



(11)

EP 4 578 986 A1

(12)

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

(43) Date of publication:
02.07.2025 Bulletin 2025/27

(21) Application number: **23857640.9**

(22) Date of filing: **17.08.2023**

(51) International Patent Classification (IPC):
C22C 38/38 ^(2006.01) **C22C 38/34** ^(2006.01)
C22C 38/06 ^(2006.01) **C22C 38/58** ^(2006.01)
C22C 38/50 ^(2006.01) **C22C 38/44** ^(2006.01)
C22C 38/42 ^(2006.01) **C21D 8/02** ^(2006.01)

(52) Cooperative Patent Classification (CPC):
C21D 8/02; C22C 38/06; C22C 38/34; C22C 38/38;
C22C 38/42; C22C 38/44; C22C 38/50; C22C 38/58

(86) International application number:
PCT/KR2023/012140

(87) International publication number:
WO 2024/043606 (29.02.2024 Gazette 2024/09)

(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 ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **22.08.2022 KR 20220104736**

(71) Applicant: **POSCO Co., Ltd**
Pohang-si, Gyeongsangbuk-do 37859 (KR)

(72) Inventors:
• **LEE, Sea-Woong**
Gwangyang-si, Jeollanam-do 57807 (KR)

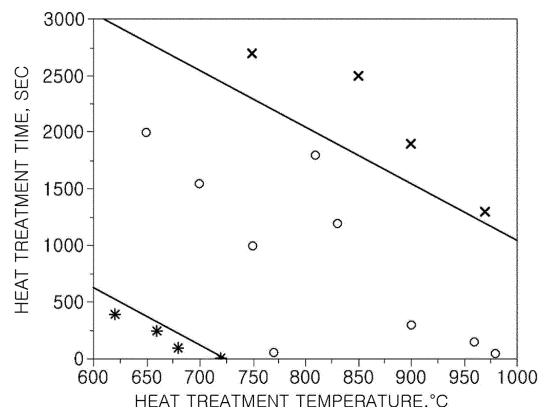
- **OH, Jin-Keun**
Gwangyang-si, Jeollanam-do 57807 (KR)
- **KIM, Seong-Woo**
Gwangyang-si, Jeollanam-do 57807 (KR)
- **KIM, Sang-Heon**
Gwangyang-si, Jeollanam-do 57807 (KR)
- **LEE, Sang-Cheol**
Gwangyang-si, Jeollanam-do 57807 (KR)
- **KIM, Kwon-Il**
Gwangyang-si, Jeollanam-do 57807 (KR)

(74) Representative: **Meissner Bolte Partnerschaft**
mbB
Patentanwälte Rechtsanwälte
Postfach 86 06 24
81633 München (DE)

(54) **COLD ROLLED STEEL SHEET FOR HOT-PRESS FORMING HAVING EXCELLENT SURFACE QUALITY, HOT-PRESS-FORMED MEMBER, AND METHOD FOR MANUFACTURING SAME**

(57) The present invention relates to a cold rolled steel sheet for hot-press forming, a hot-press-formed member, and a method for manufacturing same and, more specifically, to a cold rolled steel sheet for hot-press forming, having excellent surface quality, a hot-press-formed member, and a method for manufacturing same.

Fig 3



EP 4 578 986 A1

Description

Technical Field

5 **[0001]** The present disclosure relates to a cold-rolled steel sheet for hot press forming, a hot press formed member, and manufacturing methods thereof, and in particular, to a cold-rolled steel sheet for hot press forming and a hot press formed member that have excellent surface quality, and manufacturing methods thereof.

Background Art

10 **[0002]** Recently, a number of studies have been conducted on automobile structural members to improve fuel efficiency through weight reduction of automobiles and to improve impact resistance through high strength. In particular, a lot of members manufactured by hot press forming have been applied to automobile structural members.

15 **[0003]** Patent Document 1 suggests that ultra-high strength with a tensile strength of 1,600 MPa or more may be secured by heating an Al-Si plated steel sheet to 850°C or higher, and then performing hot press forming and quenching with a press to form a structure of a member with martensite. In addition, it is disclosed that corrosion resistance and spot weldability may be secured without shot blasting due to an alloyed layer and a diffusion layer formed by Fe diffusion from a base material to a plating layer during a heat treatment.

20 **[0004]** However, in the case of the Al-Si plated steel sheet, an Al-Si plating layer needs to be formed, and a separate plating process is required, which reduces cost efficiency and productivity.

[0005] On the other hand, in the case of non-plated materials, spot weldability cannot be secured due to an oxide layer formed during the heat treatment, a shot blasting process is necessary to remove the oxide layer, and it is difficult to secure corrosion resistance.

25 **[0006]** Therefore, there is a demand for developing a cold-rolled steel sheet for hot press forming and a hot press formed member that may secure excellent corrosion resistance and spot weldability without a plating process and a shot blasting process, and manufacturing methods thereof.

[Prior Art Document]

30 **[0007]** (Patent Document 1) U.S. Patent No. 6,296,805 (published on October 2, 2001)

Summary of Invention

Technical Problem

35 **[0008]** An aspect of the present disclosure is to provide a cold-rolled steel sheet for hot press forming and a hot press formed member that have excellent surface quality, and manufacturing methods thereof.

40 **[0009]** An object of the present disclosure is not limited to the above description. Those skilled in the art will have no difficulties in understanding the additional objects of the present disclosure from the overall descriptions of the present specification.

Solution to Problem

45 **[0010]** According to an aspect of the present disclosure, a cold-rolled steel sheet includes a base steel sheet and a first oxide layer formed on the base steel sheet, wherein the first oxide layer contains two or more of Fe, Mn, Cr, and Si, and has a thickness of 5 to 500 nm.

[0011] The base steel sheet may contain, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3 to 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.

50 **[0012]** The base steel sheet may contain one or more of 0.001 to 0.4% of Ti, 0.001 to 0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

[0013] A sum of contents of Si, Mn, and Cr in the first oxide layer may be 30% or more in terms of wt%.

[0014] The cold-rolled steel sheet may have a microstructure containing 5 area% or more of ferrite and cementite.

55 **[0015]** According to another aspect of the present disclosure, a member includes a base steel sheet; a first oxide layer formed on the base steel sheet; and a second oxide layer formed on the first oxide layer,

wherein the first oxide layer contains two or more of Fe, Mn, Cr, and Si, and

the second oxide layer is formed of an Fe-based oxide and has a thickness of 0.1 to 10 μm .

[0016] The base steel sheet may contain, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3% or more and less than 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.

[0017] The base steel sheet may contain one or more of 0.001 to 0.4% of Ti, 0.001 to 0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

[0018] A sum of contents of Si, Mn, and Cr in the second oxide layer may be less than 30% in terms of wt%.

[0019] The member may have a microstructure containing martensite or bainite as a main phase.

[0020] A tensile strength of the member may be 500 MPa or more.

[0021] According to still another aspect of the present disclosure, a manufacturing method of a cold-rolled steel sheet includes: reheating a steel slab;

hot rolling the reheated steel slab;

cooling and coiling the hot-rolled steel sheet;

cold rolling the coiled steel sheet; and

performing continuous annealing on the cold-rolled steel sheet,

wherein during the continuous annealing, a temperature increase rate at an atmosphere temperature of room temperature to 700°C is 3.0 to 20.0°C/s, a temperature increase rate at an atmosphere temperature of 700 to 800°C is 0.08 to 1.5°C/s, a temperature increase rate at an atmosphere temperature of 800 to 900°C is 0.01 to 1.5°C/s, and a temperature increase rate at an atmosphere temperature of 900 to 1,000°C is 0.01 to 1.0°C/s.

[0022] The steel slab may contain, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3 to 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.

[0023] The steel slab may contain one or more of 0.001 to 0.4% of Ti, 0.001 to 0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

[0024] The reheating may be performed in a temperature range of 1,000 to 1,300°C,

the hot rolling may be performed at a finish rolling temperature of Ar3 to 1,000°C,

the coiling may be performed in a temperature range of Ms to 750°C, and

the cold rolling may be performed at a reduction ratio of 30 to 80%.

[0025] The continuous annealing may be performed in a steel sheet temperature range of 700 to 900°C, and a continuous annealing time may be 1 to 1,000 seconds.

[0026] According to still another aspect of the present disclosure, a manufacturing method of a member includes: performing a heat treatment on a cold-rolled steel sheet; and

performing hot press forming on the heat-treated steel sheet and then cooling the hot press formed steel sheet, wherein during the heat treatment, an A value defined in the following Relational Expression 1 is 0.6 to 1.0:

[Relational Expression 1]

$$A = (T + 0.2 t) / 1,210$$

(wherein T represents a heating temperature and a unit thereof is °C, and t represents a total heating time and a unit thereof is a second).

[0027] During the heat treatment, the heating may be performed to the heating temperature at an atmosphere temperature increase rate of 1 to 1,000°C/s.

[0028] During the heat treatment, the heating temperature may be 700 to 1,000°C, and the heating time may be 150 to 1,000 seconds.

[0029] After the hot press forming, during the cooling, the cooling may be performed to an Mf temperature or lower at a cooling rate of 10 to 1,000°C/s.

Advantageous Effects of Invention

[0030] According to an aspect of the present disclosure, it is possible to provide a cold-rolled steel sheet for hot press forming and a hot press formed member that have excellent surface quality, and manufacturing methods thereof.

[0031] According to an aspect of the present disclosure, it is possible to provide a cold-rolled steel sheet for hot press forming and a hot press formed member that may be applied to an automobile structural reinforcement or reinforcing material and have excellent surface quality and impact resistance without a plating process and a shot blasting process, and manufacturing methods thereof.

Brief Description of Drawings

[0032]

FIG. 1 illustrates surface quality after hot press forming of each of Inventive Example 2 and Comparative Example 10.

FIG. 2 illustrates phosphate coverage after hot press forming of each of Inventive Example 1 and Comparative Example 2.

FIG. 3 illustrates a change in surface quality according to hot press forming conditions.

FIG. 4 illustrates photographs obtained by observing surfaces after hot press forming of Invention Example 11 and Comparative Example 24.

Best Mode for Invention

[0033] Hereinafter, preferred exemplary embodiments in the present disclosure will be described. The exemplary embodiments in the present disclosure may be modified in various forms, and the scope of the present disclosure should not be interpreted to be limited to the exemplary embodiments set forth below. The exemplary embodiments are provided in order to describe the present disclosure in more detail to those skilled in the art to which the present disclosure pertains.

[0034] The inventors of the present disclosure have recognized a problem that, in the case of a non-plated cold-rolled steel sheet for hot press forming, excellent surface quality of a member cannot be secured due to an oxide layer formed during a heat treatment performed in the manufacture of a hot press formed member, and a shot blasting process is absolutely necessary to remove the oxide layer, and have conducted intensive studies to solve the problem while securing excellent surface quality.

[0035] As a result, the inventors of the present disclosure have confirmed that a composite oxide layer having a target thickness may be formed during annealing by precisely controlling an alloy composition and manufacturing conditions, in particular, contents of Cr, Si, and Mn and a rate of change in atmosphere temperature during annealing, and excellent surface quality may be secured without a shot blasting process by controlling hot press forming process conditions, thereby completing the present disclosure.

[0036] Hereinafter, the present disclosure will be described in detail.

[0037] Hereinafter, a cold-rolled steel sheet of the present disclosure will be described in detail.

[0038] A cold-rolled steel sheet according to an aspect of the present disclosure may include a base steel sheet and a first oxide layer formed on the base steel sheet.

[0039] Hereinafter, a composition of the base steel sheet of the cold-rolled steel sheet according to an aspect of the present disclosure will be described in detail.

[0040] In the present disclosure, unless otherwise specified, % indicating a content of each element is based on weight.

[0041] The base steel sheet of the cold-rolled steel sheet according to an aspect of the present disclosure may contain, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3 to 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.

Carbon (C): 0.05 to 0.4%

[0042] Carbon (C) is an essential element for increasing strength of a heat-treated member and needs to be added appropriately. When a content of carbon (C) is less than 0.05%, it may be difficult to secure sufficient strength. On the other hand, when the content of carbon (C) exceeds 0.4%, when a hot-rolled material is cold-rolled, cold rollability of the hot-rolled material is significantly deteriorated because the strength of the hot-rolled material is excessively high, and spot weldability may be significantly deteriorated. According to another aspect of the present disclosure, a lower limit of carbon (C) may be 0.06%. According to still another aspect of the present disclosure, an upper limit of carbon (C) may be 0.38%, and according to still another aspect, the upper limit may be 0.36%.

Silicon (Si): 0.5 to 3.0%

[0043] Silicon (Si) may play an important role in forming a silicon (Si)-based oxide layer by being concentrated on a surface of a cold-rolled steel sheet when annealing the cold-rolled steel sheet on a continuous annealing line, and may also play a role in securing spot weldability of a member by suppressing the formation of Fe, Mn, and Cr oxide layers in a hot press forming process. When a content of silicon (Si) is less than 0.5%, the effects described above may be insufficient. According to another aspect of the present disclosure, a lower limit of silicon (Si) may be 0.8%. On the other hand, when the content of silicon (Si) exceeds 3.0%, an excessively thick Si-based amorphous oxide layer is formed, which may cause deterioration of spot weldability. According to still another aspect of the present disclosure, an upper limit of silicon (Si) may be 2.8%.

Chromium (Cr): 0.3 to 5.0%

[0044] Chromium (Cr) may serve to not only improve hardenability of a steel sheet, but also help a Si-based amorphous oxide layer to be stably formed on a surface layer by an appropriate reaction with Si. When a content of chromium (Cr) is less than 0.3%, the effects described above may be insufficient. According to another aspect of the present disclosure, a lower limit of chromium (Cr) may be 0.5%. On the other hand, when the content of chromium (Cr) exceeds 5.0%, the effects may be saturated and the manufacturing costs may increase. According to still another aspect of the present disclosure, an upper limit of chromium (Cr) may be 4.5%.

Manganese (Mn): 0.01 to 4.0%

[0045] Manganese (Mn) may be added to secure a solid solution strengthening effect and to reduce a critical cooling rate for securing martensite in a hot press formed member. When a content of manganese (Mn) is less than 0.01%, the effects described above may be insufficient. According to another aspect of the present disclosure, a lower limit of manganese (Mn) may be 0.05%. On the other hand, when the content of manganese (Mn) exceeds 4.0%, since strength of a steel sheet before a hot press forming process increases excessively, it may be difficult to perform a blanking work, and due to excessive addition of alloy iron, costs of raw materials may increase and spot weldability may be deteriorated. According to another aspect of the present disclosure, an upper limit of manganese (Mn) may be 3.9%, and according to still another aspect, the upper limit may be 3.8%.

Aluminum (Al): 0.001 to 0.4%

[0046] Aluminum (Al) may increase cleanness of the steel, together with Si, through deoxidation action in steelmaking. When a content of aluminum (Al) is less than 0.001%, the effects described above may be insufficient. According to another aspect of the present disclosure, a lower limit of aluminum (Al) may be 0.005%. On the other hand, when the content of aluminum (Al) exceeds 0.4%, an Ac3 temperature increases excessively, and thus, a heating temperature may need to be increased. According to still another aspect of the present disclosure, an upper limit of aluminum (Al) may be 0.3%, and according to still another aspect, the upper limit may be 0.2%.

Phosphorus (P): 0.001 to 0.05%

[0047] Phosphorus (P) is an impurity, and a lot of manufacturing costs may be required to control a content of phosphorus (P) to less than 0.001%, and thus, a lower limit of the content of phosphorus (P) may be limited to 0.001%. On the other hand, when the content of phosphorus (P) exceeds 0.05%, weldability of a hot press formed member may be significantly deteriorated. According to another aspect of the present disclosure, an upper limit of phosphorus (P) may be 0.03%.

Sulfur (S): 0.0001 to 0.02%

[0048] Sulfur (S) is an impurity, and a lot of manufacturing costs may be required to control a content of sulfur (S) to less than 0.0001%, and thus, a lower limit of the content of sulfur (S) may be limited to 0.0001%. On the other hand, when the content of sulfur (S) exceeds 0.02%, ductility, impact properties, and weldability of a member may be deteriorated. According to another aspect of the present disclosure, an upper limit of sulfur (S) may be 0.01%.

Nitrogen (N): 0.001 to 0.02%

[0049] Nitrogen (N) is an impurity, and a lot of manufacturing costs may be required to control a content of nitrogen (N) to

less than 0.001%, and thus, a lower limit of the content of nitrogen (N) may be limited to 0.001%. On the other hand, a content of nitrogen (N) exceeds 0.02%, a slab may be sensitive to cracks during casting, and impact properties may be deteriorated. According to an aspect of the present disclosure, an upper limit of nitrogen (N) may be 0.01%.

[0050] The steel material of the present disclosure may contain a balance of iron (Fe) and unavoidable impurities in addition to the composition described above. Since the unavoidable impurities may be unintentionally incorporated in a general manufacturing process, the unavoidable impurities may not be excluded. Since these impurities are known to those skilled in a general steel manufacturing field, all the contents thereof are not particularly described in the present specification.

[0051] The base steel sheet of the cold-rolled steel sheet according to an aspect of the present disclosure may contain one or more of 0.001 to 0.4% of Ti, 0.001 to 0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

Titanium (Ti), niobium (Nb), zirconium (Zr), and vanadium (V): 0.001 to 0.4%

[0052] Titanium (Ti), niobium (Nb), zirconium (Zr), and vanadium (V) are effective in improving strength of a heat-treated member by forming fine precipitates and are effective in stabilizing retained austenite and improving impact toughness by inducing grain refinement. When a content of titanium (Ti), niobium (Nb), zirconium (Zr), and vanadium (V) (in a case where two or more types are added, the sum of these elements) is less than 0.001%, the effects described above may be insufficient, and when the content of titanium (Ti), niobium (Nb), zirconium (Zr), and vanadium (V) exceeds 0.4%, the effects may be saturated, and an increase in cost may be caused due to excessive addition of alloy iron.

Boron (B): 0.0001 to 0.01%

[0053] Boron (B) is an element that may improve hardenability even with a small amount of addition, and segregates at prior austenite grain boundaries and thus may suppress brittleness of a hot press formed member caused by boundary segregation of P and/or S. When a content of boron (B) is less than 0.001%, the effects described above may be insufficient, and when the content of boron (B) exceeds 0.01%, the effects may be saturated, and hot brittleness may occur when a hot rolling is performed. According to an aspect of the present disclosure, an upper limit of boron (B) may be 0.005%.

Molybdenum (Mo) and tungsten (W): 0.001 to 1.0%

[0054] Molybdenum (Mo) and tungsten (W) may be added to improve hardenability and strength through a precipitation strengthening effect and to refine grains. When a content of molybdenum (Mo) and tungsten (W) is less than 0.001%, the effects described above may be insufficient, and when the content of molybdenum (Mo) and tungsten (W) exceeds 1.0%, the effects may be saturated, and an increase in costs may occur.

Copper (Cu) and nickel (Ni): 0.005 to 2.0%

[0055] Copper (Cu) may be added as an element that improves strength by forming fine precipitates. In addition, when copper (Cu) is added alone, hot brittleness may occur, and thus, nickel (Ni) may be added, if necessary. When a content of copper (Cu) and nickel (Ni) is less than 0.005%, the effects described above may be insufficient, and when the content of copper (Cu) and nickel (Ni) exceeds 2.0%, costs may increase excessively.

Antimony (Sb) and tin (Sn): 0.001 to 1.0%

[0056] Antimony (Sb) and tin (Sn) have the effect of suppressing the formation of oxides that may be formed at grain boundaries on a surface layer of a hot-rolled material of a steel to which Si is added, and thus may suppress dent defects caused by separation of the grain boundaries on the surface layer during annealing of a cold-rolled material. In order to obtain these effects, antimony (Sb) and tin (Sn) may be added in an amount of 0.001% or more. On the other hand, when the content of antimony (Sb) and tin (Sn) exceeds 1.0%, costs may increase excessively, and these elements may be solid-dissolved in slab grain boundaries, causing coil edge cracks during hot rolling.

Rare earth element (REM): 0.0001 to 0.02%

[0057] A rare earth element (REM) may control the activity of Fe in steel, such that a thickness of Fe scale formed on the surface layer during hot press forming may be controlled. In order to obtain these effects, it is preferable that the REM

element is added in an amount of 0.0001% or more. On the other hand, the content of the rare earth element (REM) exceeds 0.02%, the ability to control Fe activity may be lost, resulting in deterioration of surface quality. According to an aspect of the present disclosure, the rare earth element (REM) may be controlled to 0.01% or less.

[0058] The first oxide layer according to an aspect of the present disclosure may contain two or more of Fe, Mn, Cr, and Si, and may have a thickness of 5 to 500 nm.

[0059] The first oxide layer is a composite oxide layer containing two or more of Fe, Mn, Cr, and Si, in which two or more of the elements are formed, and in order to control a thickness of the second oxide layer of the member after hot press forming, precise thickness control is required by controlling an atmosphere temperature increase rate when a cold-rolled steel sheet is manufactured. According to an aspect of the present disclosure, a sum of contents of Si, Mn, and Cr in terms of wt% of the first oxide layer itself may be 30% or more, and according to another aspect, the sum of the contents may be 90% or less.

[0060] When the thickness of the first oxide layer is less than 5 nm, after hot press forming, the second oxide layer is formed excessively thick, and thus, the effect of improving surface quality may be insufficient, and it is difficult to secure excellent surface quality. On the other hand, when the thickness exceeds 500 nm, it is not easy to form a second oxide layer after hot press forming, and thus, phosphatability may be deteriorated, which may make it difficult to secure excellent surface quality and to secure sufficient plating corrosion resistance. According to an aspect of the present disclosure, an upper limit of the thickness may be 490 nm, and according to another aspect, a lower limit of the thickness may be 5.5 nm. The first oxide layer of the present disclosure may be formed continuously or discontinuously.

[0061] The first oxide layer according to an aspect of the present disclosure may contain two or more of Fe, Mn, Cr, and Si, and may have a thickness of 5.0 to 500.0 nm.

[0062] Hereinafter, a microstructure of the cold-rolled steel sheet of the present disclosure will be described in detail.

[0063] In the present disclosure, unless otherwise specified, % indicating a fraction of a microstructure is based on area.

[0064] The cold-rolled steel sheet according to an aspect of the present disclosure may contain ferrite and cementite. In the present disclosure, an area fraction thereof is not particularly limited, and more preferably, the area fraction of ferrite and cementite may be 5 area% or more.

[0065] When a blank is manufactured using a cold-rolled steel sheet to manufacture a hot press formed member, if strength of the cold-rolled steel sheet is excessive, mold abrasion may easily occur. More specifically, the microstructure features may refer to a microstructure of the base steel sheet of the cold-rolled steel sheet. Without considering this, bainite, martensite, and the like may be contained without exclusion.

[0066] Hereinafter, a member of the present disclosure will be described in detail.

[0067] The member according to an aspect of the present disclosure may include a base steel sheet, a first oxide layer formed on the base steel sheet, and a second oxide layer formed on the first oxide layer.

[0068] The composition of the base steel sheet of the member according to an aspect of the present disclosure is the same as the composition of the cold-rolled steel sheet described above, and thus will not be described.

[0069] The second oxide layer according to an aspect of the present disclosure may be formed of an Fe-based oxide and may have a thickness of 0.1 to 10 μm .

[0070] When the thickness of the second oxide layer exceeds 10 μm , there is a problem that it is difficult to secure excellent surface quality, such as oxide peeling on the surface layer after hot press forming due to excessive oxide formation. On the other hand, when the thickness is less than 0.1 μm , phosphatability may be deteriorated, which may make it difficult to secure excellent surface quality. According to an aspect of the present disclosure, a sum of contents of Si, Mn, and Cr in terms of wt% of the second oxide layer itself may be less than 30%, and preferably exceeds 0%.

[0071] Hereinafter, a microstructure of the member of the present disclosure will be described in detail.

[0072] In the present disclosure, unless otherwise specified, % indicating a fraction of a microstructure is based on area.

[0073] The member according to an aspect of the present disclosure may have a microstructure containing martensite or bainite as a main phase.

[0074] The hot press formed member of the present disclosure may contain martensite or bainite as a main phase to secure high strength. More specifically, the microstructure features may refer to a microstructure of the base steel sheet of the member. In the present disclosure, the main phase may refer to a phase having the largest area fraction among several phases forming the microstructure. The area fraction of the main phase is not particularly limited, and according to an aspect of the present disclosure, the area fraction of the main phase may be 5 area% or more.

[0075] Hereinafter, manufacturing methods of a cold-rolled steel sheet and a member of the present disclosure will be described in detail.

[0076] A cold-rolled steel sheet according to an aspect of the present disclosure may be manufactured by subjecting a steel slab satisfying the alloy composition described above to reheating, hot rolling, coiling, cool rolling, and continuous annealing.

Reheating

[0077] A steel slab satisfying the alloy composition of the present disclosure may be reheated to a temperature range of 1,000 to 1,300°C.

- 5 **[0078]** When the reheating temperature is lower than 1,000°C, it is difficult to homogenize a slab structure, and when the temperature exceeds 1,300°C, excessive oxide formation and an increase in manufacturing costs may occur.

Hot rolling

- 10 **[0079]** The reheated steel slab may be hot-rolled at a finish rolling temperature of Ar3 to 1,000°C.
[0080] When the finish rolling temperature is lower than Ar3, two-phase region rolling may easily occur, such that a mixed grain structure may occur on a surface layer, and it may be difficult to control the shape of the hot-rolled steel sheet. On the other hand, when the temperature exceeds 1,000°C, grains of the hot-rolled steel sheet may be coarsened.

15 Cooling and coiling

[0081] The hot-rolled steel sheet may be cooled and coiled in a temperature range of Ms to 750°C.

- [0082]** When the coiling temperature is lower than Ms (martensite transformation start temperature), the strength of the hot-rolled steel sheet increases excessively, which may cause deterioration of cold rollability. On the other hand, when the temperature exceeds 750°C, an increase in thickness of the oxide layer and grain boundary oxidation on the surface layer occur, and thus, pickling properties may be deteriorated, and separation of grain boundaries on the surface layer may occur during annealing in a continuous annealing furnace. During cooling, a cooling rate is not particularly limited, and air cooling may be performed.

25 Cold rolling

[0083] The coiled steel sheet may be cold-rolled.

[0084] In the present disclosure, a reduction ratio of the cold rolling is not particularly limited, and the cold rolling may be performed at a reduction ratio of 30 to 80% to secure a target thickness.

- 30 **[0085]** In the present disclosure, the cold rolling may be performed to control the thickness of the steel sheet more precisely, and pickling may be performed before the cold rolling.

Continuous annealing

- 35 **[0086]** The cold-rolled steel sheet may be subjected to continuous annealing, and during the continuous annealing, a temperature increase rate at an atmosphere temperature of room temperature to 700°C may be 3.0 to 20.0°C/s, a temperature increase rate at an atmosphere temperature of 700 to 800°C may be 0.08 to 1.5°C/s, a temperature increase rate at an atmosphere temperature of 800 to 900°C may be 0.01 to 1.5°C/s, and a temperature increase rate at an atmosphere temperature of 900 to 1,000°C may be 0.01 to 1.0°C/s.

- 40 **[0087]** During the continuous annealing, in order to precisely control the thickness of the first oxide layer on the surface layer, in the present disclosure, a temperature increase rate of the atmosphere temperature is more strictly controlled. When the temperature increase rate of the atmosphere temperature is below the suggested lower limit, since the first oxide layer is formed excessively and the thickness thereof exceeds 500 nm, a second oxide layer having a sufficient thickness is not secured after hot press forming, and thus, phosphatability may be deteriorated, and excellent surface quality may not be secured. On the other hand, when the temperature increase rate of the atmosphere temperature exceeds the suggested upper limit, since the formation of the first oxide layer is insufficient, the second oxide layer is formed excessively after hot press forming, which may cause deterioration of surface quality such as surface scale peeling.

- 45 **[0088]** According to an aspect of the present disclosure, the continuous annealing may be performed in a steel sheet temperature range of 700 to 900°C. When the annealing temperature is lower than 700°, it may be difficult to restore and recrystallize a rolled structure created by cold rolling. On the other hand, when the temperature exceeds 900°C, the annealing equipment may be deteriorated, which may lead to an increase in process costs due to frequent equipment replacement.

- 50 **[0089]** According to an aspect of the present disclosure, a continuous annealing time may be 1 to 1,000 seconds. When the annealing time is shorter than 1 second, it is difficult to obtain the annealing effect, and when the time is longer than 1,000 seconds, the productivity may be reduced.

- 55 **[0090]** The member according to an aspect of the present disclosure may be manufactured by subjecting a cold-rolled steel sheet manufactured by the method described above to a heat treatment, hot press forming, and cooling.

Heat treatment

[0091] The cold-rolled steel sheet according to an aspect of the present disclosure may be subjected to a heat treatment, in which an A value defined in the following Relational Expression 1 may be 0.6 to 1.0, and the heat treatment may be performed by heating the cold-rolled steel sheet to the heating temperature at a temperature increase rate of 1 to 1,000°C/s.

[0092] In the present disclosure, in order to precisely control the thickness of the second oxide layer, the heating temperature and the heating time may be controlled through Relational Expression 1. When the A value defined in Relational Expression 1 is less than 0.6, in the case where the heat treatment is performed, the thickness of the second oxide layer is insufficient, such that phosphatability may be deteriorated, resulting in difficulties in securing excellent surface quality. On the other hand, when the value exceeds 1.0, the thickness of the second oxide layer is excessive, which makes it difficult to secure excellent surface quality due to peeling of the oxide layer.

[0093] The temperature increase rate in the heat treatment step may mean a temperature increase rate of the atmosphere in the continuous annealing furnace. When the temperature increase rate is less than 1°C/s, it may be difficult to secure sufficient productivity, and when the rate exceeds 1,000°C/s, an equipment requiring excessive costs may be required. According to an aspect of the present disclosure, the heating temperature may be 700°C or higher and 1,000°C or lower. The heating time according to an aspect of the present disclosure may be 150 seconds or longer and 1,000 seconds or shorter.

[Relational Expression 1]

$$A = (T + 0.2 t) / 1,210$$

[0094] (In the expression, T represents a heating temperature and a unit thereof is °C, and t represents a total heating time and a unit thereof is a second.)

Hot press forming and cooling

[0095] The heat-treated steel sheet may be subjected to hot press forming, and then cooled to an Mf temperature or lower at a cooling rate of 10 to 1,000°C/s.

[0096] When the cooling rate is less than 10°C/s, unwanted ferrite and pearlite may be formed, and it is difficult to secure a desired level of tensile strength. On the other hand, when the rate exceeds 1,000°C/s, an expensive special cooling equipment is required to control the rate, which may reduce productivity.

[0097] In a case where cooling is stopped when a cooling end temperature exceeds Mf (martensite transformation end temperature) and then cooling is performed to room temperature again, it may be difficult to secure shape fixability of the hot press formed member.

[0098] The hot press formed member according to an aspect of the present disclosure manufactured as described above has a tensile strength of 500 MPa or more, and may secure excellent strength and impact resistance.

[0099] Hereinafter, the present disclosure will be described in more detail with reference to Examples. However, the following Examples are provided to illustrate and describe the present disclosure in detail, but are not intended to limit the scope of the present disclosure.

Mode for Invention

[0100] Hereinafter, the present disclosure will be described in more detail with reference to Examples. However, the following Examples are provided to illustrate and describe the present disclosure in detail, but are not intended to limit the scope of the present disclosure.

(Examples)

[0101] Slabs having the compositions shown in Table 1 and having a thickness of 40 mm were melted in vacuum, heated at 1,200°C for 1 hour in a heating furnace, and hot-rolled at a finish rolling temperature of 900°C, thereby manufacturing hot-rolled steel sheets having a final thickness of 3 mm. The hot-rolled steel sheets were air-cooled and coiled at 600°C, and then, the hot-rolled steel sheets were pickled and then cold-rolled at a cold reduction ratio of 50%, thereby manufacturing cold-rolled steel sheets.

EP 4 578 986 A1

[Table 1]

Steel type	Alloy composition (wt%)										
	C	Si	Mn	P	S	Al	Cr	Mo	Ti	B	N
A	0.33	1.93	3.46	0.0056	0.0082	0.002	4.89	0.489	0.021	0.0025	0.0024
B	0.32	0.94	2.00	0.0066	0.0015	0.009	0.85	0.085	0.015	0.0020	0.0023
C	0.06	2.66	2.18	0.0046	0.0001	0.008	0.65	0.065	0.025	0.0011	0.0021
D	0.16	1.21	2.43	0.0033	0.0026	0.007	1.40	0.140	0.017	0.0230	0.0041
E	0.10	2.15	1.66	0.0027	0.0086	0.001	3.90	0.390	0.018	0.0000	0.0028
F	0.18	2.92	1.78	0.0090	0.0043	0.005	0.33	0.033	0.021	0.0018	0.0045
G	0.33	1.52	1.70	0.0055	0.0083	0.002	0.46	0.012	0.010	0.0000	0.0049
H	0.10	0.06	3.62	0.0092	0.0071	0.001	4.90	0.490	0.095	0.0020	0.0037
I	0.36	1.93	0.42	0.0027	0.0036	0.008	5.12	0.512	0.004	0.0000	0.0047
J	0.25	1.44	0.86	0.0016	0.0045	0.005	5.75	0.575	0.072	0.0004	0.0028
K	0.24	1.39	0.63	0.0038	0.0047	0.004	0.21	0.021	0.100	0.0024	0.0048
L	0.32	0.35	1.00	0.0079	0.0070	0.007	1.62	0.162	0.061	0.0000	0.0043
M	0.07	1.09	2.50	0.0080	0.0085	0.008	6.66	0.666	0.069	0.0015	0.0021
N	0.19	0.26	2.32	0.0120	0.0014	0.007	0.05	0.013	0.053	0.0019	0.0050
O	0.08	2.45	3.81	0.0033	0.0095	0.007	0.20	0.410	0.041	0.0023	0.0048
P	0.39	3.02	3.89	0.0035	0.0003	0.007	7.86	0.250	0.051	0.0000	0.0034
Q	0.14	0.90	0.009	0.0050	0.0007	0.006	1.80	0.180	0.057	0.0009	0.0031
R	0.14	0.90	4.23	0.0050	0.0007	0.006	1.75	0.175	0.057	0.0250	0.0025

[0102] The cold-rolled steel sheets manufactured as described above were subjected to continuous annealing under the conditions shown in Table 2, and at this time, the continuous annealing was performed at a steel sheet temperature of 780°C. In addition, a heat treatment was performed under the conditions shown in Table 2, and cooling was performed after hot press forming. During the heat treatment, a temperature increase rate of 5°C/s was applied, and after hot press forming, cooling was performed to room temperature at a cooling rate of 30°C/s.

[Table 2]

Specimen Nos.	Steel type	Continuous annealing				Heat treatment		
		Atmosphere temperature increase rate according to temperature section (°C/s)				Temperature (°C)	Time (s)	Relational Expression 1
		Room temperature to 700 (°C)	700 to 800 (°C)	800 to 900 (°C)	90 to 1000 (°C)			
1	A	18.0	1.19	1.20	0.50	900.0	300.0	0.793
2	B	7.3	1.39	0.12	0.13	900.0	300.0	0.793
3	C	9.2	0.12	1.34	0.98	900.0	300.0	0.793
4	D	9.0	1.44	1.42	0.90	900.0	300.0	0.793
5	E	4.4	0.16	0.92	0.49	900.0	300.0	0.793
6	F	3.8	0.10	0.88	0.88	900.0	300.0	0.793
7	G	6.7	0.97	0.25	0.30	900.0	300.0	0.793
8	H	6.8	0.25	0.05	0.70	900.0	300.0	0.793
9	I	10.1	0.92	0.51	0.24	900.0	300.0	0.793

EP 4 578 986 A1

(continued)

5	Specimen Nos.	Steel type	Continuous annealing				Heat treatment		
			Atmosphere temperature increase rate according to temperature section (°C/s)				Temperature (°C)	Time (s)	Relational Expression 1
			Room temperature to 700 (°C)	700 to 800 (°C)	800 to 900 (°C)	90 to 1000 (°C)			
10	10	J	5.6	1.02	0.61	0.41	900.0	300.0	0.793
	11	K	10.4	0.84	1.29	0.55	900.0	300.0	0.793
	12	L	4.4	1.45	0.39	0.21	900.0	300.0	0.793
15	13	M	9.7	0.74	0.13	0.14	900.0	300.0	0.793
	14	N	17.4	0.43	0.58	0.88	900.0	300.0	0.793
	15	O	3.2	0.38	0.19	0.09	900.0	300.0	0.793
20	16	P	5.6	0.13	1.09	0.16	900.0	300.0	0.793
	17	Q	6.5	1.43	0.63	0.59	900.0	300.0	0.793
	18	R	9.6	1.18	0.85	0.56	900.0	300.0	0.793
25	19	A	18.04	1.19	1.20	0.50	900.0	300.0	0.793
	20	A	6.78	0.13	1.82	0.78	900.0	300.0	0.793
	21	A	8.74	0.07	0.29	0.39	900.0	300.0	0.793
30	22	A	8.73	0.76	0.006	0.20	900.0	300.0	0.793
	23	A	8.43	0.21	1.12	1.22	900.0	300.0	0.793
	24	C	9.22	0.12	1.34	0.98	900.0	300.0	0.793
35	25	C	1.77	0.96	1.44	0.30	900.0	300.0	0.793
	26	C	8.34	1.96	0.84	0.02	900.0	300.0	0.793
	27	C	7.63	0.10	2.46	0.18	900.0	300.0	0.793
40	28	C	5.17	0.90	0.61	0.008	900.0	300.0	0.793
	29	D	8.98	1.44	1.42	0.90	900.0	300.0	0.793
	30	D	25.0	0.19	0.07	0.64	900.0	300.0	0.793
45	31	D	1.92	0.19	1.20	2.18	900.0	300.0	0.793
	32	D	5.50	1.77	0.00	0.54	900.0	300.0	0.793
	33	B	7.3	1.39	0.12	0.13	900.0	300.0	0.79
50	34	B	7.3	1.39	0.12	0.13	700	10	0.58
	35	B	7.3	1.39	0.12	0.13	1000	2400	1.22
	36	E	4.4	0.16	0.92	0.49	900.0	300.0	0.79
55	37	E	4.4	0.16	0.92	0.49	720	10	0.59
	38	E	4.4	0.16	0.92	0.49	980	2800	1.27
	39	F	3.8	0.10	0.88	0.88	900.0	300.0	0.79
55	40	F	3.8	0.10	0.88	0.88	690	10	0.57
	41	F	3.8	0.10	0.88	0.88	1020	2000	1.17
	42	G	6.7	0.97	0.25	0.30	900.0	300.0	0.79
55	43	G	6.7	0.97	0.25	0.30	670	100	0.57
	44	G	6.7	0.97	0.25	0.30	970	3600	1.40

[Relational Expression 1] $A = (T + 0.2 t) / 1,210$

[0103] (In the expression, T represents a heating temperature and a unit thereof is °C, and t represents a total heating time and a unit thereof is a second.)

[0104] Table 3 shows the measured thickness of the first oxide layer of the cold-rolled steel sheet after continuous annealing, and also shows the thickness of the second oxide layer of the member after the subsequent heat treatment, hot press forming, and cooling. Here, the thickness of the first oxide layer was measured using a transmission electron microscope (TEM), and the thickness of the second oxide layer was measured at three locations using a transmission electron microscope (TEM) and electron beam microanalysis (EPMA) and then was expressed as the average result. In addition, for the items with quality deterioration, scale peeling was observed with the naked eye and shown, and in the observation with the naked eye, when peeling of scale with an area of 5 mm² or more occurred at 10 points or more, it was determined that the quality was deteriorated. Phosphate coverage was determined by observing a structure with a scanning electron microscope (SEM) and then measuring an area of a portion where phosphate crystals were not formed to determine whether the quality was deteriorated. At this time, when the portion where phosphate crystals were formed exceeded 70%, it was determined that the phosphate properties were good. In addition, the yield strength, the tensile strength, and the elongation of the manufactured members were measured and shown. For the yield strength, the tensile strength, and the elongation, a tensile test was performed at room temperature using JIS-5 specimens according to the ISO 6892 standard.

[Table 3]

Specimen Nos.	Steel type	Cold-rolled steel sheet	Member		Member				Classification	
			Second oxide layer	Thickness (μm)	Items with quality deterioration	Phosphate coverage (%)	Physical properties			
							Yield strength (MPa)	Tensile strength (MPa)		Elongation (%)
1	A	474.4	0.19	-	86.1	1410	2012	5.3	Inventive Example 1	
2	B	8.3	8.53	-	98.2	1352	2009	6	Inventive Example 2	
3	C	36.0	7.59	-	92.9	425	639	15.2	Inventive Example 3	
4	D	151.8	4.60	-	75.0	715	1109	9.8	Inventive Example 4	
5	E	291.1	2.62	-	81.1	826	1084	13.5	Inventive Example 5	
6	F	149.4	5.58	-	90.8	979	1210	12.6	Inventive Example 6	
7	G	5.1	9.66	-	95.1	1495	2162	4.8	Inventive Example 7	
8	H	3.9	12.15	Scale	-	908	1127	13	Comparative Example 1	
9	I	641.1	0.080	Phosphate	58.3	1347	1982	4.3	Comparative Example 2	
10	J	965.5	0.032	Phosphate	61.8	1125	1610	6.2	Comparative Example 3	
11	K	4.2	11.86	Scale	-	1059	1477	7.4	Comparative Example 4	
12	L	1.7	22.58	Scale	-	1455	1962	4.7	Comparative Example 5	
13	M	933.1	0.042	Phosphate	57.7	853	1066	17.1	Comparative Example 6	
14	N	2.5	17.15	Scale	-	988	1077	19.3	Comparative Example 7	
15	O	713.3	0.060	Phosphate	67.1	1001	1225	7.8	Comparative Example 8	
16	P	999.4	0.011	Phosphate	55.1	1465	2062	4.5	Comparative Example 9	
17	Q	1.45	30.97	Scale	-	894	1250	11.5	Comparative Example 10	
18	R	726.5	0.057	Phosphate	68.0	901	1267	12.3	Comparative Example 11	
19	A	474.4	0.19	-	86.1	1418	2010	5.2	Inventive Example 8	
20	A	2.1	19.10	Scale	-	1476	2053	5.3	Comparative Example 12	
21	A	761.2	0.05	Phosphate	48.3	1400	2072	3.4	Comparative Example 13	

(continued)

Specimen Nos.	Steel type	Cold-rolled steel sheet	Member		Member				Classification	
			Second oxide layer	Thickness (μm)	Items with quality deterioration	Phosphate coverage (%)	Physical properties			
							Yield strength (MPa)	Tensile strength (MPa)		Elongation (%)
22	A	686.7	0.05		Phosphate	57.8	1398	2025	5.3	Comparative Example 14
23	A	4.7	16.97		Scale	-	1415	2007	5.2	Comparative Example 15
24	C	36.0	7.59		-	92.9	421	637	14.4	Inventive Example 9
25	C	604.7	0.08		Phosphate	53.5	411	633	13.9	Comparative Example 16
26	C	4.6	15.67		Scale	-	471	654	16	Comparative Example 17
27	C	3.9	17.84		Scale	-	486	699	16.2	Comparative Example 18
28	C	717.0	0.05		Phosphate	63.5	493	696	13.6	Comparative Example 19
29	D	151.8	4.60		-	75.0	728	1160	9.3	Inventive Example 10
30	D	540.0	0.09		Phosphate	48.5	723	1017	9.6	Comparative Example 20
31	D	861.2	0.04		Phosphate	54.0	712	1143	9.5	Comparative Example 21
32	D	848.0	0.04		Phosphate	60.0	736	1037	9.6	Comparative Example 22
33	B	8.3	8.53		-	98.2	1362	2056	5.9	Inventive Example 11
34	B	8.3	0.069		Phosphate	47.7	1334	1998	5.2	Comparative Example 23
35	B	8.3	27.36		Scale	-	1366	2016	5.2	Comparative Example 24
36	E	291.1	2.62		-	81.1	862	1023	13.8	Inventive Example 12
37	E	291.1	0.079		Phosphate	55.8	855	1012	12.6	Comparative Example 25
38	E	291.1	29.70		Scale	-	861	1017	12.1	Comparative Example 26
39	F	149.4	5.58		-	90.8	974	1274	11.1	Inventive Example 13
40	F	149.4	0.06		Phosphate	64.9	963	1237	11.6	Comparative Example 27
41	F	149.4	17.84		Scale	-	955	1231	12.7	Comparative Example 28
42	G	5.1	9.66		-	95.1	1516	2136	4.4	Inventive Example 14

(continued)

Specimen Nos.	Steel type	Cold-rolled steel sheet	Member	Member				Classification		
		Fist oxide layer	Second oxide layer	Items with quality deterioration	Phosphate coverage (%)	Physical properties				
		Thickness (nm)	Thickness (μm)			Yield strength (MPa)	Tensile strength (MPa)		Elongation (%)	
43	G	5.1	0.05		Phosphate	42.7	1526	2196	4.6	Comparative Example 29
44	G	5.1	35.16		Scale	-	1438	2158	4.5	Comparative Example 30

[0105] In the cold-rolled steel sheet and the member satisfying the alloy composition and the manufacturing conditions of the present disclosure, the first oxide layer and the second oxide layer were formed within the thickness ranges suggested in the present disclosure, and excellent surface quality was secured even after hot press forming.

[0106] FIG. 1 illustrates photographs of the surface quality after hot press forming of each of Inventive Example 2 and Comparative Example 10. In Comparative Example 10, a thick oxide was formed compared to Inventive Example 2, and it was confirmed that the quality was deteriorated.

[0107] FIG. 2 illustrates the phosphate coverage after hot press forming of each of Inventive Example 1 and Comparative Example 2. In Comparative Example 2, it was confirmed that less than 70% of phosphate crystals were formed.

[0108] FIG. 3 illustrates the change in surface quality according to the heat treatment temperature and time conditions. The surface state was observed by controlling the hot press forming temperature and time, and it was confirmed that, when the heat treatment conditions were outside the ranges limited by Relational Expression 1, scale peeling occurred on the surface layer due to excessive formation of the second oxide layer on the surface layer after the heat treatment, or phosphatability was deteriorated due to excessive formation of the first oxide layer, which showed that the surface quality was deteriorated.

[0109] FIG. 4 illustrates photographs obtained by observing the surfaces after hot press forming of Inventive Example 11 and Comparative Example 24. In Comparative Example 24 in which the heat treatment conditions exceeded the heat treatment conditions limited by Relational Expression 1, when the surface was observed with the naked eye in comparison with Inventive Example 11, scale was confirmed.

[0110] In Comparative Examples 1, 4, 5, 7, and 10, since the content of each element was below the required range suggested by the present disclosure, the formation of the first oxide layer was not appropriate, and as illustrated in FIG. 1, the thickness of the second oxide layer after hot press forming exceeded 10 μm , and surface scale was excessively formed after hot press forming; thus, excellent surface quality was not secured.

[0111] In Comparative Examples 2, 3, 6, 8, 9, and 11, the content of each component exceeded the required range suggested by the present disclosure, and thus, the first oxide layer was excessively formed after annealing. Due to this, a sufficient second oxide layer was not formed during hot press forming, and less than 70% of phosphate crystals were formed, and thus, the surface quality was deteriorated.

[0112] In addition, in the cases of Comparative Examples 12, 15, 17, 18, and 20 in which, during the continuous annealing, the temperature increase rate in each section exceeded any one of the ranges suggested by the present disclosure, as the first oxide layer was not sufficiently formed, the second oxide layer was excessively formed after hot press forming, and thus, scale peeling on the surface layer occurred and excellent surface quality was not secured.

[0113] In the cases of Comparative Examples 13, 14, 16, and 19, as the atmosphere temperature increase rate in each section was below the lower limit of the temperature increase rate limited in the present disclosure, phosphatability was deteriorated due to excessive formation of the first oxide layer, and thus, excellent surface quality was not secured.

[0114] In addition, even in the cases of Comparative Examples 21 and 22 in which some of the atmosphere temperatures in the respective sections were below the lower limit value or exceeded the upper limit value, as the first oxide layer was excessively formed and the second oxide layer was not easily formed after hot press forming, phosphatability was deteriorated, and thus, excellent surface quality was not secured.

[0115] In the cases of Comparative Examples 23, 25, 27, and 29, as the conditions were below the lower limits of the conditions limited in Relational Expression 1, the second oxide layer was not sufficiently formed, resulting in deterioration of phosphatability, and in the cases of Comparative Examples 24, 26, 28, and 30 in which the conditions exceeded the upper limits of the suggested ranges, as the thickness of the formed second oxide layer was thick, a large amount of Fe scale was formed, and thus, the surface quality was deteriorated.

[0116] Hereinabove, the present disclosure has been described in detail with reference to the exemplary embodiments, but other exemplary embodiments having different forms are possible. Therefore, the technical spirit and scope of the claims set forth below are not limited by the exemplary embodiments.

Claims

1. A cold-rolled steel sheet comprising: a base steel sheet and a first oxide layer formed on the base steel sheet, wherein the first oxide layer contains two or more of Fe, Mn, Cr, and Si, and has a thickness of 5 to 500 nm.
2. The cold-rolled steel sheet of claim 1, wherein the base steel sheet contains, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3 to 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.
3. The cold-rolled steel sheet of claim 2, wherein the base steel sheet contains one or more of 0.001 to 0.4% of Ti, 0.001 to

0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

4. The cold-rolled steel sheet of any one of claims 1 to 3, wherein a sum of contents of Si, Mn, and Cr in the first oxide layer is 30% or more in terms of wt%.

5. The cold-rolled steel sheet of any one of claims 1 to 4, wherein the cold-rolled steel sheet has a microstructure containing 5 area% or more of ferrite and cementite.

6. A member comprising: a base steel sheet; a first oxide layer formed on the base steel sheet; and a second oxide layer formed on the first oxide layer,

wherein the first oxide layer contains two or more of Fe, Mn, Cr, and Si, and the second oxide layer is formed of an Fe-based oxide and has a thickness of 0.1 to 10 μm .

7. The member of claim 6, wherein the base steel sheet contains, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3% or more and less than 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.

8. The member of claim 7, wherein the base steel sheet contains one or more of 0.001 to 0.4% of Ti, 0.001 to 0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

9. The member of any one of claims 6 to 8, wherein a sum of contents of Si, Mn, and Cr in the second oxide layer is less than 30% in terms of wt%.

10. The member of any one of claims 6 to 9, wherein the member has a microstructure containing martensite or bainite as a main phase.

11. The member of any one of claims 6 to 10, wherein a tensile strength of the member is 500 MPa or more.

12. A manufacturing method of a cold-rolled steel sheet, comprising:

reheating a steel slab;
hot rolling the reheated steel slab;
cooling and coiling the hot-rolled steel sheet;
cold rolling the coiled steel sheet; and
performing continuous annealing on the cold-rolled steel sheet,
wherein during the continuous annealing, a temperature increase rate at an atmosphere temperature of room temperature to 700°C is 3.0 to 20.0°C/s, a temperature increase rate at an atmosphere temperature of 700 to 800°C is 0.08 to 1.5°C/s, a temperature increase rate at an atmosphere temperature of 800 to 900°C is 0.01 to 1.5°C/s, and a temperature increase rate at an atmosphere temperature of 900 to 1,000°C is 0.01 to 1.0°C/s.

13. The manufacturing method of claim 12, wherein the steel slab contains, by wt%, 0.05 to 0.4% of C, 0.5 to 3.0% of Si, 0.3 to 5.0% of Cr, 0.01 to 4.0% of Mn, 0.001 to 0.4% of Al, 0.001 to 0.05% of P, 0.0001 to 0.02% of S, 0.001 to 0.02% of N, and a balance of Fe and other unavoidable impurities.

14. The manufacturing method of claim 13, wherein the steel slab contains one or more of 0.001 to 0.4% of Ti, 0.001 to 0.4% of Nb, 0.001 to 0.4% of Zr, 0.001 to 0.4% of V, 0.0001 to 0.01% of B, 0.001 to 1.0% of Mo, 0.001 to 1.0% of W, 0.005 to 2.0% of Cu, 0.005 to 2.0% of Ni, 0.001 to 1.0% of Sb, 0.001 to 1.0% of Sn, and 0.0001 to 0.02% of REM.

15. The manufacturing method of any one of claims 12 to 14, wherein the reheating is performed in a temperature range of 1,000 to 1,300°C,

the hot rolling is performed at a finish rolling temperature of Ar₃ to 1,000°C,
the coiling is performed in a temperature range of Ms to 750°C, and
the cold rolling is performed at a reduction ratio of 30 to 80%.

16. The manufacturing method of any one of claims 12 to 15, wherein the continuous annealing is performed in a steel sheet temperature range of 700 to 900°C, and a continuous annealing time is 1 to 1,000 seconds.

17. A manufacturing method of a member, comprising:

performing a heat treatment on the cold-rolled steel sheet of any one of claims 12 to 16; and
performing hot press forming on the heat-treated steel sheet and then cooling the hot press formed steel sheet,
wherein during the heat treatment, an A value defined in the following Relational Expression 1 is 0.6 to 1.0:

[Relational Expression 1]

$$A = (T + 0.2 \ t) / 1,210$$

where T represents a heating temperature and a unit thereof is °C, and t represents a total heating time and a unit thereof is a second.

18. The manufacturing method of claim 17, wherein during the heat treatment, the heating is performed to the heating temperature at an atmosphere temperature increase rate of 1 to 1,000°C/s.

19. The manufacturing method of claim 17 or 18, wherein during the heat treatment, the heating temperature is 700 to 1,000°C, and the heating time is 150 to 1,000 seconds.

20. The manufacturing method of any one of claims 17 to 19, wherein after the hot press forming, during the cooling, the cooling is performed to an Mf temperature or lower at a cooling rate of 10 to 1,000°C/s.

Fig 1

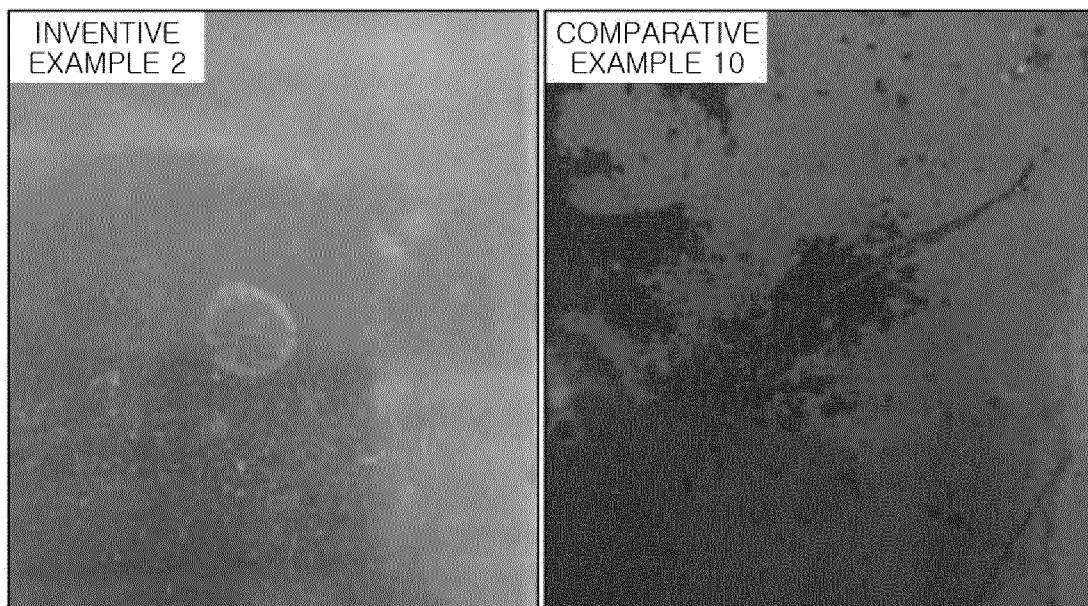


Fig 2

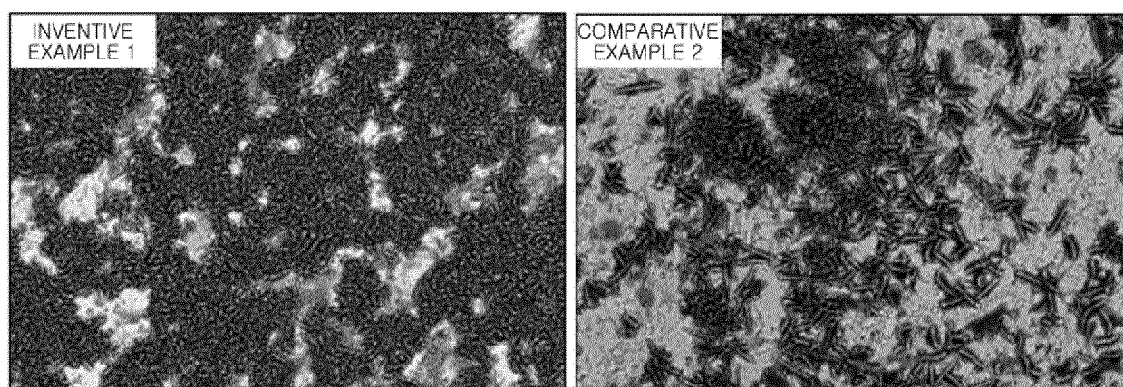


Fig 3

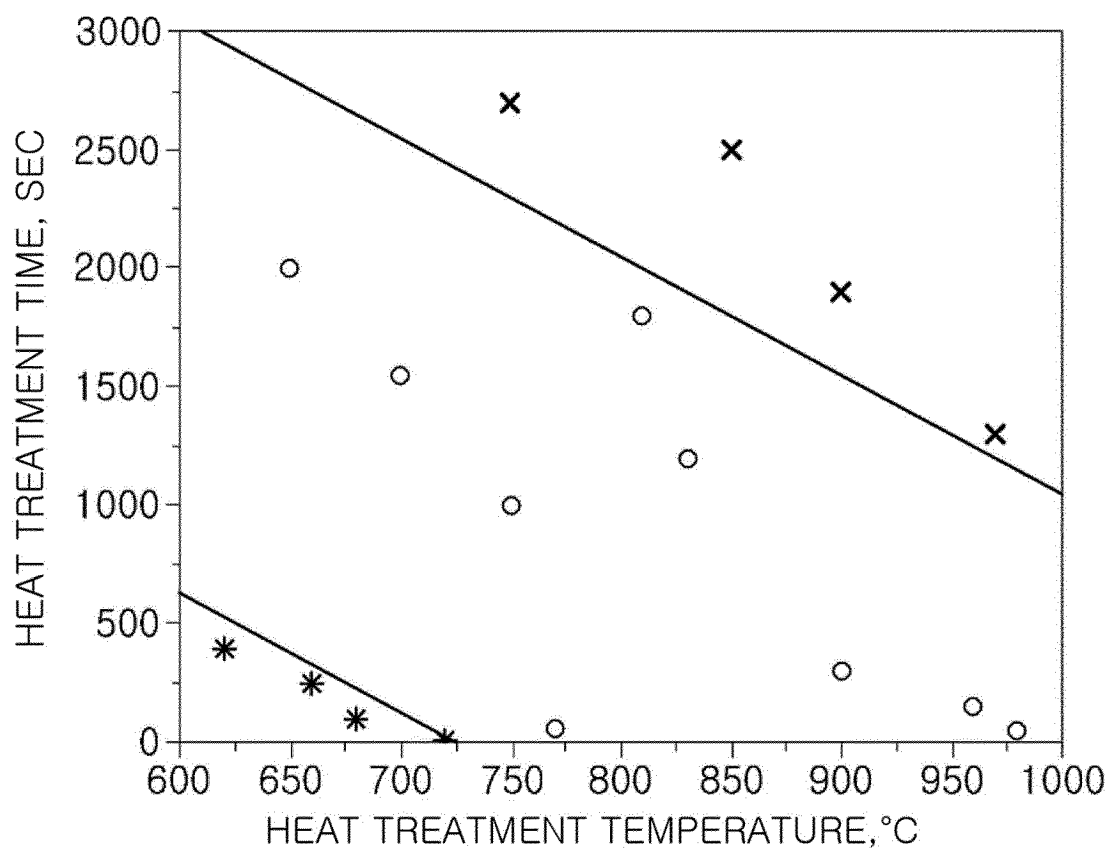
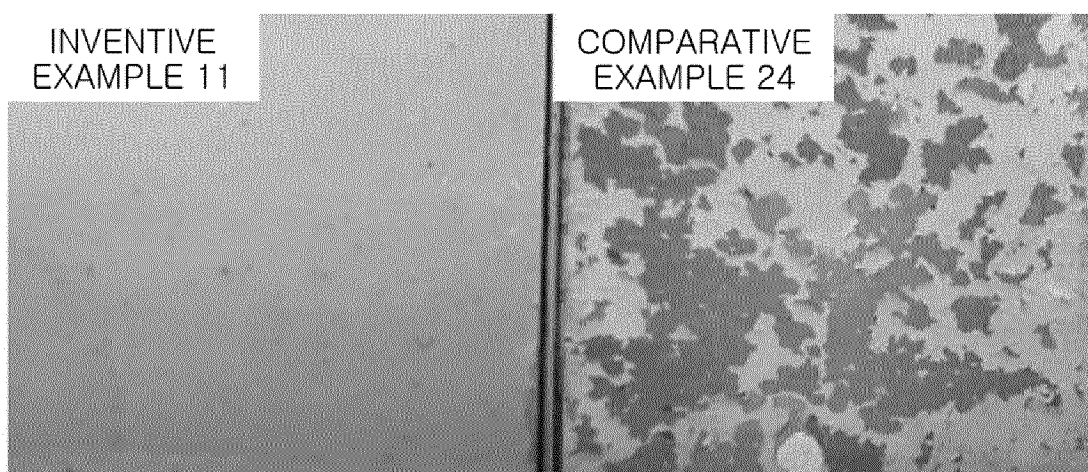


Fig 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2023/012140

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/38(2006.01)i; C22C 38/34(2006.01)i; C22C 38/06(2006.01)i; C22C 38/58(2006.01)i; C22C 38/50(2006.01)i;
C22C 38/44(2006.01)i; C22C 38/42(2006.01)i; C21D 8/02(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)

C22C 38/38(2006.01); B21D 22/02(2006.01); B21D 37/16(2006.01); B32B 15/18(2006.01); C21D 8/02(2006.01);
C21D 9/46(2006.01); C21D 9/56(2006.01); C22C 38/02(2006.01); C22C 38/04(2006.01); C22C 38/14(2006.01)

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

Korean utility models and applications for utility models: IPC as above

Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 내식성(corrosion resistance), 점용접성(spot weldability), 열간성형(hot press forming), 냉연강판(cold rolled steel sheet), 산화물층(oxide layer)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-1830527 B1 (POSCO) 21 February 2018 (2018-02-21) See paragraphs [0079], [0109] and [0147] and claims 1-3, 5-7, 9-13, 15-16 and 18-19.	1-3,5-8,10-11
Y		4,9,12-20
Y	KR 10-2017-0075046 A (POSCO) 03 July 2017 (2017-07-03) See paragraph [0041] and claim 4.	4,9
Y	CN 114045441 A (PANZHIHUA IRON & STEEL RESEARCH INSTITUTE, PANGANG GROUP) 15 February 2022 (2022-02-15) See claims 1 and 8.	12-20
A	KR 10-1852277 B1 (ARCELORMITTAL INVESTIGACION Y DESARROLLO SL) 04 June 2018 (2018-06-04) See claims 1-2 and 17.	1-20

☒ 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

“D” document cited by the applicant in the international application

“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

21 November 2023

Date of mailing of the international search report

21 November 2023

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208

Facsimile No. +82-42-481-8578

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2023/012140

5

10

15

20

25

30

35

40

45

50

55

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2016-0078851 A (POSCO) 05 July 2016 (2016-07-05) See claims 1-5.	1-20
A	JP 2009-091640 A (JFE STEEL K.K.) 30 April 2009 (2009-04-30) See claim 1.	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2023/012140

5	Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
10	KR 10-1830527 B1	21 February 2018	CN 109844142 A	04 June 2019
15			CN 109844142 B	03 September 2021
			EP 3517636 A1	31 July 2019
			EP 3517636 B1	14 July 2021
			ES 2892278 T3	03 February 2022
			JP 2019-533083 A	14 November 2019
			JP 6872009 B2	19 May 2021
			US 11441205 B2	13 September 2022
			US 11624100 B2	11 April 2023
			US 11788166 B2	17 October 2023
			US 2020-0385833 A1	10 December 2020
			US 2022-0389533 A1	08 December 2022
			US 2023-0235423 A1	27 July 2023
20			WO 2018-056792 A1	29 March 2018
25	KR 10-2017-0075046 A	03 July 2017	CN 108430662 A	21 August 2018
			CN 108430662 B	24 March 2020
			EP 3395465 A1	31 October 2018
			EP 3395465 B1	27 October 2021
			ES 2902910 T3	30 March 2022
			JP 2019-506297 A	07 March 2019
			JP 6656379 B2	04 March 2020
			KR 10-1889230 B1	16 August 2018
30			US 2018-0363117 A1	20 December 2018
			WO 2017-111431 A1	29 June 2017
			WO 2017-111431 A8	01 February 2018
35	CN 114045441 A	15 February 2022	CN 114045441 B	20 September 2022
	KR 10-1852277 B1	04 June 2018	BR 112015032233 A2	25 July 2017
			BR 112015032233 B1	15 October 2019
			CA 2915776 A1	08 January 2015
			CA 2915776 C	07 August 2018
			CN 105358719 A	24 February 2016
			CN 105358719 B	04 September 2018
40			EP 3017073 A1	11 May 2016
			EP 3017073 B1	30 August 2017
			ES 2641853 T3	14 November 2017
			HU E035159 T2	02 May 2018
			JP 2016-529392 A	23 September 2016
45			JP 6404917 B2	17 October 2018
			MA 38660 A1	31 October 2016
			MA 38660 B1	31 July 2017
			MX 2015017874 A	11 November 2016
			PL 3017073 T3	28 February 2018
50			RU 2016103568 A	10 August 2017
			RU 2648722 C2	28 March 2018
			UA 117134 C2	25 June 2018
			US 10400315 B2	03 September 2019
			US 2016-0194739 A1	07 July 2016
55			WO 2015-001367 A1	08 January 2015
			WO 2015-001414 A1	08 January 2015
			ZA 201508970 B	25 January 2017

Form PCT/ISA/210 (patent family annex) (July 2022)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2023/012140

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
KR	10-2016-0078851	A	05 July 2016	KR	10-1696052	B1	13 January 2017
JP	2009-091640	A	30 April 2009	JP	4900179	B2	21 March 2012

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

- US 6296805 B [0007]