(19)



# (11) **EP 2 927 339 A1**

(12)

# **EUROPEAN PATENT APPLICATION**

published in accordance with Art. 153(4) EPC

(43) Date of publication: 07.10.2015 Bulletin 2015/41

(21) Application number: 14743980.6

(22) Date of filing: 23.01.2014

(51) Int Cl.: C22C 38/00 (2006.01) C22C 38/50 (2006.01)

C21D 8/02 (2006.01)

(86) International application number: **PCT/JP2014/000320** 

(87) International publication number: WO 2014/115549 (31.07.2014 Gazette 2014/31)

(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** 

(30) Priority: 24.01.2013 JP 2013010976

(71) Applicant: JFE Steel Corporation Tokyo, 100-0011 (JP)

(72) Inventors:

 GOTO, Sota Tokyo 100-0011 (JP)  TOYODA, Shunsuke Tokyo 100-0011 (JP)

 OKABE, Takatoshi Tokyo 100-0011 (JP)

 OKAZAKI, Yukihiko Tokyo 100-0011 (JP)

(74) Representative: Hoffmann Eitle
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

## (54) HOT-ROLLED STEEL PLATE FOR HIGH-STRENGTH LINE PIPE

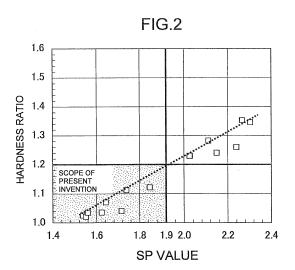
(57) Provided is an electric resistance welded steel pipe for a high strength linepipe excellent in terms of HIC resistance

A hot-rolled steel sheet for a high strength linepipe, the steel sheet having a chemical composition containing, by mass%, C: 0.02% or more and 0.06% or less, Si: 0.05% or more and 0.25% or less, Mn: 0.60% or more and 1.10% or less, P: 0.008% or less, S: 0.0010% or less, Nb: 0.010% or more and 0.060% or less, Ti: 0.001% or more and 0.020% or less, Mo: 0.05% or less, Cr: 0.05% or more and 0.50% or less, Al: 0.01% or more and 0.08% or less, Ca: 0.0005% or more and 0.0050% or less, O: 0.005% or less, one or more selected from among Cu: 0.50% or less, Ni: 0.50% or less, and V: 0.10% or less, and the balance being Fe and inevitable impurities, and a metallic structure composed of bainitic-ferrite, in which expression (1) below is satisfied, and in which the ratio of the hardness of a center segregation part to the hardness of a non-segregation part is less than 1.20.

 $SP \leq 1.90 \cdots (1)$ 

where SP is derived from SP = Mn + Mo + 11.3  $\times$  C + 0.29  $\times$  (Cu + Ni) + 0.60  $\times$  Cr + 0.88  $\times$  V, and where

atomic symbols in the equation respectively represent the contents (mass%) of the corresponding chemical elements.



P 2 927 339 A1

## Description

[Technical Field]

**[0001]** The present invention relates to a hot-rolled steel sheet having hydrogen induced cracking resistance (hereinafter, called HIC resistance) and a strength of X52 or more in accordance with API (American Petroleum Institute) standards which can preferably be used as a material for an electric resistance welded steel pipe. The electric resistant welded steel pipe is used as a line pipe for transporting energy resources such as crude oil and a natural gas. The present invention also relates to a method for manufacturing the steel sheet.

[Background Art]

10

15

30

35

40

45

**[0002]** Although UOE steel pipes have been mainly used for linepipes to date from the viewpoint of transport efficiency because UOE steel pipes can be manufactured to have a large diameter and a large thickness, high strength electric resistance welded steel pipes, which are manufactured with a high productivity from less expensive material, hot-rolled steel sheets, in a coil shape (hot-rolled steel strips), are being increasingly used instead of UOE steel pipes nowadays. Electric resistance welded steel pipes have an advantage in that they are superior to UOE steel pipes in terms of variation in wall thickness and roundness in addition to cost. On the other hand, since the pipe production method for electric resistance welded steel pipes involves cold roll forming, it is characteristic that, when pipe production is performed, plastic strain given to the cold-rolled steel pipes is significantly large compared to that given to UOE steel pipes.

**[0003]** Nowadays, in exploitation of crude oil and natural gas, there is an increasing tendency for oil fields and gas fields to be developed in the polar areas or in deeper regions due to an increase in the demand for energy and due to the progress of drilling technology. Linepipes which are used at such places are required to have so-called sour resistance such as HIC resistance and sulfate stress corrosion cracking resistance (SSC) in addition to strength, toughness and weldability. In the case of linepipes, which are not subjected to stress after having been laid, HIC resistance is particularly important.

**[0004]** HIC is a phenomenon in which hydrogen ions, which have been generated by a corrosion reaction, increase internal pressure by becoming hydrogen atoms at the surface of a steel sheet, by entering the steel, and by accumulating around inclusions such as MnS, around carbides having a large grain diameter such as NbC, and around a second hard phase so as to cause the steel material to eventually crack. In addition, in the case where a steel material is given plastic strain, since many dislocations are formed around the inclusions, the carbides, and the second hard phase mentioned above, hydrogen atoms are more likely to accumulate, which results in HIC being more likely to occur.

[0005] To date, various solutions have been proposed in order to solve the problem of HIC described above.

[0006] Patent Literature 1 discloses a method for improving HIC resistance in which inclusions, which become the origins of HIC, are rendered harmless by controlling the total contents of chemical elements which combine respectively with S (sulfur), O (oxygen), and N (nitrogen) to form inclusions to be 0.01% or less or by controlling the maximum diameter of inclusions to be 5  $\mu$ m or less, and in which the hardness of a center segregation part is controlled to be Hv 330 or less. [0007] Patent Literature 2 discloses a method for decreasing the area ratio of HIC by decreasing the size of TiN grains, which become the origin of HIC. Specifically, the size of Al-Ca-based sulfides in molten steel is decreased by controlling a weight ratio CaO/Al<sub>2</sub>O<sub>3</sub> to be 1.2 to 1.5 as a result of controlling the contents of Al and Ca in order to control the grain diameter of Al-Ti-Ca-based compound inclusions, which are formed using the sulfides as nuclei, to be 30  $\mu$ m or less. [0008] In addition, Patent Literature 3 discloses a method in which the formation of carbonitrides of Nb and Ti, which become the origins of HIC, is less likely to occur by controlling Nb concentration to be 0.06% or less and Ti concentration to be 0.025% or less in a region located at a distance in the thickness direction of 5% of the thickness from the central part in the thickness direction.

**[0009]** Patent Literature 4 discloses a method for manufacturing a high strength linepipe excellent in terms of HIC resistance in which HIC resistance is improved by decreasing the degree of center segregation as a result of decreasing Mn content in steel and in which Cr and Mo, which are comparatively less likely to undergo center segregation, are utilized.

50 [Citation List]

[Patent Literature]

## [0010]

55

[PTL 1] Japanese Unexamined Patent Application Publication No. 2006-63351

[PTL 2] Japanese Patent No. 4363403 (International Publication No. WO2005/075694)

[PTL 3] Japanese Unexamined Patent Application Publication No. 2011-63840

[PTL 4] Japanese Patent No. 2647302 (Japanese Unexamined Patent Application Publication No. 5-271766)

[Summary of Invention]

## 5 [Technical Problem]

**[0011]** However, in the case of the technique according to Patent Literature 1, since the hardness of a center segregation part is still high, there is a problem in that sufficient HIC resistance cannot be achieved in the case of an electric resistance welded steel pipe, which is given large plasticity when forming is performed, even if it is possible to render inclusions, which become the origins, harmless.

**[0012]** In addition, in the case of the techniques according to Patent Literature 2 and Patent Literature 3, since no specific measure is taken in order to control the hardness of a center segregation part, there is still a problem in that a large HIC occurs in the case of an electric resistance welded steel pipe even if it is possible to render inclusions, which become the origins, harmless.

**[0013]** In addition, in the case of the technique according to Patent Literature 4, since there is an increase in the hardness of a center segregation part as a result of the formation of a second hard phase such as martensite being promoted by the excessive addition of Cr and Mo, there is a problem in that it is necessary to further decrease the hardness of a center segregation part in the case of an electric resistance welded steel pipe, which is given a large plasticity when forming is performed.

[0014] The present invention has been completed in view of the problems described above, and an object of the present invention is to provide an electric resistance welded steel pipe for a high strength linepipe excellent in terms of HIC resistance which can preferably be used for an electric resistance welded steel linepipe and with which, for example, a crack length ratio (herein after, called CLR) is 15% or less when HIC occurs after the linepipe is given 10% of plastic strain.

[0015] Here, "excellent in terms of HIC resistance" refers to a case where a crack length ratio (CLR) is 15% or less after a steel sheet has been immersed in a NACE solution (NACE TM-0284 solution A: 5%NaCl + 0.5%CH<sub>3</sub>OOH, 1 atmosphere of saturated H<sub>2</sub>S, and pH = 3.0 to 4.0) for 96 hours.

## [Solution to Problem]

35

45

50

55

[0016] The present invention has been completed in order to decrease the hardness of a center segregation part and in order to achieve desired strength on the basis of the knowledge which has been obtained by conducting many experiments regarding the relationship between the hardness of a center segregation part and steel chemical composition and the relationship of constituent microstructures to HIC performance and manufacturing conditions.

**[0017]** First, the relationship between the HIC performance of a product and the hardness of a center segregation part was investigated. As a result, it was found that it is possible to achieve a crack length rate (CLR) of 15% or less in the case where the Vickers hardness of a center segregation part is HV 230 or less. The finding, that is, the fact that the hardness of a center segregation part is controlled in order to improve HIC resistance, is conventionally known as described in Patent Literature 1.

**[0018]** However, from the results of further collecting the data of products, since it was found that there is a case where a CLR is more than 15% even if the highest hardness of a center segregation part is controlled to be Hv 230 or less, the reason for that was investigated from the viewpoint of material uniformity. Fig. 1 illustrates the relationship between the hardness ratio of a center segregation part to a non-segregation part (the Vickers hardness of a center segregation part/the Vickers hardness of a non-segregation part) and a crack length ratio (CLR). As Fig. 1 indicates, it was found that a CLR is 15% or less in the case where the hardness ratio is 1.20 or less.

[0019] This is thought to be because, in the case where hardness distribution in the thickness direction is not uniform, since strain is concentrated at the interface between a portion having a high hardness in a center segregation part and the other portion when a steel sheet is given large plastic strain, the interface becomes the trap site of hydrogen atoms. [0020] Subsequently, by investigating the chemical composition of steel, with which a hardness ratio of a center segregation part to a non-segregation part being less than 1.20 is achieved, an SP value (= Mn + Mo + 11.3 x C + 0.29  $\times$  (Cu + Ni) + 0.60 x Cr + 0.88 x V) was derived by incorporating the segregation coefficients of constituent chemical elements in continuously cast slab, which had been calculated using a unique computation simulation, into the carbon equivalent equation (CEQ = C + Mn / 6 + (Cr + Mo + V) / 5 + (Cu + Ni) / 15). Fig. 2 illustrates the relationship between the hardness ratio of a center segregation part to a non-segregation part and an SP value. From the results, it was found that it is necessary to control an SP value to be 1.90 or less in order to control the hardness ratio of a center segregation part to be less than 1.20.

**[0021]** The present invention has been completed on the basis of the knowledge described above and further investigations, and the subject matter of the present invention is as follows.

[0022] [1] A hot-rolled steel sheet for a high strength linepipe excellent in terms of HIC resistance, the steel sheet

having a chemical composition containing, by mass%, C: 0.02% or more and 0.06% or less, Si: 0.05% or more and 0.25% or less, Mn: 0.60% or more and 1.10% or less, P: 0.008% or less, S: 0.0010% or less, Nb: 0.010% or more and 0.060% or less, Ti: 0.001% or more and 0.020% or less, Mo: 0.05% or less, Cr: 0.05% or more and 0.50% or less, Al: 0.01% or more and 0.08% or less, Ca: 0.0005% or more and 0.0050% or less, O: 0.005% or less, one or more selected from among Cu: 0.50% or less, Ni: 0.50% or less, and V: 0.10% or less, and the balance being Fe and inevitable impurities, and a metallic structure composed of bainitic-ferrite, in which expression (1) below is satisfied, and in which the ratio of the hardness of a center segregation part to the hardness of a non-segregation part is less than 1.20.

$$SP \leq 1.90 \cdots (1)$$

where SP is derived from SP = Mn + Mo +  $11.3 \times C + 0.29 \times (Cu + Ni) + 0.60 \times Cr + 0.88 \times V$ , and where atomic symbols in the equation respectively represent the contents (mass%) of the corresponding chemical elements.

[0023] [2] The hot-rolled steel sheet for a high strength linepipe excellent in terms of HIC resistance according to item [1], the steel sheet having the chemical composition, in which expression (2) below is satisfied.

$$1.2 \le EC \le 4.0 \cdots (2)$$
,

where EC is expressed by EC = [Ca]eff / (1.25  $\times$  S), where [Ca]eff is derived from Ca - (0.18 + 130  $\times$  Ca)  $\times$  O, and where atomic symbols Ca, S, and O in the equations respectively represent the contents (mass%) of the corresponding chemical elements.

[0024] [3] The hot-rolled steel sheet for a high strength linepipe excellent in terms of HIC resistance according to item [1] or [2], the steel sheet having the chemical composition, in which the ratio of the hardness of a center segregation part to the hardness of a non-segregation part is less than 1.20.

[0025] [4] A method for manufacturing a hot-rolled steel sheet for a high strength linepipe excellent in terms of HIC resistance, the method including heating a steel slab having the chemical composition according to item [1] or [2] at a temperature of 1100°C or higher and 1300°C or lower, performing rough rolling, thereafter performing finish rolling under condition that cumulative rolling reduction ratio is 20% or more in a temperature range of 930°C or lower, performing accelerated cooling on the hot-rolled steel sheet to a temperature of 380°C or higher and 600°C or lower at an average cooling rate of 5°C/sec. or more and 100°C/sec. or less in terms of the temperature of the central part in the thickness direction, and coiling the cooled steel sheet into a coil shape.

[Advantageous Effects of Invention]

[0026] According to the present invention, by strictly controlling the hardness of a center segregation part through optimization of the steel microstructure, it is possible to manufacture a hot-rolled steel sheet for an electric resistance welded steel linepipe that has an improved HIC resistance after formation of the electric resistance welded steel pipe, which has been subjected to large plastic strain and that can be used without any problem under a harsh environment equivalent to a NACE solution. In addition, the hot-rolled steel sheet manufactured using the present invention can also be used for a spiral steel pipe for a linepipe.

[Brief Description of Drawings]

[0027]

10

15

20

25

30

35

40

45

50

55

[Fig. 1] Fig. 1 is a diagram illustrating the relationship between (the hardness of a center segregation part / the hardness of a non-segregation part) and a crack length ratio (CLR).

[Fig. 2] Fig. 2 is a diagram illustrating the relationship between an SP value and (the hardness of a center segregation part / the hardness of a non-segregation part).

[Fig. 3] Fig. 3 is a diagram illustrating the positions where the hardness of a center segregation part and the hardness of a non-segregation part were determined.

[Description of Embodiments]

[0028] The reasons for the limitations on the constituent elements of the present invention will be described hereafter.

## 1. Regarding chemical composition

**[0029]** First, the reasons for the limitations on the chemical composition of the steel according to the present invention will be described. Here, % used when describing the chemical composition always represents mass%.

C: 0.02% or more and 0.06% or less

5

10

15

20

25

30

35

40

50

55

**[0030]** C is a chemical element which significantly contributes to an increase in the strength of steel, and such an effect is realized in the case where the C content is 0.02% or more, but, in the case where the C content is more than 0.06%, since a second phase such as a pearlite microstructure is likely to be formed, there is a deterioration in HIC resistance. Therefore, the C content is set to be in a range of 0.02% or more and 0.06% or less, or preferably in a range of 0.03% or more and 0.05% or less.

Si: 0.05% or more and 0.25% or less

**[0031]** Si is a chemical element which is added for solute strengthening and added in order to decrease scale-off quantity when hot rolling is performed, and such an effect is realized in the case where the Si content is 0.05% or more, but, in the case where the Si content is more than 0.25%, since red scale excessively grows, cooling ununiformity occurs when hot rolling is performed, which results in a deterioration in the uniformity of aesthetic appearance and material properties. Therefore, the Si content is set to be in a range of 0.05% or more and 0.25% or less, or preferably 0.10% or more and 0.25% or less. In addition, since there is a deterioration in toughness in an electric resistance weld zone as a result of forming of MnSi-based oxides when electric resistance welding is performed, it is preferable that Si be added so that the ratio Mn/Si be 4.0 or more and 12 or less.

Mn: 0.60% or more and 1.10% or less

**[0032]** Mn is a chemical element which contributes to an improvement in strength and toughness as a result of decreasing the grain diameter of a steel microstructure, and such an effect is realized in the case where the Mn content is 0.60% or more. On the other hand, in the case where the Mn content is increased, since a fine martensite microstructure is more likely to be formed in center segregation part, and since MnS, which becomes the origin of HIC, is more likely to be formed, it is necessary that the Mn content be controlled to be 1.10% or less. Therefore, the Mn content is set to be in a range of 0.60% or more and 1.10% or less, or preferably in a range of 0.75% or more and 1.05% or less.

P: 0.008% or less

**[0033]** Since P is a chemical element which is contained as an inevitable impurity, and since P deteriorates HIC resistance as a result of significantly increasing the hardness of a center segregation part, it is preferable that the P content be as small as possible, however, a P content of 0.008% or less is acceptable. Moreover, since there is an increase in cost due to an increase in refining time in order to markedly decrease the P content, it is preferable that the P content be 0.002% or more.

S: 0.0010% or less

[0034] Since S is, like P, a chemical element which is inevitably contained in steel, and since S forms MnS in steel, it is preferable that the S content be as small as possible, however, a S content of 0.0010% or less is acceptable, or preferably 0.0006% or less.

Nb: 0.010% or more and 0.060% or less

[0035] Nb is a chemical element which contributes to an increase in the strength of steel as a result of precipitating in the form of fine Nb carbonitrides in a coiling process when hot-rolled steel sheet is manufactured. Also, Nb is a chemical element which contributes to an improvement in the toughness of a weld zone as a result of inhibiting the growth of austenite grains when electric resistance welding is performed. Such effects are realized in the case where the Nb content is 0.010% or more. On the other hand, in the case where the Nb content is more than 0.060%, Nb carbonitrides having a large grain diameter, which become the origins of HIC, are more likely to be formed. Therefore, the Nb content is set to be in a range of 0.010% or more and 0.060% or less, or preferably in a range of 0.030% or more and 0.060% or less.

Ti: 0.001% or more and 0.020% or less

**[0036]** Ti is a chemical element which is added in order to render N, which significantly deteriorates the toughness of steel, harmless by fixing N in the form of TiN. Such an effect is realized in the case where the Ti content is more than 0.001%. On the other hand, in the case where the Ti content is more than 0.020%, since there is an increase in the amount of Ti carbonitrides which precipitate along the cleavage plane of Fe, there is a deterioration in the toughness of steel. Therefore, the Ti content is set to be in a range of 0.001% or more and 0.020% or less, or preferably in a range of 0.005% or more and 0.015% or less.

10 Mo: 0.05% or less

15

25

30

35

40

45

55

**[0037]** Mo is a chemical element which is significantly effective for improving the toughness and strength of steel by improving hardenability, but, since Mo forms a martensite microstructure as a result of being concentrated in a center segregation part, there is a deterioration in HIC resistance. Therefore, it is preferable that the Mo content be as small as possible, however, a Mo content of 0.05% or less is acceptable. It is more preferable that the Mo content be 0.01% or less.

Cr: 0.05% or more and 0.50% or less

[0038] Cr is a chemical element which is effective for improving the toughness and strength of steel by improving hardenability, and such an effect is realized in the case where the Cr is added 0.05% or more, but, in the case where the Cr is added more than 0.50%, there is a significant deterioration in the toughness of a weld zone as a result of forming Cr oxides when electric resistance welding is performed. In order to inhibit such a deterioration, the Cr content is set to be in a range of 0.05% or more and 0.50% or less, or preferably in a range of 0.05% or more and 0.30% or less.

Al: 0.01% or more and 0.08% or less

**[0039]** Although Al is added as a deoxidation agent, there is insufficient deoxidation effect in the case where the Al content is less than 0.01%, and, on the other hand, there is a deterioration in HIC resistance and toughness due to an increase in the amount of Al-based oxides having a large grain diameter which are retained in steel in the case where the Al content is more than 0.08%. Therefore, the Al content is set to be in a range of 0.01% or more and 0.08% or less, or preferably in a range of 0.01% or more and 0.05% or less.

Ca: 0.0005% or more and 0.0050% or less

**[0040]** Ca is a chemical element which is effective for improving HIC resistance by controlling the shape of sulfide-based inclusions, and such an effect is realized in the case where the Ca content is 0.0005% or more. On the other hand, in the case where the Ca content is more than 0.0050%, such an effect becomes saturated, and, in addition, there is a deterioration in HIC resistance as a result of forming a large amount of Ca oxides. Therefore, the Ca content is set to be in a range of 0.0005% or more and 0.0050% or less, or preferably in a range of 0.0010% or more and 0.0030% or less.

O: 0.005% or less

**[0041]** Since oxygen deteriorates hot workability, corrosion resistance, toughness, and HIC resistance as a result of forming various oxides, it is preferable that the oxygen content be as small as possible, however, an oxygen content of 0.005% or less is acceptable, or preferably 0.0035% or less.

[0042] In the present invention, one or more selected from among Cu, Ni, and V may be further added in the amounts described below.

50 Cu: 0.50% or less

**[0043]** Cu is a chemical element which contributes to an improvement in the toughness and strength of steel through an improvement in hardenability, and, since Cu is less likely to be concentrated in a center segregation part than Mn and Mo which have similar effect, Cu can increase the strength of steel without deteriorating HIC resistance. Therefore, Cu is added in accordance with the strength grade. Such an effect is realized in the case where the Cu content is 0.05% or more, but, in the case where the Cu content is more than 0.50%, the effect becomes saturated and there is an unnecessary increase in cost. Therefore, the Cu content is 0.50% or less, or preferably 0.40% or less.

Ni: 0.50% or less

[0044] Ni is, like Cu, a chemical element which contributes to an improvement in the toughness and strength of steel through an improvement in hardenability, and, since Ni is less likely to be concentrated in a center segregation part than Mn and Mo which have a similar effect, Ni can increase the strength of steel without deteriorating HIC resistance. Therefore, Ni is added in accordance with the strength grade. Such an effect is realized in the case where the Ni content is 0.05% or more, but, in the case where the Ni content is more than 0.50%, the effect becomes saturated and there is an unnecessary increase in cost. Therefore, the Ni content is 0.50% or less, or preferably 0.40% or less.

10 V: 0.10% or less

15

20

30

35

40

50

**[0045]** V is a chemical element which contributes to an increase in the strength of steel through solute strengthening and precipitation strengthening in the case where the V content is 0.005% or more, but, in the case where the V content is more than 0.10%, since there is an increase in the hardness of a center segregation part, there is a deterioration in HIC resistance. Therefore, the V content is set to be 0.10% or less, or preferably 0.080% or less.

SP: 1.90 or less

[0046] In the present invention, an SP value, which is derived from the contents of various alloy chemical elements, satisfies expression (1) below.

$$SP \leq 1.90 \cdots (1)$$

where SP is derived from SP = Mn + Mo +  $11.3 \times C + 0.29 \times (Cu + Ni) + 0.60 \times Cr + 0.88 \times V$ , where atomic symbols in the equation respectively represent the contents (mass%) of the corresponding chemical elements, and where the atomic symbol of a chemical element which is not added is assigned a value of 0 (zero).

[0047] An SP value was formulated in order to estimate the hardness of a center segregation part of a hot-rolled steel sheet which is used as a raw material of an electric resistance welded steel pipe using the contents of various alloy chemical elements, and, since the chemical elements are markedly concentrated in a center segregation part in the case where the SP value is more than 1.90, the condition that the hardness ratio of a center segregation part to a non-segregation part is less than 1.20 is not satisfied. In addition, since the hardness ratio of a center segregation part to a non-segregation part decreases with decreasing SP value, it is necessary to control the upper limit of the SP value to be, for example, 1.75 in the case where it is required that HIC resistance be further improved in order to achieve a CLR of 5% or less.

EC: 1.2 or more and 4.0 or less

[0048] Moreover, in the present invention, it is preferable that an EC value which is described below satisfy expression (2) below in order to effectively render sulfide-based inclusions harmless by adding Ca.

$$1.2 \le EC \le 4.0$$
 ··· (2),

where EC is expressed by EC = [Ca]eff / (1.25  $\times$  S), where [Ca]eff is derived from Ca - (0.18 + 130  $\times$  Ca)  $\times$  O, and where atomic symbols Ca, S, and O in the equations respectively represent the contents (mass%) of the corresponding chemical elements.

[0049] The EC value indicates whether the content of Ca, which is added in order to control the shape of sulfide-based inclusions, is sufficient to form CaS, and the Ca content is insufficient in the case where the EC value is less than 1.2, which results in MnS, which becomes the origin of HIC, being formed. On the other hand, in the case where the EC value is more than 4.0, since Ca-based oxides are formed in a large amount, there is a deterioration in HIC resistance due to a deterioration in the cleaning level of steel. Therefore, it is preferable that the EC value be in a range of 1.2 or more and 4.0 or less, or more preferably in a range of 1.4 or more and 3.6 or less.

[0050] Here, the remainder of the chemical elements other than constituents described above consists of Fe and inevitable impurities. However, other trace elements may be added as long as the effects of the present invention are not decreased.

## 2. Regarding metallic structure

10

15

20

30

35

40

45

50

55

[0051] Subsequently, the metallic structure of the present invention will be described.

[0052] It is necessary to form a metallic structure composed of a bainitic-ferrite microstructure in order to achieve not only a high strength of X52 (a YS of more than 380 MPa) or more in accordance with API standards but also minimum required toughness (a ductile-brittle transition temperature of -60°C or lower in a Charpy impact test) for a steel pipe which is used for a linepipe. Since there is a deterioration in yield strength, toughness, and HIC resistance in the case where different kinds of microstructures such as ferrite, fine martensite, pearlite, and residual austenite exist in a bainitic-ferrite microstructure, it is preferable that the area fractions of the microstructures other than a bainitic-ferrite microstructure be as small as possible. However, in the case where the area fractions of the microstructures other than a bainitic-ferrite microstructure are markedly small, since the influences of the microstructures other than a bainitic-ferrite microstructure are negligible small, the microstructures other than a bainitic-ferrite microstructure may be included to some extent. Specifically, a microstructure having a total area fraction of the steel microstructures other than a bainitic-ferrite microstructure (such as a ferrite microstructure, a fine martensite microstructure, a pearlite microstructure, and a residual austenite microstructure) of less than 3% may be considered to be a single bainitic-ferrite microstructure and is included in the present invention.

**[0053]** The metallic structure described above can be achieved by using steel having the chemical composition described above and the manufacturing method described below.

## 3. Regarding the hardness of a center segregation part

**[0054]** From the results of the investigations regarding the relationship between the results of the HIC test on an electric resistance welded steel linepipe and the hardness of a center segregation part of a steel sheet, it was found that there is a case where the condition that a CLR is 15% or less cannot be satisfied even if the Vickers hardness of a center segregation part is controlled to be Hv 230 or less. From the results of the investigations regarding the reason for that conducted from the viewpoint of material uniformity, it was found that, as Fig. 1 illustrates, the CLR is 15% or less in the case where the hardness ratio of a center segregation part to a non-segregation part (the Vickers hardness of a center segregation part/the Vickers hardness of a non-segregation part) is less than 1.20. Then, from the results of the investigations regarding a steel chemical composition with which the ratio of the hardness of a center segregation part to the hardness of a non-segregation part becomes less than 1.20, it was found that, as Fig. 2 illustrates, the SP value of the steel chemical composition with which the ratio of the hardness of a center segregation part to the hardness of a non-segregation part becomes less than 1.20 is 1.90 or less.

[0055] Here, the hardness of a center segregation part and the hardness of a non-segregation part were, as Fig. 3 illustrates, respectively determined for 15 points each on a center segregation line and in a portion located at 200  $\mu$ m from the center segregation line, and the arithmetic average values of the determined values were derived, where the center segregation line was exposed by performing etching using a 2%-nital solution for a duration of 30 seconds or more on a test piece for microstructure observation.

## 4. Regarding manufacturing conditions

[0056] Subsequently, manufacturing conditions for achieving the steel microstructure described above will be described.

[0057] A slab heating temperature is set to be 1100°C or higher and 1300°C or lower. In the case where the temperature is lower than 1100°C, since the temperature is not high enough for carbides, which are formed in steel when continuous casting is performed, to completely form solid solutions, the required strength cannot be achieved. On the other hand, in the case where the temperature is higher than 1300°C, since there is a marked increase in austenite grain diameter, there is a deterioration in toughness. Here, this temperature refers to the temperature of the interior of the heating furnace, and the center of the slab is presumed to be heated to this temperature.

[0058] In finish rolling, it is necessary that finish rolling be performed under the condition that cumulative rolling reduction ratio is 20% or more at a temperature of 930°C or lower. In the case where the cumulative rolling reduction ratio is less than 20%, since there are an insufficient number of nucleation sites of a bainitic-ferrite microstructure, there is an excessive increase in the grain diameter of the microstructure, which results in a deterioration in toughness. However, in the case where the cumulative rolling reduction ratio is more than 80%, since the effect becomes saturated, and since a very high load is applied to a rolling mill, it is preferable that the upper limit of the cumulative rolling reduction ratio be 80% or less.

**[0059]** The average cooling rate for the central part in the thickness direction of a steel sheet is set to be 5°C/sec. or more and 100°C/sec. or less. In the case where the cooling rate is less than 5°C/sec, the area fractions of a ferrite microstructure and/or a pearlite microstructure become 3% or more even if hardenability increasing chemical elements

such as Cu, Ni, and Cr are added. Therefore, it is necessary that the cooling rate be 5°C/sec. or more. On the other hand, in the case where the cooling rate is more than 100°C/sec, the area fraction of a martensite microstructure becomes 3% or more. The cooling rate of the central part in the thickness direction of a steel sheet was calculated by deriving the temperature history of the central part in the thickness direction of the steel sheet by performing heat-transfer calculation using the cooling capacity (heat-transfer coefficient) of a run-out, which had been investigated in advance, and the surface temperature of the steel sheet, which had been determined using a radiation thermometer on the run-out. [0060] The cooling stop temperature is set to be in a range of 380°C or higher and 600°C or lower. In the case where the cooling stop temperature is higher than 600°C, since the area fraction of a ferrite microstructure and a pearlite microstructure becomes 3% or more, and since there is an increase in the diameter of precipitation strengthening grains such as Nb carbonitrides, there is a decrease in strength. On the other hand, in the case where the cooling stop temperature is lower than 380°C, since there is an improvement in the deformation resistance of a steel sheet, it is difficult to coil the steel sheet into a coil shape, and there is a decrease in strength due to precipitation strengthening

#### 15 [EXAMPLE 1]

grains such as Nb carbonitrides not being precipitated.

5

10

20

25

30

35

40

45

50

55

[0061] By performing hot rolling on steel materials having the chemical compositions given in Table 1 under the hot rolling conditions and the cooling conditions given in Table 2, and by coiling the hot-rolled steel sheets, hot-rolled steel sheets having the thicknesses given in Table 2 were obtained. Here, steel grade G through K are comparative example steels having a chemical composition, SP value or the like which is out of the range according to the present invention.

9

				Steel	Steel	Steel	Steel	teel	teel	ive	ive	ive	ive	ive
5			Note	Example S	Example S	Example S	Example S	Example Steel	Example Steel	Comparative Example Steel				
			EC Value*2	2.1	2.6	2.2	3.5	3.5	2.5	2.0	2.6	2.5	4.5	1.5
10			SP Valuue*1	1.68	1.57	1.50	1.63	1.62	1.87	1.79	1.79	2.00	1.83	2.13
15			0	0.0025	0.0017	0.0031	0.0022	0.0022	0.0025	0.0020	0.0018	0.0016	0.0015	0.0016
			۸		-		-	080.0	090'0	-	-	0.045	0.020	-
20			Ċ	0.15	0.10	0.10	0.25	0:30	0.08	ı	1	0.08	1	0.10
			Z	ı	1	0.34	0.10	60.0	0:30	0.14	0.15	0.42	1	
25			Cu	ı	ı	0.37	0.12	ı	0:30	0.17	0.15	0.40	1	
30	[Table 1]	mass%	Са	0.0022	0.0025	0.0028	0.0030	0.0030	0.0025	0.0025	0.0021	0.0023	0.0045	0.0025
	E	╘	AI	0.045	0.040	0.038	0.033	0.033	0.042	0.045	0.034	0.055	0.035	0.040
35			Мо	0.01	0.01	0.02	0.01	0	0	0	0.20	0	0.03	0.17
			!L	0.012	0.010	0.008	0.009	0.009	800'0	800'0	0.010	0.012	0.013	0.009
40			qN	0.045	0.025	0.042	0.035	0.035	0.044	0.028	0.042	0.025	0.055	0.034
45			S	0.0004	0.0005	0.0004	0.0004	0.0004	0.0004	9000'0	0.0004	9000.0	9000'0	0.0009
40			Ь	900'0	0.007	0.005	0.005	0.005	900'0	0.005	900'0	800.0	0.004	900.0
50			Mn	06.0	1.05	92.0	0.84	1.00	1.03	1.25	1.05	1.00	1.10	1.45
			Si	0.18	0.13	0.13	0.10	0.16	0.13	0.13	0.13	0.13	0.13	0.19
55			0	90.0	0.04	0.04	0.05	0.03	0.05	0.04	0.04	90.0	0.06	0.04
			Steel Grade	٧	В	0	Q	Ш	Ь	9	Н	_	ſ	ス

Annotation: An underlined portion indicates a value out of the range according to the present invention.
\*1 SP=Mn+Mo+11.3xC+0.29x(Cu+Ni)+0.60xCr+0.88xV, where an atomic symbols in the equation respectively represent the contents (mass%) of the corresponding chemical elements.

5	Note	Example	Comparative Example																
10	Cooling Stop Temperature (°C)	540	200	450	200	520	260	420	480	530	510	500	520	520	520	650	550	540	540
15	Average Cooling Rate of Central Part in Thickness Direction (°C/sec.)	25	80	50	20	10	25	09	55	30	10	15	20	20	2	20	30	10	15
25 30	Finishing Delivery Temperature (°C)	820	810	840	840	810	810	820	820	810	810	830	810	810	820	820	810	810	820
35	Cumulative Rolling Reduction Ratio in Finish Rolling (%)	40	55	25	45	22	99	40	40	25	22	33	55	15	55	55	09	55	40
40 45	Slab Heating Temperature (°C)	1250	1200	1200	1200	1200	1200	1200	1200	1200	1150	1200	1350	1200	1200	1200	1200	1200	1150
50	Thickness (mm)	16	22	10	12	19	25	14	16	19	18	12	19	19	19	19	22	19	16
55	Steel	4	В	ပ	၁	С	၁	Q	۵	Q	В	Ь	С	С	С	С	9	н	_
	Steel Sheet No.	~	7	ဧ	4	2	9	7	80	6	10	11	12	13	14	15	16	17	18

5	Note	Comparative Example	Comparative Example	
10	Cooling Stop Temperature (°C)	540	540	
15	g Rate of Thickness //sec.)			
20	Average Cooling Rate of Central Part in Thickness Direction (°C/sec.)	15	10	
25 (panujunoo)	Finishing Delivery Temperature (°C)	820	830	present inventior
30 (conti	ing in (%)			ling to the
35	Cumulative Rolling Reduction Ratio in Finish Rolling (%)	40	22	Annotation: An underlined portion indicates a value out of the range according to the present invention.
40	ing (°C)			lue out of
45	Slab Heating Temperature (°C)	1250	1250	indicates a va
50	Thickness (mm)	16	20	erlined portior
	Steel Grade	ſ	X	n: An und
55	Steel Sheet No.	19	20	Annotatio

**[0062]** Using test pieces which had been collected from the obtained hot-rolled steel sheet, and by performing microstructure observation, a tensile test, a Charpy impact test, hardness determination, and a HIC test, tensile properties, toughness, and HIC resistance were evaluated.

**[0063]** By collecting a test piece for microstructure observation from the obtained hot-rolled steel sheet, by polishing and etching a cross-section in the rolling direction, and by using an optical microscope (at a magnification of 400 times) and an electron scanning microscope (at a magnification of 1000 times), photographs were taken for 5 microscopic fields or more in the central part in the thickness direction of the steel sheet in order to observe the kinds of microstructures and whether or not steel microstructures other than a bainitic-ferrite microstructure (such as ferrite, fine martensite, pearlite, and residual austenite) existed.

**[0064]** A tensile test piece was collected from the obtained hot-rolled steel sheet so that the longitudinal direction was at a right angle to the rolling direction (C direction), and a tensile test was performed at room temperature in accordance with API-5L specification in order to determine yield strength YS (deformation stress for a nominal strain of 0.5%) and tensile strength TS.

[0065] A v-notched test piece was collected from the central part in the thickness direction of the obtained hot-rolled steel sheet so that the longitudinal direction was at a right angle to the rolling direction (C direction), and absorbed energy and a percent brittle fracture were determined by performing a Charpy impact test at a temperature range of -140°C to 0°C in accordance with JIS Z 2242 in order to determine a temperature (fracture transition temperature) at which a percent brittle fracture was 50%. Here, three test pieces were used for one temperature in order to obtain the arithmetic averages of the determined absorbed energy and percent brittle fracture.

[0066] The hardness of a center segregation part and the hardness of a non-segregation part were respectively determined for 15 points each on a segregation line and in a portion located at 200 µm from the segregation line, and the arithmetic average values of the determined values were derived, where the segregation line was exposed by performing etching using a 2%-nital solution for a duration of 30 seconds or more on a test piece for microstructure observation (Fig. 3). Here, the hardness was determined using a Vickers hardness meter with a testing force of 0.3 kgf. The hardness ratio was calculated by dividing the hardness of a segregation part by the hardness of a non-segregation part.

[0067] Using a HIC test piece having the thickness of the steel sheet, a width of 20 mm, and a length of 100 mm which was collected from the obtained hot-rolled steel sheet so that the longitudinal direction was the rolling direction of the steel sheet, a HIC test was performed using an A solution in accordance with NACE TM 0284 in order to evaluate HIC resistance. Here, 10 test pieces were used for one coil, and a compressive strain of 10% in a width direction was applied to the test pieces in advance in order to simulate plastic strain which is applied to a steel sheet when forming is performed in a process for manufacturing an electric resistance welded steel pipe. From the test results, in the case where CLR was 15% or less for all the test pieces for one coil, the coil was judged as satisfactory (O) in terms of HIC resistance. In the case where the CLR was more than 15% for one or more of the test pieces for one coil, the coil was judged as unsatisfactory (x) in terms of HIC resistance.

[0068] The obtained results are given in Table 3.

10

15

20

25

30

35

40

45

50

55

[Table 3]

	[Table 5]									
Steel Sheet No.	Steel Grade	Metallic Structure	Yield Strength (MPa)	Tensile Strength (MPa)	Charpy (vTrs)	Hardness Ratio	HIC Resistance	Note		
1	Α	BF	511	585	-70	1.06	0	Example		
2	В	BF	435	508	-120	1.04	0	Example		
3	С	BF	490	557	-100	1.01	0	Example		
4	С	BF	495	563	-125	1.01	0	Example		
5	С	BF	489	563	-85	1.01	0	Example		
6	С	BF	482	560	-95	1.01	0	Example		
7	D	BF	480	546	-130	1.07	0	Example		
8	D	BF	494	554	-100	1.07	0	Example		
9	D	BF	497	563	-95	1.07	0	Example		
10	E	BF	500	567	-80	1.06	0	Example		
11	F	BF	534	616	-100	1.17	0	Example		

(continued)

i	Steel Sheet No.	Steel Grade	Metallic Structure	Yield Strength (MPa)	Tensile Strength (MPa)	Charpy (vTrs)	Hardness Ratio	HIC Resistance	Note
	12	С	BF	488	558	-40	1.02	0	Comparative Example
0	13	С	BF	516	573	-50	1.01	0	Comparative Example
	14	С	BF+F+P	467	539	-50	1.02	×	Comparative Example
5	15	С	F+P	460	545	-45	1.02	×	Comparative Example
	16	G	BF	472	547	-100	1.16	×	Comparative Example
0	17	Н	BF	498	573	-110	1.15	×	Comparative Example
	18	Ī	BF	476	548	-70	<u>1.24</u>	×	Comparative Example
5	19	<u>J</u>	BF	505	582	-60	1.17	×	Comparative Example
	20	<u>K</u>	BF	533	600	-100	1.30	×	Comparative Example
	Annotation: An underlined portion indicates a value out of the range according to the present invention.								

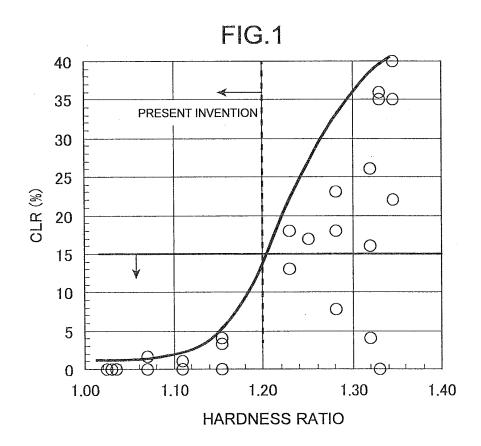
[0069] The examples of the present inventions were all steel sheets having a high yield strength YS of 380 MPa or more, minimum required toughness for a linepipe as indicated by a vTrs of -60°C or lower, and excellent HIC resistance as indicated by a hardness ratio of less than 1.20. On the other hand, the comparative examples, which were out of the range according to the present invention, did not achieve the desired properties for a hot-rolled steel sheet for a high strength electric resistance welded steel pipe excellent in terms of HIC resistance, because the desired toughness was not achieved, or because there was a deterioration in HIC resistance.

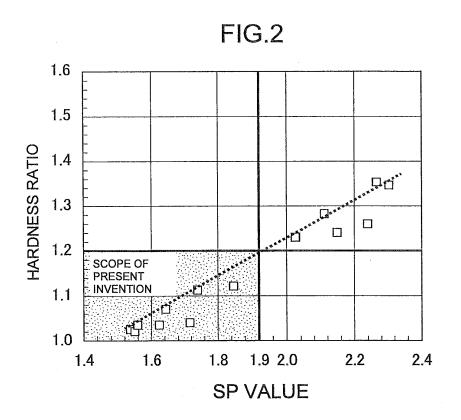
## Claims

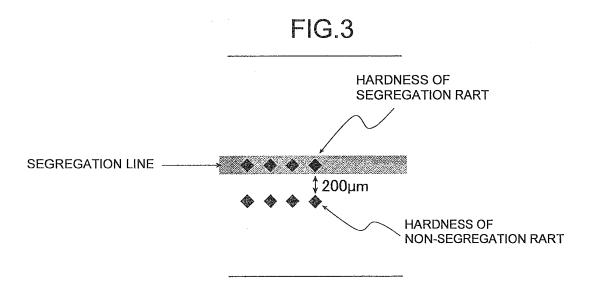
1. A hot-rolled steel sheet for a high strength linepipe, the steel sheet having a chemical composition containing, by mass%, C: 0.02% or more and 0.06% or less, Si: 0.05% or more and 0.25% or less, Mn: 0.60% or more and 1.10% or less, P: 0.008% or less, S: 0.0010% or less, Nb: 0.010% or more and 0.060% or less, Ti: 0.001% or more and 0.020% or less, Mo: 0.05% or less, Cr: 0.05% or more and 0.50% or less, Al: 0.01% or more and 0.08% or less, Ca: 0.0005% or more and 0.0050% or less, O: 0.005% or less, one or more selected from among Cu: 0.50% or less, Ni: 0.50% or less, and V: 0.10% or less, and the balance being Fe and inevitable impurities, and a metallic structure composed of bainitic-ferrite, wherein expression (1) below is satisfied, and wherein the ratio of the hardness of a center segregation part to the hardness of a non-segregation part is less than 1.20:

$$SP \leq 1.90 \cdots (1)$$

where SP is derived from SP = Mn + Mo +  $11.3 \times C + 0.29 \times (Cu + Ni) + 0.60 \times Cr + 0.88 \times V$ , and where atomic symbols in the equation respectively represent the contents (mass%) of the corresponding chemical elements.







### INTERNATIONAL SEARCH REPORT International application No. PCT/JP2014/000320 A. CLASSIFICATION OF SUBJECT MATTER 5 C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/50(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED 10 Minimum documentation searched (classification system followed by classification symbols) C22C38/00, C21D8/02, C22C38/50 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched 15 1922-1996 Jitsuyo Shinan Koho Jitsuyo Shinan Toroku Koho 1996-2014 Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. WO 2010/087512 A1 (JFE Steel Corp.), 05 August 2010 (05.08.2010), Υ 1 claims; paragraphs [0001], [0029], [0033], [0034], [0046]; examples; tables 1, 3, 5, 7, 9, 25 11 & EP 2392681 A1 & US 2012/0018056 A1 & CN 102301015 A & CN 103276291 A & CA 2750291 A & CA 2809171 A 30 & KR 10-2011-0110278 A JP 7-216500 A (Sumitomo Metal Industries, Υ 1 Ltd.), 15 August 1995 (15.08.1995), claims; paragraphs [0001], [0028] to [0035], [0044], [0045]; examples; tables 2, 5 (Family: none) 35 Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority document defining the general state of the art which is not considered — to be of particular relevance date and not in conflict with the application but cited to understand the principle or theory underlying the invention "E" earlier application or patent but published on or after the international filing 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 document which may throw doubts on priority claim(s) or which is 45 cited to establish the publication date of another citation or other special reason (as specified) 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 referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 13 February, 2014 (13.02.14) 25 February, 2014 (25.02.14) Name and mailing address of the ISA/ Authorized officer Japanese Patent Office 55 Telephone No. Form PCT/ISA/210 (second sheet) (July 2009)

# INTERNATIONAL SEARCH REPORT International application No. PCT/JP2014/000320

5	C (Continuation	). DOCUMENTS CONSIDERED TO BE RELEVANT	2014/000320
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
10	А	JP 2010-84170 A (JFE Steel Corp.), 15 April 2010 (15.04.2010), paragraphs [0001], [0038] (Family: none)	1
15	А	JP 2012-167328 A (JFE Steel Corp.), 06 September 2012 (06.09.2012), paragraphs [0001], [0051] (Family: none)	1
20			
25			
30			
35			
40			
45			
50			
55		10 (continuation of second sheet) (July 2000)	

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

## REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

- JP 2006063351 A **[0010]**
- JP 4363403 B **[0010]**
- WO 2005075694 A [0010]

- JP 2011063840 A **[0010]**
- JP 2647302 B **[0010]**
- JP 5271766 A [0010]