(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 623 631 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
07.08.2013 Bulletin 2013/32

(21) Application number: **10857890.7**

(22) Date of filing: **30.09.2010**

(51) Int Cl.:
C23C 8/14 *(2006.01)*
C21D 9/46 *(2006.01)*
C22C 38/00 *(2006.01)*
C22C 38/06 *(2006.01)*
C22C 38/58 *(2006.01)*

(86) International application number:
PCT/JP2010/067612

(87) International publication number:
WO 2012/042677 (05.04.2012 Gazette 2012/14)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(71) Applicant: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
- **FUSHIWAKI, Yusuke**
  Tokyo 100-0011 (JP)
- **SUZUKI, Yoshitsugu**
  Tokyo 100-0011 (JP)

(74) Representative: **Grünecker, Kinkeldey,**
Stockmair & Schwanhäusser
Leopoldstrasse 4
80802 München (DE)

(54) HIGH-STRENGTH STEEL SHEET AND METHOD FOR PRODUCING SAME

(57) The invention provides a high strength steel sheet which exhibits excellent chemical convertibility and corrosion resistance after electrodeposition coating even in the case where the steel sheet has a high Si content, and a method for manufacturing such steel sheets. The method includes continuous annealing of a steel sheet which includes, in terms of mass%, C at 0.01 to 0.18%, Si at 0.4 to 2.0%, Mn at 1.0 to 3.0%, Al at 0.001 to 1.0%, P at 0.005 to 0.060% and S at $\leq$ 0.01%, the balance being represented by Fe and inevitable impurities, while controlling the dew-point temperature of the atmosphere to become not less than -10°C when the heating furnace inside temperature is in the range of not less than A°C and not more than B°C during the course of heating (A: $600 \leq A \leq 780$, B: $800 \leq B \leq 900$).

Printed by Jouve, 75001 PARIS (FR)

Description

[Technical Field]

[0001] The present invention relates to a high strength steel sheet having excellent chemical convertibility and corrosion resistance after electrodeposition coating even in the case where the steel sheet has a high Si content, as well as to a method for manufacturing such steel sheets.

[Background Art]

[0002] From the viewpoint of the improvements in automobile fuel efficiency and crash safety of the automobiles, there have recently been increasing demands for car body materials to be increased in strength for thickness reduction in order to reduce the weight and increase the strength of car bodies themselves. For this purpose, the use of high strength steel sheets in automobiles has been promoted.

In general, automotive steel sheets are painted before use. As a pretreatment before painting, a chemical conversion treatment called phosphatization is performed. The chemical conversion treatment for steel sheets is one of the important treatments for ensuring corrosion resistance after painting.

[0003] The addition of silicon is effective for increasing the strength and the ductility of steel sheets. During continuous annealing, however, silicon is oxidized even if the annealing is performed in a reductive $N_2 + H_2$ gas atmosphere which does not induce the oxidation of Fe (which reduces Fe oxides). As a result, a silicon oxide (SiO_2) is formed on the outermost surface of a steel sheet. This SiO_2 inhibits a reaction for forming a chemical conversion film during a chemical conversion treatment, thereby resulting in formation of a microscopical region where any chemical conversion film is not generated. (Hereinafter, such a region will be sometimes referred to as "non-covered region"). That is, chemical convertibility is lowered.

[0004] Among conventional techniques directed to the improvement of chemical convertibility of high-Si containing steel sheets, patent document 1 discloses a method in which an iron coating layer is electroplated at 20 to 1500 mg/m^2 onto a steel sheet. However, this method entails the provision of a separate electroplating facility and increases costs correspondingly to an increase in the number of steps.

[0005] Further, patent documents 2 and 3 provide an improvement in phosphatability by specifying the Mn/Si ratio and by adding nickel, respectively. However, the effects are dependent on the Si content in a steel sheet, and a further improvement will be necessary for steel sheets having a high Si content.

[0006] Patent document 4 discloses a method in which the dew-point temperature during annealing is controlled to be -25 to 0°C so as to form an internal oxide layer which includes a Si-containing oxide within a depth of 1 μm from the surface of a steel sheet base as well as to control the proportion of the Si-containing oxide to be not more than 80% over a length of 10 μm of the surface of the steel sheet. However, the method described in patent document 4 is predicated on the idea that the dew-point temperature is controlled with respect to the entire area inside a furnace. Thus, difficulties are encountered in controlling the dew-point temperature and ensuring stable operation. If annealing is performed while the controlling of the dew-point temperature is unstable, the distribution of internal oxides formed in a steel sheet becomes nonuniform to cause a risk that chemical convertibility may be variable in a longitudinal direction or a width direction of the steel sheet (non-covered regions may be formed in the entirety or a portion of the steel sheet). Even though an improvement in chemical convertibility is attained, a problem still remains in that corrosion resistance after electrodeposition coating is poor because of the presence of the Si-containing oxide immediately under the chemical conversion coating.

[0007] Further, patent document 5 describes a method in which the steel sheet temperature is brought to 350 to 650°C in an oxidative atmosphere so as to form an oxide film on the surface of the steel sheet, and thereafter the steel sheet is heated to a recrystallization temperature in a reductive atmosphere and subsequently cooled. With this method, however, it is often the case that the thickness of the oxide film formed on the surface of the steel sheet is variable depending on the oxidation method and that the oxidation does not take place sufficiently or the oxide film becomes excessively thick with the result that the oxide film leaves residue or is exfoliated during the subsequent annealing in a reductive atmosphere, thus resulting in a deterioration in surface quality. In EXAMPLES, this patent document describes an embodiment in which oxidation is carried out in air. However, oxidation in air causes problems such as giving a thick oxide which is hardly reduced in subsequent reduction or requiring a reductive atmosphere with a high hydrogen concentration.

[0008] Furthermore, patent document 6 describes a method in which a cold rolled steel sheet containing, in terms of mass%, Si at not less than 0.1% and/or Mn at not less than 1.0% is heated at a steel sheet temperature of not less than 400°C in an iron-oxidizing atmosphere to form an oxide film on the surface of the steel sheet, and thereafter the oxide film on the surface of the steel sheet is reduced in an iron-reducing atmosphere. In detail, iron on the surface of the steel sheet is oxidized at not less than 400°C using a direct flame burner with an air ratio of not less than 0.93 and not more than 1.10, and thereafter the steel sheet is annealed in a N_2 + H_2 gas atmosphere which reduces the iron oxide, thereby forming an iron oxide layer on the outermost surface while suppressing the oxidation of SiO_2 which lowers chemical convertibility from occurring on the outermost surface. Patent document 6 does not specifically describe the heating temperature with the direct flame burner. However, in the case where Si is present at a high content (generally, 0.6% or more), the oxidation amount of silicon, which is more easily oxidized than iron, becomes large so as to suppress the oxidation of Fe or limit the oxidation of Fe itself to a too low level. As a result, the formation of a superficial reduced Fe layer by the reduction becomes insufficient and SiO_2 comes to be present on the surface of the steel sheet after the reduction, thus possibly resulting in a region which may not be covered with a chemical film.

[Citation List]

[Patent Document]

[0009]

[Patent document 1] Japanese Unexamined Patent Application Publication No. 5-320952
[Patent document 2] Japanese Unexamined Patent Application Publication No. 2004-323969
[Patent document 3] Japanese Unexamined Patent Application Publication No. 6-10096
[Patent document 4] Japanese Unexamined Patent Application Publication No. 2003-113441
[Patent document 5] Japanese Unexamined Patent Application Publication No. 55-145122
[Patent document 6] Japanese Unexamined Patent Application Publication No. 2006-45615

[Summary of Invention]

[Technical Problem]

[0010] The present invention has been made in view of the circumstances described above. It is therefore an object of the invention to provide a high strength steel sheet which exhibits excellent chemical convertibility and corrosion resistance after electrodeposition coating even in the case of a high Si content, as well as to provide a method for manufacturing such steel sheets.

[Solution to Problem]

[0011] Conventional approaches were based on simply increasing the water vapor partial pressure or the oxygen partial pressure in the entire inside of an annealing furnace so as to raise the dew-point temperature or the oxygen concentration and thereby to produce excessive internal oxidation of a steel sheet. Consequently, as mentioned above, various problems have been encountered such as difficulties in controlling the dew-point temperature or the oxidation, the occurrence of uneven chemical convertibility and a decrease in corrosion resistance after electrodeposition coating. Thus, the present inventors studied a novel approach based on an unconventional idea capable of solving the above problems. As a result, the present inventors have found that because a deterioration in corrosion resistance after electrodeposition coating can originate from a surface portion of a steel sheet, more sophisticated controlling of the microstructure and configuration of the surface portion of the steel sheet allows for obtaining a high strength steel sheet having excellent chemical convertibility and corrosion resistance after electrodeposition coating. In detail, a chemical conversion treatment is performed after annealing is carried out in such a manner that the dew-point temperature of the atmosphere is controlled to become not less than -10°C when the heating furnace inside temperature is in a limited range of not less than A°C and not more than B°C during the course of heating (A: $600 \le A \le 780$, B: $800 \le B \le 900$). In this manner, selective surface oxidation and surface segregation can be suppressed, resulting in a high strength steel sheet exhibiting excellent chemical convertibility and corrosion resistance after electrodeposition coating. Here, the term "excellent chemical convertibility" means that a steel sheet having undergone a chemical conversion treatment has an appearance without any non-covered regions or uneven results of the chemical conversion treatment.

[0012] A high strength steel sheet obtained in the above manner comes to have a microstructure and configuration in which a surface portion of the steel sheet extending from the steel sheet surface within a depth of 100 μm contains an oxide of at least one or more selected from Fe, Si, Mn, Al and P, as well as from B, Nb, Ti, Cr, Mo, Cu and Ni at 0.010 to 0.50 g/m^2 per single side surface, and in which a region extending from the steel sheet surface to a depth of 10 μm is such that a crystalline Si/Mn oxide has been precipitated in base iron grains that are within 1 μm from grain boundaries. Because of this configuration, deterioration in corrosion resistance after electrodeposition coating is realized and excellent chemical convertibility is obtained.
The present invention is based on the aforementioned findings. Features of the invention are as described below.

[0013] [1] A method for manufacturing high strength steel sheets, including continuous annealing of a steel sheet which includes, in terms of mass%, C at 0.01 to 0.18%, Si at 0.4 to 2.0%, Mn at 1.0 to 3.0%, Al at 0.001 to 1.0%, P at 0.005 to 0.060% and S at ≤ 0.01%, the balance being represented by Fe and inevitable impurities, while controlling the dew-point temperature of the atmosphere to become not less than -10°C when the heating furnace inside temperature is in the range of not less than A°C and not more than B°C during the course of heating wherein A is $600 \leq A \leq 780$ and B is $800 \leq B \leq 900$.

[0014] [2] The method for manufacturing high strength steel sheets described in [1], wherein the chemical composition of the steel sheet further includes one or more elements selected from B at 0.001 to 0.005%, Nb at 0.005 to 0.05%, Ti at 0.005 to 0.05%, Cr at 0.001 to 1.0%, Mo at 0.05 to 1.0%, Cu at 0.05 to 1.0% and Ni at 0.05 to 1.0% in terms of mass%.

[0015] [3] The method for manufacturing high strength steel sheets described in [1] or [2], further including, after the continuous annealing, electrolytically pickling the steel sheet in an aqueous solution containing sulfuric acid.

[0016] [4] A high strength steel sheet manufactured by the method described in any of [1] to [3] in which a surface portion of the steel sheet extending from the steel sheet surface within a depth of 100 μm contains an oxide of at least one or more selected from Fe, Si, Mn, Al, P, B, Nb, Ti, Cr, Mo, Cu and Ni at 0.010 to 0.50 g/m^2 per single side surface, and in which with respect to a region extending from the steel sheet surface within a depth of 10 μm, a crystalline Si/Mn oxide is present in grains that are within 1 μm from crystal grain boundaries of the steel sheet.

[0017] In the present invention, the term "high strength" means that the tensile strength TS is not less than 340 MPa. The high strength steel sheets in the invention include both cold rolled steel sheets and hot rolled steel sheets.

[Advantageous Effects of Invention]

[0018] According to the present invention, a high strength steel sheet is obtained which exhibits excellent chemical convertibility and corrosion resistance after electrodeposition coating even in the case where the steel sheet has a high Si content.

[Description of Embodiments]

[0019] The present invention will be described in detail hereinbelow. In the following description, the unit for the contents of individual elements in the chemical composition of steel is "mass%" and is indicated simply as "%" unless otherwise mentioned.

[0020] First, there will be described annealing atmosphere conditions that are the most important requirement in the invention and determine the structure of the surface of the steel sheet.
A chemical conversion treatment is performed after a steel sheet is continuously annealed in such a manner that the dew-point temperature of the atmosphere is controlled to become not less than -10°C when the heating furnace inside temperature is in a limited range of not less than A°C and not more than B°C during the course of heating in an annealing furnace (A: $600 \leq A \leq 780$, B: $800 \leq B \leq 900$). In this manner, oxides of easily oxidized elements (such as Si and Mn) are allowed to be present in appropriate amounts inside a surface portion of the steel sheet extending from the surface within a depth of 10 μm (hereinafter, such oxides will be referred to as internal oxides), thereby making it possible to suppress selective surface oxidation of such elements as Si and Mn on the steel sheet surface that deteriorate the chemical convertibility of the steel after annealing (hereinafter, this oxidation will be referred to as "surface segregation") from occurring in the surface portion of the steel sheet.

[0021] The lower limit temperature A is limited to be $600 \leq A \leq 780$ for the following reasons. When the temperature is in the range of less than 600°C, the amount of surface segregation is inherently small. Thus, a deterioration in chemical convertibility is not caused in such a temperature range even if the dew-point temperature is not controlled and internal oxides are not formed. If the temperature is raised to above 780°C without controlling of the dew-point temperature, the amount of surface segregation is so increased that the inward diffusion of oxygen is inhibited and internal oxidation is unlikely to occur. It is therefore necessary to control the dew-point temperature to become not less than -10°C at least from when the temperature is in the range of not more than 780°C. Thus, the acceptable range of A is $600 \leq A \leq 780$. For the above reason, it is preferable that A be a temperature as low as possible within this range.

[0022] The upper limit temperature B is limited to be $800 \leq B \leq 900$ for the following reasons. The formation of internal oxides decreases the amount of easily oxidized elements (such as Si and Mn) present as solutes inside a surface portion of the steel sheet extending from the surface within a depth of 10 μm (hereinafter, such a portion will be referred to as "deficient layer"), and thereby the easily oxidized elements are suppressed from diffusing from the inside of steel toward the surface. In order to form such internal oxides as well as to form the deficient layer enough to suppress the occurrence of surface segregation, the temperature B needs to satisfy $800 \leq B \leq 900$. If the temperature is less than 800°C, internal oxides are not formed sufficiently. If the temperature exceeds 900°C, internal oxides are formed in excessively large amounts and serve as starting points of a deterioration in corrosion resistance after electrodeposition coating.

[0023] The dew-point temperature is controlled to become not less than -10°C when the temperature is in the range of not less than A°C and not more than B°C for the following reasons. Increasing the dew-point temperature increases the potential of O_2 generated by the decomposition of H_2O, and therefore internal oxidation can be promoted. The amount of formed internal oxides is small if the dew-point temperature is in the range of below -10°C. The upper limit of the dew-point temperature is not particularly limited. However, the amount of oxidation of iron increases if the dew-point temperature is in excess of 90°C, causing a risk that annealing furnace walls or rollers may be degraded. Thus, the dew-point temperature is preferably not more than 90°C.

[0024] Next, the chemical composition of the high strength steel sheets of interest according to the present invention will be described.

C: 0.01 to 0.18%

[0025] Carbon increases workability by forming phases such as martensite in the steel microstructure. In order to obtain this effect, carbon needs to be contained at not less than 0.01%. On the other hand, containing carbon in excess of 0.18% causes a decrease in elongation as well as deteriorations in quality and weldability. Thus, the C content is limited to be not less than 0.01% and not more than 0.18%.

Si: 0.4 to 2.0%

[0026] Silicon increases the strength and the elongation of steel and is therefore an effective element for achieving a good quality. In order to obtain the objective strength in the present invention, silicon needs to be contained at not less than 0.4%. Steel sheets having a Si content of less than 0.4% cannot achieve a strength of interest in the invention and are substantially free of problems in terms of chemical convertibility. On the other hand, containing silicon in excess of 2.0% results in the saturation of steel strengthening effects as well as the saturation of elongation enhancement, and achieving an improvement of chemical convertibility becomes difficult. Thus, the Si content is limited to be not less than 0.4% and not more than 2.0%.

Mn: 1.0 to 3.0%

[0027] Manganese is an effective element for increasing the strength of steel. In order to ensure mechanical characteristics and strength, the Mn content needs to be not less than 1.0%. On the other hand, containing manganese in excess of 3.0% causes difficulties in ensuring weldability as well as in ensuring the balance between strength and ductility. Thus, the Mn content is limited to be not less than 1.0% and not more than 3.0%.

Al: 0.001 to 1.0%

[0028] Aluminum is added for the purpose of deoxidation of molten steel. The deoxidation effect for molten steel is obtained by adding aluminum at not less than 0.001%. On the other hand, adding aluminum in excess of 1.0% increases costs and further results in an increase in the amount of surface segregation of aluminum, thereby making it difficult to improve chemical convertibility. Thus, the Al content is limited to be not less than 0.001% and not more than 1.0%.

P: 0.005 to not more than 0.060%

[0029] Phosphorus is one of elements that are inevitably present in steel. An increase in cost is expected if the P content is reduced to below 0.005%. Thus, the P content is specified to be not less than 0.005%. On the other hand, any P content exceeding 0.060% leads to a decrease in weldability and causes a marked deterioration in chemical convertibility to such an extent that it becomes difficult to improve chemical convertibility even by the present invention. Thus, the P content is limited to be not less than 0.005% and not more than 0.060%.

S: ≤ 0.01%

[0030] Sulfur is one of inevitable elements. The lower limit is not particularly limited. However, the presence of this element in a large amount causes decreases in weldability and corrosion resistance. Thus, the S content is limited to be not more than 0.01%.

[0031] In order to control the balance between strength and ductility, one or more elements selected from 0.001 to 0.005% of B, 0.005 to 0.05% of Nb, 0.005 to 0.05% of Ti, 0.001 to 1.0% of Cr, 0.05 to 1.0% of Mo, 0.05 to 1.0% of Cu and 0.05 to 1.0% of Ni may be added as required.

The appropriate amounts of these optional elements are limited for the following reasons.

B: 0.001 to 0.005%

[0032] The effect in promoting hardening is hardly obtained if the B content is less than 0.001%. On the other hand, adding boron in excess of 0.005% results in a decrease in chemical convertibility. Thus, when boron is contained, the B content is limited to be not less than 0.001% and not more than 0.005%.

Nb: 0.005 to 0.05%

[0033] The effect in adjusting strength is hardly obtained if the Nb content is less than 0.005%. On the other hand, containing niobium in excess of 0.05% results in an increase in cost. Thus, when niobium is contained, the Nb content is limited to be not less than 0.005% and not more than 0.05%.

Ti: 0.005 to 0.05%

[0034] The effect in adjusting strength is hardly obtained if the Ti content is less than 0.005%. On the other hand, containing titanium in excess of 0.05% results in a decrease in chemical convertibility. Thus, when titanium is contained, the Ti content is limited to be not less than 0.005% and not more than 0.05%.

Cr: 0.001 to 1.0%

[0035] The effect in promoting hardening is hardly obtained if the Cr content is less than 0.001%. On the other hand, containing chromium in excess of 1.0% results in the surface segregation of chromium and a consequent decrease in weldability. Thus, when chromium is contained, the Cr content is limited to be not less than 0.001% and not more than 1.0%.

Mo: 0.05 to 1.0%

[0036] The effect in adjusting strength is hardly obtained if the Mo content is less than 0.05%. On the other hand, containing molybdenum in excess of 1.0% results in an increase in cost. Thus, when molybdenum is contained, the Mo content is limited to be not less than 0.05% and not more than 1.0%.

Cu: 0.05 to 1.0%

[0037] The effect in promoting the formation of a retained γ-phase is hardly obtained if the Cu content is less than 0.05%. On the other hand, containing copper in excess of 1.0% results in an increase in cost. Thus, when copper is contained, the Cu content is limited to be not less than 0.05% and not more than 1.0%.

Ni: 0.05 to 1.0%

[0038] The effect in promoting the formation of a retained γ-phase is hardly obtained if the Ni content is less than 0.05%. On the other hand, containing nickel in excess of 1.0% results in an increase in cost. Thus, when nickel is contained, the Ni content is limited to be not less than 0.05% and not more than 1.0%.

The balance after the deduction of the aforementioned elements is represented by Fe and inevitable impurities.

[0039] Next, there will be described a method for manufacturing the high strength steel sheets according to the invention as well as the reasons why the conditions in the method are limited. For example, a steel having the above-described chemical composition is hot rolled and is thereafter cold rolled, and subsequently the steel sheet is annealed in a continuous annealing facility and is subjected to a chemical conversion treatment. Here, in the present invention, the annealing is carried out in such a manner that the dew-point temperature of the atmosphere is controlled to become not less than -10°C when the heating furnace inside temperature is in the range of not less than A°C and not more than B°C during the course of heating (A: $600 \leq A \leq 780$, B: $800 \leq B \leq 900$). This is the most important requirement in the invention. By controlling the dew-point temperature, namely, the oxygen partial pressure in the atmosphere during the annealing step, the oxygen potential is increased with the result that easily oxidized elements such as Si and Mn are internally oxidized beforehand immediately before a chemical conversion treatment and the activities of Si and Mn in the surface portion of the steel sheet are lowered. Consequently, the external oxidation of these elements is suppressed, resulting in an improvement in chemical convertibility. In the above processing of steel, it is possible to anneal the hot rolled steel sheet without subjecting it to cold rolling.

Hot rolling

[0040] Hot rolling may be performed under usual conditions.

Pickling

[0041] It is preferable to perform a pickling treatment after hot rolling. In the pickling step, black scales formed on the surface are removed and the steel sheet is subjected to cold rolling. Pickling conditions are not particularly limited.

Cold rolling

[0042] Cold rolling is preferably carried out with a draft of not less than 40% and not more than 80%. If the draft is less than 40%, the recrystallization temperature becomes lower and the steel sheet tends to be deteriorated in mechanical characteristics. On the other hand, because the steel sheet of the invention is a high strength steel sheet, cold rolling the steel sheet with a draft exceeding 80% increases not only the rolling costs but also the amount of surface segregation during annealing, possibly resulting in a decrease in chemical convertibility.

[0043] The steel sheet that has been cold rolled or hot rolled is annealed and then subjected to a chemical conversion treatment.

[0044] In an annealing furnace, the steel sheet undergoes a heating step in which the steel sheet is heated to a predetermined temperature in an upstream heating zone and a soaking step in which the steel sheet is held in a downstream soaking zone at a predetermined temperature for a prescribed time. Next, a cooling step is performed.
As described above, the annealing is carried out in such a manner that the dew-point temperature of the atmosphere is controlled to become not less than -10°C when the heating furnace inside temperature is in the range of not less than A°C and not more than B°C (A: $600 \leq A \leq 780$, B: $800 \leq B \leq 900$). Except when the temperature is in the range of not less than A°C and not more than B°C, the dew-point temperature of the atmosphere in the annealing furnace is not particularly limited, but is preferably in the range of -50°C to -10°C.

[0045] The gas components in the annealing furnace include nitrogen, hydrogen and inevitable impurities. Other gas components may be present as long as they are not detrimental in achieving the advantageous effects of the invention. If the hydrogen concentration in the annealing furnace atmosphere is less than 1 vol%, the activation effect by reduction cannot be obtained and chemical convertibility is deteriorated. Although the upper limit is not particularly limited, costs are increased and the effect is saturated if the hydrogen concentration exceeds 50 vol%. Thus, the hydrogen concentration is preferably not less than 1 vol% and not more than 50 vol%. The gas components in the annealing furnace except hydrogen gas are nitrogen gas and inevitable impurity gases. Other gas components may be present as long as they are not detrimental in achieving the advantageous effects of the invention.
After the steel sheet is cooled from the temperature range of not less than 750°C, hardening and tempering may be performed as required. Although the conditions for these treatments are not particularly limited, it is desirable that tempering be performed at a temperature of 150 to 400°C. The reasons are because elongation tends to be deteriorated if the temperature is less than 150°C as well as because hardness tends to be decreased if the temperature is in excess of 400°C.

[0046] According to the present invention, good chemical convertibility can be ensured even without performing electrolytic pickling. However, it is preferable that electrolytic pickling be performed in order to remove trace amounts of oxides that have been inevitably generated by surface segregation during annealing and thereby to ensure better chemical convertibility.
The electrolytic pickling conditions are not particularly limited. However, in order to efficiently remove the inevitably formed surface segregation of silicon and manganese oxides formed during the annealing, alternating electrolysis at a current density of not less than 1 A/dm^2 is desirable. The reasons why alternating electrolysis is selected are because the pickling effects are low if the steel sheet is fixed to a cathode as well as because if the steel sheet is fixed to an anode, iron that is dissolved during electrolysis is accumulated in the pickling solution and the Fe concentration in the pickling solution is increased with the result that the attachment of iron to the surface of the steel sheet causes problems such as dry contamination.

[0047] The pickling solution used in the electrolytic pickling is not particularly limited. However, nitric acid or hydrofluoric acid is not preferable because they are highly corrosive to a facility and require careful handling. Hydrochloric acid is not preferable because chlorine gas can be generated from the cathode. In view of corrosiveness and environment, the use of sulfuric acid is preferable. The sulfuric acid concentration is preferably not less than 5 mass% and not more than 20 mass%. If the sulfuric acid concentration is less than 5 mass%, the conductivity is so lowered that the bath voltage is raised during electrolysis possibly to increase the power load. On the other hand, any sulfuric acid concentration exceeding 20 mass% leads to a cost problem because a large loss is caused due to drag-out.

[0048] The temperature of the electrolytic solution is preferably not less than 40°C and not more than 70°C. Because the bath temperature is raised by the generation of heat by continuous electrolysis, the pickling effect may be lowered if the temperature is less than 40°C. Further, maintaining the temperature below 40°C is sometimes difficult. Furthermore, a temperature exceeding 70°C is not preferable in view of the durability of the lining of the electrolytic cell.

[0049] The high strength steel sheets of the present invention are obtained in the above manner.
As a result, the inventive steel sheet has a characteristic structure of the surface described below.
A surface portion of the steel sheet extending from the steel sheet surface within a depth of 100 μm contains an oxide of one or more selected from Fe, Si, Mn, Al and P, as well as from B, Nb, Ti, Cr, Mo, Cu and Ni at a total amount of 0.010 to 0.50 g/m^2 per single side surface. Further, with respect to a region extending from the steel sheet surface to a depth of 10 μm, a crystalline Si/Mn complex oxide is present in base iron grains that are within 1 μm from grain boundaries.

[0050] In a high strength steel sheet containing Si and a large amount of Mn, more sophisticated controlling of the microstructure and configuration of a surface portion of the steel sheet which can be an origin of corrosion or cracks is necessary in order to achieve satisfactory corrosion resistance after electrodeposition coating. For the purpose of ensuring chemical convertibility, the present invention first provides that the dew-point temperature is controlled as described hereinabove in order to increase the oxygen potential in the annealing step. As a result of the oxygen potential being increased, easily oxidized elements such as Si and Mn are internally oxidized beforehand immediately before a chemical conversion treatment and the activities of Si and Mn in the surface portion of the steel sheet are lowered. Consequently, the external oxidation of these elements is suppressed, resulting in improvements in chemical convertibility and corrosion resistance after electrodeposition coating. These improvements are obtained by configuring the steel sheet such that the surface portion of the steel sheet extending from the steel sheet surface within a depth of 100 μm contains an oxide of at least one or more selected from Fe, Si, Mn, Al and P, as well as from B, Nb, Ti, Cr, Mo, Cu and Ni at not less than 0.010 g/m^2 per single side surface. The effects are saturated even when such oxides are present in excess of 0.50 g/m^2. Thus, the upper limit is specified to be 0.50 g/m^2.

[0051] In the case where internal oxides are present only at grain boundaries and not in grains, the intergranular diffusion of easily oxidized elements in steel can be suppressed but the intragranular diffusion thereof may not be suppressed sufficiently. Thus, as described hereinabove, the present invention provides that internal oxidation is caused to take place not only at grain boundaries but also in grains by controlling the dew-point temperature of the atmosphere to become not less than -10°C when the heating furnace inside temperature is in the range of not less than A°C and not more than B°C (A: $600 \leq A \leq 780$, B: $800 \leq B \leq 900$). In detail, a crystalline Si/Mn complex oxide is caused to be present in base iron grains that are within 1 μm from grain boundaries in a region extending from the steel sheet surface to a depth of 10 μm. Because of the oxide being present in base iron grains, the amount of solute silicon and manganese in base iron grains in the vicinity of the oxide is decreased. As a result, the surface segregation of Si and Mn due to intragranular diffusion can be suppressed.

[0052] The structure of the surface of the high strength steel sheet obtained by the manufacturing method according to the present invention is as described above. There is no problem even when the oxides have been grown so as to extend to a region that is more than 100 μm away from the steel sheet surface. Further, no problems are caused even when the crystalline Si/Mn complex oxide is caused to be present in base iron grains that are more than 1 μm away from grain boundaries in a region extending from the steel sheet surface to a depth in excess of 10 μm.

[EXAMPLE 1]

[0053] Hereinbelow, the present invention will be described in detail based on EXAMPLES.
Hot rolled steel sheets with a steel composition described in Table 1 were pickled to remove black scales and were thereafter cold rolled to give cold rolled steel sheets with a thickness of 1.0 mm. Cold rolling was omitted for some of the steel sheets. That is, as-descaled hot rolled steel sheets (thickness: 2.0 mm) were also provided.

[0054] [Table 1]

Table 1

(mass%)

Steel code	C	Si	Mn	Al	P	S	Cr	Mo	B	Nb	Cu	Ni	Ti
<u>A</u>	0.04	<u>0.1</u>	1.9	0.04	0.01	0.003	-	-	-	-	-	-	-
B	0.03	0.4	2.0	0.04	0.01	0.003	-	-	-	-	-	-	-
C	0.09	0.9	2.1	0.03	0.01	0.004	-	-	-	-	-	-	-
D	0.13	1.3	2.0	0.03	0.01	0.003	-	-	-	-	-	-	-

(continued)

(mass%)

Steel code	C	Si	Mn	Al	P	S	Cr	Mo	B	Nb	Cu	Ni	Ti
E	0.09	1.7	1.9	0.03	0.01	0.003	-	-	-	-	-	-	-
F	0.08	2.0	2.1	0.03	0.01	0.003	-	-	-	-	-	-	-
G	0.11	1.3	2.8	0.04	0.01	0.003	-	-	-	-	-	-	-
H	0.12	1.3	2.0	0.95	0.01	0.003	-	-	-	-	-	-	-
I	0.12	1.3	2.0	0.04	0.06	0.004	-	-	-	-	-	-	-
J	0.12	1.3	2.1	0.03	0.01	0.008	-	-	-	-	-	-	-
K	0.12	1.3	1.9	0.02	0.01	0.003	0.7	-	-	-	-	-	-
L	0.12	1.3	2.0	0.04	0.01	0.003	-	0.12	-	-	-	-	-
M	0.12	1.3	2.1	0.03	0.01	0.003	-	-	0.005	-	-	-	-
N	0.12	1.3	2.0	0.05	0.01	0.003	-	-	0.001	0.04	-	-	-
O	0.12	1.3	1.9	0.03	0.01	0.004	-	0.11	-	-	0.2	0.3	-
P	0.12	1.3	1.9	0.04	0.01	0.003	-	-	0.003	-	-	-	0.03
Q	0.12	1.3	2.0	0.03	0.01	0.004	-	-	-	-	-	-	0.05
R	0.20	1.3	2.1	0.04	0.01	0.003	-	-	-	-	-	-	-
S	0.12	2.1	1.9	0.04	0.01	0.003	-	-	-	-	-	-	-
T	0.12	1.3	3.1	0.04	0.01	0.004	-	-	-	-	-	-	-
U	0.12	1.3	2.0	1.10	0.01	0.004	-	-	-	-	-	-	-
V	0.12	1.3	1.9	0.03	0.07	0.003	-	-	-	-	-	-	-
W	0.12	1.3	2.1	0.04	0.01	0.015	-	-	-	-	-	-	-

Underlines indicate "outside the inventive range".

Next, the cold rolled steel sheets and the hot rolled steel sheets obtained above were introduced into a continuous annealing facility. The steel sheet was passed through the annealing facility while controlling the heating furnace inside temperature and the dew-point temperature as described in Table 2. The annealed steel sheet was thereafter subjected to water hardening and then to tempering at 300°C for 140 seconds. Subsequently, electrolytic pickling was performed by alternating electrolysis in a 5 mass% aqueous sulfuric acid solution at 40°C under current density conditions described in Table 2 while switching the polarity of the sample sheet between anodic and cathodic alternately each after 3 seconds. Thus, sample sheets were prepared. The dew-point temperature in the annealing furnace was basically set at -35°C except when the dew-point temperature was controlled as described above. The gas components in the atmosphere included nitrogen gas, hydrogen gas and inevitable impurity gases. The dew-point temperature was controlled by dehumidifying the atmosphere or by removing water in the atmosphere by absorption. The hydrogen concentration in the atmosphere was basically set at 10 vol%.
With respect to the obtained sample sheets, TS and El were measured in accordance with a tensile testing method for metallic materials described in JIS Z 2241. Further, the sample sheets were tested to examine chemical convertibility and corrosion resistance, as well as the amount of oxides present in a surface portion of the steel sheet extending immediately from the surface of the steel sheet to a depth of 100 μm (the internal oxidation amount). The measurement methods and the evaluation criteria are described below.

Chemical convertibility

[0055] Chemical convertibility was evaluated by the following method.
A chemical conversion treatment liquid (PALBOND L3080 (registered trademark)) manufactured by Nihon Parkerizing Co., Ltd. was used. A chemical conversion treatment was carried out in the following manner.

The sample sheet was degreased with degreasing liquid FINE CLEANER (registered trademark) manufactured by Nihon Parkerizing Co., Ltd., and was thereafter washed with water. Subsequently, the surface of the sample sheet was conditioned for 30 seconds with surface conditioning liquid PREPAREN Z (registered trademark) manufactured by Nihon Parkerizing Co., Ltd. The sample sheet was then soaked in the chemical conversion treatment liquid (PALBOND L3080) at 43°C for 120 seconds, washed with water and dried with hot air.
The sample sheet after the chemical conversion treatment was observed with a scanning electron microscope (SEM) at 500x magnification with respect to randomly selected five fields of view. The area ratio of the regions that had not been covered with the chemical conversion coating was measured by image processing. Chemical convertibility was evaluated based on the area ratio of the non-covered regions according to the following criteria. The symbol ○ indicates an acceptable level.

○: not more than 10%
x: more than 10%

Corrosion resistance after electrodeposition coating

[0056] A 70 mm x 150 mm test piece was cut out from the sample sheet that had been subjected to the above chemical conversion treatment. The test piece was cationically electrodeposition coated with PN-150G (registered trademark) manufactured by NIPPON PAINT Co., Ltd. (baking conditions: 170°C x 20 min, film thickness: 25 μm). Thereafter, the edges and the non-test surface were sealed with an Al tape, and the test surface was cut deep into the base steel with a cutter knife to create a cross cut pattern (cross angle: 60°), thereby preparing a sample.
Next, the sample was soaked in a 5 mass% aqueous NaCl solution (55°C) for 240 hours, removed from the solution, washed with water and dried. Thereafter, an adhesive tape was applied to the cross cut pattern and was peeled therefrom. The exfoliation width was measured and was evaluated based on the following criteria. The symbol ○ indicates an acceptable level.

○: The exfoliation width from each cut line was less than 2.5 mm.
×: The exfoliation width from each cut line was 2.5 mm or more.

Workability

[0057] To evaluate workability, a JIS No. 5 tensile test piece was sampled from the sample sheet in a direction that was 90° relative to the rolling direction. The test piece was subjected to a tensile test at a constant cross head speed of 10 mm/min in accordance with JIS Z 2241, thereby determining the tensile strength (TS/MPa) and the elongation (El %). For steel sheets with TS of less than 650 MPa, workability was evaluated to be good when $TS \times El \geq 22000$ and to be bad when $TS \times El < 22000$. For steel sheets with TS of 650 MPa to 900 MPa, workability was evaluated to be good when $TS \times El \geq 20000$ and to be bad when $TS \times El < 20000$. For steel sheets with TS of not less than 900 MPa, workability was evaluated to be good when $TS \times El \geq 18000$ and to be bad when $TS \times El < 18000$.

Internal oxidation amount in region from steel sheet surface to depth of 100 μm

[0058] The internal oxidation amount was measured by an "impulse furnace fusion-infrared absorption method". It should be noted that the amount of oxygen present in the starting material (namely, the high strength steel sheet before annealing) should be subtracted. Thus, in the invention, surface portions on both sides of the continuously annealed high strength steel sheet were polished by at least 100 μm and thereafter the oxygen concentration in the steel was measured. The measured value was obtained as the oxygen amount OH of the starting material. Further, the oxygen concentration was measured across the entirety of the continuously annealed high strength steel sheet in the sheet thickness direction. The measured value was obtained as the oxygen amount OI after internal oxidation. The difference between OI and OH (= OI - OH) was calculated wherein OI was the oxygen amount in the high strength steel sheet after internal oxidation and OH was the oxygen amount in the starting material. The difference was then converted to an amount per unit area (namely, 1 m^2) on one surface, thereby determining the internal oxidation amount (g/m^2).
The results and the manufacturing conditions are described in Table 2.

[Table 2]

No.	Steel				Annealing furnace				Internal oxidation amount (g/m^2) in region from immediately under coating to depth of 100μm	Internal oxide in region from immediately under coating to depth of 10μm		Electrolytic pickling	Current density A/dm^2	Chemical convertibility	Corrosion resistance after electrodeposition coating	TS MPa	El %	TS×El	Workability	Remarks
	Steel code	Si (mass%)	Mn (mass%)	Steel sheet	Temp. A (℃)	Temp. B (℃)	Dew-point temp. (℃) at between temp. A and temp. B	Maximum temp. (℃)		Presence	Presence of intragranular precipitate immediately under coating at depth within 1μm from grain									
1	D	1.3	2.0	Cold rolled	600	700	-5	850	0.004	×	×	Not performed	–	×	×	1051	20.8	21861	Good	COMP. EX.
2	D	1.3	2.0	Cold rolled	600	790	-5	850	0.009	×	×	Not performed	–	×	×	1029	21.1	21712	Good	COMP. EX.
3	D	1.3	2.0	Cold rolled	600	800	-5	800	0.021	○	○	Not performed	–	○	○	1031	20.4	21032	Good	INV. EX.
4	D	1.3	2.0	Cold rolled	600	800	-5	830	0.025	○	○	Not performed	–	○	○	1025	20.3	20808	Good	INV. EX.
5	D	1.3	2.0	Cold rolled	600	800	-5	860	0.028	○	○	Not performed	–	○	○	1021	20.2	20624	Good	INV. EX.
6	D	1.3	2.0	Cold rolled	600	800	-5	890	0.033	○	○	Not performed	–	○	○	1029	20.0	20580	Good	INV. EX.
7	D	1.3	2.0	Cold rolled	650	850	-5	850	0.022	○	○	Not performed	–	○	○	1034	20.7	21404	Good	INV. EX.
8	D	1.3	2.0	Cold rolled	700	850	-5	850	0.020	○	○	Not performed	–	○	○	1039	20.6	21403	Good	INV. EX.
9	D	1.3	2.0	Hot rolled	700	850	-5	850	0.123	○	○	Not performed	–	○	○	1040	20.3	21112	Good	INV. EX.
10	D	1.3	2.0	Cold rolled	750	850	-5	850	0.015	○	○	Not performed	–	○	○	1024	20.4	20890	Good	INV. EX.
11	D	1.3	2.0	Cold rolled	780	850	-5	850	0.012	○	○	Not performed	–	○	○	1031	20.8	21445	Good	INV. EX.
12	D	1.3	2.0	Cold rolled	790	850	-5	850	0.007	×	×	Not performed	–	×	×	990	20.9	20691	Good	COMP. EX.
13	D	1.3	2.0	Cold rolled	700	850	-35	850	0.006	×	×	Not performed	–	×	×	991	20.7	20514	Good	COMP. EX.
14	D	1.3	2.0	Cold rolled	700	850	-15	850	0.008	×	×	Not performed	–	×	×	1159	18.0	20862	Good	COMP. EX.
15	D	1.3	2.0	Cold rolled	700	850	-10	850	0.011	○	○	Not performed	–	○	○	1044	19.9	20776	Good	INV. EX.
16	D	1.3	2.0	Cold rolled	700	850	0	850	0.068	○	○	Not performed	–	○	○	1033	20.4	21073	Good	INV. EX.
17	D	1.3	2.0	Cold rolled	700	850	20	850	0.221	○	○	Not performed	–	○	○	1050	20.6	21630	Good	INV. EX.
18	D	1.3	2.0	Cold rolled	700	850	60	850	0.436	○	○	Not performed	–	○	○	1051	20.1	21125	Good	INV. EX.
19	D	1.3	2.0	Cold rolled	700	850	-5	850	0.021	○	○	Performed	1	○	○	1041	20.0	20820	Good	INV. EX.
20	D	1.3	2.0	Cold rolled	700	850	-5	850	0.019	○	○	Performed	5	○	○	1042	20.7	21569	Good	INV. EX.
21	D	1.3	2.0	Cold rolled	700	850	-5	850	0.020	○	○	Performed	10	○	○	1044	20.9	21820	Good	INV. EX.

Underlines indicate that manufacturing conditions are outside the inventive ranges.

[Table 2 (Cont.)]

Table 2 (Cont.)

No.	Steel				Annealing furnace				Internal oxidation amount (g/m^2) in region from immediately under coating to depth of 100μm	Internal oxide in region from immediately under coating to depth of 10μm		Electrolytic pickling	Current density A/dm^2	Chemical convertibility	Corrosion resistance after electrodeposition coating	TS MPa	El %	TS×El	Workability	Remarks
	Steel code	Si (mass%)	Mn (mass%)	Steel sheet	Temp. A (℃)	Temp. B (℃)	Dew-point temp. (℃) at between temp. A and temp. B	Maximum temp. (℃)		Presence	Presence of intragranular precipitate immediately under coating at depth within 1μm from grain									
22	A	0.1	1.9	Cold rolled	700	850	-5	850	0.021	○	○	Not performed	–	○	○	712	26.5	18868	Bad	COMP. EX.
23	B	0.4	2.0	Cold rolled	700	850	-5	850	0.009	○	○	Not performed	–	○	○	1010	20.9	21109	Good	INV. EX.
24	C	0.9	2.1	Cold rolled	700	850	-5	850	0.011	○	○	Not performed	–	○	○	1021	21.4	21849	Good	INV. EX.
25	E	1.7	1.9	Cold rolled	700	850	-5	850	0.030	○	○	Not performed	–	○	○	1036	22.8	23621	Good	INV. EX.
26	F	2.0	2.1	Cold rolled	700	850	-5	850	0.039	○	○	Not performed	–	○	○	1029	20.5	21095	Good	INV. EX.
27	G	1.3	2.8	Cold rolled	700	850	-5	850	0.021	○	○	Not performed	–	○	○	1064	19.7	20961	Good	INV. EX.
28	H	1.3	2.0	Cold rolled	700	850	-5	850	0.051	○	○	Not performed	–	○	○	1066	20.3	21640	Good	INV. EX.
29	I	1.3	2.0	Cold rolled	700	850	-5	850	0.022	○	○	Not performed	–	○	○	1145	20.1	23015	Good	INV. EX.
30	J	1.3	2.1	Cold rolled	700	850	-5	850	0.015	○	○	Not performed	–	○	○	1044	19.9	20776	Good	INV. EX.
31	K	1.3	1.9	Cold rolled	700	850	-5	850	0.016	○	○	Not performed	–	○	○	1063	19.4	20622	Good	INV. EX.
32	L	1.3	2.0	Cold rolled	700	850	-5	850	0.013	○	○	Not performed	–	○	○	1052	19.5	20514	Good	INV. EX.
33	M	1.3	2.1	Cold rolled	700	850	-5	850	0.014	○	○	Not performed	–	○	○	1037	20.9	21673	Good	INV. EX.
34	N	1.3	2.0	Cold rolled	700	850	-5	850	0.016	○	○	Not performed	–	○	○	1077	20.4	21971	Good	INV. EX.
35	O	1.3	1.9	Cold rolled	700	850	-5	850	0.015	○	○	Not performed	–	○	○	1078	21.0	22638	Good	INV. EX.
36	P	1.3	1.9	Cold rolled	700	850	-5	850	0.013	○	○	Not performed	–	○	○	811	26.7	21654	Good	INV. EX.
37	Q	1.3	2.0	Cold rolled	700	850	-5	850	0.017	○	○	Not performed	–	○	○	1055	19.7	20784	Good	INV. EX.
38	R	1.3	2.1	Cold rolled	700	850	-5	850	0.019	○	○	Not performed	–	○	○	1066	12.8	13645	Bad	COMP. EX.
39	S	2.1	1.9	Cold rolled	700	850	-5	850	0.052	○	○	Not performed	–	×	○	1212	16.4	19877	Good	COMP. EX.
40	T	1.3	3.1	Cold rolled	700	850	-5	850	0.016	○	○	Not performed	–	○	○	1125	13.4	15075	Bad	COMP. EX.
41	U	1.3	2.0	Cold rolled	700	850	-5	850	0.051	○	○	Not performed	–	×	×	1079	21.4	23091	Good	COMP. EX.
42	V	1.3	1.9	Cold rolled	700	850	-5	850	0.033	○	○	Not performed	–	×	○	1144	19.4	22194	Good	COMP. EX.
43	W	1.3	2.1	Cold rolled	700	850	-5	850	0.020	○	○	Not performed	–	○	×	1079	20.3	21904	Good	COMP. EX.

Underlines indicate that manufacturing conditions are outside the inventive ranges.

From Table 2, the high strength steel sheets manufactured by the inventive method were shown to be excellent in chemical convertibility, corrosion resistance after electrodeposition coating and workability in spite of the fact that these high strength steel sheets contained large amounts of easily oxidized elements such as Si and Mn.
On the other hand, the steel sheets obtained in COMPARATIVE EXAMPLES were poor in at least one of chemical convertibility, corrosion resistance after electrodeposition coating and workability.

[Industrial Applicability]

[0059] The high strength steel sheets according to the present invention are excellent in chemical convertibility, corrosion resistance and workability, and can be used as surface-treated steel sheets for reducing the weight and increasing the strength of bodies of automobiles. Besides automobiles, the inventive high strength steel sheets can be used as surface-treated steel sheets having corrosion resistance on the base steel sheet in a wide range of applications including home appliances and building materials.

Claims

1. A method for manufacturing high strength steel sheets, comprising continuous annealing of a steel sheet which includes, in terms of mass%, C at 0.01 to 0.18%, Si at 0.4 to 2.0%, Mn at 1.0 to 3.0%, Al at 0.001 to 1.0%, P at 0.005 to 0.060% and S at $\leq$ 0.01%, the balance being represented by Fe and inevitable impurities, while controlling the dew-point temperature of the atmosphere to become not less than -10°C when the heating furnace inside temperature is in the range of not less than A°C and not more than B°C during the course of heating wherein A is $600 \leq A \leq 780$ and B is $800 \leq B \leq 900$.

2. The method for manufacturing high strength steel sheets according to Claim 1, wherein the chemical composition of the steel sheet further includes one or more elements selected from B at 0.001 to 0.005%, Nb at 0.005 to 0.05%, Ti at 0.005 to 0.05%, Cr at 0.001 to 1.0%, Mo at 0.05 to 1.0%, Cu at 0.05 to 1.0% and Ni at 0.05 to 1.0% in terms of mass%.

3. The method for manufacturing high strength steel sheets according to Claim 1 or 2, further comprising, after the continuous annealing, electrolytically pickling the steel sheet in an aqueous solution containing sulfuric acid.

4. A high strength steel sheet manufactured by the method described in any one of Claims 1 to 3 in which a surface portion of the steel sheet extending from the steel sheet surface within a depth of 100 μm contains an oxide of at least one or more selected from Fe, Si, Mn, Al, P, B, Nb, Ti, Cr, Mo, Cu and Ni at 0.010 to 0.50 g/m^2 per single side surface, and in which with respect to a region extending from the steel sheet surface within a depth of 10 μm, a crystalline Si/Mn oxide is present in grains that are within 1 μm from crystal grain boundaries of the steel sheet.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/067612

A. CLASSIFICATION OF SUBJECT MATTER
C23C8/14(2006.01)i, *C21D9/46*(2006.01)i, *C22C38/00*(2006.01)i, *C22C38/06*(2006.01)i, *C22C38/58*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C8/00-12/02, C21D9/46, C22C38/00, C22C38/06, C22C38/58

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	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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 Y	WO 2007/043273 A1 (Nippon Steel Corp.), 19 April 2007 (19.04.2007), page 6, lines 21 to 27; page 7, lines 1 to 24; page 11, line 11 to page 12, line 16; tables 1, 2; fig. 2 & US 2009/0123651 A1 & EP 1936000 A1 & CA 2625790 A & KR 10-2008-0046241 A & CN 101287854 A	1,2 3,4
X	JP 2010-126758 A (JFE Steel Corp.), 10 June 2010 (10.06.2010), claims; paragraphs [0048], [0056] & WO 2010/061957 A1	4

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

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

Date of the actual completion of the international search
10 November, 2010 (10.11.10)

Date of mailing of the international search report
22 November, 2010 (22.11.10)

Name and mailing address of the ISA/
Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/067612

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2010-053371 A (JFE Steel Corp.), 11 March 2010 (11.03.2010), claim 1; paragraphs [0004] to [0006], [0009], [0013] (Family: none)	3,4
Y	JP 10-110300 A (Hitachi Metals, Ltd.), 28 April 1998 (28.04.1998), paragraph [0002] (Family: none)	3,4
Y	JP 09-019775 A (Yamaki Kogyo Kabushiki Kaisha), 21 January 1997 (21.01.1997), paragraph [0014] (Family: none)	3,4

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 5320952 A **[0009]**
- JP 2004323969 A **[0009]**
- JP 6010096 A **[0009]**
- JP 2003113441 A **[0009]**
- JP 55145122 A **[0009]**
- JP 2006045615 A **[0009]**