Internal oxidation amount upon hot rolling (g/m ²)	Coating appearance	TS (MPa)	EI (%)	TS×EI	LME cracking resistance	Amount of diffusible hydrogen in steel sheet		Damage to furnace body	Bendability		Category
							(mass ppm)	Rating		R/t	Rating	
1	0.2	×	1311	10.2	13372	○	0.21	○	○	0.9	⊙+	Comp. Ex.
2	0.0	×	1316	9.8	12897	○	0.19	○	○	0.9	⊙+	Comp. Ex.
3	0.0	×	1309	10.2	13352	○	0.18	○	○	0.9	⊙+	Comp. Ex.
4	0.0	×	1296	10.1	13090	○	0.19	○	○	0.9	⊙+	Comp. Ex.
5	0.0	×	1312	9.6	12595	○	0.20	○	○	0.9	⊙+	Comp. Ex.
6	0.0	×	1305	9.4	12267	○	0.15	○	○	0.9	⊙+	Comp. Ex.
7	0.0	×	1312	9.5	12464	○	0.16	○	○	0.9	⊙+	Comp. Ex.
8	0.0	×	1307	9.6	12547	○	0.21	○	○	0.9	⊙+	Comp. Ex.
9	0.0	○	1416	7.1	10054	○	0.21	○	×	0.9	⊙+	Comp. Ex.
10	0.0	○	1383	8.5	11756	×	0.51	×	○	3.1	Δ	Comp. Ex.
11	0.0	○	1318	8.8	11598	×	0.53	×	○	2.8	Δ	Comp. Ex.
12	0.0	○	1299	9.5	12341	×	0.61	×	○	4.5	×	Comp. Ex.
13	0.0	○	1312	10.1	13251	⊙	0.08	⊙	×	0.9	⊙+	Comp. Ex.
14	0.0	○	1340	9.6	12864	○	0.55	×	○	1.8	○	Comp. Ex.
15	0.0	×	1308	9.8	12818	⊙	0.09	⊙	○	0.3	⊙+	Comp. Ex.
16	0.0	○	1307	9.7	12678	⊙	0.02	⊙	×	0.0	⊙+	Comp. Ex.
17	0.0	○	1305	9.5	12398	×	0.45	×	○	4.2	×	Comp. Ex.
18	0.1	○	1322	9.0	11898	○	0.23	○	○	0.9	⊙+	Inventive Ex.
19	0.0	○	1313	9.9	12999	○	0.20	○	○	0.9	⊙+	Inventive Ex.
20	0.0	○	1302	9.8	12760	○	0.21	○	○	0.9	⊙+	Inventive Ex.
21	0.0	○	1322	9.2	12162	○	0.19	○	○	0.9	⊙+	Inventive Ex.
22	0.0	○	1318	9.4	12389	○	0.21	○	○	0.9	⊙+	Inventive Ex.
23	0.0	○	1312	9.3	12202	○	0.20	○	○	0.9	⊙+	Inventive Ex.
24	0.0	○	1314	9.2	12089	○	0.22	○	○	0.9	⊙+	Inventive Ex.

(continued)

No.	Internal oxidation amount upon hot rolling (g/m ²)	Coating appearance	TS (MPa)	EI (%)	TS×EI	LME cracking resistance	Amount of diffusible hydrogen in steel sheet		Damage to furnace body	Bendability		Category
							(mass ppm)	Rating		R/t	Rating	
25	0.0	○	1313	9.7	12736	○	0.18	○	○	0.9	⊕+	Inventive Ex.
26	0.0	○	1308	9.1	11903	○	0.16	○	○	0.9	⊕+	Inventive Ex.
27	0.0	○	1306	8.8	11493	○	0.19	○	○	0.9	⊕+	Inventive Ex.
28	0.0	○	1298	8.9	11552	○	0.20	○	○	0.9	⊕+	Inventive Ex.
29	0.0	○	1303	8.6	11206	○	0.21	○	○	0.9	⊕+	Inventive Ex.
30	0.0	○	1325	9.1	12058	○	0.19	○	○	0.9	⊕+	Inventive Ex.
31	0.0	○	1319	8.6	11343	○	0.17	○	○	0.9	⊕+	Inventive Ex.
32	0.0	○	1314	8.6	11300	○	0.18	○	○	0.9	⊕+	Inventive Ex.
33	0.0	○	1318	9.3	12257	○	0.21	○	○	0.9	⊕+	Inventive Ex.
34	0.0	○	1303	9.6	12509	○	0.23	○	○	0.9	⊕+	Inventive Ex.
35	0.0	○	1317	8.2	10799	○	0.21	○	○	0.9	⊕+	Inventive Ex.
36	0.0	○	1322	9.1	12030	○	0.21	○	○	0.9	⊕+	Inventive Ex.
37	0.0	○	1314	8.3	10906	○	0.24	○	○	0.9	⊕+	Inventive Ex.
38	0.0	○	1315	8.5	11178	○	0.25	○	○	0.9	⊕+	Inventive Ex.
39	0.0	○	1381	7.2	9943	○	0.21	○	○	0.9	⊕+	Inventive Ex.
40	0.0	○	1346	8.1	10903	○	0.16	○	○	0.9	⊕+	Inventive Ex.
41	0.0	○	1363	8.5	11586	○	0.15	○	○	0.9	⊕+	Inventive Ex.
42	0.0	○	1286	8.2	10545	○	0.18	○	○	0.9	⊕+	Inventive Ex.
43	0.0	○	1295	8.3	10749	○	0.19	○	○	0.9	⊕+	Inventive Ex.
44	0.0	○	1287	7.9	10167	○	0.21	○	○	0.9	⊕+	Inventive Ex.
45	0.0	○	1345	6.3	8474	○	0.23	○	○	0.9	⊕+	Inventive Ex.
46	0.0	○	1314	8.2	10775	⊗	0.05	⊗	○	0.1	⊕+	Inventive Ex.
47	0.0	○	1313	7.5	9848	⊗	0.06	⊗	○	0.5	⊕+	Inventive Ex.
48	0.0	○	1308	8.3	10856	○	0.21	○	○	1.8	○	Inventive Ex.

(continued)

No.	Internal oxidation amount upon hot rolling (g/m ²)	Coating appearance	TS (MPa)	EI (%)	TS×EI	LME cracking resistance	Amount of diffusible hydrogen in steel sheet (mass ppm)		Damage to furnace body	Bendability		Category
										R/t	Rating	
49	0.0	○	1328	9.0	11952	○	0.19		○	1.3	⊙	Inventive Ex.
50	0.0	○	1317	9.1	11985	○	0.23		○	1.9	○	Inventive Ex.
51	0.0	○	1185	22.5	26663	○	0.11		○	0.9	⊙+	Inventive Ex.
52	0.0	○	1215	21.9	26609	○	0.13		○	0.9	⊙+	Inventive Ex.
53	0.0	○	1358	13.8	18740	○	0.16		○	0.9	⊙+	Inventive Ex.
54	0.0	○	1353	16.5	22325	○	0.18		○	0.9	⊙+	Inventive Ex.
55	0.0	○	1216	23.9	29062	○	0.12		○	0.9	⊙+	Inventive Ex.
56	0.2	×	1231	9.4	11571	○	0.19		○	0.9	⊙+	Comp. Ex.
57	0.1	○	1225	9.3	11393	○	0.22		○	0.9	⊙+	Inventive Ex.
58	0.2	×	984	14.1	13874	○	0.21		○	-	-	Comp. Ex.
59	0.1	○	987	14.5	14312	○	0.25		○	-	-	Inventive Ex.
60	0.2	×	968	17.2	16650	○	0.21		○	-	-	Comp. Ex.
61	0.1	○	959	17.6	16878	○	0.19		○	-	-	Inventive Ex.
62	0.2	×	1415	8.3	11745	○	0.17		○	1.1	⊙	Comp. Ex.
63	0.1	○	1426	8.1	11551	○	0.18		○	1.1	⊙	Inventive Ex.
64	0.2	×	751	25.2	18925	○	0.24		○	-	-	Comp. Ex.
65	0.1	○	745	25.6	19072	○	0.23		○	-	-	Inventive Ex.
66	0.2	×	831	13.4	11135	○	0.21		○	-	-	Comp. Ex.
67	0.1	○	832	13.6	11315	○	0.23		○	-	-	Inventive Ex.
68	0.2	×	819	22.4	18346	○	0.22		○	-	-	Comp. Ex.
69	0.1	○	815	21.8	17767	○	0.24		○	-	-	Inventive Ex.
70	0.2	×	615	32.0	19680	○	0.20		○	-	-	Comp. Ex.
71	0.1	○	614	31.2	19157	○	0.19		○	-	-	Inventive Ex.
72	0.2	×	1024	17.9	18330	○	0.18		○	-	-	Comp. Ex.

(continued)

No.	Internal oxidation amount upon hot rolling (g/m ²)	Coating appearance	TS (MPa)	EI (%)	TS×EI	LME cracking resistance	Amount of diffusible hydrogen in steel sheet		Damage to furnace body	Bendability		Category
							(mass ppm)	Rating		R/t	Rating	
73	0.1	○	1023	18.6	19028	○	0.19	○	○	-	-	Inventive Ex.
74	0.2	×	791	22.4	17718	○	0.17	○	○	-	-	Comp. Ex.
75	0.1	○	794	23.5	18659	○	0.21	○	○	-	-	Inventive Ex.
76	0.2	×	1191	13.8	16436	○	0.21	○	○	-	-	Comp. Ex.
77	0.1	○	1186	13.5	16011	○	0.21	○	○	-	-	Inventive Ex.
78	0.0	○	1024	12.6	12902	○	0.22	○	○	-	-	Ref. Ex.

[0094] The data in Table 3 indicates that the steel sheets of Inventive Examples, despite being high-strength hot-dip galvanized steel sheets containing C, Si, and Mn, are excellent in the LME cracking resistance, have good coating appearance, and have a small amount of diffusible hydrogen in steel sheet, and therefore are expected to achieve good delayed fracture resistance. Further, the steel sheets caused little damage to the furnace body, and are excellent also in ductility and bendability. On the other hand, the steel sheets of Comparative Examples, each produced by a method outside the scope of the present invention, are inferior in at least one of LME cracking resistance, coating appearance, the amount of diffusible hydrogen in steel sheet, and damage to the furnace body.

Industrial Applicability

[0095] A high-strength hot-dip galvanized steel sheet, obtained by the production method of the present invention, has excellent appearance quality and excellent resistance to resistance-welding cracking, and can reduce deterioration of the delayed fracture resistance caused by hydrogen embrittlement. Such a steel sheet can be used as a surface-treated steel sheet to reduce the weight and increase the strength of an automotive body itself.

Reference Signs List

[0096]

- 1 hot-dip galvanized steel sheet for testing
- 2 test specimen
- 3 spacer
- 4 electrodes
- 5 fixing base
- 6 nugget
- 7 nugget diameter
- 8 cutting-plane line

Claims

1.

A method for producing a high-strength hot-dip galvanized steel sheet, comprising: a hot rolling step of hot-rolling a slab containing, in % by mass, C: not less than 0.05% and not more than 0.30%, Si: not less than 0.45% and not more than 2.0%, and Mn: not less than 1.0% and not more than 4.0%, and coiling the hot-rolled sheet at a temperature equal to or lower than a temperature T_C (°C) calculated from the following equation (1), followed by pickling; a cold rolling step of cold-rolling the hot-rolled sheet obtained in the hot rolling step; a step of continuously annealing the cold-rolled steel sheet, obtained in the cold rolling step, in a direct-fired furnace and in an annealing furnace comprising a radiant tube-type heating and holding furnace; and a step of hot-dip galvanizing the annealed steel sheet,

wherein in the direct-fired furnace, in an early stage, the steel sheet is heated to a temperature of not less than 400°C and not more than 670°C in an atmosphere containing 1000 ppm by volume or more of O_2 and 1000 ppm by volume or more of H_2O , and in a later stage, the steel sheet is heated to a temperature of not less than 600°C and not more than 700°C in an atmosphere containing 500 ppm by volume or less of O_2 , and

wherein in the annealing furnace comprising the radiant tube-type heating and holding furnace, the steel sheet is held at a temperature of not less than 650°C and not more than 900°C for at least 90 seconds in an atmosphere which satisfies the following conditions: the H_2O concentration is not less than 5000 ppm by volume and not more than 40000 ppm volume, the H_2 concentration is not less than 2% by volume and not more than 20% by volume, and the logarithm of the ratio of the partial pressure of H_2O (P_{H_2O}) to the partial pressure of H_2 (P_{H_2}), i.e. $\log(P_{H_2O}/P_{H_2})$, is not less than -1.1 and not more than 0.5:

$$T_C = -30([Si] + [Mn]) + 775 \quad (1)$$

where [Si] is the Si content (mass %) of the steel sheet, and [Mn] is the Mn content (mass %) of the steel sheet.

2. The method for producing a high-strength hot-dip galvanized steel sheet according to claim 1, wherein the steel sheet after the hot-dip galvanization is subjected to an alloying treatment.

3. The method for producing a high-strength hot-dip galvanized steel sheet according to claim 1 or 2, further comprising a cooling and heating step of cooling the steel sheet, which has undergone the heating and holding in the radiant tube-type heating and holding furnace, from the final holding temperature during the annealing to a temperature of 150 to 350°C at an average cooling rate of at least 10°C/sec, and then heating the steel sheet to a temperature of 350 to 600°C and holding it at that temperature for 10 to 600 seconds.
4. The method for producing a high-strength hot-dip galvanized steel sheet according to any one of claims 1 to 3, wherein the logarithm of the ratio of the partial pressure of H₂O (P_{H₂O}) to the partial pressure of H₂ (P_{H₂}), i.e. log(P_{H₂O}/P_{H₂}), is not less than -0.99 and not more than 0.5.
5. The method for producing a high-strength hot-dip galvanized steel sheet according to any one of claims 1 to 4, wherein the logarithm of the ratio of the partial pressure of H₂O (P_{H₂O}) to the partial pressure of H₂ (P_{H₂}), i.e. log(P_{H₂O}/P_{H₂}), is not less than -0.9 and not more than 0.5.
6. The method for producing a high-strength hot-dip galvanized steel sheet according to any one of claims 1 to 5, wherein the logarithm of the ratio of the partial pressure of H₂O (P_{H₂O}) to the partial pressure of H₂ (P_{H₂}), i.e. log(P_{H₂O}/P_{H₂}), is not less than -0.7 and not more than 0.5.

FIG. 1

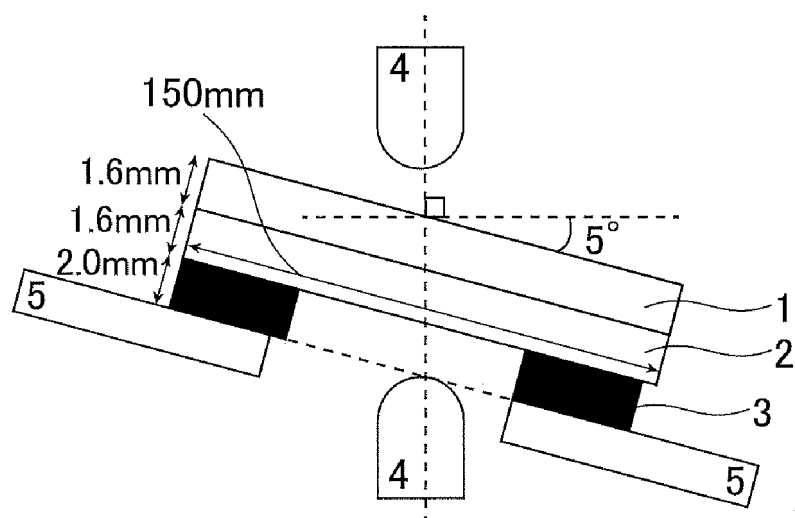
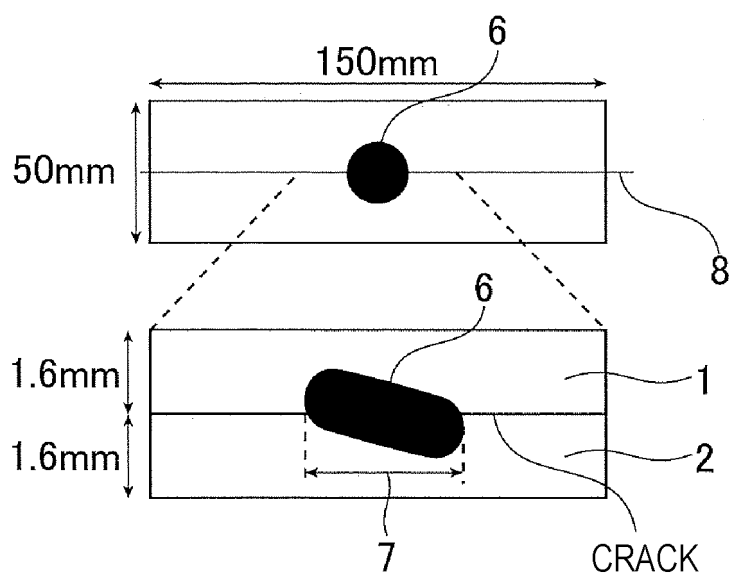


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/012038

A. CLASSIFICATION OF SUBJECT MATTER

C21D 9/46(2006.01)i; *C21D 9/56*(2006.01)i; *C22C 38/00*(2006.01)i; *C22C 38/04*(2006.01)i; *C22C 38/60*(2006.01)i;
C23C 2/02(2006.01)i; *C23C 2/06*(2006.01)i; *C23C 2/40*(2006.01)i

FI: C21D9/46 J; C21D9/56 101B; C22C38/00 301T; C22C38/04; C22C38/60; C23C2/02; C23C2/06; C23C2/40

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)

C21D9/46; C21D9/56; C22C38/00-38/60; C23C2/00-2/40

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/038801 A1 (JFE STEEL CORPORATION) 17 March 2016 (2016-03-17) claims	1-6
A	WO 2015/087549 A1 (JFE STEEL CORPORATION) 18 June 2015 (2015-06-18) claims	1-6
A	JP 2013-136809 A (NIPPON STEEL & SUMITOMO METAL CORP) 11 July 2013 (2013-07-11) claims	1-6
A	JP 2015-113504 A (JFE STEEL CORPORATION) 22 June 2015 (2015-06-22) claims	3-6

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

08 June 2023

Date of mailing of the international search report

20 June 2023

Name and mailing address of the ISA/JP

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Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/012038

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2016/038801 A1	17 March 2016	EP 3159420 A1 claims US 2017/0253943 A1 CN 106715726 A	
WO 2015/087549 A1	18 June 2015	EP 3081665 A1 claims US 2016/0304982 A1 CN 105814229 A JP 2016-53211 A	
JP 2013-136809 A	11 July 2013	(Family: none)	
JP 2015-113504 A	22 June 2015	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 6052270 B [0008]
- JP 6172297 B [0008]