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

(11) EP 2 520 680 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
26.10.2016 Bulletin 2016/43

(21) Application number: **10841182.8**

(22) Date of filing: **22.12.2010**

(51) Int Cl.:
C22C 38/00 (2006.01) *C21D 8/02* (2006.01)
B21B 3/02 (2006.01) *B21B 1/22* (2006.01)

(86) International application number:
PCT/KR2010/009225

(87) International publication number:
WO 2011/081350 (07.07.2011 Gazette 2011/27)

(54) **HIGH STRENGTH STEEL SHEET HAVING EXCELLENT RESISTANCE TO POST WELD HEAT TREATMENT AND METHOD FOR MANUFACTURING SAME**

HOCHFESTES STAHLBLECH MIT AUSGEZEICHNETER RESISTENZ GEGEN EINE NACH DEM SCHWEISSEN ERFOLGENDE WÄRMEBEHANDLUNG SOWIE VERFAHREN ZU DESSEN HERSTELLUNG

FEUILLARD D'ACIER À RÉSISTANCE MÉCANIQUE ÉLEVÉE AYANT UNE EXCELLENTE RÉSISTANCE AU TRAITEMENT THERMIQUE POST-SOUDAGE ET SON PROCÉDÉ DE FABRICATION

(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

(30) Priority: **28.12.2009 KR 20090132129**

(43) Date of publication of application:
07.11.2012 Bulletin 2012/45

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(56) References cited:

EP-A1- 2 258 884	WO-A1-2009/119368
JP-A- 8 283 905	JP-A- 8 283 905
JP-A- 61 079 745	JP-A- 61 079 745
JP-A- H11 131 177	JP-A- 2004 027 355
JP-A- 2004 027 355	JP-A- 2004 204 344
JP-A- 2004 204 344	JP-A- 2006 045 672
JP-A- 2009 041 073	US-A1- 2009 025 839

Printed by Jouve, 75001 PARIS (FR)

Description

[Technical Field]

[0001] The present invention relates to a steel sheet used for crude oil refining equipment, storage tanks, heat exchangers, reaction furnaces, condensers and the like in wet hydrogen sulfide environments, and more particularly, to a steel sheet having excellent strength and toughness even after performing a Post Weld Heat Treatment (PWHT) and a method for manufacturing the same.

[Background Art]

[0002] According to a recent trend for oilfields in poor surroundings to be actively developed due to the era of high oil prices as well as petroleum in being in recent short supply, the thickness of steel for refining and storing crude oil is being increased.

[0003] Post Weld Heat Treatment (PWHT) is carried out to eliminate stress generated during welding with the objects of stabilizing shape and size and preventing the deformation of a structure after welding if the steel is welded in addition to the above-mentioned thickening of steel. However, a steel sheet passing through the PWHT process for a lengthy period of time has a problem in that tensile strength of the steel sheet may be deteriorated due to coarsening in the structure of the steel sheet.

[0004] Document US 2009/0025839 A1 discloses a high tensile strength, refractory steel which comprises, in mass percent, approximately C: 0.04 to 0.15%, Si: 0.50% or less, Mn: 0.50 to 2.00%, P: 0.020% or less, S: 0.010% or less, Nb: 0.01 to 0.5%, Mo: 0.30% or more and less than 0.70%, Al: 0.060% or less, N: 0.0010 to 0.0060%, and the balance consisting of iron and unavoidable impurities.

[0005] That is, a lengthy PWHT process causes a phenomenon in which strength and toughness of the steel sheet are lowered at the same time depending on softening of matrix structures and grain boundaries, growth of crystal grains, coarsening of carbides, and others.

[0006] A means for preventing the deterioration of physical properties according to the above-mentioned long-time PWHT process disclosed in Japanese Patent Publication No. 1997-256037 enabled assurance time for PWHT up to 16 hours by the processes of performing heating and hot rolling on a slab comprising, by weight percent, 0.05 to 0.20% of C, 0.02 to 0.5% of Si, 0.2 to 2.0% of Mn, 0.005 to 0.10% of Al, and containing, if necessary, one or more selected from Cu, Ni, Cr, Mo, V, Nb, Ti, B and Ca, and rare-earth elements with the remainder being iron and unavoidable impurities, air cooling the hot rolled steel sheet at room temperature, and heating and slow cooling the air-cooled steel sheet at the transformation point of Ac1 to Ac3.

[0007] However, the above-mentioned technology has problems that the PWHT assurance time is very scarce if thickening and weld conditions of steel are severe, and it is impossible to apply the PWHT process conducted longer than the PWHT assurance time.

[0008] Therefore, steel having high PWHT resistance which is accompanied by severe thickening and weld conditions of steel such that strength and toughness of the steel sheet are not deteriorated even after performing PWHT for a lengthy period of time is required.

[Disclosure]

[Technical Problem]

[0009] An object of the present invention is to provide a high strength steel sheet having excellent Post Weld Heat Treatment (PWHT) resistance of which strength and toughness are not deteriorated even after performing PWHT for a lengthy period of time, and a method for manufacturing the same.

[Technical Solution]

[0010] The present invention provides a high strength steel sheet excellent in PWHT (Post Weld Heat Treatment) resistance having a composition comprising by weight percent: 0.1 to 0.3% of C; 0.15 to 0.50% of Si; 0.6 to 1.2% of Mn; 0.035% or less of P; 0.020% or less of S; optionally 0.001 to 0.05% of Al; 0.01 to 0.35% of Cr; 0.005 to 0.2% of Mo; 0.005 to 0.05% of V; 0.001 to 0.05% of Nb; 0.001 to 0.05% of Ti; 0.0005 to 0.005% of Ca; 0.05 to 0.5% of Ni; one or more selected from the group consisting of 0.005 to 0.5% of Cu, 0.005 to 0.2% of Co and 0.005 to 0.2% of W; and Fe as well as unavoidable impurities, wherein the composition satisfies the following relational expression:

Cu + Ni + Cr + Mo: 1.5% or less,

Cr + Mo: 0.4% or less,
V + Nb: 0.1% or less, and
Ca/S: 1.0 or less.

[0011] Furthermore, the present invention provides a method for manufacturing the high strength steel sheet excellent in PWHT resistance, the method comprising:

reheating a steel slab satisfying the composition range to a temperature range of 1050°C to 1250°C;
hot-rolling the reheated steel slab in a temperature range of T_{nr} to T_{nr} + 100 °C;
performing a heat treatment by holding the hot rolled steel sheet in a temperature range of 850°C to 950°C for a time period of 1.3*t + (10 to 30) in minutes, wherein t is thickness (mm) of steel; and
cooling the heat-treated steel sheet at a cooling rate of 0.1 to 10 °C/sec.

[Advantageous Effects]

[0012] According to the present invention, a steel sheet for pressure vessels which has strength of 500 MPa or more, of which strength and toughness are not deteriorated even after PWHT reaching 100 hours, and which is excellent in hydrogen-induced cracking resistance can be provided.

[Best Mode]

[0013] Hereinafter, the present invention will be described in detail.

[0014] First, a composition range of the present invention (hereinafter referred to as "weight percent (wt%)") is described in detail.

[0015] The content of carbon (C) is limited to a range of 0.1 to 0.3 wt%. C, as an element for improving strength of a steel sheet, has problems that the strength of the steel sheet in a matrix phase is lowered with a C content of less than 0.1 wt%, and segregation is generated in the structure to deteriorate hydrogen-induced cracking resistance with a C content of more than 0.3 wt%.

[0016] The content of silicon (Si) is limited to a range of 0.15 to 0.50 wt%. Si is an element that is effective in deoxidation and solid solution strengthening, and Si is an element that is added to obtain an effect of increasing the impact transition temperature. Although Si should be added in an amount of 0.15 wt% or more to accomplish such effects, there are problems that weldability is deteriorated, and an oxidation film is severely formed on the surface of the steel sheet if Si is added in an amount of more than 0.5 wt%.

[0017] The content of manganese (Mn) is limited to being within the range of 0.6 to 1.2 wt%. Mn is preferably controlled to the content of 1.2 wt% or less since Mn along with S forms MnS, an elongated nonmetallic inclusion, thereby deteriorating elongation at room temperature and low temperature toughness. However, the content of Mn is limited to being within the range of 0.6 to 1.2 wt% since it is difficult to secure proper strength due to the nature of the present invention if Mn is added to the content of less than 0.6 wt%.

[0018] The content of aluminum (Al) is optionally limited to being within the range of 0.001 to 0.5 wt%. Al together with the above-mentioned Si is one of strong deoxidizers in the steelmaking process, and has problems that the deoxidation effect is insignificant with an Al content of less than 0.001 wt%, and the deoxidation effect is saturated and manufacturing costs increases if Al is added in an amount of more than 0.05 wt%.

[0019] Although phosphorous (P) is an element that deteriorates low temperature toughness, phosphorous (P) is controlled to be within the range of 0.035 wt% or less since it costs excessively to eliminate phosphorous (P) in the steelmaking process.

[0020] Sulfur (S) along with phosphorous (P) is also an element that adversely affects low temperature toughness, it is to control sulfur (S) within the range of 0.020 wt% or less since it may cost excessively to eliminate sulfur (S) in the steelmaking process as in the case of phosphorous (P).

[0021] The content of chromium (Cr) is limited to being within the range of 0.01 to 0.35 wt%. Although Cr is added in an amount of 0.01 wt% or more to obtain the strength increasing effect in the present invention since chromium (Cr) is an element that increases strength, it is advantageous to control chromium (Cr) to the amount of 0.35 wt% or less since chromium (Cr) is a relatively expensive element, and chromium (Cr) causes manufacturing costs to be increased if chromium (Cr) is added in an amount of more than 0.35 wt%.

[0022] The content of molybdenum (Mo) is limited to being within the range of 0.005 to 0.2 wt%. Mo is an element that prevents cracking of the steel sheet due to sulfides as well as an element that is effective in increasing strength of the steel sheet as in the case of Cr. Although Mo is added to the amount of 0.005 wt% or more to obtain the effects, it is advantageous to limit the amount of Mo to 0.2 wt% or less since Mo is also a relatively expensive element and causes manufacturing costs to increase.

[0023] The content of vanadium (V) is limited to being within the range of 0.005 to 0.05 wt%. V is an element that is effective in increasing the strength of the steel sheet as in the cases of Cr and Mo. Therefore, although V is added in an amount of 0.005 wt% or more to promote the effect of increasing strength of the steel sheet, it is advantageous to add V in an amount of 0.05 wt% or less since V is a relatively expensive element.

[0024] The content of niobium (Nb) is limited to being within the range of 0.001 to 0.05 wt%. Nb is an important element that exists in the state of solid solution within austenite to increase hardenability of austenite, and that is precipitated into carbonitrides (Nb(C,N)) matching the matrix to increase strength of the steel sheet. Although Nb is added in an amount of 0.001 wt% or more to obtain the effects, it is advantageous to limit the content of Nb to 0.05 wt% or less since Nb exists in the form of coarse precipitates in the continuous casting process and functions as a site of hydrogen induced cracking if Nb is added in a large amount.

[0025] The content of titanium (Ti) is limited to being within the range of 0.001 to 0.05 wt%. Ti like Nb is an important element that is precipitated into carbonitrides (Ti(C,N)) and increases strength of the steel sheet. Although Ti is added in an amount of 0.001 wt% or more to obtain the effects, it is advantageous to limit the content of Ti to 0.05 wt% or less since Ti exists in the form of coarse precipitates in the continuous casting process and functions as a site of hydrogen induced cracking if Ti is added in a large amount.

[0026] The content of calcium (Ca) is limited to being within the range of 0.0005 to 0.005 wt.%. Ca is added in an amount of 0.0005 wt% or more such that Ca is produced into CaS to inhibit the formation of nonmetallic inclusions such as MnS. However, an upper limit value of the content is limited to 0.005 wt% since Ca is reacted with O contained in steel to produce CaO that is a nonmetallic inclusion if the content of Ca exceeds 0.005 wt%.

[0027] The content of nickel (Ni) is limited to being within the range of 0.05 to 0.5 wt%. It is advantageous to add Ni in an amount of 0.5 wt% or less since Ni is a relatively expensive element and causes manufacturing costs to increase although Ni is added in an amount of 0.05 wt% or more to obtain the effect as an element that is most effective in improving low temperature toughness of the steel sheet.

[0028] The foregoing composition of the present invention comprises one or more selected from the group consisting of Cu, Co, and W.

[0029] If Copper (Cu) is selected it is added in an amount of 0.005 to 0.5 wt%. Cu prevents strength of the steel sheet from deteriorating even after performing PWHT according to matrix strengthening by solution strengthening or e-Cu precipitation, and prevents strength and toughness of the steel sheet from deteriorating through matrix strengthening and recovery inhibition. If copper (Cu) is selected, it is advantageous to add Cu within the range of 0.005 to 0.5 wt% since it is relatively expensive.

[0030] If Cobalt (Co) is selected, cobalt (Co) is added in an amount of 0.005 to 0.2 wt%. If Cobalt (Co) is selected, cobalt (Co) is added in a range of 0.005 to 0.2 wt% since it is relatively expensive, although Co is an element that is effective in preventing softening of the matrix structure.

[0031] If Tungsten (W) is selected, it is added in an amount of 0.005 to 0.2 wt%. If Tungsten (W) is selected, it is added in an amount of 0.005 wt% or more since it has characteristics that can prevent strength and toughness of the steel sheet from deteriorating by forming WC or reducing a precipitation fraction of cementite, thereby preventing growth of cementite or coagulation inhibition of cementite. It is advantageous to add W within a range of 0.005 to 0.2 wt% since W is relatively expensive.

[0032] Contents of the following elements such as Cu, Ni, Cr, Mo, V, Nb and others satisfy the following relations when considering that steel of the present invention can be used as steel for pressure vessels.

Cu + Ni + Cr + Mo: 1.5 wt% or less
Cr + Mo: 0.4 wt% or less
V + Nb: 0.1 wt% or less
Ca/S: 1.0 or less

[0033] That is, relations of Cu + Ni + Cr + Mo, Cr + Mo and V + Nb numerical values respectively limited by the basic standard of steel for pressure vessels (ASTM A20). Accordingly, the contents Cu + Ni + Cr + Mo, Cr + Mo and V + Nb are limited to 1.5 wt% or less, 0.4 wt% or less and 0.1 wt% or less respectively. Alloy elements which are not included according to embodiments of the present invention can be calculated as 0.

[0034] The Ca/S ratio is an essential composition ratio improving hydrogen induced cracking resistance of the steel sheet by spheroidizing MnS inclusions. The ratio is controlled to 1.0 or less since its effects are difficult to expect if the Ca/S ratio exceeds 1.0.

[0035] The composition comprises Fe as well as unavoidable impurities as a remainder.

[0036] Hereinafter, the microstructure of the present invention is described in detail.

[0037] If steel having the above-mentioned composition is subjected to controlled rolling and heat treatment by a process to be described later, the microstructure of the steel may be formed in a ferrite structure or a mixed structure of ferrite and pearlite. The structure may comprise up to 10 wt% of bainite although it is preferable that low temperature structure is not included in the above-mentioned structure if possible. The reason for controlling the structure in the above-stated form is that a steel sheet of the present invention should be excellent in a target hydrogen induced cracking resistance and should have proper strength and toughness.

[0038] Furthermore, a banding index value (measured by ASTM E-1268) exhibiting how much the banding structure that is weak in hydrogen induced cracking has been formed is preferably 0.25 or less in order to secure hydrogen induced cracking resistance. Hydrogen induced cracking resistance is rapidly lowered in the microstructure if the banding index value exceeds 0.25.

[0039] The center of a steel sheet in a thickness direction (3/8 to 5/8t, t: thickness of the steel sheet) preferably has an average ferrite grain size of 50 μm or less since it is apprehended that strength and toughness of the steel sheet are deteriorated if the ferrite grains have excessive sizes. Although the crystal grain sizes do not have a lower limit, the crystal grain sizes may have 5 μm or more since it is generally difficult to obtain crystal grains of less than 5 μm from a target steel of the present invention.

[0040] Hereinafter, a manufacturing method according to the present invention is described in detail.

[0041] The manufacturing method according to the present invention comprises reheating a steel slab satisfying the above-mentioned composition range to a temperature range of 1050 to 1250°C since a solid solution of solute atoms is difficult if the reheating temperature is lower than 1050°C, and sizes of austenite crystal grains become too coarse to deteriorate properties of the steel sheet if the reheating temperature is more than 1250°C.

[0042] After performing the foregoing reheating process, processes of recrystallization controlled rolling, heat treatment, and PWHT are required to be carried out in the manufacturing method according to the present invention such that a steel sheet according to the present invention has a ferrite + pearlite dual phase structure for obtaining hydrogen induced cracking resistance, and the banding index value (measured by ASTM E-1268) becomes 0.25 or less.

[0043] The recrystallization controlled rolling is carried out by hot rolling the reheated steel slab at a no-recrystallization temperature or more. T_{nr}, the foregoing no-recrystallization temperature can be calculated by the following expression.

$$T_{nr}\ (°C) = 887+464xC+890xTi+363xAl-357xSi+(6446xNb-644xNb^{1/2})+(732xV-230xV^{1/2})$$

[0044] So as to maintain the banding index value (measured by ASTM E-1268) to 0.25 or less, recrystallization controlled rolling is the most important variable, and the recrystallization controlled rolling is preferably performed by applying 10% or more of rolling reduction per each rolling pass in a temperature range of T_{nr} to T_{nr} + 100°C, thereby imparting a cumulative rolling reduction of 30% or more since a banding index value of 0.25 or less cannot be expected if the cumulative rolling reduction is less than 30%. Further, temperature of recrystallization controlled rolling is also limited to a control banding index, thereby inhibiting the band structure in the state that crystal grains have not become coarse. More specifically, it is not preferable that the temperature is lower than a no-recrystallization temperature range (T_{nr}) since austenite is flattened into a pancake such that the banding index value is increased. On the contrary, it is not preferable that temperature is excessively high since crystal grains have excessive sizes.

[0045] Subsequently, hot rolling is conducted, and a cooled hot-rolled steel sheet is heat-treated. The heat treatment is held under conditions of a temperature range of 850°C to 950°C and a time period of 1.3xt + (10 to 30) in minutes, wherein t is thickness (mm) of steel. It is difficult to secure strength of the steel sheet since it is difficult to resolve solute atoms for solid solution if the heat treatment is conducted at a temperature of less than 850°C, whereas low temperature of the steel sheet is deteriorated since crystal grains are grown if the heat treatment is conducted at a temperature of more than 950°C.

[0046] The heat treatment holding time is limited since homogenization of the structure is difficult if the holding time is less than 1.3xt + 10 minutes (t is thickness (mm) of steel), and productivity is deteriorated if the holding time is more than 1.3*t + 30 in minutes (t is thickness (mm) of steel).

[0047] The held steel sheet is cooled to a cooling rate of 0.1 to 10 °C/sec based on the central part of the steel sheet since there are high possibilities that coarsening of ferrite grains may be generated during cooling at a cooling rate of 0.1 °C/sec or less, and an excessive second phase (10 % or more of bainite fraction) may be generated at a cooling rate of 10 °C/sec or more.

[0048] The foregoing cooling rate is controlled to adjust an average ferrite grain size in the central part of the steel sheet to 50 μm or less.

[0049] PWHT is required in a steel sheet of the present invention manufactured through the heat treatment process in order to eliminate residual stress by the welding process added during fabrication of pressure vessels. Although strength and toughness of the steel sheet are generally deteriorated after performing PWHT on a steel sheet for a lengthy period of time, the steel sheet manufactured by the present invention has a merit that welding work is possible without a large drop in strength or toughness of the steel sheet even when the steel sheet is subjected to PWHT at an ordinary

PWHT temperature of 600°C to 640°C for a lengthy period of time of up to 100 hours. Particularly, the steel sheet of the present invention has a tensile strength of 450 MPa or more even after performing PWHT for 100 hours, and satisfies a Charpy impact energy value of 50 J or more at - 50°C.

[0050] Hereinafter, embodiments of the present invention will be described in detail with reference to the following embodiments. However, the following embodiments are provided for illustrative purposes only, and the scope of the present invention should not be limited thereto in any manner.

[Embodiments]

[0051] The following table 1 exhibits chemical components of inventive steels and comparative steels respectively. Steel slabs having the same compositions as shown in the table 1 were manufactured by conducting rolling, heat treatment and cooling under conditions of steel sheet thicknesses and reheating temperatures of the table 2.

[0052] After subjecting the steel sheets manufactured under the foregoing conditions to PWHT and other processes under the same conditions as shown in the following table 2, yield strengths, tensile strengths and crack length ratios (CLR) of the steel sheets were examined, and the examination results were shown in the following table 2.

[0053] In the following table 2, low temperature toughness values were evaluated as Charpy impact energy values obtained by performing the Charpy impact test of samples having V notches at -50°C, and crack length ratios (%) were measured according to NACE Standard TM0277.

[Table 1]

Category	C	Mn	Si	P	S	Cu	Ni	Cr	Mo	V	Nb	Ti	Co	W	Ca
Inventive steel 1	0.17	1.10	0.30	0.01	0.0015	0.15	0.20	0.05	0.12	0.005	0. 015	0.003	-	0.10	0.0015
Inventive steel 2	0.18	1.05	0.35	0.08	0.0012	-	0.15	0.10	0.10	0.010	0.014	0.012	0.10	-	0.0025
Inventive steel 3	0.16	1.10	0.30	0.01	0.0015	0.20	0.20	0.05	0.12	0.005	0.015	0.015	-	0.10	0.0020
Inventive steel 4	0.15	1.05	0.25	0.08	0.0012	-	0.15	0.10	0.10	0.010	0.014	0.012	0.10	-	0.0018
Comparative steel 1	0.17	1.05	0.25	0.01	0.0015	-	0.20	0.15	0.08	0.010	0.010	0.010	-	-	0.0025
Comparative steel 2	0.15	1.15	0.25	0.01	0.0014	-	0.15	0.20	0.15	0.009	0. 012	0.012	-	-	0.0023

[Table 2]

Category	Thickness of steel sheet (mm)	Reheating Temp. (°C)	Cumulative rolling reduction (%)	Heat treatment conditions (°C,min)	Cooling rate (°C/sec)	PWHT Temp. (°C)	PWHT time (Hr)	Average ferrite grain size of central part (μm)	Banding Index	YS (MPa)	TS (MPa)	-50°C Impact Toughness (J)	CLR (%)
Inventive steel 1	13	1150	60	890,50	1.0	620	6	15	0.18	380	545	203	0.03
	25	1100	75	900,60	0.7	620	16	23	0.12	375	540	197	0.0
	50	1180	55	890,80	0.8	610	50	25	0.15	360	539	213	0.0
	80	1200	50	900,125	0.5	610	100	37	0.08	359	522	186	0.0
Inventive steel 2	30	1100	80	910,60	110	610	6	19	0.12	355	542	173	0.0
	75	1150	65	910,120	120	610	16	26	0.11	354	539	180	0.0
	80	1200	60	890,125	120	610	50	37	0.13	350	531	175	0.0
	80	1200	50	890,125	120	610	100	33	0.07	350	519	170	0.0
Inventive steel 3	30	1100	80	910,60	110	610	6	21	0.16	355	535	173	0.0
	75	1150	65	910,120	120	610	16	27	0.07	354	537	180	0.0
	80	1200	60	890,125	120	610	50	32	0.13	350	533	175	0.0
	80	1200	50	890,125	120	610	100	38	0.11	350	528	175	0.0
Inventive steel 4	50	1100	60	910,80	110	610	6	15	0.09	355	542	173	0.0
	75	1150	55	910,120	120	610	16	23	0.10	354	535	180	0.0
	80	1200	60	890,125	120	610	50	28	0.08	350	538	175	0.0
	80	1200	50	890,125	120	610	100	35	0.11	350	521	175	0.0
Comparative steel 1	50	1200	-	900,85	Air cooling	620	16	25	0.26	370	536	166	35
	50	1150	-	900,80	Air cooling	620	50	51	0.36	325	461	27	20
	75	1100	-	900,120	Air cooling	620	100	58	0.27	329	547	23	25
Comparative steel 2	50	1100	-	900,80	Air cooling	620	16	35	0.26	360	525	178	30
	60	1100	-	900,100	Air cooling	620	50	50	0.29	333	468	29	35
	75	1180	-	900,120	Air cooling	620	100	51	0.26	328	460	18	25

[0054] As can be seen from the results of tables 1 and 2, inventive steels satisfying compositions and manufacturing conditions have strength and toughness values that are not lowered although the PWHT time reaches 50 to 100 hours. On the contrary, it can be confirmed that strength and toughness values of the comparative steels are substantially deteriorated than those of the inventive steels as the PWHT time is extended to 50 hours or more although the comparative steels show strength and toughness levels that are almost equal to those of the inventive steels if the PWHT time is small when comparing the comparative steels with the invention steels.

[0055] Particularly, it can be seen that low temperature toughness values of the inventive steels were not dropped greatly even after the PWHT time of 100 hours, whereas those of the comparative steels were dropped greatly.

[0056] On the other hand, it can be seen that the inventive steels are far excellent in the CLR (Crack Length Ratio) (%) exhibiting hydrogen induced cracking resistance under the H2S gas (Sour Gas) atmosphere. Like this, it can be seen through the embodiments of the present invention that the inventive steels are excellent in the CLR (Crack Length Ratio) because the Banding Index showing the homogenization extent of microstructures formed in a composite structure of ferrite and pearlite is controlled to a lower value of 0.25 or less.

Claims

1. A high strength steel sheet excellent in PWHT (Post Weld Heat Treatment) resistance having a composition comprising by weight percent: 0.1 to 0.3% of C; 0.15 to 0.50% of Si, 0.6 to 1.2% of Mn; 0.035% or less of P; 0.020% or less of S; optionally 0.001 to 0.05 % of Al; 0.01 to 0.35% of Cr; 0.005 to 0.2% of Mo; 0.005 to 0.05% of V; 0.001 to 0.05% of Nb; 0.001 to 0.05% of Ti; 0.0005 to 0.005% of Ca; 0.05 to 0.5% of Ni; one or more selected from the group consisting of 0.005 to 0.5% of Cu, 0.005 to 0.2% of Co and 0.005 to 0.2% of W; and Fe as well as unavoidable impurities as a remainder,
   wherein the composition satisfies the following relational expression: Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or less.

2. The high strength steel sheet of claim 1, wherein the microstructure of the steel sheet is formed in a ferrite structure or a mixed structure of ferrite and pearlite, and the central part of the steel sheet has an average ferrite grain size of 50 μm or less.

3. The high strength steel sheet of claim 1, wherein the steel sheet has a banding index value (measured by ASTM E-1268) of 0.25 or less.

4. The high strength steel sheet of claim 1, wherein the steel sheet has a tensile strength of 450 MPa or more even after performing PWHT for 100 hours, and has a Charpy impact energy value of 50 J or more at -50°C.

5. A method for manufacturing a high strength steel sheet excellent in PWHT resistance, the method comprising:

   reheating a steel slab to a temperature range of 1050 to 1250°C, the steel slab having a composition comprising by weight percent: 0.1 to 0.3% of C; 0.15 to 0.50% of Si; 0.6 to 1.2% of Mn; 0.035% or less of P; 0.020% or less of S; optionally 0.001 to 0.05 % of Al; 0.01 to 0.35% of Cr; 0.005 to 0.2% of Mo; 0.005 to 0.05% of V; 0.001 to 0.05% of Nb; 0.001 to 0.05% of Ti; 0.0005 to 0.005% of Ca; 0.05 to 0.5% of Ni; one or more selected from the group consisting of 0.005 to 0.5% of Cu, 0.005 to 0.2% of Co and 0.005 to 0.2% of W; and Fe as well as unavoidable impurities as a remainder,
   wherein the composition satisfies the following relational expression: Cu + Ni + Cr + Mo: 1.5% or less, Cr + Mo: 0.4% or less, V + Nb: 0.1% or less, and Ca/S: 1.0 or less; hot-rolling the reheated steel slab in a temperature range of Tnr to Tnr + 100°C;
   performing a heat treatment by holding the hot rolled steel sheet in a temperature range of 850°C to 950°C for a time period of 1.3*t + (10 to 30) in minutes, wherein t is thickness (mm) of steel; and
   cooling the heat-treated steel sheet at a cooling rate of 0.1 to 10°C/sec.

6. The method of claim 5, wherein the hot-rolling is performed to a cumulative rolling reduction of 30% or more by applying 10% or more of rolling reduction per each rolling pass.

7. The method of claim 5, wherein the cooling is performed by controlling the cooling rate such that an average ferrite grain size in the central part of the steel sheet is adjusted to 50 μm or less.

Patentansprüche

1. Hochfestes Stahlblech von ausgezeichneter PWHT-Widerstandsfähigkeit (PWHT - Wärmebehandlung nach dem Schweißen), das eine Zusammensetzung hat, die in Gewichtsprozent umfasst: 0,1 bis 0,3% C; 0,15 bis 0,50% Si, 0,6 bis 1,2% Mn; 0,035% oder weniger P; 0,020% oder weniger S; optional 0,001 bis 0,05% Al; 0,01 bis 0,35% Cr; 0,005 bis 0,2% Mo; 0,005 bis 0,05% V; 0,001 bis 0,05% Nb; 0,001 bis 0,05% Ti; 0,0005 bis 0,005% Ca; 0,05 bis 0,5% Ni; eines oder mehr Elemente, das bzw. die aus der Gruppe ausgewählt ist bzw. sind, die aus 0,005 bis 0,5% Cu, 0,005 bis 0,2% Co und 0,005 bis 0,2% W besteht; und Fe sowie andere unvermeidliche Verunreinigungen als Rest,
wobei die Zusammensetzung den folgenden Verhältnisausdruck erfüllt: Cu + Ni + Cr + Mo: 1,5% oder weniger, Cr + Mo: 0,4% oder weniger, V + Nb: 0,1% oder weniger, und Ca/S: 1,0 oder weniger.

2. Hochfestes Stahlblech nach Anspruch 1, wobei die Mikrostruktur des Stahlblechs in einer Ferritstruktur oder einer Mischstruktur aus Ferrit und Perlit gebildet ist und der zentrale Teil des Stahlblechs eine mittlere Ferritkorngröße von 50 μm oder weniger hat.

3. Hochfestes Stahlblech nach Anspruch 1, wobei das Stahlblech einen Banding-Indexwert (gemessen durch ASTM E-1268) von 0,25 oder weniger hat.

4. Hochfestes Stahlblech nach Anspruch 1, wobei das Stahlblech, selbst nach Durchführung einer PWHT über 100 Stunden, eine Zugfestigkeit von 450 MPa oder mehr hat, und einen Charpy-Kerbschlagzähigkeitswert von 50 J oder mehr bei -50°C hat.

5. Verfahren zum Herstellen eines hochfesten Stahlblechs von ausgezeichneter PWHT-Widerstandsfähigkeit, wobei das Verfahren umfasst:

   Wiedererhitzen einer Stahlbramme auf einen Temperaturbereich von 1050 bis 1250°C, wobei die Stahlbramme eine Zusammensetzung hat, die in Gewichtsprozent umfasst:
   0,1 bis 0,3% C; 0,15 bis 0,50% Si, 0,6 bis 1,2% Mn; 0,035% oder weniger P; 0,020% oder weniger S; optional 0,001 bis 0,05% Al; 0,01 bis 0,35% Cr; 0,005 bis 0,2% Mo; 0,005 bis 0,05% V; 0,001 bis 0,05% Nb; 0,001 bis 0,05% Ti; 0,0005 bis 0,005% Ca; 0,05 bis 0,5% Ni; eines oder mehr Elemente, das bzw. die aus der Gruppe ausgewählt ist bzw. sind, die aus 0,005 bis 0,5% Cu, 0,005 bis 0,2% Co und 0,005 bis 0,2% W besteht; und Fe sowie andere unvermeidliche Verunreinigungen als Rest,
   wobei die Zusammensetzung den folgenden Verhältnisausdruck erfüllt: Cu + Ni + Cr + Mo: 1,5% oder weniger, Cr + Mo: 0,4% oder weniger, V + Nb: 0,1% oder weniger, und Ca/S: 1,0 oder weniger; Warmwalzen der wiedererhitzen Stahlbramme in einem Temperaturbereich von Tnr bis Tnr + 100°C;
   Durchführen einer Wärmebehandlung, indem das warmgewalzte Stahlblech über einen Zeitraum von 1,3*t + (10 bis 30) in Minuten in einem Temperaturbereich von 850°C bis 950°C gehalten wird, wobei t die Stahldicke (mm) ist; und
   Abkühlen des wärmebehandelten Stahlblechs mit einer Abkühlrate von 0,1 bis 10°C/sec.

6. Verfahren nach Anspruch 5, wobei das Warmwalzen bis zu einer kumulativen Abwalzreduktion von 30% oder mehr erfolgt, indem 10% oder mehr Abwalzreduktion jeweils pro Walzdurchgang eingesetzt wird.

7. Verfahren nach Anspruch 5, wobei das Abkühlen erfolgt, indem die Abkühlrate so gesteuert wird, dass eine mittlere Ferritkorngröße im zentralen Teil des Stahlblechs auf 50 μm oder weniger eingestellt wird.

Revendications

1. Feuillard d'acier à résistance élevée ayant une excellente résistance PWHT (traitement thermique post-soudage), ayant une composition comprenant, en pourcentage de poids : 0,1 à 0,3 % de C ; 0,15 à 0,50 % de Si ; 0,6 à 1,2 % de Mn ; 0,035 % ou moins de P ; 0,020 % ou moins de S ; facultativement 0,001 à 0,05 % d'Al ; 0,01 à 0,35 % de Cr ; 0,005 à 0,2 % de Mo ; 0,005 à 0,05 % de V ; 0,001 à 0,05 % de Nb ; 0,001 à 0,05 % de Ti ; 0,0005 à 0,005 % de Ca ; 0,05 à 0,5 % de Ni ; un ou plusieurs éléments sélectionnés dans le groupe constitué par 0,005 à 0,5 % de Cu, 0,005 à 0,2 % de Co et 0,005 à 0,2 % de W ; et Fe ainsi que des impuretés inévitables comme reste,
sachant que la composition satisfait à l'expression relationnelle suivante : Cu + Ni + Cr + Mo : 1,5 % ou moins, Cr + Mo : 0,4 % ou moins, V + Nb : 0,1 % ou moins, et Ca/S : 1,0 ou moins.

2. Le feuillard d'acier à résistance élevée de la revendication 1, sachant que la microstructure du feuillard d'acier est formée dans une structure de ferrite ou une structure mixte de ferrite et de perlite, et la partie centrale du feuillard d'acier a une taille de grain de ferrite moyenne de 50 μm ou moins.

3. Le feuillard d'acier à résistance élevée de la revendication 1, sachant que le feuillard d'acier a une valeur d'indice de cerclage (mesurée suivant ASTM E-1268) de 0,25 ou moins.

4. Le feuillard d'acier à résistance élevée de la revendication 1, sachant que le feuillard d'acier a une résistance à la traction de 450 MPa ou plus même après exécution d'un PWHT pendant 100 heures, et a une valeur d'énergie d'impact Charpy de 50 J ou plus à -50 °C.

5. Procédé de fabrication d'un feuillard d'acier à résistance élevée ayant une excellente résistance PWHT, le procédé comprenant :

le réchauffage d'une brame d'acier à une plage de température de 1050 à 1250 °C, la brame d'acier ayant une composition comprenant, en pourcentage de poids : 0,1 à 0,3 % de C ; 0,15 à 0,50 % de Si ; 0,6 à 1,2 % de Mn ; 0,035 % ou moins de P ;
0,020 % ou moins de S ; facultativement 0,001 à 0,05 % d'Al ; 0,01 à 0,35 % de Cr ; 0,005 à 0,2 % de Mo ; 0,005 à 0,05 % de V ; 0,001 à 0,05 % de Nb ; 0,001 à 0,05 % de Ti ; 0,0005 à 0,005 % de Ca ; 0,05 à 0,5 % de Ni ; un ou plusieurs éléments sélectionnés dans le groupe constitué par 0,005 à 0,5 % de Cu, 0,005 à 0,2 % de Co et 0,005 à 0,2 % de W ; et Fe ainsi que des impuretés inévitables comme reste,
sachant que la composition satisfait à l'expression relationnelle suivante : Cu + Ni + Cr + Mo : 1,5 % ou moins, Cr + Mo : 0,4 % ou moins, V + Nb : 0,1 % ou moins, et Ca/S : 1,0 ou moins ; le laminage à chaud de la brame d'acier réchauffée dans une plage de température de Tnr à Tnr + 100 °C ;
l'exécution d'un traitement thermique en maintenant le feuillard d'acier laminé à chaud dans une plage de température de 850 °C à 950 °C pendant une période de 1,3*t + (10 à 30) en minutes, sachant que t est l'épaisseur (mm) d'acier ; et
le refroidissement du feuillard d'acier traité thermiquement à un taux de refroidissement de 0,1 à 10 °C/s.

6. Le procédé de la revendication 5, sachant que le laminage à chaud est exécuté à une réduction de laminage cumulative de 30 % ou plus en appliquant 10 % ou plus de réduction de laminage pour chaque passe de laminage.

7. Le procédé de la revendication 5, sachant que le refroidissement est exécuté en régulant le taux de refroidissement de telle sorte qu'une taille de grain de ferrite moyenne dans la partie centrale du feuillard d'acier soit ajustée à 50 μm ou moins.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20090025839 A1 **[0004]**
- JP 9256037 A **[0006]**