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(54) PROCESS FOR PRODUCING STEEL SHEET AND DEVICE FOR CONTINUOUSLY ANNEALING STEEL SHEET

(57) The present method for manufacturing a high strength steel sheet having a tensile strength of 780 MPa or higher includes continuous annealing by heating a steel sheet having a predetermined chemical composition to 750°C to 900°C and holding the steel sheet in the temperature range for 0 seconds to 300 seconds, in which, during heating and holding, a hydrogen concentration in a furnace atmosphere is less than 10 volume%, when a temperature of the steel sheet is 700°C or lower, a furnace body average value is higher than -3.01 and lower than -0.07, when the temperature is higher than 700°C and 800°C or lower, the value is higher than -1.36 and lower than -0.07, when the temperature is higher than 800°C, the value is higher than -3.01 and -0.53 or lower, and a dew point is lower than -10°C.

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Description

[Technical Field of the Invention]

[0001] The present invention relates to a method for manufacturing a steel sheet and a device for continuous annealing a steel sheet and particularly to a method for manufacturing a high strength steel sheet which contains 0.050 mass% or more of C, 0.10 mass% or more of Si, and 1.20 mass% or more of Mn and has a tensile strength of 780 MPa or higher and a device for continuous annealing a steel sheet which is suitable for the method for manufacturing a high strength steel sheet.

[Related Art]

[0002] Recently, in the automotive field, for the purpose of the weight reduction of vehicle bodies which is intended to improve gas mileage or reduce the amount of CO_2 emitted and the improvement of collision safety, there has been an intensifying need for the use of high strength steel sheets for vehicle bodies, parts, and the like. Recently, high strength steel sheets having a tensile strength of 780 MPa or higher or 980 MPa or higher also have been in use.

[0003] However, the high-strengthening of steel sheets generally deteriorates material properties such as formability (workability) and the like. On the other side, these high strength steel sheets need to be, similar to soft steel sheets, formed in large quantities at a low cost and be provided as a variety of members. Therefore, the above described high strength steel sheets also need to have high ductility and favorable workability as well as high strength.

[0004] Here, in high strength steel sheets having a tensile strength of 780 MPa or higher, in order to impart high ductility and favorable workability, it is common to add an alloying element such as Si or Mn to steel.

[0005] On the other side, in the annealing of a steel sheet containing Si or Mn at a peak temperature of 800°C to 900°C, there has been a concern that Si or Mn may be precipitated, concentrated, and oxidized in the surface layer of a steel sheet and thus a Si oxide or a Si-Mn oxide may be exposed on the surface. In a case where a Si oxide or a Si-Mn oxide is exposed on the surface of a steel sheet as described above, there is a problem in that the plating property during plating treatments is deteriorated or the chemical convertibility before painting is degraded.

[0006] Regarding the above described problem, for example, Patent Document 1 proposes a technique in which, in a heat treatment of a high strength steel sheet in which the Si content is 0.4 mass% to 2.0 mass%, the steel sheet is reduced in a reducing atmosphere in which the air ratio in a direct flame reducing burner in a direct flame reduction furnace is set to 0.6 or higher or lower than 0.9, a Si oxide film is controlled to be thin, and then the logarithm log (P_{H2O}/P_{H2}) of the water partial pressure P_{H2O} to the hydrogen partial pressure P_{H2} in an indirect heating furnace which is intended to carry out hydrogen reduction is set to -1.6 or higher and -0.5 or lower, thereby suppressing the exposure of the Si oxide on the steel sheet surface and improving the plating property of the steel sheet.

[0007] In addition, Patent Document 2 proposes a method in which, in a continuous annealing line having a direct flame heating furnace and an indirect reduction furnace, a steel sheet is oxidized by direct flame heating before reduction in the reduction furnace, and then, in a case where the peak temperature of the steel sheet is set to T (923K ≤ T ≤ 1,173K), the logarithm log P_{O2} of the oxygen partial pressure in the atmosphere of the furnace is reduced in a range of $-0.000.074 \times T^2 + 0.105 \times T - 0.2 \times [Si\%]^2 + 2.1 \times [Si\%] - 98.8 \leq \log P_{O2} \leq -0.000.078 \times T^2 + 0.107 \times T - 90.4$, thereby manufacturing a high strength galvannealed steel sheet having excellent formability.

[0008] Furthermore, Patent Document 3 proposes a technique in which, in the continuous annealing of a cold rolled steel sheet, during warming, the steel sheet is heated using a direct flame burner in which the steel sheet temperature is 550°C or higher and the air ratio is 0.95 or higher so as to oxidize the surface of the steel sheet, then, the steel sheet is heated and warmed using a direct flame burner in which the air ratio is 0.89 or lower until the steel sheet temperature reaches 750°C or higher, and then the steel sheet is soaking-annealed in a furnace in which the dew point is -25°C or lower, thereby improving the chemical convertibility.

[0009] In addition, Patent Document 4 proposes a technique in which, in the continuous annealing of a steel sheet, in a heating process, the dew point in the atmosphere is set to -40°C or lower in a case where the temperature in a heating furnace is 600°C or higher and A°C or lower (650 ≤ A ≤ 780), and the dew point in the atmosphere is set to -10°C or higher in a case where the temperature in the heating furnace is higher than A°C and B°C or lower (800 ≤ B ≤ 900), thereby improving the chemical convertibility.

[0010] In addition, Patent Documents 5 and 6 propose a technique in which, during the continuous annealing including a preheating, a warming, and a recrystallization of a steel sheet, in the preheating, the ratio (P_{H2O}/P_{H2}) of the water vapor partial pressure to the hydrogen partial pressure in the continuous annealing atmosphere is controlled so as to satisfy a condition of Expression (1) below from the relationship with the preheating temperature Tp, in the warming, the recrystallization temperature Tr is set to 650°C to 900°C, the ratio (P_{H2O}/P_{H2}) of the water vapor partial pressure to the hydrogen partial pressure in in the annealing atmosphere is controlled so as to satisfy a condition of Expression (2) below from the relationship with the recrystallization temperature Tr and the warming rate reaches 1 °C/second to 20

°C/second, and, in the recrystallization, the ratio (P_{H2O}/P_{H2}) of the water vapor partial pressure to the hydrogen partial pressure in the annealing atmosphere is controlled so as to satisfy a condition of Expression (3) below from the relationship with the recrystallization temperature Tr and the holding time reaches 40 seconds to 600 seconds, thereby improving the chemical convertibility.

$$\text{(1) Expression: } \log (P_{H2O}/P_{H2}) \leq -2.8 \times 10^{-6} T_P^2 + 6.8 \times 10^{-3} T_p - 4.8$$

$$\text{(2) Expression: } 5.3 \times 10^{-8} \times T_r^2 + 1.4 \times 10^{-5} \times T_r - 0.01 \leq P_{H2O}/P_{H2} \leq 6.4 \times 10^{-7} \times T_r^2 + 1.7 \times 10^{-4} T_r - 0.1$$

$$\text{(3) Expression: } P_{H2O}/P_{H2} \leq 5.3 \times 10^{-8} \times T_r^2 + 1.4 \times 10^{-5} \times T_r - 0.01$$

[0011] In addition, Patent Document 7 discloses a method for manufacturing a hot-dip galvanized steel sheet in which a steel sheet containing Si, Mn, and Al in a specific ratio is controlled so that the logarithm ratio between the hydrogen partial pressure and the water vapor partial pressure in the atmospheric gas in a reduction furnace satisfies -

$$1.39 \leq \log (P_{H2O}/P_{H2}) \leq -0.695.$$

[0012] However, the above described techniques described in Patent Documents 1 to 7 have the following problems.

[0013] That is, Patent Documents 1 to 3 are characterized in that a direct flame heated portion is provided and the air ratio in a direct flame burner is controlled. However, in recent years, annealing devices constituted of indirect heating furnaces alone without direct flame heated portions have been the mainstream of device for continuous annealing that anneals steel sheets. To the above described continuous annealing furnaces not having any direct flame heated portions, the application of methods in which the air ratio in a direct flame burner is controlled as described in Patent Documents 1 to 3 is not possible. In addition, in methods in which a steel sheet is oxidized using a direct flame burner before reduction as described in Patent Documents 1 to 3, it becomes impossible to ensure a predetermined air ratio due to the high-temperature deterioration of the burner facility, a change in the amount of heat generated from combustion gas, or the like, and consequently, thick oxide films generated are incapable of completely preventing the formation of build-up (bumps) on a furnace roll in the furnace. The oxide films generated in the direct flame heating furnace peel off from the steel sheet and attach to the roll surface while the steel sheet is being wound around the roll in the furnace and generate pressing defect on the steel sheet, which is not preferable.

[0014] In addition, in a case where the atmosphere of the furnace is controlled under the conditions described in Patent Document 4, it is possible to suppress the exposure of the Si oxide on the surface, however it is necessary to set the dew point to -10°C or higher, and thus there is a problem in that the decarburization of the steel sheet is proceeded and the tensile strength or fatigue strength of the steel sheet is degraded. Particularly, in high strength steel sheets containing a large amount of C, decarburization-induced strength degradation is a significant problem.

[0015] In addition, in the conditions described in Patent Documents 5 and 6, there is a problem in that it is difficult to guarantee the appropriate conditions of the P_{H2O}/P_{H2} value in Expression (1) and Expression (3), the dew point, and the like due to an external change in the amount of moisture in gas or the deterioration of production facilities.

[0016] In addition, Patent Document 7 suggests that, in the manufacturing of a hot-dip galvanized steel sheet using a horizontal reduction furnace, the hydrogen concentration in the atmospheric gas in the furnace is set to 10% or higher. However, setting the hydrogen concentration in the atmospheric gas to 10% or higher requires a special facility, and thus a significant facility investment becomes necessary for the application of the above described suggestion.

[Prior Art Document]

[Patent Document]

[0017]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2007-191745

[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. 2006-233333

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. 2013-253322

[Patent Document 4] Japanese Unexamined Patent Application, First Publication No. 2012-072452

[Patent Document 5] Japanese Unexamined Patent Application, First Publication No. 2008-069445

[Patent Document 6] Japanese Unexamined Patent Application, First Publication No. 2008-121045

[Patent Document 7] Japanese Unexamined Patent Application, First Publication No. 2012-12683

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0018] The present invention has been made in consideration of the above described circumstances, and an object of the present invention is to provide a method for manufacturing a high strength steel sheet in which, in a continuous annealing furnace not having a direct flame heated portion, the atmosphere during annealing is controlled, whereby the exposure of Si oxides on the surface of the steel sheet is suppressed by oxidizing Si in the steel sheet, and the progress of decarburization of the steel sheet can be suppressed and a device for continuous annealing a steel sheet which is suitable for the above described method for manufacturing a high strength steel sheet. In the present invention, a high strength means that the tensile strength is 780 MPa or higher.

[Means for Solving the Problem]

[0019] As a result of intensive studies for achieving the above described object, the present inventors obtained the following findings.

(a) During heating for annealing, the internal oxidation of Si and decarburization are initiated in a temperature range of a steel sheet of 700°C to 750°C.
(b) In a range of 700°C to 800°C, particularly, 700°C to 750°C, when log (P_{H2O}/P_{H2}) which is a relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of a furnace is adjusted to an appropriate range, it is possible to oxidize Si in the furnace and suppress decarburization.
(c) Furthermore, in a range for heating a steel sheet of 700°C or lower or higher than 800°C, when log(P_{H2O}/P_{H2}) is adjusted to an appropriate range, it is possible to prevent the oxidation of the surface of the steel sheet or accelerate internal oxidation and suppress decarburization.
(d) When the dew point of the atmosphere in the furnace is set to lower than - 10°C during heating the steel sheet at higher than 800°C, it is possible to suppress decarburization and prevent the degradation of strength.

[0020] The present invention has been made on the basis of the above described findings. The gist thereof will be described below.

(1) A method for manufacturing a steel sheet according to an aspect of the present invention is a method for manufacturing a high strength steel sheet having a tensile strength of 780 MPa or higher, the method includes: a continuous annealing by heating a steel sheet containing as a chemical composition, by mass%, C: 0.050% to 0.40%, Si: 0.10% to 2.50%, Mn: 1.20% to 3.50%, Cr: 0% to 0.80%, Ni: 0% to 5.00%, Cu: 0% to 3.00%, Nb: 0% to 0.10%, Mg: 0% to 0.010%, Ti: 0% to 0.10%, B: 0% to 0.010%, and Mo: 0% to 0.5% and a remainder being Fe and impurities, in which P: limited to 0.100% or less, S: limited to 0.010% or less, Al: limited to 1.200% or less, and N: limited to 0.0100% or less, up to a temperature range of 750°C to 900°C and holding the steel sheet in the temperature range for 0 seconds to 300 seconds, in the continuous annealing, during the heating up to the temperature range and the holding in the temperature range, a hydrogen concentration in an atmosphere of a furnace is less than 10 volume%, when a temperature of the steel sheet is 700°C or lower, a furnace body average value of log (P_{H2O}/P_{H2}) which is a relationship between a water partial pressure P_{H2O} and a hydrogen partial pressure P_{H2} in the atmosphere of the furnace is in a range of Expression (i) below, when the temperature of the steel sheet is higher than 700°C and 800°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace is in a range of Expression (ii) below, and, when the temperature of the steel sheet is higher than 800°C, the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace is in a range of Expression (iii) below, and a dew point is lower than -10°C.

$$-3.01 < \log (P_{H2O}/P_{H2}) < -0.07 \quad (i)$$

$$-1.36 < \log (P_{H2O}/P_{H2}) < -0.07 \quad (ii)$$

$$-3.01 < \log (P_{H2O}/P_{H2}) < -0.53 \quad (iii)$$

(2) In the method for manufacturing a steel sheet according to (1), the steel sheet may contain, by mass%, one or more of Cr: 0.01% to 0.80%, Ni: 0.01% to 5.00%, Cu: 0.01% to 3.00%, Nb: 0.001% to 0.10%, Mg: 0.0001% to 0.010%, Ti: 0.001% to 0.10%, B: 0.0001% to 0.010%, and Mo: 0.01% to 0.5%.

(3) In the method for manufacturing a steel sheet according to (1) or (2), when the temperature of the steel sheet is higher than 700°C and 800°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace may be in a range of Expression (vii) below.

$$-1.00 < \log (P_{H2O}/P_{H2}) < -0.67 \quad (vii)$$

(4) A device for continuous annealing a steel sheet according to another aspect of the present invention is a device for continuous annealing a steel sheet containing as a chemical composition, by mass%, C: 0.050% to 0.40%, Si: 0.10% to 2.50%, Mn: 1.20% to 3.50%, Cr: 0% to 0.80%, Ni: 0% to 5.00%, Cu: 0% to 3.00%, Nb: 0% to 0.10%, Mg: 0% to 0.010%, Ti: 0% to 0.10%, B: 0% to 0.010%, and Mo: 0% to 0.5% and a remainder being Fe and impurities, in which P: limited to 0.100% or less, S: limited to 0.010% or less, Al: limited to 1.200% or less, and N: limited to 0.0100% or less, the device includes: an in-furnace atmosphere adjustment unit for setting a hydrogen concentration in an atmosphere of a furnace to less than 10 volume%, when a temperature of the steel sheet is 700°C or lower, adjusting a furnace body average value of log (P_{H2O}/P_{H2}) which is a relationship between a water partial pressure P_{H2O} and a hydrogen partial pressure P_{H2} in the atmosphere of the furnace to be in a range of Expression (iv) below, when the temperature of the steel sheet is higher than 700°C and 800°C or lower, adjusting the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace to be in a range of Expression (v) below, when the temperature of the steel sheet is higher than 800°C, adjusting the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace to be in a range of Expression (vi) below, and adjusting a dew point to be lower than -10°C.

$$-3.01 < \log (P_{H2O}/P_{H2}) < -0.07 \quad (iv)$$

$$-1.36 < \log (P_{H2O}/P_{H2}) < -0.07 \quad (v)$$

$$-3.01 < \log (P_{H2O}/P_{H2}) \leq -0.53 \quad (vi)$$

[Effects of the Invention]

[0021] According to the method for manufacturing a steel sheet according to the above described aspect of the present invention which is constituted as described above, in the furnace in which the hydrogen concentration in the atmosphere is set to less than 10 volume%, in a temperature range of higher than 700°C and 800°C or lower in which the internal oxidation of Si and decarburization is initiated, the furnace body average value of log (P_{H2O}/P_{H2}) which is relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace is set to lower than -0.07, and thus it is possible to suppress the occurrence of decarburization. In addition, in the above described temperature range of the steel sheet, the furnace body average value of log (P_{H2O}/P_{H2}) is set to higher than -1.36, it is possible to oxidize Si in the steel sheet and suppress the exposure of Si oxides on the steel sheet surface. In addition, in a temperature range of 700°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) is set in a range of $-3.01 < \log (P_{H2O}/P_{H2}) < -0.07$, in a range for heating steel sheet of higher than 800°C, the furnace body average value of log (P_{H2O}/P_{H2}) is set in a range of $-3.01 < \log (P_{H2O}/P_{H2}) < -0.53$, and the dew point is set to lower than - 10°C, and thus the it is possible to prevent the surface oxidation of the steel sheet or accelerate the internal oxidation. In addition, it is possible to cause the internal oxidation of Si and reliably suppress the progress of decarburization.

[0022] According to the method for manufacturing a steel sheet according to the above described aspect of the present invention, it becomes possible to manufacture a high strength steel sheet having a tensile strength of 780 MPa or higher is ensured and the fatigue strength, the plating property, and the chemical convertibility are excellent without deteriorating properties such as elongation or workability more than in the related art.

[0023] In addition, according to the device for continuous annealing a steel sheet having the above descried constitution, since the in-furnace atmosphere adjustment unit for setting the furnace body average value of log (P_{H2O}/P_{H2}) which is the relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace to a range of -1.36 < log (P_{H2O}/P_{H2}) < -0.07 in a temperature range in which the temperature of the steel sheet during heating is higher than 700°C and 800°C or lower is provided, it is possible to suppress the exposure of Si oxides on the surface of the steel sheet through the internal oxidation of Si and suppress decarburization. Therefore, the use of the device for continuous annealing a steel sheet having the above described constitution enables the manufacturing of a high strength steel sheet having a tensile strength of 780 MPa or higher and, furthermore, is excellent in terms of a plating property and a chemical convertibility. In addition, in a temperature range of 700°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) is set in a range of -3.01 < log (P_{H2O}/P_{H2}) < -0.07, and in a range that the steel sheet is heated at higher than 800°C, the furnace body average value of log (P_{H2O}/P_{H2}) is set in a range of -3.01 < log (P_{H2O}/P_{H2}) < -0.53 in, whereby it is possible to prevent surface oxidation, accelerate internal oxidation, and suppress decarburization.

[0024] That is, according to the above described aspect of the present invention, it is possible to provide a method for manufacturing a high strength steel sheet in which the atmosphere during annealing is controlled, whereby the exposure of Si oxides on the surface of the steel sheet is suppressed by oxidizing Si in the steel sheet, and the progress of decarburization of the steel sheet can be suppressed and a device for continuous annealing a steel sheet which is suitable for the above described method for manufacturing a high strength steel sheet. In addition, steel sheets obtained using the manufacturing method and the device for continuous annealing have a high strength and are excellent in terms of a plating property and a chemical convertibility.

[Brief Description of the Drawings]

[0025] Fig. 1 is a schematic explanatory view showing a device for continuous annealing a steel sheet which is used in a method for manufacturing a steel sheet according to an embodiment of the present invention.

[Embodiments of the Invention]

[0026] Hereinafter, a method for manufacturing a steel sheet according to an embodiment of the present invention (in some cases, referred to as a method for manufacturing a steel sheet according to the present embodiment) and a device for continuous annealing a steel sheet according to an embodiment of the present invention (in some cases, referred to as a device for continuous annealing a steel sheet according to the present embodiment) will be described with reference to the accompanying drawing. However, the present invention is no limited to the following embodiment.

[0027] In the present embodiment, the subject is the manufacturing of a high strength steel sheet which is used, for example, in automotive applications and the like and has a tensile strength of 780 MPa or higher and preferably 980 MPa or higher.

[0028] The method for manufacturing a steel sheet according to the present embodiment has continuous annealing by heating a steel sheet containing as a chemical composition, by mass%, C: 0.050% to 0.40%, Si: 0.10% to 2.50%, Mn: 1.20% to 3.50%, Cr: 0% to 0.80%, Ni: 0% to 5.00%, Cu: 0% to 3.00%, Nb: 0% to 0.10%, Mg: 0% to 0.010%, Ti: 0% to 0.10%, B: 0% to 0.010%, and Mo: 0% to 0.5% and a remainder being Fe and impurities.

[0029] Here, processes other than the continuous annealing are not particularly limited and may be carried out using a well-known method depending on desired properties of the steel sheet. For example, as processes other than the continuous annealing which are generally carried out as necessary, processes of casting steel for obtaining a slab, hot rolling the slab for obtaining a steel sheet, cold rolling the steel sheet, pickling, temper rolling, or the like may be carried out using a well-known method. However, it is necessary that the continuous annealing is carried out under conditions described below.

[0030] First, the reasons for limiting the chemical composition of the steel sheet (high strength steel sheet) which is the manufacturing subject in the present embodiment will be described.

C: 0.050 mass% or more and 0.40 mass% or less

[0031] C is an essential element to form hard structures such as martensite, tempered martensite, bainite, and residual austenite and improve the strength of the steel sheet. Therefore, in order to set the tensile strength of the steel sheet to 780 MPa or higher after continuous annealing, the C content is set to 0.050 mass% or higher. In order to sufficiently increase the strength, the C content is preferably 0.075 mass% or more. On the other hand, when the C content is excessively increased, the weldability of the steel sheet is deteriorated, and thus the C content is set to 0.40 mass% or lower. The C content is preferably 0.30 mass% or lower.

Si: 0.10 mass% or more and 2.50 mass% or less

[0032] Si is an element having an action effect that ensures the elongation of the steel sheet so as to improve the strength without significantly impairing the workability. Therefore, in order to significantly ensure the workability and the strength, the Si content is set to 0.10 mass% or higher. In order to further improve the workability and the strength, the Si content is preferably 0.45 mass% or higher. On the other hand, when the Si content is excessively increased, the toughness is degraded and, conversely, the workability is deteriorated. Therefore, the Si content is set to 2.50 mass% or lower. The Si content is preferably 2.30 mass% or lower.

Mn: 1.20 mass% or more and 3.50 mass% or less

[0033] Mn is an element having the same action effect as Si. Therefore, in order to significantly ensure the workability and the strength, the Mn content is set to 1.20 mass% or higher. In order to further improve the workability and the strength, the Mn content is preferably 1.50 mass% or higher. On the other hand, when the Mn content is excessively increased, the weldability is deteriorated. Therefore, the Mn content is set to 3.50 mass% or lower. The Mn content amount is preferably 3.30 mass% or lower.

[0034] The high strength steel sheet which is the subject of the present embodiment, basically, contains the above described chemical compositions and has a remainder being Fe and impurities. However, in order to satisfy the required properties, although not essential, Cr, Ni, Cu, Nb, Mg, Ti, B, and Mo may be added to the steel sheet in ranges described below for the purpose of additional high strengthening or further improving the formability. In addition, even when the Cr content, Ni content, Cu content, Nb content, Mg content, Ti content, B content, and Mo content are below the lower limits of the contents described below, the effects of the present invention are not impaired. None of Cr, Ni, Cu, Nb, Mg, Ti, B, and Mo is essential to satisfy the required properties, and thus the lower limits of the contents thereof are 0%.

[0035] The impurities refer to elements that are incorporated during the industrial manufacturing of steel due to raw materials such as minerals or scraps or other causes. The amount of the impurities is preferably small, and regarding P content, S content, Al content, and N content among impurities, particularly, it is preferably that P: limited to 0.100 mass% or lower, S: limited to 0.010 mass% or lower, Al: limited to 1.200 mass% or lower, and N: 0.0100 mass% or lower.

Cr: 0.01 mass% or more and 0.80 mass% or less

[0036] Cr is an element having an effect for suppressing phase transformation at high temperatures and increasing the strength of the steel sheet. In the case of obtaining the above described effect, the Cr content is preferably 0.01 mass% or higher. On the other hand, when the C content exceeds 0.80 mass%, the workability in hot rolling is impaired, and the productivity is degraded. Therefore, even when Cr is added to the steel sheet, the Cr content is set to 0.80 mass% or lower. The Cr content is preferably 0.40 mass% or lower.

Ni: 0.01 mass% or more and 5.00 mass% or less

[0037] Ni is an element having an effect for suppressing phase transformation at high temperatures and increasing the strength of the steel sheet. In the case of obtaining the above described effect, the Ni content is preferably 0.01 mass% or higher. On the other hand, when the Ni content exceeds 5.00 mass%, the weldability is impaired. Therefore, even when in Ni is added to the steel sheet, the Ni content is set to 5.00 mass% or lower. The Ni content is preferably 2.00 mass% or lower.

Cu: 0.01 mass% or more and 3.00 mass% or less

[0038] Cu is an element that increases the strength of the steel sheet when Cu is in the steel as fine particles. In the case of obtaining the above described effect, the Cu content is preferably 0.01 mass% or higher. On the other hand, when the Cu content exceeds 5.00 mass%, the weldability is impaired. Therefore, even when Cu is added to the steel sheet, the Cu content is set to 3.00 mass% or lower. The Cu content is preferably 2.00 mass% or lower.

Nb: 0.001 mass% or more and 0.10 mass% or less

[0039] Nb is an element that contributes to an increase in the strength of the steel sheet due to precipitation strengthening, fine grain strengthening by the suppression of the growth of ferrite crystal grains, and dislocation strengthening through the suppression of recrystallization. In the case of obtaining the above described effect, the Nb content is preferably 0.001 mass% or higher. On the other hand, when the Nb content exceeds 0.10 mass%, the amount of a carbonitride precipitated is increased, and the formability is deteriorated. Therefore, even when Nb is added to the steel sheet, the Nb content is set to 0.10 mass% or lower. The Nb content is preferably 0.05 mass% or lower.

Mg: 0.0001 mass% or more and 0.010 mass% or less

[0040] Mg is an effective element for improving the formability. In the case of obtaining the above described effect, the Mg content is preferably 0.0001 mass% or higher. On the other hand, when the Mg content exceeds 0.010 mass%, conversely, there is a concern that the ductility may be impaired. Therefore, even when Mg is added to the steel sheet, the Mg content is set to 0.010 mass% or lower. The Mg content is preferably 0.005 mass% or lower.

Ti: 0.001 mass% or more and 0.10 mass% or less

[0041] Ti is an element that contributes to an increase in the strength of the steel sheet due to precipitation strengthening, fine grain strengthening by the suppression of the growth of ferrite crystal grains, and dislocation strengthening through the suppression of recrystallization. In the case of obtaining the above described effect, the Ti content is preferably 0.001 mass% or higher. On the other hand, when the Ti content exceeds 0.10 mass%, the amount of a carbonitride precipitated is increased, and the formability is deteriorated. Therefore, even when Ti is added to the steel sheet, the Ti content is set to 0.10 mass% or lower. The Ti content is preferably 0.05 mass% or lower.

B: 0.0001 mass% or more and 0.010 mass% or less

[0042] B is an effective element for suppressing phase transformation at high temperatures and increasing the strength of the steel sheet. In the case of obtaining the above described effect, the B content is preferably 0.0001 mass% or higher. On the other hand, when the B content exceeds 0.010 mass%, the workability in hot rolling is impaired, and the productivity is degraded. Therefore, even when in B is added to the steel sheet, the B content is set to 0.010 mass% or lower. The B content is preferably 0.005 mass% or lower.

Mo: 0.01 mass% or more and 0.5 mass% or less

[0043] Mo is an effective element for suppressing phase transformation at high temperatures and increasing the strength of the steel sheet. In the case of obtaining the above described effect, the Mo content is preferably 0.01 mass% or higher. On the other hand, when the Mo content exceeds 0.5 mass%, the workability in hot rolling is impaired, and the productivity is degraded. Therefore, even when Mo is added to the steel sheet, the Mo content is set to 0.5 mass% or lower. The Mo content is preferably 0.25 mass% or lower.

[0044] Next, the continuous annealing will be described.

[0045] In the continuous annealing, a steel sheet 1 mounted in a device for continuous annealing steel sheet 10 as shown in Fig. 1 is heated to, for example, 750°C to 900°C, held in the temperature range for 0 seconds to 300 seconds, and then cooled.

[0046] At this time, if the atmosphere of a furnace is not controlled, there are cases in which Si and Mn in the steel sheet 1 are precipitated and concentrated in the surface layer of the steel sheet 1 and are exposed on the surface of the steel sheet 1 in a Si oxide or a Si-Mn oxide form. In addition, there are cases in which annealing causes decarburization and degrades the strength of the steel sheet 1. Holding the steel sheet for zero seconds means that the steel sheet is warmed and then immediately cooled at a point in time at which the steel sheet reaches a predetermined temperature of 750°C to 900°C.

[0047] In the continuous annealing of the method for manufacturing a steel sheet according to the present embodiment, it is possible to suppress the formation of oxides on the surface of the steel sheet 1 by controlling the furnace body average value of log (P_{H2O}/P_{H2}) which is a relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace as described below. In the case of carrying out the above described control, a device for continuous annealing a steel sheet according to the present embodiment described below is preferably used.

<Furnace Body Average Value of log (P_{H2O}/P_{H2}) When Temperature of Steel Sheet Is Higher Than 700°C and 800°C or Lower>

[0048] In the continuous annealing of the method for manufacturing a steel sheet according to the present embodiment, when the temperature of the steel sheet 1 is higher than 700°C and 800°C or lower in which the internal oxidation of Si and decarburization are initiated, the furnace body average value of log (P_{H2O}/P_{H2}) which is a relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace of the device for continuous annealing 10 is set to higher than -1.36 and lower than -0.07. When log (P_{H2O}/P_{H2}) is set in the above described range, it is possible to oxidize Si in the steel sheet 1, suppress the exposure of Si oxides on the surface of the steel sheet 1, and suppress the occurrence of decarburization. As a result, the tensile strength and the fatigue strength are ensured, and furthermore, it becomes possible to manufacture high strength steel sheets having an excellent plating property and an excellent chemical convertibility. Here, "log" indicates a common logarithm.

[0049] In a case where the furnace body average value of log (P_{H2O}/P_{H2}) which is above described relationship is -1.36 or lower, the internal oxidation of Si is not sufficiently caused, Si oxides are exposed on the surface of the steel sheet 1, and the plating property and the chemical convertibility are deteriorated. On the other side, when the furnace body average value of log (P_{H2O}/P_{H2}) which is above described relationship is -0.07 or higher, decarburization is proceeded, and there is a concern that the strength of the steel sheet 1 may be degraded.

[0050] In order to further suppress the exposure of Si oxides on the surface and further decrease decarburization from the steel sheet, in a temperature range in which the temperature of the steel sheet is higher than 700°C and 800°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) which is relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace is preferably set in a range of -1.00 < log (P_{H2O}/P_{H2}) < -0.67.

[0051] Here, the reason for specifying log (P_{H2O}/P_{H2}) in the steel sheet temperature range of higher than 700°C and 800°C or lower is that, in a case where the furnace body average value of log (P_{H2O}/P_{H2}) is set to -1.36 < log (P_{H2O}/P_{H2}) < -0.07 only in a range of 700°C to 750°C which is a temperature range during occurring an internal oxidation, there are cases in which internal oxidation is uneven and insufficient. When the steel sheet is heated up to a range of 800°C or lower at the above described P_{H2O}/P_{H2}, internal oxidation is sufficiently caused, and it also becomes possible to suppress decarburization.

<Furnace Body Average Value of log (P_{H2O}/P_{H2}) When Temperature of Steel Sheet Is Higher Than 800°C>

[0052] In the method for manufacturing a steel sheet according to the present embodiment, in a case where the temperature of the steel sheet is higher than 800°C (including when the steel sheet is heated and when the steel sheet is held), the furnace body average value of log (P_{H2O}/P_{H2}) is controlled so as to be in a range of -3.01 < log (P_{H2O}/P_{H2}) < -0.53. When log (P_{H2O}/P_{H2}) is set in the above described range, internal oxidation is sufficiently satisfied, and the suppression of decarburization becomes possible.

[0053] In a case where the furnace body average value of log (P_{H2O}/P_{H2}) becomes higher than -0.53 in a temperature range of higher than 800°C, decarburization is proceeded, and there is a concern that the strength of the steel sheet 1 may be degraded. In order to further decrease decarburization, the furnace body average value of log (P_{H2O}/P_{H2}) in the temperature range of higher than 800°C is preferably lower than - 0.67. In addition, in order to further decrease decarburization, the furnace body average value of log (P_{H2O}/P_{H2}) in the temperature range of higher than 800°C is also preferably lower than the furnace body average value of log (P_{H2O}/P_{H2}) in the temperature range of higher than 700°C and 800°C or lower.

[0054] On the other side, regarding the lower limits of each log (P_{H2O}/P_{H2}) in a case where the temperature of the steel sheet is 700°C or lower and a case where the temperature of the steel sheet is higher than 800°C, an achievable value in terms of actual manufacturing is set to -3.01 outside a range of 700°C to 800°C.

[0055] In a case where the annealing temperature of the steel sheet is set to 800°C or lower, it is not necessary to consider log (P_{H2O}/P_{H2}) at higher than 800°C.

<Furnace Body Average Value of log (P_{H2O}/P_{H2}) When Temperature of Steel Sheet Is 700°C or Lower>

[0056] In a case where the temperature of the steel sheet is 700°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) is controlled so as to be higher than - 3.01 and lower than -0.07, that is, -3.01 < log (P_{H2O}/P_{H2}) < -0.07.

[0057] In a temperature range of 700°C or lower as well, in a case where the furnace body average value of log (P_{H2O}/P_{H2}) reaches -0.07 or higher, the surface of the steel sheet 1 is oxidized, and it becomes impossible to accelerate internal oxidation at a subsequent temperature of higher than 700°C and 800°C or lower. Therefore, the furnace body average value of log (P_{H2O}/P_{H2}) is set to lower than -0.07. The furnace body average value of log (P_{H2O}/P_{H2}) is preferably lower than -0.67.

[0058] On the other side, regarding the lower limits of each log (P_{H2O}/P_{H2}) in a case where the temperature of the steel sheet is 700°C or lower and a case where the temperature of the steel sheet is higher than 800°C, an achievable value in terms of actual manufacturing is set to -3.01 outside the range of 700°C to 800°C.

[0059] A method for controlling log (P_{H2O}/P_{H2}) in the respective temperature ranges is not limited; however, in a case where the device for continuous annealing steel sheet 10 according to the present embodiment is used, log (P_{H2O}/P_{H2}) can be controlled by introducing water vapor or humidified gas into the furnace that is set to an atmosphere including a predetermined H_2 gas through atmospheric gas introduction portions 15. In addition, in the case of more finely controlling log (P_{H2O}/P_{H2}) in the respective temperature ranges, the atmospheric gas introduction portions may be provided in individual heating bands and soaking bands respectively. In this case, atmospheric gases or water vapors having different compositions may be introduced from the respective atmospheric gas introduction portions.

[0060] Here, the internal oxidation of Si refers to a phenomenon in which oxygen and Si diffused in the steel sheet 1 react with each other and thus a Si oxide is precipitated. The internal oxidation occurs at a location approximately 0.1 to 20 μm deep from the surface of the steel sheet 1.

[0061] In the present embodiment, in ferrite in a surface layer area of the steel sheet, a region in which the number of Si oxide grains having a maximum length of 25 nm or longer is 1.0 x 10^{12} grains/m^2 or more will be defined as an internal oxidation layer of Si, and, when the depth of the internal oxidation layer is 0.1 μm or more, it is possible to determine that internal oxidation is sufficient. The depth location of the internal oxidation layer of Si can be obtained as described below. A specimen is sampled from a sheet thickness cross section parallel to the rolling direction of the steel sheet as an observed section, the observed section is polished and Nital-etched, and regions having a rectangular shape that is 1.0 μm long in the thickness direction of the steel sheet and 20 μm long in the rolling direction are set at three or more places using a field emission scanning electron microscope (FE-SEM) at a magnification of 5,000 times or higher. The number of Si oxide grains is counted in each of the regions, in a case where 10 or more Si oxide grains are present, the region is considered as the internal oxidation layer of Si, and the average value of the maximum depths of regions in which 10 or more Si oxide grains are present is considered as the depth location of the internal oxidation layer of Si.

[0062] The internal oxidation of Si occurs in a case where the diffusion rate of oxygen into the inside of the steel sheet 1 is faster than the diffusion rate of Si into the surface of the steel sheet 1 and is more likely to occur in a case where the concentration of oxygen in the atmosphere is high and the amount of Si in the steel sheet 1 is small. Therefore, log (P_{H2O}/P_{H2}) and the dew point of the atmospheric gas in the furnace in the above described temperature range are preferably adjusted depending on the amount of Si in the steel sheet 1.

[0063] In the above description, the Si oxide has been described, however Mn is also an element that is likely to be precipitated and concentrated in the surface layer together with Si during annealing and is an element having a concern of being exposed on the surface of the steel sheet as a Si-Mn oxide and thus deteriorating the plating property and the chemical convertibility. However, according to the method for manufacturing a steel sheet according to the present embodiment, the atmosphere of the furnace is controlled during heating for annealing, whereby it is possible to suppress the exposure of not only a Si oxide but also a Si-Mn oxide on the surface of the steel sheet, and it becomes possible to manufacture high strength steel sheets having an excellent plating property and an excellent chemical convertibility.

[0064] In addition, in the present embodiment, when the thickness of a decarburization layer is 70 μm or less, it is possible to determine that the progress of decarburization can be suppressed. In the present embodiment, an area fraction S1 of a hard structure at a sheet thickness 1/4 portion of the steel sheet and an area fraction S2 of the hard structure in the surface layer area of the steel sheet are compared with each other, and the maximum depth location at which S2/S1 reaches 0.40 or less is considered as the thickness of the decarburization layer. The hard structure refers to a structure made of one or more of martensite, tempered martensite, bainite, and residual austenite. Regarding an area ratio, a specimen is sampled from a sheet thickness cross section parallel to the rolling direction of the steel sheet as an observed section, the observed section is polished and Nital-etched, and regions are observed and obtained at three or more places using a field emission scanning electron microscope (FE-SEM) at a magnification of 500 times to 3,000 times. That is, in individual observation regions, 50 μm or longer parallel lines are drawn on the sheet surface of the steel sheet, the total length L of the lines overlapping the hard structure is obtained, the ratios L/L0 to the length L0 of the line are obtained, and the average value thereof is considered as the area fraction S2 of the hard structure at the depth location.

[0065] The furnace body average value of log (P_{H2O}/P_{H2}) in each of the temperature ranges can be measured as described below.

[0066] First, at each of a location in the furnace at which the temperature reaches 700°C or lower, a location at which the temperature reaches higher than 700°C and 800°C or lower, and a location at which the temperature reaches higher than 800°C, the dew points and the concentrations of hydrogen are measured using a well-known measurement instrument at a total of five places including at least one place from each of the upper stage, the middle stage, and the lower stage of the furnace body. In addition, the average values are considered as the dew point and the hydrogen concentration in the corresponding temperature range. In addition, on the basis of the measured dew points, the water partial pressure (P_{H2O}) in the corresponding temperature range is obtained using the Tetens expression.

[0067] On the other side, the temperature of the steel sheet in the furnace becomes the same as the temperature in the furnace. That is, for example, at a location at which the temperature in the furnace reaches higher than 700°C and 800°C or lower, the temperature of the steel sheet also reaches higher than 700°C and 800°C or lower.

[0068] According to the method for manufacturing a steel sheet according to the present embodiment, it is possible to manufacture high strength steel sheets having an excellent plating property and an excellent chemical convertibility and having a tensile strength of 780 MPa or higher.

[0069] Next, the device for continuous annealing steel sheet 10 according to the present embodiment will be described with reference to the accompanying drawing. The device for continuous annealing steel sheet 10 according to the present embodiment is suitable to carry out the above described continuous annealing according to the present embodiment.

[0070] The device for continuous annealing steel sheet 10 shown in Fig. 1 is a device for annealing the steel sheet 1 while travelling the steel sheet, and the steel sheet 1 is mounted in the device for continuous annealing steel sheet 10 from the bottom left of Fig. 1. The device for continuous annealing steel sheet 10 includes a first heating band 11 which is located on the upstream side in the travelling direction of the steel sheet 1 and heats the steel sheet up to 700°C or lower, a second heating band 12 which is located on the downstream side of the first heating band 11 and heats the steel sheet up to higher than 700°C and 800°C or lower, a third heating band 13 which is located on the downstream side of the second heating band 12 and heats the steel sheet to a temperature range of higher than 800°C, and a soaking band 14 which is located on the rear stage side of the third heating band 13. In the device for continuous annealing 10, the first heating band 11, the second heating band 12, the third heating band 13, and the soaking band 14 are all indirect heating type atmospheric furnaces. The inside of the furnace is controlled to an atmosphere having a predetermined hydrogen concentration.

[0071] In addition, in the second heating band 12 of the device for continuous annealing steel sheet 10 according to the present embodiment, the atmospheric gas introduction portions 15 (in-furnace atmosphere adjustment unit) for supplying water vapor or humidified gas into the furnace are provided so as to face the upstream side in the travelling direction of the steel sheet 1.

[0072] Due to the supply of water vapor or the like from the atmospheric gas introduction portions 15, when the steel sheet is heated at a temperature at which the temperature of the steel sheet 1 is higher than 700°C and 800°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) which is the relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace can be controlled in a range of $-1.36 < \log (P_{H2O}/P_{H2}) < -0.07$.

[0073] In addition, due to the supply of water vapor or the like from the atmospheric gas introduction portions 15, in the first heating band 11, the furnace body average value of log (P_{H2O}/P_{H2}) can be controlled to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.07$, in a range of higher than 800°C in the third heating band 13, the furnace body average value of log (P_{H2O}/P_{H2}) can be controlled to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.53$, and, in the soaking band 14, the furnace body average value of log (P_{H2O}/P_{H2}) can be controlled to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.07$ in a case where the temperature is 800°C or lower and in a range of $-3.01 < \log (P_{H2O}/P_{H2}) < -0.53$ in a case where the temperature is higher than 800°C. In order to more accurately control log (P_{H2O}/P_{H2}) of the first heating band 11, the third heating band 13, or the soaking band 14, atmospheric gas introduction portions may be further provided in the first heating band 11, the third heating band 13, or the soaking band 14.

[0074] In addition, due to the supply of water vapor or the like from the atmospheric gas introduction portions, it is also possible to control the dew point of the atmosphere in the furnace or the hydrogen concentration in the atmosphere of the furnace in the furnace when the temperature of the steel sheet is higher than 800°C.

[0075] When continuous annealing is carried out using the device for continuous annealing steel sheet 10 according to the present embodiment, it is possible to manufacture high strength steel sheets which have a predetermined strength and have an excellent plating property and an excellent chemical convertibility.

[0076] Hitherto, the method for manufacturing a steel sheet and the device for continuous annealing steel sheet according to the present embodiment have been described. However, the present invention is not limited thereto and can be appropriately modified within the scope of the technical concept of the invention.

[0077] For example, the composition of the steel sheet is not limited to the composition exemplified in the present embodiment, and other elements may also be added to the composition depending on required properties.

[0078] In addition, in the method for manufacturing a steel sheet according to the present embodiment, the continuous annealing has been described to be preferably carried out using the device for continuous annealing shown in Fig. 1, however the present invention is not limited thereto. That is, a different continuous annealing furnace including an in-furnace atmosphere adjustment unit which is capable of controlling the furnace body average value of log (P_{H2O}/P_{H2}) which is the relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace to $-1.36 < \log (P_{H2O}/P_{H2}) < -0.07$ in a range in which the steel sheet is heated so that the temperature of the steel sheet 1 under heating reaches higher than 700°C and 800°C or lower, to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.07$ in a range in which the steel sheet is heated so that the temperature of the steel sheet 1 reaches 700°C or lower, and to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.53$ in a range in which the steel sheet is heated at higher than 800°C and controlling log (P_{H2O}/P_{H2}) to ranges according to the controls in the above described temperatures during heating in temperature maintaining bands by the highest heating temperature may also be used.

[Examples]

[0079] The results of experiments carried out to confirm the effects of the present invention will be described.

[0080] Continuous annealing was carried out on a cold rolled steel sheet having a sheet thickness of 1.2 mm which was manufactured using the device for continuous annealing steel sheet described in the above described embodiment and a well-known method. The composition of a steel sheet subjected to the annealing is as shown in Table 1.

[Table 1]

Steel type	Chemical composition (by mass%) / Remainder is Fe and impurities															
	C	Si	Mn	P	S	Al	N	Cr	Mo	Cu	Ni	Nb	Ti	Mg	B	Note
A	0.115	1.23	1.88	0.013	0.0009	0.052	0.0045									Invention Steel
B	0.078	1.55	3.20	0.015	0.0032	0.230	0.0071	0.25	0.05							Invention Steel
C	0.281	2.24	2.35	0.012	0.0018	0.069	0.0031			0.15	0.25					Invention Steel
D	0.205	0.38	2.95	0.021	0.0028	1.050	0.0022					0.025	0.035			Invention Steel
E	0.155	0.85	2.10	0.009	0.0027	0028	0.0028							0.005	0.002	Invention Steel
F	0.021	1.65	1.75	0.009	0.0040	0.035	00043									Comparative Steel
G	0.135	0.05	231	0.010	0.0021	0.090	0.0054									Comparative Steel
H	0.163	0.65	0.58	0.012	0.0025	0.120	0.0025									Comparative Steel

[0081] In a continuous annealing, continuous annealing was carried out under conditions (holding sheet temperatures and holding times) shown in Tables 2 to 8 using the device for continuous annealing steel sheet. The upper limit of the highest heating temperature was set to 900°C as an achievable value in terms of actual manufacturing. In addition, the furnace body average values of log (P_{H2O}/P_{H2}) which is the relationship between expression the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace during heating and holding were set to the conditions shown in Tables 2 to 8. The hydrogen concentration in the atmosphere of the furnace was 1.0% to 5.0%, and, when the steel sheet temperature exceeded 800°C, the dew points were all lower than -10°C.

[Table 2]

Test No.	Steel type	$\log(P_{H20}/P_{H2})$			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
1	A	-0.07	-	-	1.0	300	700	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
2	A	-0.07	-0.07	-0.07	1.0	300	900	19.6	86	GOOD	GOOD	GOOD	POOR	Comparative Example
3	A	-0.14	-0.14	-0.14	1.0	300	900	18.8	83	GOOD	GOOD	GOOD	POOR	Comparative Example
4	A	-0.22	-0.22	-0.22	1.0	300	900	18.0	81	GOOD	GOOD	GOOD	POOR	Comparative Example
5	A	-0.37	-0.37	-0.37	1.0	300	900	15.9	72	GOOD	GOOD	GOOD	POOR	Comparative Example
6	A	-0.53	-0.53	-0.53	1.0	300	900	13.2	66	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
7	A	-0.67	-0.67	-0.67	1.0	300	825	5.2	41	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
8	A	-0.67	-0.67	-0.67	1.0	300	850	6.9	48	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
9	A	-0.67	-0.67	-0.67	1.0	300	875	9.1	53	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
10	A	-0.67	-0.67	-0.67	1.0	300	900	11.6	59	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
11	A	-0.78	-0.78	-0.78	1.5	300	900	9.5	50	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
12	A	-0.89	-0.89	-0.89	2.0	300	900	6.9	43	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample

(continued)

Test No.	Steel type	$\log(P_{H20}/P_{H2})$ 700°C or lower	$\log(P_{H20}/P_{H2})$ Higher than 700°C and 800°C or lower	$\log(P_{H20}/P_{H2})$ Higher than 800°C	Concentration of hydrogen in furnace (%)	Holding time (sec)	Holding sheet temperature (°C)	Location of internal oxidation (µm)	Thickness of decarburization layer (µm)	Chemical conversion treatment	Plating property: Appearance	Plating property: Peeling test	Tensile strength	Note
13	A	-1.00	-1.00	-1.00	2.0	300	900	3.2	27	GOOD	GOOD	GOOD	GOOD	Invention Example
14	A	-1.17	-1.17	-1.17	3.0	300	825	0.3	0	FAIR	GOOD	GOOD	GOOD	Invention Example
15	A	-1.17	-1.17	-1.17	30	300	850	0.5	0	FAIR	GOOD	GOOD	GOOD	Invention Example
16	A	-1.17	-1.17	-1.17	4.0	300	875	0.9	1	FAIR	GOOD	GOOD	GOOD	Invention Example
17	A	-1.17	-1.17	-1.17	4.0	300	900	11	1	GOOD	GOOD	GOOD	GOOD	Invention Example
18	A	-1.26	-1.26	-1.26	5.0	300	900	0.4	0	FAIR	GOOD	GOOD	GOOD	Invention Example
19	A	-1.36	-1.36	-1.36	1.0	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
20	A	-0.53	-0.53	-	1.0	90	750	2.1	24	GOOD	GOOD	GOOD	GOOD	Invention Example
21	A	-0.53	-0.53	-	1.0	90	800	3.3	32	GOOD	GOOD	GOOD	GOOD	Invention Example
22	A	-0.67	-0.67	-	1.0	90	750	1.7	20	GOOD	GOOD	GOOD	GOOD	Invention Example
23	A	-0.67	-0.67	-	1.0	90	800	2.7	24	GOOD	GOOD	GOOD	GOOD	Invention Example
24	A	-0.78	-0.78	-	1.5	90	750	1.1	7	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	$\log(P_{H2O}/P_{H2})$			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of decarburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(µm)	(µm)		Appearance	Peeling test		
25	A	-0.78	-0.78	-	1.5	90	800	2.3	19	GOOD	GOOD	GOOD	GOOD	Invention Example
26	A	-0.89	-0.89	-	2.0	90	800	1.9	16	GOOD	GOOD	GOOD	GOOD	Invention Example
27	A	-1.00	-1.00	-	2.0	90	750	0.8	0	FAIR	GOOD	GOOD	GOOD	Invention Example
28	A	-1.00	-1.00	-	2.0	90	800	1.2	7	GOOD	GOOD	GOOD	GOOD	Invention Example
29	A	-1.17	-1.17	-	4.0	90	800	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

[Table 3]

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
30	B	-0.07	-	-	1.0	300	700	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
31	B	-0.07	-0.07	-0.07	1.0	300	900	20.3	87	GOOD	GOOD	GOOD	POOR	Comparative Example
32	B	-0.14	-0.14	-0.14	1.0	300	900	18.7	83	GOOD	GOOD	GOOD	POOR	Comparative Example
33	B	-0.22	-0.22	-0.22	1.0	300	900	18.2	79	GOOD	GOOD	GOOD	POOR	Comparative Example
34	B	-0.37	-0.37	-0.37	1.0	300	900	16.5	71	GOOD	GOOD	GOOD	POOR	Comparative Example
35	B	-0.53	-0.53	-0.53	1.0	300	900	13.2	63	GOOD	GOOD	GOOD	GOOD	Invention Example
36	B	-0.67	-0.67	-0.67	1.0	300	825	5.5	38	GOOD	GOOD	GOOD	GOOD	Invention Example
37	B	-0.67	-0.67	-0.67	1.0	300	850	7.6	45	GOOD	GOOD	GOOD	GOOD	Invention Example
38	B	-0.67	-0.67	-0.67	1.0	300	875	9.1	50	GOOD	GOOD	GOOD	GOOD	Invention Example
39	B	-0.67	-0.67	-0.67	1.0	300	900	12.0	56	GOOD	GOOD	GOOD	GOOD	Invention Example
40	B	-0.78	-0.78	-0.78	1.5	300	900	9.8	47	GOOD	GOOD	GOOD	GOOD	Invention Example
41	B	-0.89	-0.89	-0.89	2.0	300	900	7.2	40	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holding sheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(µm)	(µm)		Appearance	Peeling test		
42	B	-1.00	-1.00	-1.00	2.0	300	900	3.4	24	GOOD	GOOD	GOOD	GOOD	Invention Example
43	B	-1.17	-1.17	-1.17	3.0	300	825	0.4	0	FAIR	GOOD	GOOD	GOOD	Invention Example
44	B	-1.17	-1.17	-1.17	3.0	300	850	0.5	0	FAIR	GOOD	GOOD	GOOD	Invention Example
45	B	-1.17	-1.17	-1.17	4.0	300	875	0.8	1	FAIR	GOOD	GOOD	GOOD	Invention Example
46	B	-1.17	-1.17	-1.17	4.0	300	900	1.2	1	GOOD	GOOD	GOOD	GOOD	Invention Example
47	B	-1.26	-1.26	-1.26	50	300	900	0.4	0	FAIR	GOOD	GOOD	GOOD	Invention Example
48	B	-1.36	-1.36	-1.36	1.0	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
49	B	-0.53	-0.53	-	1.0	90	750	2.4	22	GOOD	GOOD	GOOD	GOOD	Invention Example
50	B	-0.53	-0.53	-	1.0	90	800	3.5	29	GOOD	GOOD	GOOD	GOOD	Invention Example
51	B	-0.67	-0.67	-	1.0	90	750	1.7	18	GOOD	GOOD	GOOD	GOOD	Invention Example
52	B	-0.67	-0.67	-	1.0	90	800	2.8	22	GOOD	GOOD	GOOD	GOOD	Invention Example
53	B	-0.78	-0.78	-	1.5	90	750	1.2	5	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
54	B	-0.78	-0.78	-	1.5	90	800	2.5	17	GOOD	GOOD	GOOD	GOOD	Invention Example
55	B	-0.89	-0.89	-	2.0	90	800	1.9	13	GOOD	GOOD	GOOD	GOOD	Invention Example
56	B	-1.00	-1.00	-	2.0	90	750	0.7	0	FAIR	GOOD	GOOD	GOOD	Invention Example
57	B	-1.00	-1.00	-	2.0	90	800	1.5	5	GOOD	GOOD	GOOD	GOOD	Invention Example
58	B	-1.17	-1.17	-	4.0	90	800	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

[Table 4]

Test No.	Steel type	$\log(P_{H2O}/P_{H2})$ 700°C or lower	$\log(P_{H2O}/P_{H2})$ Higher than 700°C and 800°C or lower	$\log(P_{H2O}/P_{H2})$ Higher than 800°C	Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property: Appearance	Plating property: Peeling test	Tensile strength	Note
					%	(sec)	(°C)	(μm)	(μm)					
59	C	-0.07	-	-	1.0	300	700	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
60	C	-0.07	-0.07	-0.07	1.0	300	900	19.8	90	GOOD	GOOD	GOOD	POOR	Comparative Example
61	C	-0.14	-0.14	-0.14	1.0	300	900	18.9	84	GOOD	GOOD	GOOD	POOR	Comparative Example
62	C	-0.22	-0.22	-0.22	1.0	300	900	18.3	82	GOOD	GOOD	GOOD	POOR	Comparative Example
63	C	-0.37	-0.37	-0.37	1.0	300	900	16.2	76	GOOD	GOOD	GOOD	POOR	Comparative Example
64	C	-0.53	-0.53	-0.53	1.0	300	900	13.1	68	GOOD	GOOD	GOOD	GOOD	Invention Example
65	C	-0.67	-0.67	-0.67	1.0	300	825	5.3	42	GOOD	GOOD	GOOD	GOOD	Invention Example
66	C	-0.67	-0.67	-0.67	1.0	300	850	6.4	49	GOOD	GOOD	GOOD	GOOD	Invention Example
67	C	-0.67	-0.67	-0.67	1.0	300	875	9.2	55	GOOD	GOOD	GOOD	GOOD	Invention Example
68	C	-0.67	-0.67	-0.67	1.0	300	900	12.1	61	GOOD	GOOD	GOOD	GOOD	Invention Example
69	C	-0.78	-0.78	-0.78	1.5	300	900	9.3	52	GOOD	GOOD	GOOD	GOOD	Invention Example
70	C	-0.89	-0.89	-0.89	2.0	300	900	6.8	45	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H2O}/P_{H2}) 700°C or lower	log (P_{H2O}/P_{H2}) Higher than 700°C and 800°C or lower	log (P_{H2O}/P_{H2}) Higher than 800°C	Concentration of hydrogen in furnace %	Holding time (sec)	Holding sheet temperature (°C)	Location of internal oxidation (µm)	Thickness of decarburization layer (µm)	Chemical conversion treatment	Plating property Appearance	Plating property Peeling test	Tensile strength	Note
71	C	-1.00	-1.00	-1.00	2.0	300	900	3.2	28	GOOD	GOOD	GOOD	GOOD	Invention Example
72	C	-1.17	-1.17	-1.17	3.0	300	825	0.3	0	FAIR	GOOD	GOOD	GOOD	Invention Example
73	C	-1.17	-1.17	-1.17	3.0	300	850	0.4	0	FAIR	GOOD	GOOD	GOOD	Invention Example
74	C	-1.17	-1.17	-1.17	4.0	300	875	0.8	1	FAIR	GOOD	GOOD	GOOD	Invention Example
75	C	-1.17	-1.17	-1.17	4.0	300	900	1.1	1	GOOD	GOOD	GOOD	GOOD	Invention Example
76	C	-1.26	-1.26	-1.26	50	300	900	0.4	0	FAIR	GOOD	GOOD	GOOD	Invention Example
77	C	-1.36	-1.36	-1.36	1.0	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
78	C	-0.53	-0.53	-	1.0	90	750	1.7	25	GOOD	GOOD	GOOD	GOOD	Invention Example
79	C	-0.53	-0.53	-	1.0	90	800	3.6	35	GOOD	GOOD	GOOD	GOOD	Invention Example
80	C	-0.67	-0.67	-	1.0	90	750	1.7	22	GOOD	GOOD	GOOD	GOOD	Invention Example
81	C	-0.67	-0.67	-	1.0	90	800	2.5	25	GOOD	GOOD	GOOD	GOOD	Invention Example
82	C	-0.78	-0.78	-	1.5	90	750	1.0	7	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H2O}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
83	C	-0.78	-0.78	-	1.5	90	800	2.3	20	GOOD	GOOD	GOOD	GOOD	Invention Example
84	C	-0.89	-0.89	-	2.0	90	800	2.1	15	GOOD	GOOD	GOOD	GOOD	Invention Example
85	C	-1.00	-1.00	-	2.0	90	750	0.5	0	FAIR	GOOD	GOOD	GOOD	Invention Example
86	C	-1.00	-1.00	-	2.0	90	800	1.4	7	GOOD	GOOD	GOOD	GOOD	Invention Example
87	C	-1.17	-1.17	-	4.0	90	800	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

[Table 5]

Test No.	Steel type	$\log (P_{H20}/P_{H2})$			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
88	D	-007	-	-	1.0	300	700	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
89	D	-0.07	-0.07	-0.07	1.0	300	900	19.1	86	GOOD	GOOD	GOOD	POOR	Comparative Example
90	D	-0.14	-0.14	-0.14	1.0	300	900	18.5	81	GOOD	GOOD	GOOD	POOR	Comparative Example
91	D	-0.22	-0.22	-0.22	1.0	300	900	17.4	76	GOOD	GOOD	GOOD	POOR	Comparative Example
92	D	-0.37	-0.37	-0.37	1.0	300	900	15.2	71	GOOD	GOOD	GOOD	POOR	Comparative Example
93	D	-0.53	-0.53	-0.53	1.0	300	900	123	65	GOOD	GOOD	GOOD	GOOD	Invention Example
94	D	-0.67	-0.67	-0.67	1.0	300	825	5.4	40	GOOD	GOOD	GOOD	GOOD	Invention Example
95	D	-0.67	-0.67	-0.67	1.0	300	850	6.6	48	GOOD	GOOD	GOOD	GOOD	Invention Example
96	D	-0.67	-0.67	-0.67	1.0	300	875	9.0	52	GOOD	GOOD	GOOD	GOOD	Invention Example
97	D	-0.67	-0.67	-0.67	1.0	300	900	11.4	60	GOOD	GOOD	GOOD	GOOD	Invention Example
98	D	-0.78	-0.78	-0.78	1.5	300	900	9.3	51	GOOD	GOOD	GOOD	GOOD	Invention Example
99	D	-0.89	-0.89	-0.89	2.0	300	900	6.3	44	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holding sheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
100	D	-1.00	-1.00	-1.00	2.0	300	900	3.7	25	GOOD	GOOD	GOOD	GOOD	Invention Example
101	D	-1.17	-1.17	-1.17	3.0	300	825	0.2	0	FAIR	GOOD	GOOD	GOOD	Invention Example
102	D	-1.17	-1.17	-1.17	3.0	300	850	0.6	0	FAIR	GOOD	GOOD	GOOD	Invention Example
103	D	-1.17	-1.17	-1.17	4.0	300	875	0.7	1	FAIR	GOOD	GOOD	GOOD	Invention Example
104	D	-1.17	-1.17	-1.17	4.0	300	900	1.1	1	GOOD	GOOD	GOOD	GOOD	Invention Example
105	D	-126	-1.26	-1.26	5.0	300	900	0.3	0	FAIR	GOOD	GOOD	GOOD	Invention Example
106	D	-1.36	-1.36	-1.36	1.0	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
107	D	-0.53	-0.53	-	1.0	90	750	2.1	24	GOOD	GOOD	GOOD	GOOD	Invention Example
108	D	-0.53	-0.53	- -	1.0	90	800	3.2	32	GOOD	GOOD	GOOD	GOOD	Invention Example
109	D	-0.67	-0.67	-	1.0	90	750	1.6	20	GOOD	GOOD	GOOD	GOOD	Invention Example
110	D	-0.67	-0.67	-	1.0	90	800	2.3	24	GOOD	GOOD	GOOD	GOOD	Invention Example
111	D	-0.78	-0.78	-	1.5	90	750	1.1	8	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
112	D	-0.78	-0.78	-	1.5	90	800	2.2	19	GOOD	GOOD	GOOD	GOOD	Invention Example
113	D	-0.89	-0.89	-	2.0	90	800	1.8	15	GOOD	GOOD	GOOD	GOOD	Invention Example
114	D	-1.00	-1.00	-	2.0	90	750	0.7	0	FAIR	GOOD	GOOD	GOOD	Invention Example
115	D	-1.00	-1.00	-	2.0	90	800	1.5	7	GOOD	GOOD	GOOD	GOOD	Invention Example
116	D	-1.17	-1.17	-	4.0	90	800	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

[Table 6]

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
117	E	-0.07	-	-	1.0	300	700	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
118	E	-0.07	-0.07	-0.07	1.0	300	900	18.8	86	GOOD	GOOD	GOOD	POOR	Comparative Example
119	E	-0.14	-0.14	-0.14	1.0	300	900	17.8	81	GOOD	GOOD	GOOD	POOR	Comparative Example
120	E	-0.22	-0.22	-0.22	1.0	300	900	17.3	81	GOOD	GOOD	GOOD	POOR	Comparative Example
121	E	-0.37	-0.37	-0.37	1.0	300	900	15.4	74	GOOD	GOOD	GOOD	POOR	Comparative Example
122	E	-0.53	-0.53	-0.53	1.0	300	900	12.6	67	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
123	E	-0.67	-067	-0.67	1.0	300	825	4.9	39	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
124	E	-0.67	-0.67	-0.67	1.0	300	850	6.5	52	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
125	E	-0.67	-0.67	-0.67	1.0	300	875	8.4	53	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
126	E	-0.67	-0.67	-0.67	1.0	300	900	11.1	58	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
127	E	-0.78	-0.78	-0.78	1.5	300	900	9.0	50	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample
128	E	-0.89	-0.89	-0.89	2.0	300	900	67	47	GOOD	GOOD	GOOD	GOOD	Invention Ex-ample

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holding sheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
129	E	-1.00	-1.00	-1.00	2.0	300	900	29	23	GOOD	GOOD	GOOD	GOOD	Invention Example
130	E	-1.17	-1.17	-1.17	3.0	300	825	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example
131	E	-1.17	-1.17	-1.17	3.0	300	850	0.5	0	FAIR	GOOD	GOOD	GOOD	Invention Example
132	E	-1.17	-1.17	-1.17	4.0	300	875	0.7	1	FAIR	GOOD	GOOD	GOOD	Invention Example
133	E	-1.17	-1.17	-1.17	4.0	300	900	1.1	1	GOOD	GOOD	GOOD	GOOD	Invention Example
134	E	-1.26	-126	-1.26	5.0	300	900	06	0	FAIR	GOOD	GOOD	GOOD	Invention Example
135	E	-1.36	-1.36	-1.36	1.0	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
136	E	-0.53	-0.53	-	1.0	90	750	1.8	23	GOOD	GOOD	GOOD	GOOD	Invention Example
137	E	-0.53	-0.53	-	1.0	90	800	3.0	34	GOOD	GOOD	GOOD	GOOD	Invention Example
138	E	-0.67	-0.67	-	1.0	90	750	1.6	20	GOOD	GOOD	GOOD	GOOD	Invention Example
139	E	-0.67	-0.67	-	1.0	90	800	3.0	22	GOOD	GOOD	GOOD	GOOD	Invention Example
140	E	-0.78	-0.78	-	1.5	90	750	0.9	6	GOOD	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
141	E	-0.78	-0.78	-	1.5	90	800	2.4	21	GOOD	GOOD	GOOD	GOOD	Invention Example
142	E	-0.89	-0.89	-	2.0	90	800	1.8	17	GOOD	GOOD	GOOD	GOOD	Invention Example
143	E	-1.00	-1.00	-	2.0	90	750	0.6	0	FAIR	GOOD	GOOD	GOOD	Invention Example
144	E	-1.00	-1.00	-	2.0	90	800	1	6	GOOD	GOOD	GOOD	GOOD	Invention Example
145	E	-1.17	-1.17	-	4.0	90	800	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

[Table 7]

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
146	A	-0.07	0.14	-0.07	1.00	300	900	19.7	95	GOOD	GOOD	GOOD	POOR	Comparative Example
147	A	-0.07	-1.36	-1.36	1.00	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
148	A	-0.14	-0.14	-0.07	1.00	300	900	19.5	96	GOOD	GOOD	GOOD	POOR	Comparative Example
149	A	-1.36	-1.17	-2.83	5.00	300	900	01	0	FAIR	GOOD	GOOD	GOOD	Invention Ex-ample
150	A	-0.14	-1.36	-0.07	1.00	300	900	17.3	87	GOOD	GOOD	GOOD	POOR	Comparative Example
151	A	-1.36	-0.14	-0.07	1.00	300	900	19.7	96	GOOD	GOOD	GOOD	POOR	Comparative Example
152	A	-2.83	-1.17	-1.36	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Ex-ample
153	B	-0.07	-0.14	-0.07	1.00	300	900	19.4	97	GOOD	GOOD	GOOD	POOR	Comparative Example
154	B	-0.07	-1.36	-1.36	1.00	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
155	B	-0.14	-0.14	-0.07	1.00	300	900	19.4	97	GOOD	GOOD	GOOD	POOR	Comparative Example
156	B	-1.36	-1.17	-2.83	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Ex-ample
157	B	-0.14	-1.36	-0.07	1.00	300	900	17.1	86	GOOD	GOOD	GOOD	POOR	Comparative Example

(continued)

Test No.	Steel type	log (P_{H2O}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holding sheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
158	B	-1.36	-0.14	-0.07	1.00	300	900	19.8	94	GOOD	GOOD	GOOD	POOR	Comparative Example
159	B	-2.83	-1.17	-1.36	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example
160	C	-0.07	-0.14	-0.07	1.00	300	900	19.2	94	GOOD	GOOD	GOOD	POOR	Comparative Example
161	C	-0.07	-1.36	-1.36	1.00	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
162	C	-0.14	-0.14	-0.07	1.00	300	900	18.9	96	GOOD	GOOD	GOOD	POOR	Comparative Example
163	C	-1.36	-1.17	-2.83	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example
164	C	-0.14	-1.36	-0.07	1.00	300	900	16.8	86	GOOD	GOOD	GOOD	POOR	Comparative Example
165	C	-1.36	-0.14	-0.07	1.00	300	900	19.6	96	GOOD	GOOD	GOOD	POOR	Comparative Example
166	C	-2.83	-1.17	-1.36	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention
167	D	-0.07	-0.14	-0.07	1.00	300	900	19.2	93	GOOD	GOOD	GOOD	POOR	Comparative Example
168	D	-0.07	-1.36	-1.36	1.00	300	900	0	0	POOR	POOR	GOOD	GOOD	Comparative Example
169	D	-0.14	-0.14	-0.07	1.00	300	900	19.8	93	GOOD	GOOD	GOOD	POOR	Comparative Example
170	D	-1.36	-1.17	-2.83	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μm)	(μm)		Appearance	Peeling test		
171	D	-0.14	-1.36	-0.07	1.00	300	900	17.9	88	GOOD	GOOD	GOOD	POOR	Comparative Example
172	D	-1.36	-0.14	-0.07	1.00	300	900	19.1	95	GOOD	GOOD	GOOD	POOR	Comparative Example
173	D	-2.83	-1.17	-1.36	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example

[Table 8]

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μM)	(μm)		Appearance	Peeling test		
174	E	-0.07	-0.14	-0.07	1.00	300	900	19	98	GOOD	GOOD	GOOD	POOR	Comparative Example
175	E	-0.07	-1.36	-1.36	1.00	300	900	0	0	POOR	POOR	POOR	GOOD	Comparative Example
176	E	-0.14	-0.14	-0.07	1.00	300	900	19.3	97	GOOD	GOOD	GOOD	POOR	Comparative Example
177	E	-1.36	-1.17	-2.83	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example
178	E	-0.14	-1.36	-0.07	1.00	300	900	17.5	88	GOOD	GOOD	GOOD	POOR	Comparative Example
179	E	-1.36	-0.14	-0.07	1.00	300	900	19.2	96	GOOD	GOOD	GOOD	POOR	Comparative Example
180	E	-2.83	-1.17	-1.36	5.00	300	900	0.1	0	FAIR	GOOD	GOOD	GOOD	Invention Example
181	F	-2.83	-2.83	-2.83	5.00	300	900	0	0	POOR	POOR	GOOD	POOR	Comparative Example
182	F	-2.83	-2.83	-2.83	5.00	300	800	0	0	POOR	POOR	GOOD	POOR	Comparative Example
183	G	-2.83	-2.83	-2.83	5.00	300	900	0	0	POOR	POOR	GOOD	POOR	Comparative Example
184	G	-2.83	-2.83	-2.83	5.00	300	800	0	0	POOR	POOR	GOOD	POOR	Comparative Example
185	H	-2.83	-2.83	-2.83	5.00	300	900	0	0	POOR	POOR	GOOD	POOR	Comparative Example

(continued)

Test No.	Steel type	log (P_{H20}/P_{H2})			Concentration of hydrogen in furnace	Holding time	Holdingsheet temperature	Location of internal oxidation	Thickness of de-carburization layer	Chemical conversion treatment	Plating property		Tensile strength	Note
		700°C or lower	Higher than 700°C and 800°C or lower	Higher than 800°C	%	(sec)	(°C)	(μM)	(μm)		Appearance	Peeling test		
186	H	-2.83	-2.83	-2.83	5.00	300	800	0	0	POOR	POOR	GOOD	POOR	Comparative Example

[0082] For the annealed steel sheets, the depth of the internal oxidation layer of Si and the thickness of the carburization layer were evaluated as described above.

(Depth Location of Internal Oxidation Layer of Si)

[0083] In ferrite in a surface layer area of the steel sheet, a region in which the number of Si oxide grains having a maximum length of 25 nm or longer was 1.0 x 10^{12} grains/m^2 or more was defined as an internal oxidation layer of Si.

[0084] Specifically, a specimen was sampled from a sheet thickness cross section parallel to the rolling direction of the steel sheet as an observed section, and the observed section was polished, Nital-etched, and observed using a field emission scanning electron microscope (FE-SEM) at a magnification of 5,000 times or higher. Regions having a rectangular shape that was 1.0 μm long in the thickness direction of the steel sheet and 20 μm long in the rolling direction were set at three random places. In each of the three places, the number of Si oxide grains was counted in the region, in a case where 10 or more Si oxide grains were present, the region was considered as the internal oxidation layer of Si, and the average value of the maximum depths of regions in which 10 or more Si oxide grains were present at the three places was considered as the depth location of the internal oxidation layer of Si. The evaluation results are shown in Table 1. When the depth of the internal oxidation layer was 0.1 μm or more, it was determined that internal oxidation was sufficient.

(Thickness of Decarburization Layer)

[0085] An area fraction S1 of a hard structure at a sheet thickness 1/4 portion of the steel sheet and an area fraction S2 of the hard structure in the surface layer area of the steel sheet were compared with each other, and the maximum depth location at which S2/S1 reached 0.40 or less was considered as the thickness of the decarburization layer. The hard structure refers to a structure made of one or more of martensite, tempered martensite, bainite, and residual austenite. Regarding an area ratio, a specimen was sampled from a sheet thickness cross section parallel to the rolling direction of the steel sheet as an observed section, the observed section was polished and Nital-etched, and regions were observed and obtained at three or more places using a field emission scanning electron microscope (FE-SEM) at a magnification of 500 times to 3,000 times. That is, in individual observation regions, 50 μm or longer parallel lines were drawn on the sheet surface of the steel sheet, the total length L of the lines overlapping the hard structure was obtained, the ratios L/LO to the length L0 of the line were obtained, and the average value thereof was considered as the area fraction S2 of the hard structure at the depth location. The evaluation results are shown in Table 1. When the thickness of the decarburization layer was 70 μm or less, it was determined that it was possible to suppress the progress of decarburization.

[0086] Furthermore, for these steel sheets, the chemical convertibility, the plating property, and the tensile strength were evaluated.

(Chemical Convertibility)

[0087] First, the continuous annealed steel sheet was cut to a 70 mm x 150 mm test piece, an aqueous solution of 18 g of a defatting agent (trade name: FINE CLEANER E2083) manufactured by Nihon Parkerizing Co., Ltd. was sprayed to the test piece at 40°C for 120 seconds so as to wash the test piece with water, thereby removing fats. Next, the defatted cold rolled steel sheet was immersed in an aqueous solution of 0.5 g of a surface conditioner (trade name: PREPALENE XG) manufactured by Nihon Parkerizing Co., Ltd. at normal temperature for 60 seconds. After that, the steel sheet was immersed in a zinc phosphate treatment agent (trade name: PALBOND L3065) manufactured by Nihon Parkerizing Co., Ltd. for 120 seconds, washed with water, and dried, thereby carrying out a chemical conversion treatment. After that, three places (the central portion and both end portions) along the longitudinal direction of the chemical conversion treated test piece were observed using a scanning electron microscope at a magnification of 1,000 times, and the degree of attachment of crystal grains of a zinc phosphate coating was observed.

[0088] In a case where zinc phosphate crystals of the chemical conversion treatment coating were densely attached, the chemical convertibility was evaluated as "GOOD", in a case where zinc phosphate crystals were not dense, and a small number of voids (portions to which the zinc phosphate coating was not attached and which are generally referred to as "lack of hiding") are visible between adjacent crystals, the chemical convertibility was evaluated as "FAIR", and, in a case where places not coated with the chemical conversion treatment coating were clearly visible, the chemical convertibility was evaluated as "POOR".

(Tensile Strength)

[0089] A No. 5 test piece described in JIS Z2201 was cut out from the continuous-annealed steel sheet in a direction orthogonal to the rolling direction, and a tensile test was carried out at a normal temperature according to JIS Z2241, thereby obtaining a tensile strength and an elongation.

[0090] In addition, in a case where the tensile strength was 780 MPa or higher and the tensile strength degraded by less than 1.0% compared with the tensile strength of a test piece obtained by cutting portions outside 80% of the test piece from the sheet thickness center in the thickness direction, the tensile strength was evaluated as "GOOD". On the other hand, in a case where the tensile strength was lower than 780 MPa and a case where the tensile strength was 780 MPa or higher, however the tensile strength degraded by 1.0% or more compared with the tensile strength of the test piece obtained by cutting portions outside 80% of the test piece from the sheet thickness center in the thickness direction, the tensile strength was evaluated as "POOR".

(Plating Property)

[0091] A hot dip galvanizing treatment was carried out on the continuous-annealed steel sheet using a well-known method, the external appearance of the hot dip galvanized steel sheet was visually evaluated, and a plating peeling test was carried out, thereby evaluating the adhesion. Specifically, the adhesion was evaluated as described below.

"External Appearance Inspection"

[0092] Regarding the external appearance of the surface of the hot dip galvanized steel sheet, five samples having a length of 1 m were continuously sampled from the steel sheet through the entire width, and the status of the generation of unplated portions was visually determined using the following standards.

GOOD: No unplated portions having a diameter of 0.5 mm or larger were observed (practically permissible external appearance).

POOR: Unplated portions having a diameter of 0.5 mm or larger were observed (outside the permissible range of external appearance).

"Plating Peeling Test"

[0093] A plating peeling test was carried out according to the "Metallic Materials-Bend Testing Method" described in JIS Z2248 which evaluates plate adhesion in a process in which a compressive stress is applied to a steel sheet. Specifically, as disclosed in document "Hot Dip Galvanized Steel Sheet Manual, p. 53 to 55", a 60° V bend test was carried out using each steel sheet, then, tape was attached to the inside of a bent portion, and the tape was peeled off. In addition, the plate adhesion was evaluated using the following standards from the peeling status of the plated layer peeled off together with the tape. As the tape, "CELLOTAPE" (registered trademark) manufactured by Nichiban Co., Ltd. was used.

GOOD: The peeled width was shorter than 7.0 mm (practically permissible)

POOR: The peeled width was 7.0 mm or longer (practically not permissible)

[0094] In Test No. 1, No. 30, No. 59, No. 88, and No. 117, the steel sheet temperatures during annealing were 700°C or lower, and neither the internal oxidation of Si nor decarburization was occurred. In Test No. 19, No. 48, No. 77, No. 106, and No. 135, the steel sheet temperatures during heating were higher than 700°C and 800°C or lower, in the range of heating the steel sheets, the furnace body average values of log (P_{H2O}/P_{H2}) which is the relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace were -1.36 or lower, and the internal oxidation of Si was not sufficient.

[0095] In Test No. 2, No. 31, No. 60, No. 89, and No. 118, the temperatures of the steel sheets during heating and holding were 900°C, however the furnace body average values of log (P_{H2O}/P_{H2}) which is a relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace were -0.07 or higher, and the decarburization thicknesses became excessively thick.

[0096] In Test Nos. 3 to 5, Nos. 32 to 34, Nos. 61 to 63, Nos. 90 to 92, and Nos. 119 to 121, the furnace body average values of log (P_{H2O}/P_{H2}) at higher than 800°C were - 0.54 or higher, and the decarburization thicknesses became excessively thick.

[0097] In addition, in Test Nos. 146 to 148, No. 150, No. 151, Nos. 153 to 155, No. 157, No. 158, Nos. 160 to 162, No. 164, No. 165, No. 167 to No. 169, No. 171, No. 172, Nos. 172 to 176, No. 178, No. 179, and Nos. 181 to 186, the furnace body average values of log (P_{H2O}/P_{H2}) were deviated from the present invention at all of the steel sheet temperatures of 700°C or lower, higher than 700°C and 800°C or lower, and higher than 800°C, the internal oxidation was not sufficient, and the decarburization thicknesses became excess or the tensile strength or the plating property was deteriorated.

[0098] In contrast, in Test Nos. 6 to 18, Nos. 20 to 29, Nos. 35 to 47, Nos. 49 to 58, Nos. 64 to 76, Nos. 78 to 87, Nos. 93 to 105, Nos. 107 to 116, Nos. 122 to 134, Nos. 136 to 145, No. 149, No. 152, No. 156, No. 159, No. 163, No. 166, No. 170, No. 173, No. 177, and No. 180 in which, in the continuous annealing of heating the steel sheets at a temperature of 750°C to 900°C during heating and holding of the steel sheets, the furnace body average values of log (P_{H2O}/P_{H2}) which is a relationship between the water partial pressure P_{H2O} and the hydrogen partial pressure P_{H2} in the atmosphere of the furnace at a steel sheet of higher than 700°C and 800°C or lower were set in a range of $-1.36 < \log (P_{H2O}/P_{H2}) < -0.07$, the furnace body average values of log (P_{H2O}/P_{H2}) at a steel sheet temperature of 700°C or lower were set to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.07$, and the furnace body average values of log (P_{H2O}/P_{H2}) at higher than 800°C were set to $-3.01 < \log (P_{H2O}/P_{H2}) < -0.53$, the depth locations of the internal oxidation layers of Si were sufficiently deep, and the thicknesses of the decarburization layer became thin.

[0099] From what has been described above, it was confirmed that, according to the present invention, Si is oxidized in a steel sheet, thereby suppressing the exposure of Si oxides on the surface of the steel sheet, and the progress of decarburization from the steel sheet can be suppressed.

[Industrial Applicability]

[0100] It is possible to provide a method for manufacturing a high strength steel sheet in which the atmosphere during annealing is controlled, whereby the exposure of Si oxides on the surface of the steel sheet is suppressed by oxidizing Si in the steel sheet, and the progress of decarburization of the steel sheet can be suppressed and a device for continuous annealing steel sheet which is suitable for the above described method for manufacturing a high strength steel sheet.

[Brief Description of the Reference Symbols]

[0101]

1 STEEL SHEET
10 DEVICE FOR CONTINUOUS ANNEALING STEEL SHEET
11 FIRST HEATING BAND
12 SECOND HEATING BAND
13 THIRD HEATING BAND
14 SOAKING BAND
15 ATMOSPHERIC GAS INTRODUCTION PORTION (IN-FURNACE ATMOSPHERE ADJUSTMENT UNIT)

Claims

1. A method for manufacturing a high strength steel sheet having a tensile strength of 780 MPa or higher, the method comprising:

continuous annealing by heating a steel sheet containing as a chemical composition, by mass%, C: 0.050% to 0.40%, Si: 0.10% to 2.50%, Mn: 1.20% to 3.50%, Cr: 0% to 0.80%, Ni: 0% to 5.00%, Cu: 0% to 3.00%, Nb: 0% to 0.10%, Mg: 0% to 0.010%, Ti: 0% to 0.10%, B: 0% to 0.010%, and Mo: 0% to 0.5% and a remainder being Fe and impurities, in which P: limited to 0.100% or less, S: limited to 0.010% or less, Al: limited to 1.200% or less, and N: limited to 0.0100% or less, up to a temperature range of 750°C to 900°C and holding the steel sheet in the temperature range for 0 seconds to 300 seconds,
wherein, in the continuous annealing, during the heating up to the temperature range and the holding in the temperature range,
a hydrogen concentration in an atmosphere of a furnace is less than 10 volume%,
when a temperature of the steel sheet is 700°C or lower, a furnace body average value of log (P_{H2O}/P_{H2}) which is a relationship between a water partial pressure P_{H2O} and a hydrogen partial pressure P_{H2} in the atmosphere of the furnace is in a range of Expression (i) below,
when the temperature of the steel sheet is higher than 700°C and 800°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace is in a range of Expression (ii) below, and,
when the temperature of the steel sheet is higher than 800°C, the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace is in a range of Expression (iii) below, and a dew point is lower than -10°C,

$$-3.01 < \log (P_{H2O}/P_{H2}) < -0.07 \qquad (i)$$

$$-1.36 < \log (P_{H2O}/P_{H2}) < -0.07 \qquad (ii)$$

$$-3.01 < \log (P_{H2O}/P_{H2}) < -0.53 \qquad (iii).$$

2. The method for manufacturing a steel sheet according to claim 1, wherein the steel sheet contains, by mass%, one or more of
Cr: 0.01% to 0.80%,
Ni: 0.01% to 5.00%,
Cu: 0.01% to 3.00%,
Nb: 0.001% to 0.10%,
Mg: 0.0001% to 0.010%,
Ti: 0.001% to 0.10%,
B: 0.0001% to 0.010%, and
Mo: 0.01% to 0.5%.

3. The method for manufacturing a steel sheet according to claim 1 or 2, wherein, when the temperature of the steel sheet is higher than 700°C and 800°C or lower, the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace is in a range of Expression (vii) below,

$$-1.00 < \log (P_{H2O}/P_{H2}) < -0.67 \qquad (vii).$$

4. A device for continuous annealing a steel sheet containing as a chemical composition, by mass%, C: 0.050% to 0.40%, Si: 0.10% to 2.50%, Mn: 1.20% to 3.50%, Cr: 0% to 0.80%, Ni: 0% to 5.00%, Cu: 0% to 3.00%, Nb: 0% to 0.10%, Mg: 0% to 0.010%, Ti: 0% to 0.10%, B: 0% to 0.010%, and Mo: 0% to 0.5% and a remainder being Fe and impurities, in which P: limited to 0.100% or less, S: limited to 0.010% or less, Al: limited to 1.200% or less, and N: limited to 0.0100% or less, the device comprising:

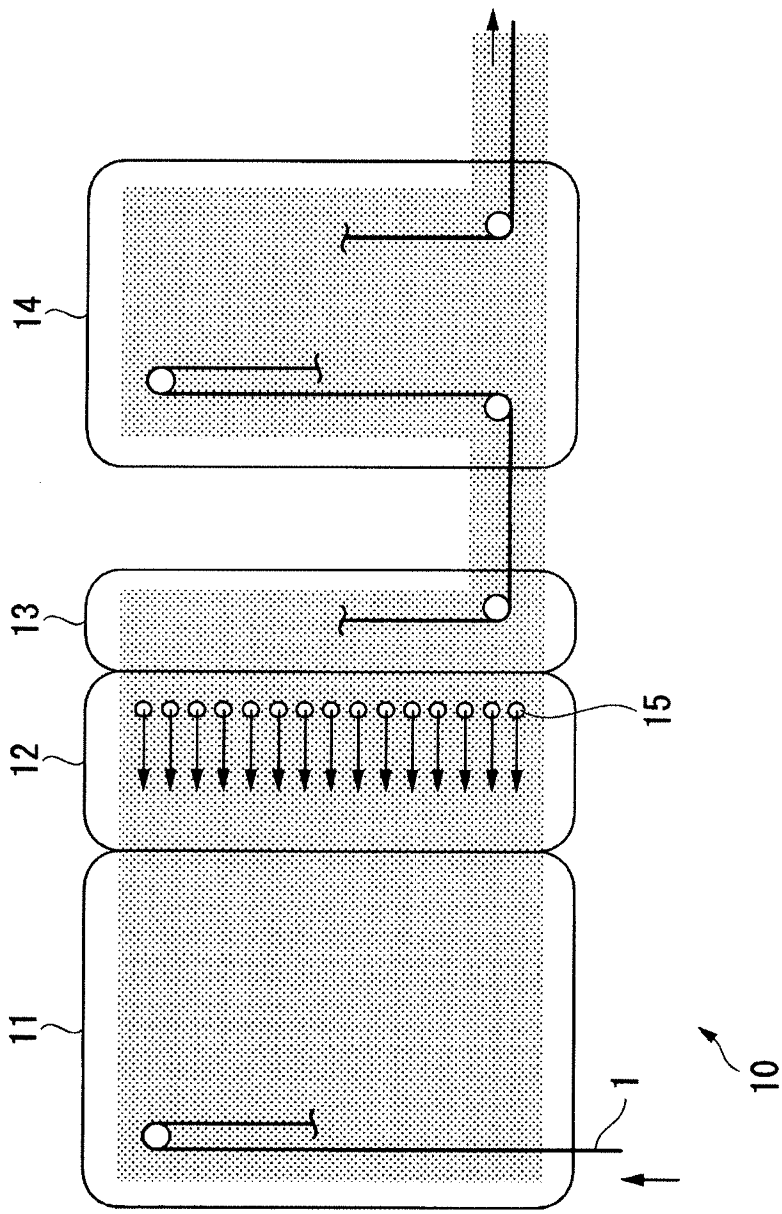
an in-furnace atmosphere adjustment unit for
setting a hydrogen concentration in an atmosphere of a furnace to less than 10 volume%,
when a temperature of the steel sheet is 700°C or lower, adjusting a furnace body average value of log (P_{H2O}/P_{H2}) which is a relationship between a water partial pressure P_{H2O} and a hydrogen partial pressure P_{H2} in the atmosphere of the furnace to be in a range of Expression (iv) below,
when the temperature of the steel sheet is higher than 700°C and 800°C or lower, adjusting the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace to be in a range of Expression (v) below,
when the temperature of the steel sheet is higher than 800°C, adjusting the furnace body average value of log (P_{H2O}/P_{H2}) in the atmosphere of the furnace to be in a range of Expression (vi) below, and
adjusting a dew point to be lower than -10°C,

$$-3.01 < \log (P_{H2O}/P_{H2}) < -0.07 \qquad (iv)$$

$$-1.36 < \log (P_{H2O}/P_{H2}) < -0.07 \qquad (v)$$

$$-3.01 < \log (P_{H2O}/P_{H2}) \leq -0.53 \qquad (vi).$$

[FIGURE 1]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/055601

A. CLASSIFICATION OF SUBJECT MATTER
C21D9/56(2006.01)i, *C23C2/02*(2006.01)n, *C23C2/06*(2006.01)n, *C23C22/12*(2006.01)n, *C23C22/78*(2006.01)n

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C21D9/56, C23C2/00-2/40, C23C22/12, C23C22/78

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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.
X	JP 2011-111673 A (Nippon Steel Corp.), 09 June 2011 (09.06.2011), experimental example P-5 (Family: none)	1-4
X	JP 2011-111675 A (Nippon Steel Corp.), 09 June 2011 (09.06.2011), experimental example 66 (Family: none)	1,2,4
A	JP 2013-142198 A (Nippon Steel & Sumitomo Metal Corp.), 22 July 2013 (22.07.2013), claims (Family: none)	1-4

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

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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

International application No. PCT/JP2016/055601

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/018739 A1 (Nippon Steel & Sumitomo Metal Corp.), 07 February 2013 (07.02.2013), examples & US 2014/0212684 A1 examples & EP 2738280 A1 & CA 2842897 A1 & MX 2014000882 A & RU 2014106991 A & ZA 201401349 A & VN 37971 A & IN 201401276 P1 & TW 201309815 A & CN 103717773 A & KR 10-2014-0041833 A	1-4
A	WO 2015/037241 A1 (JFE Steel Corp.), 19 March 2015 (19.03.2015), examples & CN 105531389 A	1-4
A	WO 2015/037242 A1 (JFE Steel Corp.), 19 March 2015 (19.03.2015), examples & CN 105531390 A	1-4

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2012012683 A **[0017]**

Non-patent literature cited in the description

- *Hot Dip Galvanized Steel Sheet Manual,* 53-55 **[0093]**