Provided is an ultra-high-strength steel sheet having high phosphatability and hole expandability, including, by wt %, carbon (C): 0.08% to 0.2%, silicon (Si): 0.05% to 1.3%, manganese (Mn): 2.0% to 3.0%, phosphorus (P): 0.001% to 0.10%, sulfur (S): 0.010% or less, aluminum (Al): 0.01% to 0.1%, chromium (Cr): 0.3% to 1.2%, boron (B): 0.0010% to 0.0030%, titanium (Ti): 0.01% to 0.05%, nitrogen (N): 0.001% to 0.01%, and a balance of iron (Fe) and inevitable impurities, satisfying 3.4 ≤ Ti/Ne ≤ 10, 1.0 × Mn/(Si + Cr), and 0.7 ≤ Mn*/(Si* + Cr*) ≤ Mn/(Si + Cr) where Ti, N, Mn, Si, and Cr refer to a weight percent (wt %), and Mn*, Si*, and Cr* refer to an average of values obtained by GDS component analysis from the surface to the 0.1 μm position in the thickness direction.
ULTRA-HIGH STRENGTH STEEL SHEET HAVING EXCELLENT PHOSPHATABILITY AND HOLE EXPANDABILITY AND METHOD FOR MANUFACTURING SAME

TECHNICAL FIELD

[0001] The present disclosure relates to an ultra-high-strength steel sheet for automobiles or the like, and more particularly, to an ultra-high-strength steel sheet having high phosphatability and hole expandability, and a method for manufacturing the ultra-high-strength steel sheet.

BACKGROUND ART

[0002] In recent years, the use of ultra-high-strength steel sheets for automobiles has increased to deal with fuel efficiency regulations for protecting the environment and to guarantee crash safety. When manufacturing such ultra-high-strength steels, it is not easy to ensure sufficient strength and ductility through using only general steel materials strengthened by the solid-solution strengthening or precipitation strengthening effect.

[0003] Thus, transformation-strengthened steels having strength and ductility improved by using transformation phases have been developed, and examples thereof include dual phase (DP) steel, complex phase (CP) steel, and transformation induced plasticity (TRIP) steel.

[0004] Among such transformation-strengthened steels, DP steel includes hard martensite finely uniformly distributed in soft ferrite to ensure high strength and ductility. CP steel has two or three phases selected from ferrite, martensite, and bainite, and includes precipitation strengthening elements such as titanium (Ti) or niobium (Nb) for strength improvements. The strength and ductility of the TRIP steel are guaranteed by martensite transformation induced by processing finely, uniformly distributed retained austenite at room temperature.


[0006] Although it has been attempted to guarantee elongation using various transformation phases as described above so as to deal with the accelerated use of high-strength steels for automobiles, it is still practically difficult to ensure sufficient elongation.

[0007] In particular, as regulations on crashworthiness have been tightened for passenger safety, the use of ultra-high-strength steels for crashworthy members has been increased. However, although such ultra-high-strength steels have high yield strength, the ultra-high-strength steels may easily fracture or may not smoothly absorb energy in a crash.

[0008] Therefore, it is needed to improve the hole expandability of ultra-high-strength steels so as to smoothly absorb energy without fractures and suppress flange cracking during a complex process such as a bending process or a roll forming process.

[0009] Hot-rolled high-burging steel is representative of a steel material having high hole expandability, and it has been attempted to minimize a hardness difference between phases so as to improve hole expandability. In general, a ferrite single phase including nano-sized fine precipitates, or a bainite single phase or a ferrite-bainite complex phase including precipitates has been proposed as a basic structure of high-burging steel, and similar attempts have been made on cold-rolled steel sheets.

[0010] In addition, it is necessary to utilize transformation phases and precipitates so as to develop CP steel having ultra-high-strength and hole expandability. However, CP steel has ductility and bending workability markedly varying with phase fractions, and proper fractions of phases and manufacturing ranges for CP steel have not yet been studied. Thus, research into CP steel is increasingly required.

[0011] In addition, it is necessary to add large amounts of solid-solution strengthening elements such as silicon (Si) or chromium (Cr) so as to guarantee stable formation of hard phases and reduce a hardness difference between phases. However, the addition of silicon (Si) or chromium (Cr) leads to the formation of surface oxides during an annealing process, and the surface oxides may not be easily removed in a pickling process after the annealing process. Therefore, final products have poor phosphatability.

[0012] Therefore, it is needed to develop a technique for guaranteeing ultra-high-strength, hole expandability, and phosphatability as well.


DISCLOSURE

Technical Problem

[0016] Aspects of the present disclosure may provide an ultra-high-strength steel sheet having high hole expandability and phosphatability owing to optimized alloying element contents and manufacturing conditions, and a method for manufacturing the ultra-high-strength steel sheet.

Technical Solution

[0017] According to an aspect of the present disclosure, an ultra-high-strength steel sheet having high phosphatability and hole expandability may include, by wt %, carbon (C): 0.08% to 0.2%, silicon (Si): 0.05% to 1.3%, manganese (Mn): 2.0% to 3.0%, phosphorus (P): 0.001% to 0.10%, sulfur (S): 0.010% or less, aluminum (Al): 0.01% to 0.1%, chromium (Cr): 0.3% to 1.2%, boron (B): 0.0010% to 0.0030%, titanium (Ti): 0.01% to 0.05%, nitrogen (N): 0.001% to 0.01%, and a balance of iron (Fe) and inevitable impurities.

[0018] wherein titanium (Ti) and nitrogen (N) may satisfy Formula 1 below, manganese (Mn), silicon (Si), and chromium (Cr) may satisfy Formula 2 below, contents of manganese (Mn), silicon (Si), and chromium (Cr) in a surface layer ranging from a surface to a 0.1 μm position in a thickness direction may satisfy Formula 3 below, and the
The present disclosure provides an ultra-high-strength steel sheet having a tensile strength of 1 GPa or greater, a yield ratio of 0.8 or greater, high hole expandability for preventing flange cracking during forming process, a high crash energy absorbing ability, and high phosphatability.

BEST MODE

The inventor has conducted in-depth research into developing an ultra-high-strength steel sheet having high hole expandability and phosphatability in addition to having high tensile strength, and found that a steel sheet having the intended properties could be provided by optimizing the contents of alloying elements and manufacturing conditions to guarantee phase fraction proper for the objects. Based on this knowledge, the inventor has invented the present invention.

Embodiments of the present disclosure will now be described in detail.

According to an aspect of the present disclosure, an ultra-high-strength steel sheet having high phosphatability and hole expandability has an alloying composition including, by wt %, carbon (C): 0.08% to 0.2%, silicon (Si): 0.05% to 1.3%, manganese (Mn): 2.0% to 3.0%, phosphorus (P): 0.001% to 0.10%, sulfur (S): 0.010% or less, aluminum (Al): 0.01% to 0.1%, chromium (Cr): 0.3% to 1.2%, boron (B): 0.0010% to 0.0030%, titanium (Ti): 0.01% to 0.05%, and nitrogen (N): 0.001% to 0.01%, wherein the content ratio of manganese (Mn), silicon (Si), an chromium (Cr) may be properly controlled.

First, reasons for controlling the contents of alloying elements of the ultra-high-strength steel sheet of the present disclosure and relationships between the alloying elements will be described in detail. In the following description, the content of each element is given in wt % unless otherwise specified.

- Carbon (C): 0.08% to 0.2%
- Manganese (Mn): less than 0.08%, it is difficult to obtain a tensile strength of 1 GPa or greater. Conversely, if the content of carbon (C) is less than 0.08%, it is difficult to obtain a tensile strength of 1 GPa or greater.

- Silicon (Si): 0.05% to 1.3%
- Phosphorus (P): 0.001% to 0.10%
- Chromium (Cr): 0.3% to 1.2%
- Boron (B): 0.0010% to 0.0030%
- Titanium (Ti): 0.01% to 0.05%
- Nitrogen (N): 0.001% to 0.01%

Advantageous Effects

The present disclosure provides an ultra-high-strength steel sheet having high hole expandability and phosphatability in addition to having high tensile strength, and found that a steel sheet having the intended properties could be provided by optimizing the contents of alloying elements and manufacturing conditions to guarantee phase fraction proper for the objects. Based on this knowledge, the inventor has invented the present invention.

According to the present disclosure, it may be preferable that the carbon content (C) be within the range of 0.08% to 0.2%.

According to the present disclosure, it may be preferable that the content of silicon (Si) be within the range of 0.05% to 1.3%.

Manganese (Mn) is an element having a significantly high solid-solution strengthening effect.

If the content of manganese (Mn) is less than 2.0%, it is difficult to guarantee an intended degree of strength in the present disclosure. Conversely, if the content of manganese (Mn) is greater than 3.0%, weldability is poor, and the possibility of problems such as an increase in the load of a cold rolling mill is high. In addition, annealing oxides are formed in large amounts, and thus, phosphatability is poor.

Therefore, according to the present disclosure, it may be preferable that the content of manganese (Mn) be within the range of 2.0% to 3.0%.

Phosphorus (P) is an element effective in strengthening steel.

However, if the content of phosphorus (P) is less than 0.001%, this effect may not be obtained, and manufacturing costs may increase to adjust the content of phosphorus (P) to be an excessively low value during steel making processes. Conversely, if the content of phosphorus (P) is greater than 0.10%, poor impact properties are resulted from grain boundary segregation, thereby making steel brittle.

Therefore, according to the present disclosure, it may be preferable that the content of phosphorus (P) be within the range of 0.001% to 0.10%.

Formulas:

- Formula 1: \[ \text{Formula 1} \]
- Formula 2: \[ \text{Formula 2} \]
- Formula 3: \[ \text{Formula 3} \]
- Formula 5: \[ \text{Formula 5} \]
- Formula 6: \[ \text{Formula 6} \]

References:

1. Carbon (C): 0.08% to 0.2%
2. Silicon (Si): 0.05% to 1.3%
3. Manganese (Mn): 2.0% to 3.0%
4. Phosphorus (P): 0.001% to 0.10%
5. Chromium (Cr): 0.3% to 1.2%
6. Boron (B): 0.0010% to 0.0030%
7. Titanium (Ti): 0.01% to 0.05%
8. Nitrogen (N): 0.001% to 0.01%
9. Manganese (Mn), Silicon (Si), and Chromium (Cr) content ratio may be properly controlled.
Sulfur (S): 0.010% or less

Sulfur (S), an element existing in steel as an impurity, lowers the ductility, hole expandability, and weldability of the steel. Thus, the content of sulfur (S) is adjusted to be as low as possible.

If the content of sulfur (S) is greater than 0.010%, MnS forms, thereby increasing the possibility of a significant decrease in hole expandability and decreases in ductility and weldability. Thus, it may be preferable that the content of sulfur (S) be within the range of 0.010% or less.

Aluminum (Al): 0.01% to 0.1%

Aluminum (Al) has a deoxidizing effect by combining with oxides contained in steel during steel making processes, and together with silicon (Si), aluminum (Al) facilitates the distribution of carbon (C) to austenite during phase transformation.

To this end, it may be preferable that the content of aluminum (Al) be within the range of 0.01% or greater. However, if the content of aluminum (Al) is greater than 0.1%, the surface quality of steel slabs decreases, and manufacturing costs increase.

Therefore, according to the present disclosure, it may be preferable that the content of aluminum (Al) be within the range of 0.01% to 0.1%.

Chromium (Cr): 0.3% to 1.2%

Chromium (Cr) is an element added to improve the hardenability of steel and guarantee high strength, and in the present disclosure, chromium (Cr) is an element effective in inducing the formation of bainite by delaying the transformation of ferrite.

However, if the content of chromium (Cr) is less than 0.3%, it is difficult to obtain these effects. Conversely, if the content of chromium (Cr) is greater than 1.2%, these effects may be saturated, and the load of a cold rolling mill may increase because the strength of a hot-rolled material may be excessively high, thereby markedly increasing manufacturing costs. In addition, annealing oxides are formed during an annealing heat treatment, and thus it may be difficult to control a pickling process, thereby resulting in markedly poor phosphatability.

Therefore, according to the present disclosure, it may be preferable that the content of chromium (Cr) be within the range of 0.3% to 1.2%.

Boron (B): 0.0010% to 0.0030%

Boron (B) is an element effective in increasing the fraction of bainite by suppressing austenite-to-ferrite transformation during cooling in an annealing process.

However, if the content of boron (B) is less than 0.0010%, it is difficult to obtain this effect. Conversely, if the content of boron (B) is greater than 0.0030%, this effect is saturated because of grain boundary segregation of boron (B), and phosphatability is poor because of surface concentration of boron (B) during an annealing heat treatment.

Therefore, according to the present disclosure, it may be preferable that the content of boron (B) be within the range of 0.0010% to 0.0030%.

Titanium (Ti): 0.01% to 0.05%

Titanium (Ti) is an element added to steel for increasing the strength of the steel and scavenging nitrogen (N) from the steel.

If the content of titanium (Ti) is less than 0.01%, it is difficult to obtain these effects. Conversely, if the content of titanium (Ti) is greater than 0.05%, these effects are saturated, and process errors such as nozzle clogging may occur during a continuous casting process.

Therefore, according to the present disclosure, it may be preferable that the content of titanium (Ti) be within the range of 0.01% to 0.05%.

Nitrogen (N): 0.001% to 0.01%

Together with carbon (C), nitrogen (N) is representative of interstitial solid solution strengthening elements. In general, nitrogen (N) is added from air, and the content of nitrogen (N) is controlled through a degasification process during steel making processes.

If the content of nitrogen (N) is less than 0.001%, production costs increases because of excessive degasification, and if the content of nitrogen (N) is greater than 0.01%, high-temperature ductility is low because of excessive formation of precipitates such as AlN or TiN.

Therefore, according to the present disclosure, it may be preferable that the content of nitrogen (N) be within the range of 0.001% to 0.01%.

In addition, titanium (Ti) and nitrogen (N) of the above-described alloying elements of the steel sheet of the present disclosure may satisfy a content relationship expressed by Formula 1 below.

\[
3.4\%{\text{Ti}}/\%{\text{N}} \leq 10
\]  

(Formula 1)

(In Formula 1, each of Ti and N refers to the weight percent (wt %) of the element.)

If the ratio of Ti/N is less than 3.4, the amount of titanium (Ti) added is insufficient compared to the amount of dissolved nitrogen (N). Therefore, remaining nitrogen (N) may form Nb or the like, and thus the effect of increasing strength by adding boron (B) may be lowered, thereby causing a decrease in strength. Conversely, if the ratio of Ti/N is greater than 10, costs for denitrification increase, and the possibility of problems such as nozzle clogging increases during a continuous casting process.

Along with this, manganese (Mn), and silicon (Si) and chromium (Cr) of the above-described alloying elements may satisfy a content relationship expressed by Formula 2 below, and the contents of manganese (Mn), silicon (Si), and chromium (Cr) in a steel surface layer (from a surface to a 0.1 μm position in a thickness direction) may satisfy Formula 3 below.

\[
0.75\%{\text{Mn}}/\%{\text{Si}} + \%{\text{Cr}} \leq 1
\]  

(Formula 2)

\[
1.0\%{\text{Mn}}/\%{\text{Si}} + \%{\text{Cr}} \leq 2
\]  

(Formula 3)

(In Formulas 2 and 3, each of Mn, Si, and Cr refers to the weight percent (wt %) of the element, and in Formula 3, each of Mn*, Si*, and Cr* refers to the average of GDS component analysis values.)

Formulas 2 and 3 are conditions for guaranteeing the phosphatability of the ultra-high-strength steel sheet of the present disclosure. If the value of Formula 2 is less than 1, a very dense Si and Cr oxide layer is formed during an annealing heat treatment process, and it is not easy to remove the oxide layer even in the case that a final pickling process is enhanced. In addition, if the oxide layer is removed under conditions of an excessively high acid content and an excessively high temperature, relatively weak grain boundaries are first eroded, and thus the workability and fatigue characteristics of the steel sheet are markedly decreased.

In addition, if the value of Formula 3 indicating contents of elements in the surface of the steel sheet after a
final pickling process is less than 0.7, Si or Cr oxides, or an Si-rich or Cr-rich layer having poor phosphatability remains in a very near surface layer or grain boundaries of the steel sheet, thereby hindering the formation of phosphate crystals. Conversely, if the value is greater than the ratio of Mn/(Si+Cr), Mn-containing oxides formed in a very near surface layer is oxidized during initial heating in an annealing heat treatment process and is then partially reduced in a reducing atmosphere inside an annealing furnace, or Mn-containing oxides are initially selectively coarsened, thereby making it difficult to properly remove the Mn-containing oxides in a final pickling process. In this case, when phosphate crystals are formed, deviation occurs to result in poor phosphatability.

[0072] In addition to the above-described alloying elements, the ultra-high-strength steel sheet of the present disclosure may further include at least one of niobium (Nb), molybdenum (Mo), vanadium (V), and tungsten (W) in an amount described below.

[0073] Niobium (Nb): 0.01% to 0.05%

[0074] Molybdenum (Mo), representative of precipitation strengthening elements, is added to increase the strength of steel and induce grain refinement.

[0075] If the content of niobium (Nb) is less than 0.01%, it is difficult to sufficiently obtain these effects. Conversely, if the content of niobium (Nb) is greater than 0.05%, manufacturing costs may excessively increase, and ductility may markedly decrease because of excessive formation of precipitates.

[0076] Therefore, according to the present disclosure, it may be preferable that the content of niobium (Nb) be within the range of 0.01% to 0.05%.

[0077] Each of molybdenum (Mo), vanadium (V), and tungsten (W): 0.01% to 0.20%

[0078] Molybdenum (Mo), vanadium (V), and tungsten (W) are elements having a function similar to that of niobium (Nb). If the content of each of these elements is less than 0.01%, it is difficult to have sufficient strength increasing and grain refinement effects on steel, and if the content of any one of these elements is greater than 0.20%, manufacturing costs may excessively increase compared to the effect of increasing strength.

[0079] Therefore, according to the present disclosure, when molybdenum (Mo), vanadium (V), or tungsten (W) is added, the content of the element may preferably be within the range of 0.01% to 0.20%.

[0080] In addition, niobium (Nb), molybdenum (Mo), vanadium (V), and tungsten (W) may satisfy Formula 4 below.

\[
0.01 \leq Nb + 0.2(Mo + V + W) \leq 0.05
\]  

[Formula 4]

[0081] (In Formula 4, each of Nb, Mo, V, and W refers to the weight percent (wt %) of the element.)

[0082] If the relational value of Nb, Mo, V, and W is less than 0.01, it is difficult to obtain the grain refinement and precipitation strengthening effects, and if the relation value is greater than 0.05, production costs may excessively increase, as compared to the above-described effects.

[0083] The other component of the ultra-high-strength steel sheet of the present disclosure is iron (Fe). However, impurities of raw materials or steel manufacturing environments may be inevitably included in the ultra-high-strength steel sheet, and such impurities may not be removed from the ultra-high-strength steel sheet. Such impurities are well-known to those of ordinary skill in the steel manufacturing industry, and thus descriptions thereof will not be provided in the present disclosure.

[0084] The ultra-high-strength steel sheet of the present disclosure may have a microstructure including martensite or tempered martensite in an area fraction of 50% to 80%, bainite in an area fraction of 10% to 30%, retained austenite in an area fraction of less than 5%, and the balance of ferrite. In this case, since the fractions of tempered martensite and bainite are maximized, and the fraction of ferrite causing a great hardness difference between phases is reduced, the formation of voids in a hole punching process is suppressed.

[0085] More preferably, martensite including tempered martensite may be included in a fraction of 50% to 80%, and if the fraction is less than 50%, it is difficult to obtain intended ultra-high-strength within the range of 1 GPa or greater in tensile strength, and guarantee hole expandability. Conversely, if the fraction is greater than 80%, poor hole expandability is obtained because of an excessive increase in strength.

[0086] In addition, if the fraction of bainite is less than 10%, hole expandability may markedly decrease due to an excessive increase in strength, and thus it may be difficult to obtain the value of tensile strength (MPa) x hole expanding ratio (HER) within an intended range of 40000 or greater. Conversely, if the fraction of bainite is greater than 30%, it is difficult to guarantee ultra-high-strength.

[0087] Tempered martensite, formed at high temperature is a key phase for guaranteeing hole expandability intended in the present disclosure, and tempered martensite may be formed in large amounts by performing slow cooling in a temperature range immediately below a martensite start temperature during a cooling process.

[0088] In addition, if the fraction of retained austenite is 5% or more, delayed fracture resistance property is poor. Thus, it may be preferable that the fraction of retained austenite be adjusted to be less than 5%.

[0089] In addition, although the fraction of ferrite is not particularly limited, it may be preferable that the fraction of ferrite be within the range of 20% or less for guaranteeing hole expandability.

[0090] The ultra-high-strength steel sheet of the present disclosure having the above-described microstructure may have a tensile strength of 1 GPa or greater and the value of tensile strength (MPa) x hole expanding ratio (HER) within the range of 40000 or greater for guaranteeing hole expandability to a degree in which flange cracking does not occur in a press forming process or roll forming process.

[0091] If the above-mentioned value is less than 40000, it may be difficult to guarantee ultra-high-strength even in the case that high hole expandability is obtained, or poor hole expandability may be obtained even in the case that ultra-high-strength is obtained, or the ability of absorbing impact energy may be poor.

[0092] In addition, the ultra-high-strength steel sheet of the present disclosure may have a yield ratio of 0.8 or greater. If the yield ratio of the ultra-high-strength steel sheet is less than 0.8, the fraction of ferrite is generally high, thereby resulting in a decrease in strength and poor hole expandability.

[0093] The ultra-high-strength steel sheet of the present disclosure having a tensile strength of 1000 MPa or greater
and high hole expandability is processable through a press forming process and a roll forming process and has high crashworthiness.

[0096] The ultra-high-strength steel sheet of the present disclosure may be a cold-rolled steel sheet or a hot-dip galvanized steel sheet.

[0097] Hereinafter, a method for manufacturing an ultra-high-strength steel sheet having high phosphatability and high expandability will be described in detail according to the present disclosure.

[0098] First, a steel material having the above-described alloying composition and component relationships is prepared, and a hot rolling process and a cold rolling process may be performed on the steel material to manufacture a cold-rolled steel sheet.

[0099] In this case, the hot rolling process and the cold rolling process may be performed according to methods generally used to manufacture an ultra-high-strength steel sheet. For example, hot rolling and cold rolling conditions for a complex phase (CP) steel manufacturing method may be used. However, this is a non-limiting example.

[0100] The cold-rolled steel sheet manufactured as described above may be annealed preferably at 800°C to 850°C.

[0101] If the temperature of the annealing heat treatment is less than 800°C, the fraction of ferrite may exceed 20%, and thus it may be difficult to guarantee intended ultra-high-strength and hole expandability. Conversely, if the temperature of the annealing heat treatment is greater than 850°C, although hole expandability is improved, elements such as silicon (Si), manganese (Mn), chromium (Cr), or boron (B) form surface oxides or concentrated substances in large amounts during the high-temperature annealing heat treatment and remain on surface regions even after a subsequent pickling process, thereby resulting in poor phosphatability.

[0102] The annealing heat treatment may be performed in an annealing furnace under reducing atmosphere conditions provided by hydrogen and nitrogen gases, and in this case, the atmosphere of the annealing furnace may be adjusted to have a dew point within the range of −35°C to −50°C. If the dew point is higher than −35°C, elements having a high oxygen affinity such as manganese (Mn), silicon (Si), chromium (Cr), or boron (B) included in the steel sheet may easily form surface oxides or concentrated substances and may not be easily removed in a later pickling process. In addition, such elements may be attached to rolls of the annealing furnace and cause dent defects. Conversely, if the dew point is lower than −50°C, manufacturing costs may markedly increase.

[0103] The cold-rolled steel sheet annealed as described above may be rapidly cooled to a temperature ranging within a predetermined cooling stop temperature range and may be maintained at the temperature.

[0104] In this case, the cooling stop temperature range may preferably range from Ms (martensite start temperature) to Bs (bainite start temperature), and the cold-rolled steel sheet may be maintained within the cooling stop temperature range for a predetermined period of time. The cold-rolled steel sheet may be maintained for a period of time expressed by Formula 5 below.

\[
300 \div 4729 + 71T + 25Mn + 16Si + 117Cr - 20.17T + 0.0197T^2 < 500
\]  

(Formula 5)

[0109] In more detail, according to the present disclosure, the temperature of an acid is controlled in addition to the concentration of the acid. Specifically, although the concentration of hydrochloric acid may be adjusted according to the alloying composition of the steel sheet, the concentration of hydrochloric acid may preferably be adjusted to be within the range of 5% to 20%. If the concentration of hydrochloric acid is less than 5%, oxides may not be properly removed. Conversely, if the concentration of hydrochloric acid is greater than 20%, erosion may rapidly occur by the acid, and selective grain boundary erosion may markedly occur, thereby resulting in poor workability and fatigue characteristics. Although the temperature of hydrochloric acid may also be adjusted according to the alloying composition of the steel sheet, the temperature of hydrochloric acid may preferably be adjusted to be within the range of 50°C to 80°C. If the temperature of hydrochloric acid is less than 50°C, oxides may not be easily removed because of low reactivity, and if the temperature of hydrochloric acid is greater than 80°C, selective erosion may occur because of excessively rapid reactions.

[0110] In addition, when the post-pickling process is performed under the above-described conditions, the concen-
tation and temperature of hydrochloric acid may have a relationship with alloying compositions as expressed by Formula 6.

\[(\text{HCl concentration}) \times \text{(HCl temperature)} = (1.33 + \text{Mn} + 1.1) \times (48 + 0.8 + \text{Si} + 0.7 + 1.1)\]  
[Formula 6]

[0111] In Formula 6, each of Mn, Si, and Cr refers to the weight percent (wt %) of the element.

[0112] If the value of Formula 6 is less than 1, pickling properties deteriorate, and thus annealing oxides may not be properly removed at a given concentration and temperature of hydrochloric acid. That is, when the value of Formula 6 is 1 or greater, surface oxides may easily be removed from a surface layer of the steel sheet.

[0113] In addition, the post-pickling process may preferably be performed for 5 seconds to 15 seconds. If the pickling time is less than 5 seconds, the post-pickling process may not be completely performed, and if the pickling time is greater than 15 seconds, the productivity of the post-pickling process may be lowered.

[0114] After the process of removing surface oxides is completed as described above, the contents of manganese (Mn), silicon (Si), and chromium (Cr) in a surface layer (from a surface to a 0.1 \( \mu \)m position in a thickness direction) of the ultra-high-strength steel sheet of the present disclosure satisfies Formula 3 described above, thereby guaranteeing high phosphatability.

**MODE FOR INVENTION**

[0115] Hereinafter, the present disclosure will be described more specifically through examples. However, the following examples should be considered in a descriptive sense only and not for purposes of limitation. The scope of the present invention is defined by the appended claims, and modifications and variations may be reasonably made therefrom.

**EXAMPLES**

[0116] A hot rolling process and a cold rolling process were performed on steel slabs having alloying compositions shown in Table 1 below under general process conditions to manufacture cold-rolled steel sheets, and an annealing process, a cooling process, and a post-pickling process were performed on the cold-rolled steel sheets under conditions shown in Table 2 below.

[0117] Thereafter, phosphatoc processability (phosphatability) of the cold-rolled steel sheets was analyzed, and surface GDS analysis was performed on the cold-rolled steel sheets. Results thereof are shown in Table 3 below.

[0118] In this case, the GSD analysis was performed by measuring the contents of elements in a region from the surface to a 0.1 \( \mu \)m depth position of each cold-rolled steel sheet, and calculating the averages of the measured contents.

[0119] In addition, the phosphatability was evaluated using a phosphate solution prepared using four chemicals: Chemfos #740A, Chemfos #740R, Chemfil Buffer, and an accelerator together with Rinse Conditioner (surface modifier) and CHEMKLEEN #177 (degreaser) available from Pittsburgh Plate Glass (PPG). Phosphatability was evaluated as being acceptable or not acceptable by observing a surface enlarged 1000 times using a SEM, checking a portion not coated with phosphate, and checking whether a measured weight of phosphate coating was within the range of 2 g/m\(^2\) to 3 g/m\(^2\).

[0120] In addition, microstructure fractions and mechanical properties (yield strength, tensile strength, elongation, and hole expanding ratio (HER)) of each cold-rolled steel sheet were measured, and results of the measurement are shown in Table 4 below.

[0121] In this case, a SEM image of the microstructure of each cold-rolled steel sheet was captured at a magnification of 3000 times, and the area fraction of each phase was measured using an image analyzer. In addition, the fraction of retained austenite was measured based on the peak intensity of austenite using XRD.

[0122] A tension test was performed using JIS-5 specimens at a rate of 10 mm/min.

[0123] In addition, HERs were measured according to JIS T 1001-1996.

[0124] Results of the tension test and the HER test are average values obtained by performing each test three times.

**TABLE 1**

<table>
<thead>
<tr>
<th>Alloying composition (wt %)</th>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Cr</th>
<th>B*</th>
<th>Ti</th>
<th>N*</th>
<th>Nb</th>
<th>Mo</th>
<th>V</th>
<th>W</th>
<th>F1</th>
<th>F2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IS 1</strong></td>
<td>0.10</td>
<td>0.5</td>
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### TABLE 1-continued

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<th>Ti</th>
<th>N*</th>
<th>Nb</th>
<th>Mo</th>
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</table>

*IS: Inventive Steel,
**CS: Comparative Steel,
***F: Formula

[0125] (In Table 1 above, the contents of B* and N* are in ppm. In addition, Comparative Steels 3, 4, 5, 9, and 10 of Table 1 above were processed under manufacturing conditions shown in Table 2 below which did not satisfy conditions proposed in the present disclosure, and were thus named as Comparative Steels.)

### TABLE 2

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<th>Pickling conditions</th>
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<td>Cooling rate (°C/min)</td>
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*IS: Inventive Steel,
**CS: Comparative Steel,
***F: Formula

[0126] (In Table 2 above, rapid cooling of Inventive Steels 1 to 11, and Comparative Steels 1 to 10 was performed within the range of Ms to Bs.)

### TABLE 3

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<th>Phosphat- ability</th>
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**CE 1**

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*IE: Inventive Example, **CE: Comparative Example

[0127] In Table 3 above, each of Mn*, Si*, and Cr* is the average of values measured by GDS component analysis from a surface to a 0.1 μm position.

TABLE 4

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*IE: Inventive Example, **CE: Comparative Example

[0128] In Table 4 above, B refers to bainite, M refers to martensite, F refers to ferrite, and γ refers to retained austenite. In addition, YS refers to yield strength, TS refers to tensile strength, El refers to elongation, HER refers to a hole expanding ratio, and property formula refers to tensile strength (MPa) hole expanding ratio (HER).

[0129] As shown in Tables 1 to 4, Inventive Examples 1 to 11, satisfying both the alloy composition and the manufacturing conditions proposed in the present disclosure, satisfied phosphatability requirements, that is, had high phosphatability.

[0130] In addition, bainite and martensite were formed in proper fractions in Inventive Examples 1 to 11, and thus Inventive Examples 1 to 11 had a tensile strength of 1 GPa or greater, a yield ratio of 0.8 or greater, and the value of tensile strength (MPa) hole expanding ratio (HER) within the range of 40000 or greater.

[0131] These results show that inventive steels of the present disclosure have high hole expandability in addition to having high phosphatability.

[0132] However, Comparative Examples 1 to 10, not satisfying one or more of the alloy composition and the manufacturing conditions proposed in the present disclosure, satisfied not all the physical property conditions intended in the present disclosure.

[0133] Comparative Examples 1 and 2 had carbon (C) and manganese (Mn) contents outside the ranges proposed in the present disclosure, and thus did not have a tensile strength of 1 GPa or greater and the value of tensile strength (MPa) hole expanding ratio (HER) within the range of 40000 or greater. In addition, Comparative Examples 1 and 2 had a yield ratio of less than 0.8, and thus did not satisfy the yield ratio range proposed in the present disclosure.

[0134] Comparative Examples 3 and 4 did not satisfy the maintaining process condition (Formula 5) after rapid cool-
post-pickling condition (Formula 6) of the present disclosure. Thus, the phosphatability of Comparative Example 8 was poor.

[0138] Although the alloying compositions of Comparative Examples 9 and 10 satisfied the conditions proposed in the present disclosure, Comparative Examples 9 and 10 did not satisfy the post-pickling process condition (Formula 6), and thus surface oxides remained on Comparative Examples 9 and 10 after pickling. As a result, Comparative Examples 9 and 10 did not satisfy Formula 3 of the present disclosure and thus had poor phosphatability.

[0139] As described above, only when the alloying composition and manufacturing conditions, particularly, Formulas 1 to 6 of the present disclosure are satisfied, an ultra-high-strength steel sheet having ultra-high-strength, hole expandability, and phosphatability may be manufactured as intended in the present disclosure.

1. An ultra-high-strength steel sheet having high phosphatability and hole expandability, comprising, by wt %, carbon (C): 0.08% to 0.2%, silicon (Si): 0.05% to 1.3%, manganese (Mn): 2.0% to 3.0%, phosphorus (P): 0.001% to 0.10%, sulfur (S): 0.010% or less, aluminum (Al): 0.01% to 0.1%, chromium (Cr): 0.3% to 1.2%, boron (B): 0.0010% to 0.0030%, titanium (Ti): 0.01% to 0.05%, nitrogen (N): 0.001% to 0.01%, and a balance of iron (Fe) and inevitable impurities,

wherein titanium (Ti) and nitrogen (N) satisfy Formula 1 below, manganese (Mn), silicon (Si), and chromium (Cr) satisfy Formula 2 below, contents of manganese (Mn), silicon (Si), and chromium (Cr) in a surface layer ranging from a surface to a 0.1 μm position in a thickness direction satisfy Formula 3 below, and the ultra-high-strength steel sheet has a yield ratio of 0.8 or greater,

\[
3.4s\text{Ti}/N\leq10
\]

[Formula 1]

\[
1.0s\text{Mn}/(\text{Si}+\text{Cr})
\]

[Formula 2]

\[
0.7s\text{Mn}^*/s\text{Si}^*+s\text{Cr}^*/s\text{Mn}/(\text{Si}+\text{Cr})
\]

[Formula 3]

where in Formulas 1 and 3, each of Ti, N, Mn, Si, and Cr refers to a weight percent (wt %) of the element, and in Formula 3, each of Mn*, Si*, and Cr* refers to an average of values obtained by GDS component analysis from the surface to the 0.1 μm position in the thickness direction.

2. The ultra-high-strength steel sheet of claim 1, further comprising, by wt %, at least one of niobium (Nb): 0.01% to 0.05%, molybdenum (Mo): 0.01% to 0.20%, vanadium (V): 0.01% to 0.20%, and tungsten (W): 0.01% to 0.20%, wherein the ultra-high-strength steel sheet satisfies Formula 4 below,

\[
0.01s\text{Nb}+0.2(Mo+V+W)\leq0.05
\]

[Formula 4]

where each of Nb, Mo, V, and W refers to a weight percent (wt %) of the element.

3. The ultra-high-strength steel sheet of claim 1, wherein the ultra-high-strength steel sheet has a microstructure comprising martensite or tempered martensite in an area fraction of 50% to 80%, bainite in an area fraction of 10% to 30%, retained austenite in an area fraction of less than 5%, and a balance of ferrite.

4. The ultra-high-strength steel sheet of claim 1, wherein the ultra-high-strength steel sheet has a value of tensile strength (MPa):hole expanding ratio (HER) within a range of 40000 or greater.

5. The ultra-high-strength steel sheet of claim 1, wherein the ultra-high-strength steel sheet is a cold-rolled steel sheet or a hot-dip galvanized steel sheet.

6. A method for manufacturing an ultra-high-strength steel sheet having high phosphatability and hole expandability, the method comprising:

preparing a steel material comprising, by wt %, carbon (C): 0.08% to 0.2%, silicon (Si): 0.05% to 1.3%, manganese (Mn): 2.0% to 3.0%, phosphorus (P): 0.001% to 0.10%, sulfur (S): 0.010% or less, aluminum (Al): 0.01% to 0.1%, chromium (Cr): 0.3% to 1.2%, boron (B): 0.0010% to 0.0030%, titanium (Ti): 0.01% to 0.05%, nitrogen (N): 0.001% to 0.01%, and a balance of iron (Fe) and inevitable impurities, wherein titanium (Ti) and nitrogen (N) satisfy Formula 1 below, and manganese (Mn), silicon (Si), and chromium (Cr) satisfy Formula 2 below;

hot rolling and cold rolling the steel material to manufacture a cold-rolled steel sheet;

annealing the cold-rolled steel sheet at 800°C to 850°C;

rapidly cooling the annealed cold-rolled steel sheet to a temperature range of a martensite start temperature (Ms) to a bainite start temperature (Bs) and then maintaining the cold-rolled steel sheet;

after the maintaining, cooling the cold-rolled steel sheet at a rate of 10°C/min to 50°C/min; and

after the cooling, removing surface oxides from the cold-rolled steel sheet,

wherein the maintaining of the cold-rolled steel sheet is performed for a period of time satisfying Formula 5 below, and the removing of the surface oxides is performed in conditions satisfying Formula 6 below,

\[
3.4s\text{Ti}/N\leq10
\]

[Formula 1]

\[
1.0s\text{Mn}/(\text{Si}+\text{Cr})
\]

[Formula 2]

\[
3.5s\text{Mn}+7\text{Ti}+25\text{Mo}+16\text{Si}+11\text{Cr}+20.1\text{T}+0.01991t^2+500
\]

[Formula 5]

\[
\text{(HCl concentration)}\times\text{HCl temperature}/(1.34\text{Mn}+7.45s\text{Si}+0.8\text{Cr})\times(47+2.1\text{Mn}+13.9\text{Si}+4.3\text{Cr})=1
\]

[Formula 6]

where in Formulas 1 to 6, each of Ti, N, Mn, Si, Cr, and C refers to a weight percent (wt %) of the element, and T in Formula 5 refers to a rapid cooling stop temperature (°C), and a value calculated by Formula 5 is in seconds.

7. The method of claim 6, wherein the steel material further comprising, by wt %, at least one of niobium (Nb): 0.01% to 0.05%, molybdenum (Mo): 0.01% to 0.20%, vanadium (V): 0.01% to 0.20%, and tungsten (W): 0.01% to 0.20%, and the steel material satisfies Formula 4 below,

\[
0.01s\text{Nb}+0.2(Mo+V+W)\leq0.05
\]

[Formula 4]

where each of Nb, Mo, V, and W refers to a weight percent (wt %) of the element.

8. The method of claim 6, wherein the annealing of the cold-rolled steel sheet is performed in an environment having a dew point of −35°C to −50°C.

9. The method of claim 6, wherein the rapid cooling of the annealed cold-rolled steel sheet is performed at a cooling rate of 100°C/min to 600°C/min.
10. The method of claim 6, wherein contents of manganese (Mn), silicon (Si), chromium (Cr) in a surface layer ranging from a surface to a 0.1 μm position in a thickness direction of the ultra-high-strength steel sheet satisfy Formula 3 below,

\[
0.7a_{\text{Mn}*}/(\text{Si}^* + \text{Cr}^*)a_{\text{Mn}}/(\text{Si} + \text{Cr}) \quad \text{[Formula 3]}
\]

where in Formula 3, each of Mn, Si, and Cr refers to a weight percent (wt %) of the element, and each of Mn*, Si*, and Cr* refers to an average of values obtained by GDS component analysis from the surface to the 0.1 μm position in the thickness direction.

* * * * *