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

(11) EP 3 305 936 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
11.04.2018 Bulletin 2018/15

(21) Application number: **15893419.0**

(22) Date of filing: **28.05.2015**

(51) Int Cl.:
C22C 38/16 *(2006.01)*
C21D 8/02 *(2006.01)*
C22C 38/04 *(2006.01)*
C22C 38/06 *(2006.01)*
C22C 38/60 *(2006.01)*

(86) International application number:
PCT/KR2015/005381

(87) International publication number:
WO 2016/190467 (01.12.2016 Gazette 2016/48)

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

(71) Applicant: **POSCO**
Gyeongsangbuk-do 790-300 (KR)

(72) Inventors:
- **YOON, Jeong-Bong**
Pohang-si
Gyeongsangbuk-do 790-360 (KR)
- **LEE, Byoung-Ho**
Pohang-si
Gyeongsangbuk-do 790-360 (KR)
- **KIM, Jong-Hwa**
Pohang-si
Gyeongsangbuk-do 790-360 (KR)

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

(54) HOT-ROLLED STEEL SHEET HAVING EXCELLENT COMPOSITE CORROSION RESISTANCE TO SULFURIC ACID AND HYDROCHLORIC ACID AND MANUFACTURING METHOD THEREFOR

(57) Disclosed are: a hot-rolled steel sheet having excellent composite resistance to sulfuric acid and hydrochloric acid; and a manufacturing method therefor. An aspect of the present invention provides a hot-rolled steel sheet having excellent composite corrosion resistance to sulfuric acid and hydrochloric acid, the hot-rolled steel sheet containing, by weight%, 0.05-0.1% of C, 0.5-1.5% of Mn, 0.02% or less of P, 0.02% or less of S, 0.01-0.1% of Al, 0.2-0.6% of Cu, 0.05-0.1% of Sb, the remainder Fe, and inevitable impurities, wherein Cu and Sb are enriched within 500 nm from the surface in the thickness direction, and the mass loss to a solution of 16.9 vol% of sulfuric acid + 0.35 vol% of hydrochloric acid is 2.0 mg/cm2/hr.

Printed by Jouve, 75001 PARIS (FR)

Description

[Technical Field]

[0001] The present disclosure relates to a hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid and applicable as a material for thermal power plant equipment such as desulfurization equipment, denitrification equipment, preheaters, or parts thereof, and a method for manufacturing the hot-rolled steel sheet.

[Background Art]

[0002] Steels having resistance to sulfuric acid corrosion or sulfuric acid-hydrochloric acid composite corrosion are used as materials for desulfurization equipment and denitrification equipment in thermal power plants in which sulfuric acid corrosion or sulfuric acid-hydrochloric acid composite corrosion is serious, due to sulfuric acid and hydrochloric acid produced by a reaction between moisture and exhaust gas containing sulfurous acid gas and chlorine gas generated when fossil fuels such as coal or petroleum are combusted, pipes of combined cycle power plants, and gas-gas heater (GGH) heat elements required to be made of relatively thick steel sheets, etc.

[0003] In general, it has been commonly known that a large amount of copper (Cu) may be added to steel having resistance to sulfuric acid-hydrochloric acid composite corrosion so as to decrease the rate of corrosion in a composite atmosphere of sulfuric acid and hydrochloric acid, as compared to the rate of corrosion of normal steels.

[0004] Although copper (Cu) is more effective than other alloying elements in decreasing the rate of sulfuric acid corrosion, copper (Cu) added in large amounts causes problems such as the formation of cracks in steel sheets during a hot rolling process, and thus, steels to which an appropriate amount of copper (Cu) and other elements are added have been developed (Japanese Patent Application Laid-open Publication No. 1997-025536, Japanese Patent Application Laid-open Publication No. 1998-110237, Korean Patent Application Laid-open Publication No. 2009-0070249, etc) .

[0005] As described above, although the corrosion resistance of steels resistant to sulfuric acid-hydrochloric acid composite corrosion is improved as the content of copper (Cu) is increased, copper (Cu) is a relatively expensive alloying element, and thus production costs may be increased in proportion to the amount of copper (Cu). In addition, copper (Cu), having a low melting point, may be segregated or easily cause cracks, even if only a small amount of deformation occurs in copper-rich regions. Therefore, cracks may be easily formed in portions such as slab corners undergoing a large amount of processing during a continuous casting process, and thus, surface defects undergoing corrosion earlier that other portions may remain after a hot rolling process.

[0006] Therefore, there is a need for a method of imparting high composite corrosion resistance to steel resistant to sulfuric acid-hydrochloric acid composite corrosion while minimizing the content of copper (Cu) in the steel.

[Disclosure]

[Technical Problem]

[0007] Aspects of the present disclosure may provide a hot-rolled steel sheet having high corrosion resistance in a composite corrosive environment containing sulfuric acid and hydrochloric acid, and a method for manufacturing the hot-rolled steel sheet.

[Technical Solution]

[0008] According to an aspect of the present disclosure, a hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid may include, by wt%, carbon (C): 0.05% to 0.1%, manganese (Mn): 0.5% to 1.5%, phosphorus (P) : 0.02% or less, sulfur (S): 0.02% to less, aluminum (Al): 0.01% to 0.1%, copper (Cu): 0.2% to 0.6%, antimony (Sb): 0.05% to 0.1%, and a balance of iron (Fe) and inevitable impurities, wherein copper (Cu) and antimony (Sb) may be concentrated in a region from a surface to a 500-nm position in a thickness direction of the hot-rolled steel sheet, and the hot-rolled steel sheet may have a corrosion loss of 2.0 mg/cm^2/hr or less in a solution of 16.9 volume% sulfuric acid and 0.35 volume% hydrochloric acid.

[0009] According to another aspect of the present disclosure, a method for manufacturing a hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid may include: reheating a steel slab to 1100°C to 1300°C, the steel slab including, by wt%, carbon (C): 0.05% to 0.1%, manganese (Mn): 0.5% to 1.5%, phosphorus (P): 0.02% or less, sulfur (S): 0.02% or less, aluminum (Al): 0.01% to 0.1%, copper (Cu): 0.2% to 0.6%, antimony (Sb): 0.05% to 0.1%, and a balance of iron (Fe) and inevitable impurities; obtaining a hot-rolled steel sheet by hot rolling the reheated steel slab and finish hot rolling the steel slab at a temperature of 850°C to 950°C; rapidly cooling the hot-rolled steel sheet at a rate of 120°C/s to 150°C/s; coiling the cooled hot-rolled steel sheet at a temperature of 650°C to 750°C; and slowly cooling the coiled hot-rolled steel sheet at a rate of 30°C/hr to 40°C/hr to a cooling finish temperature of 350°C to 400°C.

[0010] The above-described aspects of the present disclosure do not include all aspects or features of the present disclosure. Other aspects or features, and effects of the present disclosure will be clearly understood from the following descriptions of exemplary embodiments.

[Advantageous Effects]

[0011] The present disclosure may provide a hot-rolled steel sheet having high composite corrosion resistance even though the hot-rolled steel sheet has lower amounts of alloying elements than steel sheets of the related art having composite corrosion resistance to sulfuric acid and hydrochloric acid. In addition, the hot-rolled steel sheet of the present disclosure may be used as a material, required to have a relatively thick thickness, for denitrification equipment and desulfurization equipment of power plants, exhaust gas pipes of boilers, and preheaters, and may markedly increase the lifespans of such facilities and apparatuses.

[Best Mode]

[0012] The inventors have repeatedly conducted research into compositions of steel sheets and methods of manufacturing steel sheets in order to provide a method of imparting high composite corrosion resistance to steel resistant to sulfuric acid-hydrochloric acid composite corrosion while minimizing the content of copper (Cu) in the steel. As a result, the inventors have found that if antimony (Sb) is added to a steel sheet as an alloying element, and cooling conditions after a hot rolling process and a coiling process are properly controlled, a Cu-Sb rich layer, guaranteeing high composite corrosion resistance, is formed on the steel sheet to an appropriate thickness in a corrosive environment containing sulfuric acid and hydrochloric acid. Based on this knowledge, the inventors have invented the present invention.

[0013] Hereinafter, a hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid will be described in detail according to an aspect of the present disclosure.

[0014] First, the alloying composition of the hot-rolled steel sheet of the present disclosure will be described in detail.

Carbon (C): 0.05 wt% to 0.1 wt%

[0015] Carbon (C) is effective in increasing the strength of a steel sheet. If the content of copper (Cu) is less than 0.05 wt%, it is difficult to obtain a desired degree of strength, and wear resistance reduces. Conversely, if the content of carbon (C) is greater than 0.1 wt%, the weldability of the steel sheet markedly reduces, thereby markedly increasing the possibility of defects during welding and decreasing the corrosion resistance of the steel sheet. Therefore, according to the present disclosure, it may be preferable that the content of copper (Cu) be within the range of 0.05 wt% to 0.1 wt%.

Manganese (Mn): 0.5 wt% to 1.5 wt%

[0016] Manganese (Mn) dissolves in steel and precipitates sulfur (S) in the form of manganese sulfide, thereby preventing hot shortness caused by dissolved sulfur (S) and having a solid-solution strengthening effect. If the content of manganese (Mn) is less than 0.5 wt%, manganese sulfide is not sufficiently precipitated. Thus, hot shortness may be caused by dissolved sulfur (S), and it may be difficult to obtain a desired degree of strength. Conversely, if the content of manganese (Mn) is greater than 1.5 wt%, the above-described effects are saturated, and product cost markedly increases. Thus, according to the present disclosure, it may be preferable that the content of manganese (Mn) be within the range of 0.5 wt% to 1.5 wt%.

Phosphorus (P): 0.02 wt% or less

[0017] Phosphorus (P) is an element inevitably added to steel, and if the content of phosphorus (P) is greater than 0.02 wt%, composite corrosion resistance may markedly decrease from a desired value. Therefore, it may be preferable that the content of phosphorus (P) be within the range of 0.02 wt% or less.

Sulfur (S): 0.02 wt% or less

[0018] Sulfur (S) is an element dissolved in steel causing hot shortness, and thus, the content of sulfur (S) is adjusted to be as low as possible. If the content of sulfur (S) is greater than 0.02 wt%, there is a high possibility that defects will be formed due to hot shortness. Therefore, it may be preferable that the content of sulfur (S) be within the range of 0.02 wt% or less.

Aluminum (Al): 0.01 wt% to 0.1 wt%

[0019] Aluminum (Al) is an element inevitably added to Alkilled steel, and it may be preferable that the content of aluminum (Al) be within the range of 0.01 wt% or greater for the effect of deoxidation. However, if the content of aluminum (Al) is greater than 0.1 wt%, surface defects may very likely be formed on the steel sheet, and the weldability of the steel sheet may be decreased. Therefore, according to the present disclosure, it may be preferable that the content of aluminum (Al) be within the range of 0.01 wt% to 0.1 wt%.

Copper (Cu): 0.2 wt% to 0.6 wt%

[0020] Copper (Cu) is an element added for composite corrosion resistance to sulfuric acid and hydrochloric acid. If the content of copper (Cu) is excessively low, it may be difficult to obtain desired composite corrosion resistance. Thus, preferably, copper (Cu) may be added in an amount of 0.2% or greater, and more preferably in an amount of 0.3% or greater. Although composite corrosion resistance increases in proportion to the content of copper (Cu), if the content of copper (Cu) is excessively high, the increase of corrosion resistance is markedly lowered, and production costs may be markedly increased. In addition, surface defects known as star cracks may be formed. Therefore, according to the present disclosure, preferably, the upper limit of the content of copper (Cu) may be set to be 0.6 wt%, and more preferably 0.5 wt%.

Antimony (Sb): 0.05 wt% to 0.1 wt%

[0021] Together with copper (Cu), antimony (Sb) is a key element for improving composite corrosion resistance. In particular, antimony (Sb) forms a Cu-Sb composite oxide in a corrosive environment, thereby effectively improving composite corrosion resistance. If the content of antimony (Sb) is less than 0.05 wt%, it is difficult to obtain the above-described effects. Conversely, if the content of antimony (Sb) is greater than 0.1 wt%, the above-described effects are saturated, and production costs markedly increase. Thus, preferably, the content of antimony (Sb) may be adjusted to be 0.1 wt% or less.

[0022] The steel sheet includes iron (Fe) and inevitable impurities in addition to the above-described alloying elements. Although the addition of elements other than the above-described elements is not excluded, it may be preferable that the total content of tungsten (W), molybdenum (Mo), cobalt (Co), and nickel (Ni) be adjusted to be less than 10 ppm. The reason for this is that these elements may deteriorate the properties of the hot-rolled steel sheet, for example, ductility.

[0023] Furthermore, in the hot-rolled steel sheet of the present disclosure, copper (Cu) and antimony (Sb) may be concentrated in a region from the surface to a 500-nm position in the thickness direction of the hot-rolled steel sheet. These elements are concentrated in the surface of the hot-rolled steel sheet during manufacturing processes, and if the hot-rolled steel sheet is exposed to a corrosive environment containing sulfuric acid and hydrochloric acid, the elements change into a Cu-Sb composite oxide, thereby markedly improving the corrosion resistance of the hot-rolled steel sheet.

[0024] In this case, the contents of concentrated copper (Cu) and antimony (Sb) are not particularly limited. As described below, the contents of concentrated copper (Cu) and antimony (Sb) may be adjusted such that an oxide layer having a thickness of 400 nm or greater from the surface of the hot-rolled steel sheet may be formed in a corrosive environment containing sulfuric acid and hydrochloric acid. If the thickness of the oxide layer is less than 400 nm, it may be difficult to obtain a degree of corrosion resistance intended in the present disclosure. Since corrosion resistance increases as the thickness of the oxide layer increases, the upper limit of the thickness of the oxide layer is not particularly set in the present disclosure. However, if the thickness of the oxide layer is greater than 500 nm, the effect of improving corrosion resistance is relatively low when the addition of large amounts of alloying elements is considered, and production costs may be excessively increased. Thus, it may be more preferable that the thickness of the oxide layer be within the range of 400 nm to 500 nm.

[0025] The hot-rolled steel sheet of the present disclosure has a corrosion loss of 2.0 mg/cm^2/hr or less in a solution of 16.9 volume% sulfuric acid and 0.35 volume% hydrochloric acid.

[0026] Hereinafter, a method for manufacturing a hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid will be described in detail, according to another aspect of the present disclosure.

[0027] First, a steel slab having the above-described composition is prepared and reheated to a temperature of 1100°C to 1300°C. If the reheating temperature is lower than 1100°C, it is difficult to secure a temperature for a subsequent hot rolling process. Conversely, if the reheating temperature is higher than 1300°C, copper (Cu) having a relatively low melting point may melt out, and thus cracks may very likely be formed in the surface of the steel slab.

[0028] Thereafter, the reheated steel slab is subjected to hot rolling, and is then subjected to finish hot rolling at a temperature of 850°C to 950°C, to obtain a hot-rolled steel sheet. If the finish hot rolling temperature is lower than 850°C, the elongation of the hot-rolled steel sheet is markedly decreased due to elongated grains, and properties of the hot-rolled steel sheet have directional deviations. Conversely, if the finish hot rolling temperature is higher than 950°C, austenite grains become coarse, and thus hardenability markedly increases.

[0029] Thereafter, the hot-rolled steel sheet is rapidly cooled at a rate of 120°C/s to 150°C/s, based on the surface temperature of the hot-rolled steel sheet. The rapid cooling may provide driving force such that alloying elements improving corrosion resistance may move to the surface of the hot-rolled steel sheet after a coiling process. If the cooling rate is less than 120°C/s, the surface temperature of the hot-rolled steel sheet may be too high to sufficiently drive oxide-forming elements from the interior to the surface of the hot-rolled steel sheet, and thus when the hot-rolled steel sheet is exposed to a composite corrosive environment, oxides may not be sufficiently formed. Conversely, if the cooling rate is greater than 150°C/s, the interior temperature of the hot-rolled steel sheet becomes excessively low, and thus heat recuperation may not occur to a desired temperature after a coiling process. In this case, alloying elements effective in forming an oxide layer may not move smoothly. Therefore, preferably, the cooling rate may be set to be within the range of 120°C/s to 150°C/s.

[0030] Thereafter, the cooled hot-rolled steel sheet is coiled at a temperature of 650°C to 750°C. If the coiling temperature is lower than 650°C, atoms may not easily move during the coiling process. As a result, a rich layer may not be easily formed, and thus an oxide layer may not be formed in a corrosive environment. That is, corrosion resistance may not be sufficiently guaranteed. If the coiling temperature is higher than 750°C, heat recuperation occurs to an excessively high temperature, and thus, defects such as dents may be formed on the coiled hot-rolled steel sheet. Therefore, the coiling temperature may preferably be set to be within the range of 650°C to 750°C.

[0031] In addition, during the coiling process, it may be preferable that the surface of the hot-rolled steel sheet have a temperature of 720°C to 750°C owing to a heat recuperation phenomenon. Although the interior temperature of the hot-rolled steel sheet is adjusted to be within the range of 650°C to 750°C through the cooling process, the surface temperature of the hot-rolled steel sheet is lower than the range because of rapid cooling. Therefore, the hot-rolled steel sheet may be allowed to undergo heat recuperation so as to activate the movement of alloying elements effective in forming an oxide layer and thus to form a rich layer having a sufficient thickness. To sufficiently obtain these effects, the surface temperature of the hot-rolled steel sheet may preferably be 720°C or higher after heat recuperation. However, the surface temperature of the hot-rolled steel sheet will not exceed 750°C even if the heat recuperation is sufficient.

[0032] The coiled hot-rolled steel sheet is slowly cooled to a cooling finish temperature of 350°C to 400°C at a rate of 30°C/hr to 40°C/hr. If the slow cooling rate is excessively high, copper (Cu) forming a rich layer may not sufficiently move, and thus it may be difficult to form a rich layer having a sufficient thickness. Therefore, it may be preferable that the slow cooling rate be within the range of 40°C/hr or less. However, if the slow cooling rate is less than 30°C/hr, the size of grains may increase excessively, and thus, the strength of the hot-rolled steel sheet may decrease. Thus, the slow cooling rate may preferably be within the range of 30°C/hr to 40°C/hr. In addition, if the cooling finish temperature is lower than 350°C, properties of the hot-rolled steel sheet such as ductility may deteriorate, and productivity may decrease. Conversely, if the cooling finish temperature is higher than 400°C, a rich layer having a sufficient thickness may not be formed, and thus the hot-rolled steel sheet may have poor corrosion resistance. Therefore, the cooling finish temperature may preferably be within the range of 350°C to 400°C.

[Mode for Invention]

[0033] Hereinafter, the present disclosure will be described more specifically through examples. However, the following examples should be considered in a descriptive sense only, and are 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)

[0034] Steel ingots, manufactured through a melting process and having compositions as illustrated in Table 1 below, were maintained in a heating furnace for one hour at 1200°C and were subjected to a hot rolling process. In this case, finish hot rolling was performed at 900°C, and hot-rolled steel sheets having a thickness of 4.5 mm were ultimately manufactured. Thereafter, the hot-rolled steel sheets were cooled, coiled, and maintained under the conditions shown in Table 2 below. Thereafter, the hot-rolled steel sheets were slowly cooled to 380°C at a rate of 35°C/h, thereby completing the manufacturing of the hot-rolled steel sheets.

[0035] To observe corrosion characteristics of the hot-rolled steel sheets, specimens of the hot-rolled steel sheets were placed in a solution having a temperature of 60°C and containing 16.9 volume% sulfuric acid and 0.35 volume% hydrochloric acid for 6 hours, and subsequently, the corrosion loss of each specimen was measured as shown in Table 2 below.

[0036] In addition, after the immersion in the sulfuric acid-hydrochloric acid composite corrosive environment, the thickness of an oxide layer (corrosion-resistant layer) of each hot-rolled steel sheet was measured as shown in Table 2.

[Table 1]

Steels	Composition (wt%)						
	C	Mn	P	S	Al	Cu	Sb
Inventive Steel 1	0.075	0.69	0.012	0.009	0.033	0.32	0.08
Inventive Steel 2	0.068	0.67	0.011	0.009	0.029	0.39	0.06
Inventive Steel 3	0.074	0.75	0.009	0.01	0.029	0.44	0.05
Comparative Steel 1	0.069	0.74	0.012	0.011	0.035	0.28	-

[Table 2]

Steels	Cooling Rate (°C/s)	Coiling Temperature (°C)	Corrosion Loss (mg/cm^2/hr)	Thickness of Oxide Layer (nm)	Examples
Inventive Steel 1	130	700	1.8	420	Inventive Example 1
	130	500	4.5	57	Comparative Example 1
	10	700	3.8	63	Comparative Example 2
Inventive Steel 2	130	700	1.6	440	Inventive Example 2
	10	700	3.6	69	Comparative Example 3
Inventive Steel 3	130	700	1.4	460	Inventive Example 3
	10	700	3.2	75	Comparative Example 4
Comparative Steel 1	130	700	8.8	220	Comparative Example 5

[0037] As shown in Tables 1 and 2, Inventive Examples 1 to 3 satisfying the alloying composition and manufacturing conditions proposed in the present disclosure had a corrosion loss of 2.0 mg/cm^2/hr or less in the sulfuric acid-hydrochloric acid corrosive environment owing to the formation of oxide layers having a thickness of 400 nm or greater. That is, Inventive Examples 1 to 3 had high corrosion resistance.

[0038] Although Comparative Example 1 satisfied the alloying composition of the present disclosure, the coiling temperature of Comparative Example 1 was low, 500°C. Thus, an oxide layer was not sufficiently formed, resulting in corrosion loss of 4.5 mg/cm^2/hr. That is, Comparative Example 1 had poor corrosion resistance.

[0039] Although Comparative Examples 2 to 4 satisfied the alloying composition of the present disclosure, the cooling rate of Comparative Example 2 to 4 was low, 10°C/s. Thus, oxide layers were not sufficiently formed, resulting in a corrosion loss of 3.2 mg/cm^2/hr or greater. That is, Comparative Examples 2 to 4 had poor corrosion resistance.

[0040] Although Comparative Example 5 satisfied the manufacturing conditions of the present disclosure, antimony (Sb) was not added to Comparative Example 5, resulting in a corrosion loss of 8.8 mg/cm^2/hr in the sulfuric acid-hydrochloric acid corrosive environment. That is, Comparative Example 5 had poor corrosion resistance. The reason for this is that a Cu-Sb composite oxide having high corrosion resistance was not formed in an oxide layer.

[0041] While exemplary embodiments have been shown and described above, it will be apparent to those skilled in the art that modifications and variations could be made without departing from the scope of the present invention as defined by the appended claims.

Claims

1. A hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid, the hot-rolled steel sheet comprising, by wt%, carbon (C) : 0.05% to 0.1%, manganese (Mn): 0.5% to 1.5%, phosphorus (P): 0.02% or less, sulfur (S) : 0.02% or less, aluminum (Al): 0.01% to 0.1%, copper (Cu): 0.2% to 0.6%, antimony (Sb): 0.05% to 0.1%, and a balance of iron (Fe) and inevitable impurities, wherein copper (Cu) and antimony (Sb) are concentrated in a region from a surface to a 500-nm position in a thickness direction of the hot-rolled steel sheet, and the hot-rolled steel sheet has a corrosion loss of 2.0 mg/cm^2/hr or less in a solution of 16.9 volume% sulfuric acid and 0.35 volume% hydrochloric acid.

2. The hot-rolled steel sheet of claim 1, wherein the inevitable impurities comprise tungsten (W), molybdenum (Mo), cobalt (Co), and nickel (Ni) in a total amount of less than 10 ppm.

3. The hot-rolled steel sheet of claim 1, wherein the concentrated copper (Cu) and antimony (Sb) form an oxide layer comprising a Cu-Sb composite oxide in a corrosive environment containing sulfuric acid and hydrochloric acid.

4. The hot-rolled steel sheet of claim 3, wherein the oxide layer has a thickness of 400 nm to 500 nm from the surface of the hot-rolled steel sheet in the thickness direction of the hot-rolled steel sheet.

5. A method for manufacturing a hot-rolled steel sheet having high composite corrosion resistance to sulfuric acid and hydrochloric acid, the method comprising:

   reheating a steel slab to 1100°C to 1300°C, the steel slab comprising, by wt%, carbon (C): 0.05% to 0.1%, manganese (Mn): 0.5% to 1.5%, phosphorus (P): 0.02% or less, sulfur (S) : 0.02% or less, aluminum (Al): 0.01% to 0.1%, copper (Cu): 0.2% to 0.6%, antimony (Sb): 0.05% to 0.1%, and a balance of iron (Fe) and inevitable impurities;
   obtaining a hot-rolled steel sheet by hot rolling the reheated steel slab and finish hot rolling the steel slab at a temperature of 850°C to 950°C;
   rapidly cooling the hot-rolled steel sheet at a rate of 120°C/s to 150°C/s;
   coiling the cooled hot-rolled steel sheet at a temperature of 650°C to 750°C; and
   slowly cooling the coiled hot-rolled steel sheet at a rate of 30°C/hr to 40°C/hr to a cooling finish temperature of 350°C to 400°C.

6. The method of claim 5, wherein during the coiling of the cooled hot-rolled steel sheet, a surface of the hot-rolled steel sheet reaches a temperature of 720°C to 750°C through a heat recuperation phenomenon.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2015/005381

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i, C22C 38/16(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 38/00; C21D 8/02; C22C 38/60; C22C 38/16; B21B 3/00

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: hot rolled steel sheets, composite corrosion resistance, antimony, oxide layer, corrosion mass loss, winding temperature, cooling velocity

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2015-0029468 A (POSCO) 18 March 2015 See abstract, paragraphs [0013]-[0032] and claims 1, 2, 5-7.	1-4
A		5,6
A	KR 10-2013-0143374 A (POSCO) 31 December 2013 See abstract, paragraphs [0018]-[0034] and claims 1-6.	1-6
A	JP 2012-177190 A (JFE STEEL CORP.) 13 September 2012 See abstract, paragraphs [0023]-[0033] and claims 1, 2.	1-6
A	JP 2007-262558 A (JFE STEEL K.K.) 11 October 2007 See abstract, paragraphs [0015]-[0021] and claims 1-5.	1-6
A	JP 09-025536 A (SUMITOMO METAL IND., LTD.) 28 January 1997 See abstract, paragraphs [0017]-[0028] and claim 1.	1-6

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

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

Date of the actual completion of the international search 28 OCTOBER 2015 (28.10.2015)	Date of mailing of the international search report **28 OCTOBER 2015 (28.10.2015)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2015/005381

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-2015-0029468 A	18/03/2015	KR 10-1518578 B1 WO 2015-037783 A1	07/05/2015 19/03/2015
KR 10-2013-0143374 A	31/12/2013	KR 10-1417294 B1	08/07/2014
JP 2012-177190 A	13/09/2012	CN 104105806 A EP 2808411 A1 KR 10-2014-0105862 A WO 2013-111355 A1	15/10/2014 03/12/2014 02/09/2014 01/08/2013
JP 2007-262558 A	11/10/2007	JP 4997808 B2	08/08/2012
JP 09-025536 A	28/01/1997	NONE	

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 9025536 A **[0004]**
- JP 10110237 A **[0004]**
- KR 20090070249 **[0004]**