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

(11) EP 3 561 126 A1

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

(43) Date of publication:
30.10.2019 Bulletin 2019/44

(21) Application number: **17885245.5**

(22) Date of filing: **21.12.2017**

(51) Int Cl.:
C22C 38/42 $^{(2006.01)}$
C22C 38/44 $^{(2006.01)}$
C22C 38/00 $^{(2006.01)}$
C22C 38/04 $^{(2006.01)}$
C22C 38/58 $^{(2006.01)}$
C21D 8/02 $^{(2006.01)}$
C21D 9/46 $^{(2006.01)}$

(86) International application number:
PCT/KR2017/015294

(87) International publication number:
WO 2018/117715 (28.06.2018 Gazette 2018/26)

(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 MD TN

(30) Priority: **22.12.2016 KR 20160177202**

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

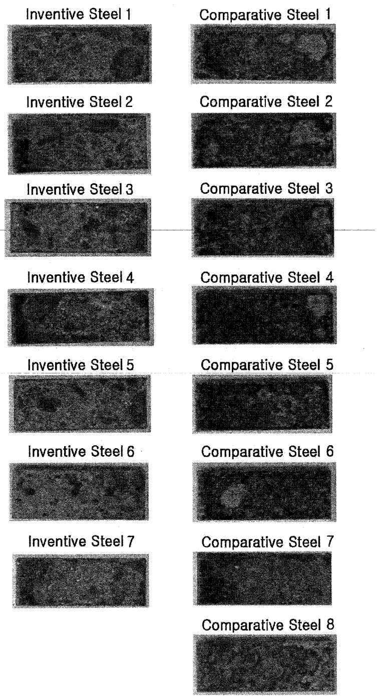
(72) Inventors:
- **PARK, Jin-Ho**
  Pohang-si
  Gyeongsangbuk-do 37877 (KR)
- **UM, Kyung-Keun**
  Pohang-si
  Gyeongsangbuk-do 37877 (KR)

(74) Representative: **Potter Clarkson**
The Belgrave Centre
Talbot Street
Nottingham NG1 5GG (GB)

(54) STEEL MATERIAL HAVING EXCELLENT CORROSION RESISTANCE IN DEW CONDENSATION ENVIRONMENT CONTAINING SULFIDE AND METHOD FOR PRODUCING SAME

(57) The present invention relates to a steel material having excellent corrosion resistance for use in an oil tanker, a crude oil tank, and the like and, particularly to a steel material having excellent corrosion resistance in a dew condensation environment containing a sulfide gas and a method for producing the same.

[FIG. 2]



EP 3 561 126 A1

Description

[Technical Field]

[0001] The present disclosure relates to a steel material, having excellent corrosion resistance for use in an oil tanker, a crude oil tank, and the like, and particularly, to a steel material having excellent corrosion resistance in a dew condensation environment containing a sulfide gas and a method for producing the steel material.

[Background Art]

[0002] Among various steels for use in ships, a steel material for use in a crude oil tank for an oil tanker may suffer from significantly serious corrosion damage due to an internal environment of the crude oil tank. In the crude oil tank, various types of corrosion occur due to volatile components in crude, or inert gas, sent into the tank to achieve explosion proofing of, mixed seawater, salt in oilfield brine, or dew condensation, caused by an internal temperature difference, and the like. Additionally, a corrosion rate is significantly higher than a corrosion rate in a typical brine environment.

[0003] In a top plate of a crude tank, hydrogen sulfide gas, evaporated from crude, and gas such as CO_2, SO_2, O_2, or the like in inert gas, introduced to achieve explosion proof, may react with dew condensation, formed on a surface of a steel material by a temperature difference, to contain a large amount of hydrogen sulfide and sulfur dioxide components. Accordingly, corrosion occurs. Corrosion caused by the dew condensation, i.e. condensed water, is similar to atmospheric corrosion of atmospheric corrosion resistant steel because of the corrosion at the thin water film, and moisture is periodically and repeatedly condensed and dried due to a daily temperature range. For this reason, the corrosion, caused by condensed water, may be separately classified as dew point corrosion.

[0004] During the daytime, dew condensation does not occur on the deckhead of a crude oil transport ship, running while loaded with crude oil, because an internal temperature of the deckhead rises to about 50°C. During the nighttime, evaporated moisture forms on a lower portion of the deckhead because the internal temperature of the deckhead drops to about 25 degrees Celsius. In the case of a 300,000 ton crude oil transport ship, up to 30 tons of water may condense on an upper portion of a deckhead to cause corrosion. Therefore, corrosion, caused by the condensed water, is not negligible.

[0005] In addition, carbon dioxide and sulfur dioxide, combustible gases, are injected into an empty space in a tank of a crude oil transport ship to prevent the explosion of a hull. Such gases are dissolved in moisture, together with sulfur and hydrogen sulfide, already contained in crude oil, to form an atmosphere proximate to corrosion caused by acidic condensed water when dew condensation occurs. Generally, as acidity is increased, an amount of H^+ ions, participating in a corrosion reaction, is increased. Therefore, a corrosion rate may be further increased.

[0006] Patent Documents 1 and 2 have been proposed to improve corrosion resistance of a steel material for a ship. However, since a steel material for a ship of Patent Document 1 was designed without consideration of corrosion caused by hydrogen sulfide when crude coil contains the hydrogen sulfide, the steel material for ship is insufficient to be used in an actual crude oil tank.

[0007] (Patent Documents 1) Japanese Patent Publication Laid-Open 2000-017381

[Disclosure]

[Technical Problem]

[0008] An aspect of the present disclosure is to provide a steel material which may optimize steel components and may identify a relationship between components to secure improved corrosion resistance, even in a dew condensation environment, including sulfides and a method for producing the steel material.

[Technical Solution]

[0009] According to an aspect of the present disclosure, there is provided a steel material, having excellent corrosion resistance in a dew condensation environment containing a sulfide gas, comprising, by weight percent (wt%), 0.02 to 0.2% of carbon (C), 0.1 to 1.0% of silicon (Si), 0.2 to 2.0% of manganese (Mn), 0.03% or less of phosphorus (P), 0.03% or less of sulfur (S), 0.05 to 0.5% of copper (Cu), 0.05 to 0.5% of nickel (Ni), 0.02 to 0.5% of molybdenum (Mo), 0.1% or less of aluminum (Al), 0.05 to 0.5% of chromium (Cr), 0.001 to 0.01% of calcium (Ca), and the balance of iron (Fe) and inevitable impurities.

[0010] A sensitivity index of sulfide dew point corrosion, given by Relational Expression 1, is 1.7 or more to 2.5 or less

(Relational Expression 1)

$$\text{Sensitivity Index of Sulfide Dew point corrosion} = 0.4Ca/S + 5Cr + 6Mo + 2Cu + Ni - 0.5Mn$$

(where Ca, S, Cr, Mo, Cu, Ni, and Mn denote contents (wt%) of corresponding elements).

[0011] According to another aspect of the present disclosure, there is provided a method for producing a steel material, having excellent corrosion resistance in a dew condensation environment containing a sulfide gas, by hot-rolling and cooling a slab comrpising, by weight percent (wt%), 0.02 to 0.2% of carbon (C), 0.1 to 1.0% of silicon (Si), 0.2 to 2.0% of manganese (Mn), 0.03% or less of phosphorus (P), 0.03% or less of sulfur (S), 0.05 to 0.5% of copper (Cu), 0.05 to 0.5% of nickel (Ni), 0.02 to 0.5% of molybdenum (Mo), 0.1% or less of aluminum (Al), 0.05 to 0.5% of chromium (Cr), 0.001 to 0.01% of calcium (Ca), and the balance of iron (Fe) and inevitable impurities,

[0012] A sensitivity index of sulfide dew point corrosion, given by Relational Expression 1, is 1.7 or more to 2.5 or less

(Relational Expression 1)

$$\text{Sensitivity Index of Sulfide Dew point corrosion} = 0.4Ca/S + 5Cr + 6Mo + 2Cu + Ni - 0.5Mn$$

(where Ca, S, Cr, Mo, Cu, Ni, and Mn denote contents (wt%) of corresponding elements).
wherein the cooling is performed at a cooling rate of 10°C/s or higher between a cooling start temperature, higher than or equal to Ar3 temperature, and cooling stop temperature of (Ae1-30°C) to 600°C.

[Advantageous Effects]

[0013] As set forth above, according to an example embodiment in the present disclosure, steel components may be optimized to satisfy a sensitivity index of sulfide dew point corrosion. Thus, resistance against the sulfide dew point corrosion may be improved.

[Description of Drawings]

[0014]

FIG. 1 illustrates a test apparatus for simulating a sulfide dew condensation test in the present disclosure.
FIG. 2 is an image illustrating a result of a sulfide dew point corrosion test performed for 100 days according to an example embodiment in the present disclosure.

[Best Mode for Invention]

[0015] Hereinafter, the present disclosure will be described in detail.

[0016] The present inventors have conducted researches to address the above-described issues of the related art. The inventors found that in order to improve resistance against corrosion in a dew condensation environment containing sulfide gas, a composition of each component needs to be appropriately controlled, as set forth below. In addition, the inventors found that that relationships between components such as Ca, S, Cr, Mo, Ni, Mn, and the like, affecting sensitivity of dew point corrosion, needs to be appropriately controlled. For these reasons, the inventors conceived the present invention.

[0017] First, an alloy composition range of a steel material according to the present disclosure will be described in detail. The steel material comprises, by weight percent (wt%), 0.02 to 0.2% of carbon (C), 0.1 to 1.0% of silicon (Si), 0.2 to 2.0% of manganese (Mn), 0.03% or less of phosphorus (P), 0.03% or less of sulfur (S), 0.05 to 0.5% of copper (Cu), 0.05 to 0.5% of nickel (Ni), 0.02 to 0.5% of molybdenum (Mo), 0.1% or less of aluminum (Al), 0.05 to 0.5% of chromium (Cr), 0.001 to 0.01% of calcium (Ca), and a balance of iron (Fe) and inevitable impurities.

Carbon (C): 0.02 to 0.2 wt%

[0018] Carbon (C) is an element added to improve strength. When a content of carbon (C) is increased, hardenability may be increased to improve strength. However, as the amount of added carbon is increased, general corrosion resistance is reduced. And since precipitation of carbide or the like is promoted, localized corrosion resistance is also affected. The content of carbon (C) should be decreased to improve the general corrosion resistance and the localized corrosion resistance. However, when the content of carbon (C) is less than 0.02 wt%, it is difficult to secure strength. When carbon (C) is more than 0.2 wt%, weldability is deteriorated to be inappropriate for, in detail, steel for welded structure. Therefore, carbon (C) has a range, in detail, from 0.02 to 0.2 wt%. Under a viewpoint of corrosion resistance, the content of carbon (C) may be set to, in detail, be 0.16 wt% or less and may be set to, in further detail, 0.14 wt% or less to improve casting cracking and to reduce a carbon equivalent.

Silicon (Si): 0.1 to 1.0 wt%

[0019] Silicon (Si) needs to be present in amount of 0.1 wt% or more to serve as a deoxidizer and to serve to increase strength of steel. In addition, since silicon (Si) contributes to improvement in general corrosion resistance, it is advantageous to increase the content of silicon (Si). However, when the content of silicon (Si) is greater than 1.0 wt%, toughness and weldability are deteriorated. And since it is difficult to detach a scale during rolling, the scale causes a surface defect. Therefore, the content of silicon (Si) is limited to, in detail, 0.1 to 1.0 wt%. In further detail, silicon (Si) is added in an amount of 0.2 wt% or more to improve corrosion resistance.

Manganese (Mn): 0.2 to 2.0 wt%

[0020] Manganese (Mn) is an element effect in increasing the strength without reducing toughness. However, when an excessive amount of manganese (MN) is added, an electrochemical reaction rate of a steel surface may be increased during a corrosion reaction to reduce corrosion resistance. When manganese (Mn) is added in an amount of less than 0.2 wt%, it is difficult to secure durability of a structural steel. When the content of manganese (Mn) is increased, hardenability is increased to improve strength. However, when manganese (Mn) is added in an amount greater than 2.0 wt%, weldability and corrosion resistance are reduced. Therefore, the content of manganese (Mn) is set to be, in detail, 0.2 to 2.0 wt%.

Phosphorus (P): 0.03 wt% or less

[0021] Phosphorus (P) is an impurity element. When the phosphorous (P) is added in an amount greater than 0.03 wt%, weldability is significantly reduced and toughness is deteriorated. Therefore, the content of phosphorous (P) is limited to, in detail, 0.03 wt% or less.

Sulfur (S): 0.03 wt% or less

[0022] Sulfur (S) is also an impurity element. When the content of sulfur (S) is greater than 0.03 wt%, ductility, impact toughness, and weldability of steel are deteriorated. Accordingly, the content of sulfur (S) is limited to, in detail, 0.03 wt% or less. Sulfur (S) is apt to react with manganese (Mn) to form an elongated inclusion like manganese sulfide (MnS), and voids, formed on both ends of the elongated inclusion, may be a starting point of localized corrosion. Therefore, the content of sulfur (S) is limited to, in further detail, 0.01 wt% or less.

Copper (Cu): 0.05 to 0.5 wt%

[0023] When copper (Cu) is contained in an amount of 0.05 wt% or more together with nickel (Ni), exudation of iron (Fe) is delayed, which is effective in improving general corrosion resistance and localized corrosion resistance. However, when the amount of copper (Cu) is greater than 0.5 wt%, copper (Cu) in a liquid state melts into a grain boundary during production of a slab. Thus, cracking occurs during hot working, which is called "hot shortness" phenomenon. Therefore, the content of copper (Cu) is set to, in detail, be 0.05 to 0.5 wt%. Since surface cracking, occurring during production of the slab, interact with the contents of carbon (C), nickel (Ni), and manganese (Mn), a frequency of occurrence of the surface cracking may vary, depending on the content of each element, but the content of copper (Cu) is set to, in further detail, be 0.5 wt% or less.

Nickel (Ni): 0.05 to 0.5 wt%

[0024] Similarly to the case of copper (Cu), when nickel (Ni) is contained in an amount of 0.05 wt% or more, it is effective in improving general corrosion resistance and localized corrosion resistance. In addition, when nickel (Ni) is added together with copper (Cu), nickel (Ni) reacts with copper (Cu) in such a manner that formation of a copper (Cu) phase is suppressed to prevent hot shortness from occurring. Nickel (Ni) is also an element effective in improving toughness of a base material. However, since nickel (Ni) is an expensive element, the addition of nickel (Ni) in an amount of 0.5 wt% or more is disadvantageous in terms of economical efficiency and weldability. Therefore, the content of nickel (Ni) is set to, in detail, be 0.05 to 0.5 wt%.

[0025] Since an influence of nickel (Ni) on improvement of corrosion resistance is not higher than an influence of copper (Cu), the content of nickel (Ni) is greater than or equal to the content of copper (Cu), in detail, 1.5 times or less the content of copper (Cu) to suppress surface cracking caused by addition of copper (Cu), rather than containing a great amount of nickel (Ni) to improve corrosion resistance. The content of nickel (Ni) is limited to, in further detail, 0.3 wt% or less.

Molybdenum (Mo): 0.02 to 0.5 wt%

[0026] Molybdenum (Mo) is an element contributing to improvement of corrosion resistance and strength and should be added in an amount of 0.02 wt% or more to achieve such an effect. However, molybdenum (Mo) should be dissolved in steel to improve corrosion resistance. For example, the dissolved molybdenum (Mo) improves the corrosion resistance to the condensed water containing hydrogen sulfide. However, molybdenum (Mo), contained in an amount greater than a dissolution limit, may reacts with sulfur (S) in such a manner Mo_2S is formed to reduce corrosion resistance. Therefore, when an excessive amount of molybdenum (Mo) is added, corrosion resistance against condensed water, containing hydrogen sulfide, may be reduced. Hence, an upper limit thereof is, in detail, 0.5 wt%. In addition, a precipitate of molybdenum (Mo) serves to improve strength, but coarsely precipitated molybdenum (Mo) may cause localized corrosion of the steel. Therefore, molybdenum (Mo) is added in an amount of, in further detail, 0.1 wt% or less.

Aluminum (Al): 0.1 wt% or less

[0027] Aluminum (Al) is an element, added for deoxidation, and reacts with nitrogen (N) in the steel in such a manner that an aluminum nitride (AlN) is formed and austenite grains are refined to improve toughness. However, when aluminum (Al) is contained in an amount greater than 0.1 wt%, an inclusion is formed in a coarse oxide during a steelmaking process and a stretched inclusion, crushed and elongated during rolling, is formed according to aluminum oxide-based characteristics. Since the formation of such an elongated inclusion promotes the formation of a void around the inclusion and such a void serves as a starting point for localized corrosion, the elongated inclusion serves to reduce the localized corrosion resistance. Therefore, the content of aluminum (Al) is set to, in detail, be 0.1 wt% or less. Since deoxidation effect may be obtained by another deoxidizing element such as silicon (Si) or the like even when aluminum (Al) is added, a lower limit of aluminum (Al) is not limited. However, in detail, at least 0.001 wt% or more of aluminum (Al) may be added to expect a deoxidation effect achieved by aluminum (Al).

Chromium (Cr): 0.05 to 0.5 wt%

[0028] Chromium (Cr) is an element which increases the corrosion resistance by forming a chrome-containing oxide layer on a surface of the steel in a corrosive environment. Chromium (Cr) should be contained in an amount of 0.05 wt% or more to exhibit a corrosion resistance effect depending on addition of chromium (Cr). However, when chromium (Cr) is contained in an amount greater than 0.5 wt%, toughness and weldability are adversely affected. Therefore, the content of chromium (Cr) is set to, in detail, be 0.05 to 0.5 wt%.

Calcium (Ca): 0.001 to 0.01 wt%

[0029] Calcium (Ca) reacts with aluminum (Al), silicon (Si), and oxygen (O) in a molten steel to form a composite oxide and then reacts with sulfur (S) to form calcium sulfide (CaS). Such a calcium sulfide (CaS) inclusion is dissolved in water in a dew condensation environment to increase pH of the surface of the steel. Thus, formation of a stable phase is promoted under suppress of an electrochemical reaction of the steel to improve corrosion resistance characteristics. To improve the corrosion resistance, calcium (Ca) should be added in an amount of at least 0.001 wt%. However, when the content of calcium (Ca) is greater than 0.01 wt%, refractories may be melted during a steelmaking process. Therefore, the content of Ca is set to, in detail, be 0.001 to 0.01 wt%. Additionally, calcium (Ca) is added in an amount of, in further detail, 0.002 wt% or more to secure a sulfide dew point corrosion sensitivity index.

[0030] In addition to the above components, the balance includes iron (Fe) and inevitable impurities. However, the addition of other alloying elements is not excluded, without departing from the scope of the present disclosure.

[0031] In the steel material of the present disclosure, the sulfide condensation corrosion sensitivity index, defined as Relational Expression 1, satisfies, in detail, 1.7 to 2.3.

Relational Expression 1

$$\text{Sensitivity Index of Sulfide Dew point corrosion} = 0.4Ca/S + 5Cr + 6Mo + 2Cu + Ni - 0.5Mn$$

(where Ca, S, Cr, Mo, Cu, Ni, and Mn denote contents (wt%) of corresponding elements).

[0032] The above Ca, Cr, Mo, Cu, Ni, and Mn are components affecting a corrosion resistance effect in a sulfide dew condensation environment depending on amounts of addition thereof. An influence of each of these components on the corrosion resistance was quantitatively derived, and a relationship between the components was expressed by Relational Expression 1. When the sensitivity index of sulfide dew point corrosion, defined as Relational Expression 1, is 1.7 to 2.5, improved corrosion resistance may be secured in a corresponding environment.

[0033] The steel of the present disclosure, having the advantageous composition, may be easily produced using knowledge in the art by a person of ordinary skill in the art without excessively repeated tests. A producing method, more advantageous than the method found by the present inventors, for example, a method for producing the steel material is proposed in the present disclosure.

[0034] The method for producing a steel material according to the present disclosure is a method for producing a steel material through conventional hot rolling and cooling, and is characterized in that the cooling is performed at a cooling rate of 10°C/sec or less in such a manner that cooling starting temperature is Ar3 temperature or higher and cooling stop temperature ranges from (Ae1-30°C) to 600°C. Hereinafter, cooling conditions of the present disclosure will be described.

Cooling Section: cooled from Ar3 temperature or higher to(Ae1-30°C)~600°C

[0035] According to a result of tests performed by the present inventors, when molybdenum (Mo), added to achieve the advantageous effect, forms a great amount of precipitate, the added molybdenum (Mo) has an adverse influence on general corrosion, localized corrosion, or the like. Meanwhile, when an excessive amount of molybdenum (Mo) is dissolved, molybdenum (Mo) has an adverse influence on corrosion resistance in an environment containing hydrogen sulfide. Therefore, it is necessary to appropriately control a ratio of molybdenum (Mo), forming the precipitate, and the dissolved molybdenum (Mo). Since molybdenum (Mo) tends to form precipitates at temperature between 700 and 550°C, a portion of the section needs to be rapidly cooled to prevent that molybdenum (Mo) forms a precipitate and the other portions of the section needs to be slowly cooled to prevent that molybdenum (Mo) is excessively dissolved.

[0036] When cooling is started at temperature lower than or Ar3 temperature, copper (Cu) is segregated to pearlite to accelerate corrosion caused by a galvanic pair of the pearlite and ferrite. Accordingly, the cooling needs to be started at temperature, higher than or equal to the Ar3 temperature, and needs to be performed to a temperature of (Ael-30°C) or lower at which precipitates such as molybdenum (Mo) are appropriately formed without forming pearlite. When the cooling is performed to significantly low temperature, molybdenum (Mo) is not appropriately precipitated and is excessively dissolved. Therefore, molybdenum (Mo) may bond to sulfur (S) at a condensed water atmosphere, containing hydrogen sulfide, to form Mo_2S and may deteriorate corrosion resistance of the steel material. As a result, the cooling needs to be finished at temperature of 600°C or higher.

Cooling Rate: 10°C/s or higher

[0037] Since time, taken to pass through a temperature range in which a precipitate of molybdenum (Mo) is easily formed, is increased when the cooling rate is low, the precipitate may be excessively formed. Therefore, the cooling rate needs to be 10°C/s or higher. Even if the cooling rate is high, there is no problem in achieving objects of the present disclosure. Accordingly, it is unnecessary to determine an upper limit of the cooling rate. However, since there may be a limitation in capability of cooling equipment, the upper limit may be determined to be 50°C/s in consideration of the limitation in capability to apply a significantly high cooling rate.

[Mode for Invention]

[0038] Hereinafter, an example embodiment in the present disclosure will be described in detail. However, the present disclosure is not limited to the example embodiment described herein.

(Embodiment)

[0039] A steel slab was produced using continuous casting after preparing molten steel having a composition (weight percent (wt%), the balance including iron (Fe) and inevitable impurities) listed in Table 1. The produced steel slab was hot-rolled under normal conditions and then cooled under conditions in Table 2.

Table 1

Steel No.	C	Si	Mn	P	S	Ni	Mo	Al	Cu	Cr	Ca
IS 1	0.06	0.45	0.9	0.015	0.003	0.35	0.05	0.025	0.25	0.2	0.004
IS 2	0.08	0.61	1.1	0.02	0.002	0.26	0.03	0.03	0.22	0.15	0.004
IS 3	0.09	0.81	1.2	0.02	0.004	0.4	0.12	0.029	0.1	0.09	0.008
IS 4	0.04	0.75	0.9	0.019	0.003	0.31	0.04	0.034	0.14	0.12	0.007
IS 5	0.12	0.51	0.8	0.012	0.003	0.4	0.05	0.031	0.3	0.11	0.006
IS 6	0.16	0.31	1.4	0.022	0.006	0.29	0.03	0.027	0.19	0.3	0.002
IS 7	0.15	0.5	0.7	0.011	0.005	0.24	0.06	0.021	0.21	0.25	0.003
CS 1	0.07	0.45	0.9	0.012	0.004	0.21	0	0.035	0.15	0.15	0.002
CS 2	0.11	0.52	1.2	0.018	0.004	0.22	0.02	0.031	0.16	’0.21	0.001
CS 3	0.09	0.49	0.8	0.017	0.004	0.16	0.04	0.029	0.12	0.2	0.003
CS 4	0.1	0.51	1.1	0.016	0.005	0.19	0.05	0.034	0.14	0.25	0.001
CS 5	0.06	0.68	1.5	0.015	0.003	0.45	0.02	0.036	0	0.2	0.004
CS 6	0.1	0.56	1.2	0.018	0.005	0.4	0.05	0.036	0.3	0	0.006
CS 7	0.1	0.6	1.3	0.018	0.008	0.15	0.2	0.029	0.1	0.35	0.001
CS 8	0.08	0.55	1.2	0.013	0.007	0.21	0.17	0.027	0.12	0.31	0.002
*IS: Inventive Steel *CS: Comparative Steel											

Table 2

Steel No.	Ar3 (°C)	Cooling Starting Temperature (°C)	Cooling Ending Temperature (°C)	Cooling Rate (°C/s)
IS 1	794	815	658	17.3
IS 2	780	812	634	19.7
IS 3	757	805	647	17.5
IS 4	807	829	622	21.8
IS 5	781	819	634	20.1
IS 6	728	778	651	14.6
IS 7	788	809	647	17.5
CS 1	806	820	644	19.2
CS 2	766	791	618	18.5
CS 3	807	834	634	20.9

(continued)

Steel No.	Ar3 (°C)	Cooling Starting Temperature (°C)	Cooling Ending Temperature (°C)	Cooling Rate (°C/s)
CS 4	776	807	627	19.8
CS 5	748	798	613	20.1
CS 6	757	789	618	18.5
CS 7	750	781	616	17.9
CS 8	763	777	620	17.1
*IS: Inventive Steel *CS: Comparative Steel				

[0040] As can be seen from the Table 1, inventive steels refer to steel sheets having compositions satisfying a composition range defined in the present disclosure. However, comparative steels 1, 5, and 6 illustrate a case in which essential additive elements, selected in the present disclosure, such as Mo, Cu, and Cr are not added. Comparative steels 2, 3, 4, 7, and 8 illustrate a case in which essential elements are added but the sensitivity index of sulfide dew point corrosion, expressed as Relational Expression 1, does not satisfy a required range because the sensitivity index is less than 1.7 or more than 2.5, as described later. Such components of the comparative steels are significantly reduced in corrosion resistance than those of the inventive steels. Accordingly, since corrosion of the steel material cannot be prevented in the sulfide dew point corrosion environment, the corrosion resistance may be reduced and a replacement cycle may be increased.

[0041] Table 3 below lists measurement results of sensitivity indices of sulfide dew point corrosion and corrosion rates of inventive steels and comparative steels. The corrosion rates, listed in Table 3, were results measured by the test apparatus illustrated in FIG. 1. For example, as illustrated in FIG. 1, in order to simulate the sulfide dew condensation environment, an airtight container was filled with distilled, water and a corrosive gas such as SO_2, H_2S, CO_2, O_2, or the like was continuously purged into the distilled water. Then a sample, having a size of 60mm × 20mm × 5mm, to measure a corrosion rate was polished with #600 sandpaper and located on top of the airtight container. A cover of the airtight container was provided with a gas inlet, an outlet, and a heating/cooling water circulation system. After being air-tightened, the airtight container was mounted in a thermostat and a temperature cycle of (50°C, 20 hours) → (25°C, 4 hours) was given for 100 days. A gas, introduced into the test apparatus, was a gas simulating the sulfide dew point corrosion environment of an upper deck of the crude oil tank, and has a composition below.

Gas Composition: by volume percent, 5% of O_2 - 15% of CO_2 - 0.011% of SO_2 - 0.055% of H_2S - balance N_2

[0042] After a corrosion test for 100 days, a derusting treatment was performed in a corrosion product removal solution. Mass loss of each sample was divided by a surface area of an initial sample. For relative comparison, the corrosion rate of the comparative steel 1 was set to 100, and relative corrosion rates are listed in Table 3.

Table 3

Steel No.	Sensitivity Index of Sulfide Dew point corrosion	Relative Corrosion Rate
IS 1	2.23	38
IS 2	1.88	49
IS 3	1.97	42
IS 4	1.91	45
IS 5	2.25	34
IS 6	1.78	57
IS 7	2.16	37
CS 1	1.01	100
CS 2	1.21	95
CS 3	1.54	90

(continued)

Steel No.	Sensitivity Index of Sulfide Dew point corrosion	Relative Corrosion Rate
CS 4	1.55	90
CS 5	1.35	88
CS 6	1.18	85
CS 7	2.70	69
CS 8	2.53	65
*IS: Inventive Steel *CS: Comparative Steel		

[0043] As can be seen from Table 2, when the corrosion resistance element such as Mo, Cu, Cr, or the like is not added at all or is insufficiently added and the sensitivity index of sulfide dew condensation does not satisfy a range of more than 1.7 to less than 2.3 proposed in the present disclosure, a relative corrosion rate is at most twice as high as that of the inventive steel. Such a phenomenon occurred in all comparative steels although the degree thereof was slightly different, which is determined to result from the fact that the sensitivity index of sulfide dew condensation, proposed in the present disclosure, was not satisfied.

[0044] FIG. 2 is an image of samples of the inventive steels 1 to 7 and the comparative steels 1 to 8 observed after a sulfide dew point corrosion test performed for 100 days. As described above, the inventive steels 1 to 7, in which the sensitivity index of sulfide dew corrosion satisfies the range of 1.7 or more to 2.5 or less proposed as Relational Expression 1 of the present disclosure, had a dense structure in which corrosion products had bright colors. In the case of the comparative steels 1 to 8, dark-colored corrosion products are visible to the naked eye.

[0045] As described above, as illustrated in Table 3 and FIG. 2, the sensitivity index of sulfide corrosion, proposed in the present disclosure, should be satisfied to prevent sulfide dew point corrosion. When the sensitivity index is not satisfied, sufficient corrosion resistance is not secured to stably use a steel material in a corresponding environment, and thus life of a corresponding structure may not be secured.

Claims

1. A steel material, having excellent corrosion resistance in a dew condensation environment containing a sulfide gas, comprising, by weight percent (wt%), 0.02 to 0.2% of carbon (C), 0.1 to 1.0% of silicon (Si), 0.2 to 2.0% of manganese (Mn), 0.03% or less of phosphorus (P), 0.03% or less of sulfur (S), 0.05 to 0.5% of copper (Cu), 0.05 to 0.5% of nickel (Ni), 0.02 to 0.5% of molybdenum (Mo), 0.1% or less of aluminum (Al), 0.05 to 0.5% of chromium (Cr), 0.001 to 0.01% of calcium (Ca), and the balance of iron (Fe) and inevitable impurities,
   wherein a sensitivity index of sulfide dew point corrosion, given by Relational Expression 1, is 1.7 or more to 2.5 or less

   (Relational Expression 1)

   $$\text{Sensitivity Index of Sulfide Dew point corrosion} = 0.4Ca/S + 5Cr + 6Mo + 2Cu + Ni - 0.5Mn$$

   where Ca, S, Cr, Mo, Cu, Ni, and Mn denote contents (wt%) of corresponding elements.

2. The steel material of claim 1, wherein a content of the Ni is greater than or equal to a content of the Cu, and is 1.5 times or less the content of the Cu.

3. The steel material of claim 1, wherein the Cu is 0.002 to 0.01%.

4. A method for producing a steel material, having excellent corrosion resistance in a dew condensation environment containing a sulfide gas, by hot-rolling and cooling a slab comprising, by weight percent (wt%), 0.02 to 0.2% of carbon (C), 0.1 to 1.0% of silicon (Si), 0.2 to 2.0% of manganese (Mn), 0.03% or less of phosphorus (P), 0.03% or less of sulfur (S), 0.05 to 0.5% of copper (Cu), 0.05 to 0.5% of nickel (Ni), 0.02 to 0.5% of molybdenum (Mo), 0.1%

or less of aluminum (Al), 0.05 to 0.5% of chromium (Cr), 0.001 to 0.01% of calcium (Ca), and the balance of iron (Fe) and inevitable impurities,
wherein a sensitivity index of sulfide dew point corrosion, given by Relational Expression 1, is 1.7 or more to 2.5 or less

(Relational Expression 1)

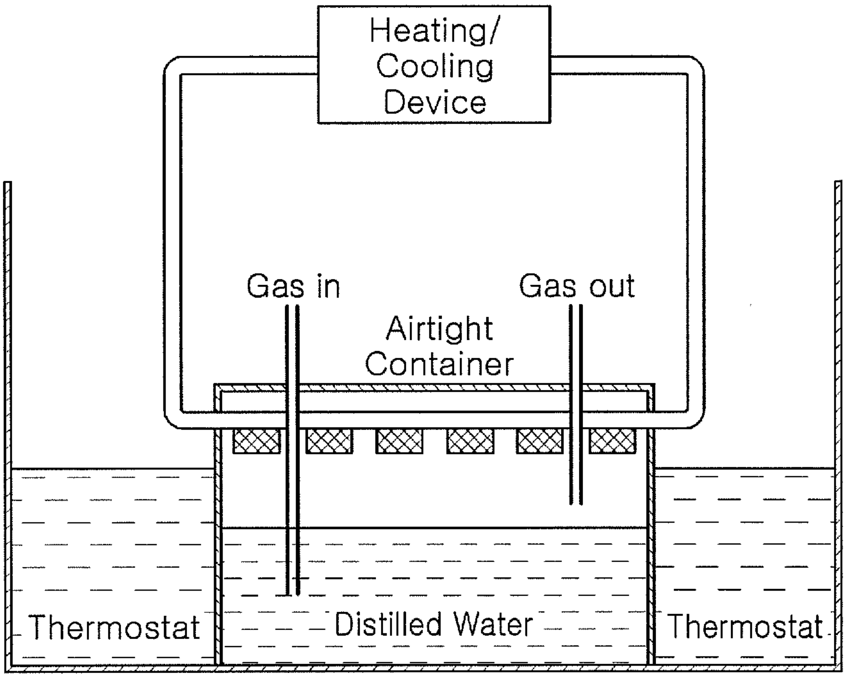
$$\text{Sensitivity Index of Sulfide Dew point corrosion} = 0.4\text{Ca}/\text{S} + 5\text{Cr} + 6\text{Mo} + 2\text{Cu} + \text{Ni} - 0.5\text{Mn}$$

where Ca, S, Cr, Mo, Cu, Ni, and Mn denote contents (wt%) of corresponding elements, and
wherein the cooling is performed at a cooling rate of 10°C/s or higher between cooling start temperature, higher than or equal to Ar3 temperature, and cooling stop temperature of (Ae1-30°C) to 600°C.

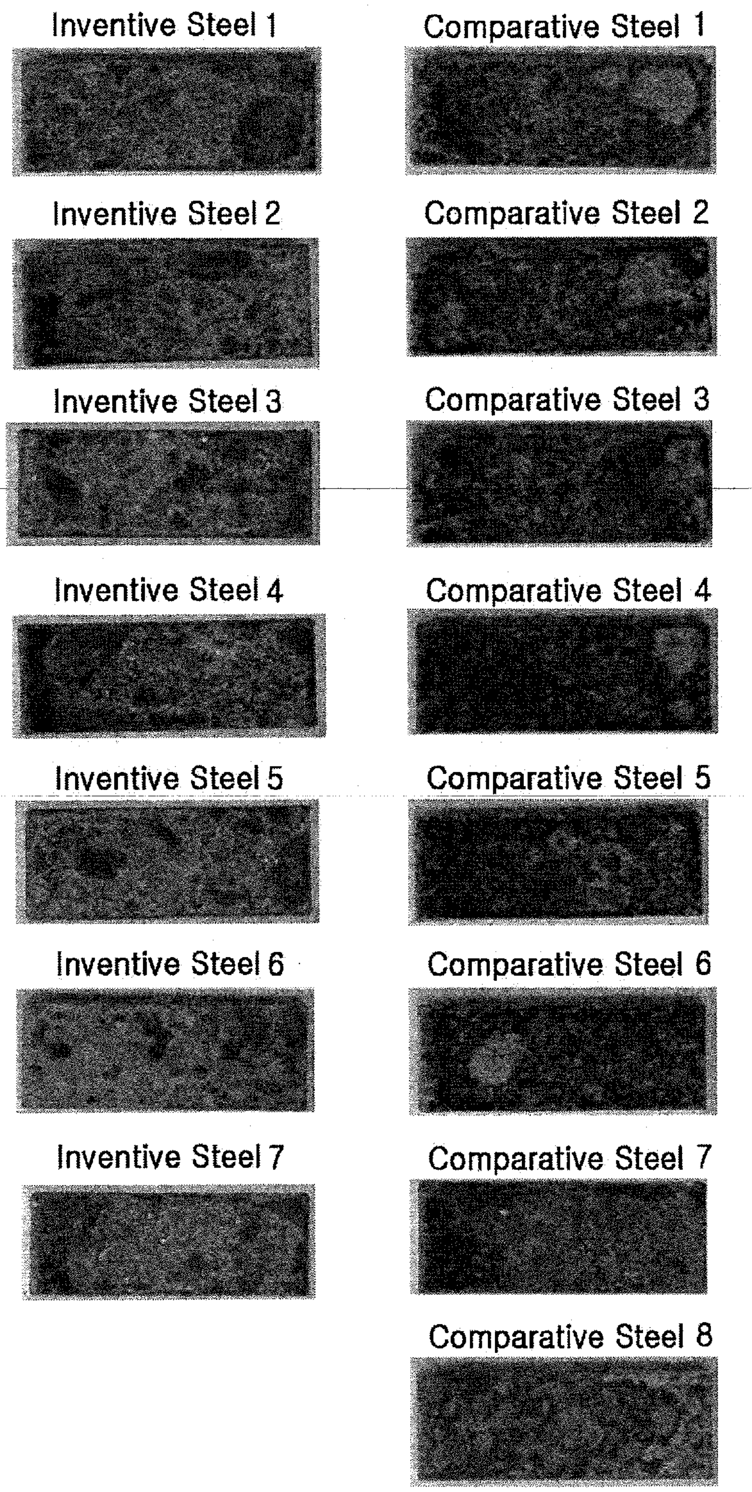
5. The method of claim 4, wherein a content of the Ni is greater than or equal to a content of the Cu, and is 1.5 times or less the content of the Cu.

6. The method of claim 4, wherein the Cu is 0.002 to 0.01%.

[FIG. 1]


Heating/
Cooling
Device
Gas in
Gas out
Airtight
Container
Thermostat
Distilled Water
Thermostat

[FIG. 2]



Inventive Steel 1

Comparative Steel 1

Inventive Steel 2

Comparative Steel 2

Inventive Steel 3

Comparative Steel 3

Inventive Steel 4

Comparative Steel 4

Inventive Steel 5

Comparative Steel 5

Inventive Steel 6

Comparative Steel 6

Inventive Steel 7

Comparative Steel 7

Comparative Steel 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2017/015294

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/42(2006.01)i, C22C 38/44(2006.01)i, C22C 38/00(2006.01)i, C22C 38/04(2006.01)i, C22C 38/58(2006.01)i, C21D 8/02(2006.01)i, C21D 9/46(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 38/42; C22C 38/26; C21D 8/02; C22C 38/00; C22C 38/08; C22C 38/18; C22C 38/38; C22C 38/16; C22C 38/44; C22C 38/04; C22C 38/58; C21D 9/46

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: sulfide, dew condensation corrosion, hot rolling, slab, corrosion resistance, sensitivity index

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2016-0085311 A (JFE STEEL CORPORATION) 15 July 2016 See paragraphs [0090]-[0094]; claims 1-3; and figure 1.	1,3-4,6
Y		2,5
Y	KR 10-2010-0067510 A (POSCO) 21 June 2010 See paragraphs [0039], [0060]-[0064]; claims 1-6; and figure 2.	2,5
A	KR 10-2016-0099063 A (POSCO) 19 August 2016 See paragraphs [0051]-[0066]; claims 1-6; and figure 1.	1-6
A	JP 2014-201759 A (JFE STEEL CORP.) 27 October 2014 See paragraphs [0036]-[0039]; claims 1-2; and figure 1.	1-6
A	JP 2002-173736 A (KAWASAKI STEEL CORP.) 21 June 2002 See paragraphs [0015]-[0029]; claims 1-7; and figure 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 04 APRIL 2018 (04.04.2018)	Date of mailing of the international search report **04 APRIL 2018 (04.04.2018)**
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. +82-42-481-8578	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2017/015294

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-2016-0085311 A	15/07/2016	CN 105793454 A	20/07/2016
		JP 2015-113507 A	22/06/2015
		JP 6048385 B2	21/12/2016
		KR 10-1786413 B1	17/10/2017
		TW 201536931 A	01/10/2015
		TW I534275 B	21/05/2016
		WO 2015-087532 A1	18/06/2015
KR 10-2010-0067510 A	21/06/2010	KR 10-1069981 B1	04/10/2011
KR 10-2016-0099063 A	19/08/2016	KR 10-1696157 B1	13/01/2017
		KR 10-2016-0077417 A	04/07/2016
JP 2014-201759 A	27/10/2014	NONE	
JP 2002-173736 A	21/06/2002	JP 3570376 B2	29/09/2004

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000017381 A **[0007]**