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(54) **THICK STEEL PLATE HAVING EXCEPTIONAL HAZ TOUGHNESS AT VERY LOW TEMPERATURES**

(57) This thick steel plate satisfies a prescribed chemical composition, and has a Di value of 2.5-5.0, a sol. N parameter of 20 ppm or less, and an Ni-Ti balance of 0.0024 × ([Ni] - 7.5)^2 + 0.010 - [Ti] or less, and furthermore has a crystal grain diameter of 4.0 μm or less after heating at 700°C × 5s and cooling from 700°C to 500°C in 19 s.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a thick steel plate that is used as a material of structural member requiring cryogenic-temperature properties, for a storage tank for LNG (liquefied natural gas) and so on, particularly a thick steel plate having excellent HAZ toughness at cryogenic temperatures.

BACKGROUND ART

[0002] A natural gas contains methane as a main ingredient and is liquefied at cryogenic temperatures under atmospheric pressure. On that occasion, its volume is decreased to about 1/600. For that reason, a way of storing or transporting the natural gas in the form of a liquid rather than a gas is advantageous. Meanwhile, it is necessary to hold the natural gas at cryogenic temperatures, and therefore, a material having excellent cryogenic-temperature properties is required for an LNG storage tank and so on.

[0003] A thick steel plate that is used for an LNG storage tank and so on is ferrite-based steel. In general, this ferrite-based steel becomes brittle at low temperatures and possibly results in fracture as in ceramics. However, it is possible to overcome such a defect by increasing the addition amount of Ni. On the other hand, for a reason that Ni is an expensive element, a reduction of the Ni content is always required. From the standpoint of a balance between those matters, it is the present situation that 9% Ni steel is used as the material of structural member requiring excellent cryogenic-temperature properties, for an LNG storage tank and so on.

[0004] In general, in order to improve the toughness of steel, it is said that refinement of the microstructure, insurance of stable retained-γ, reduction of fracture starting point, such as MA (Martensite Austenite constituent), coarse inclusions, etc., and improvement of toughness of the matrix are effective. The addition of Ni improves all of the above-described factors without particularly brining harmful influences. Conversely, it may be said that when the steel is subjected to reduction of Ni content, it becomes difficult to obtain the toughness.

[0005] In view of such actual circumstances, in order to overcome the problem of reduction of the toughness to be caused due to the reduction of Ni content, there are made various proposals of ensuring the toughness of a base metal by figuring out heat treatment to ensure mainly a retained-γ fraction in PTL 1 and so on.

[0006] Meanwhile, in a heat affected zone (HAZ), the base metal microstructure formed by heat treatment vanishes, and hence, it is difficult to ensure the retained-γ. For that reason, in order to ensure the HAZ toughness while reducing the Ni content, it is necessary to take measures by any of refinement of microstructure, reduction of fracture starting point, or improvement of toughness of the matrix. There have hitherto been taken techniques of refinement of microstructure or a combination of refinement of microstructure and reduction of fracture starting point as described in NPL 1 and NPL 2. However, according to those conventional techniques, it was not achieved to thoroughly ensure the HAZ toughness at cryogenic temperatures while reducing the Ni content.

CITATION LIST

PATENT LITERATURE

[0007] PTL 1: JP-A-2011-241419

NON-PATENT LITERATURE

[0008]

NPL 1: Kaoru KIMURA, et al., "Improvement of Toughness of 51/2% Ni Steel-Welded Portion (Development VI of Nickel Steels for Low Temperature", Iron and Steel, The Iron and Steel Institute of Japan, Vol. 58 (1972), p.228

NPL 2: Yukito OGIWARA, et al., "Development of 7% Ni-TMCP Steel Plates for LNG Tank (Second Report)", Proceedings of Welding Structure Symposium 2011, Japan Welding Society, Welding Structure Research Committee, 2011, p.459

SUMMARY OF INVENTION

SOLUTION TO PROBLEM

[0009] In order to solve the above-described prior art problems, an object of the present invention is to provide a thick steel plate having excellent HAZ toughness at cryogenic temperatures, that is capable of ensuring HAZ toughness at cryogenic temperatures while minimizing the addition amount of expensive Ni as far as possible.

TECHNICAL SOLUTION

[0010] The thick steel plate having HAZ toughness at a cryogenic temperature in the present invention includes, in terms of mass %, 0.02 to 0.10% of C, 0.40% or less (not including 0%) of Si, 0.5 to 2.0% of Mn, 0.007% or less (not including 0%) of P, 0.007% or less (not including 0%) of S, 0.005 to 0.05% of Al, 5.0 to 7.5% of Ni, 0.025% or less (not including 0%) of Ti, and 0.010% or less (not including 0%) of N, with the remainder being iron and inevitable impurities, and a Di value determined according to the following formula is 2.5 or more and 5.0 or less: $([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times (1.7 - 0.09 \times 6.5)$, a sol. N parameter is 20 ppm or less, an Ni-Ti balance is $\{0.0024 \times ([Ni] - 7.5)^2 + 0.010 - [Ti]\} \geq 0$, and a grain size after heating at 700°C for 5 seconds and cooling from 700°C to 500°C over 19 seconds is 4.0 μm or less, provided that in each of the formulae, [ ] expresses mass %.

[0011] In addition, it is preferred that the thick steel plate further includes, in terms mass %, one or two or more of 1.0% or less (not including 0%) of Cu, 1.2% or less (not including 0%) of Cr, and 1.0% or less (not including 0%) of Mo in terms of mass %.

[0012] In addition, it is preferred that the thick steel plate further includes, in terms mass %, one or two or more of 0.1% or less (not including 0%) of Nb, 0.5% or less (not including 0%) of V, 0.005% or less (not including 0%) of B, and 0.005% or less (not including 0%) of Zr in terms of mass %.

[0013] In addition, it is preferred that the thick steel plate further includes, in terms mass %, one or two of 0.003% or less (not including 0%) of Ca and 0.005% or less (not including 0%) of REM in terms of mass %.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] In accordance with the thick steel plate of the present invention, it is possible to ensure thorough HAZ toughness at cryogenic temperatures to be required in a storage tank for LNG and so on while minimizing the addition amount of expensive Ni to an extent of 5.0 to 7.5 mass % as far as possible.

DESCRIPTION OF EMBODIMENTS

[0015] In order to obtain a thick steel plate having excellent HAZ toughness at cryogenic temperatures, that satisfies a requirement of ($vE_{-196} \geq 41$ J) in a Charpy impact absorption test while minimizing the addition amount of Ni to an extent of 5.0 to 7.5 mass % as far as possible, for the reason that though Ni is added for the purpose of ensuring the toughness, but it is expensive, the present inventors carried out extensive and intensive investigations regarding researches and experiments.

[0016] As a result, it has been found that by not only regulating a component composition of the thick steel plate to a predetermined component composition but also regulating a Di value determined by a component balance that is an indicator of hardenability during quenching to 2.5 or more and 5.0 or less and a sol. N parameter to 20 ppm or less, an Ni-Ti balance to $\{0.0024 \times ([Ni] - 7.5)^2 + 0.010 - [Ti]\} \geq 0$, respectively, and further regulating a grain size after a heat cycle of heating at 700°C for 5 seconds and cooling from 700°C to 500°C over 19 seconds to 4.0 μm or less, the desired excellent HAZ toughness at cryogenic temperatures can be realized, leading to accomplishment of the present invention.

[0017] It is to be noted that the test using a Charpy impact test specimen having a size of several cm as taken from the thick steel plate of the present invention is performed at a cryogenic temperature as -196°C, whereas the test using a large-sized test specimen of a meter size is performed at -165°C. In addition, actual storage tanks for LNG and so on are used at -165°C. Accordingly, the cryogenic temperature as intended in the present invention refers to from -165°C to -196°C.

[0018] Examples of a method of improving the toughness in high Ni steel may include methods, such as insurance of retained-γ fraction, refinement of microstructure size, reduction of low-temperature YS (= improvement in toughness of the matrix), etc. In a heat affected zone (HAZ) where the microstructure formed by heat treatment vanishes by a heat cycle, it may be considered that among those methods, it is an effective method of adopting refinement of the microstructure size or reduction of low-temperature YS. In addition, with respect to the reduction of low-temperature YS, an attention has been paid to control of solute N that is a cause of bringing an increase of YS due to the Cottrell atmosphere and the Ni quantity that is said to be able to reduce low-temperature YS of the matrix.

(The Di value is 2.5 or more and 5.0 or less)

[0019] In the present invention, the Di value that is an indicator of hardenability during quenching can be determined according to the following formula:

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times (1.7 - 0.09 \times 6.5)$$

[0020] In order to obtain a microstructure of a fine size, it is effective to prescribe the Di value for the sake of convenience. In the case where the Di value is less than 2.5, the microstructure becomes rough, and vE_{-196} in the Charpy impact absorption test is decreased. On the other hand, when the Di value is more than 5.0, the hardness increases, and in this case, vE_{-196} in the Charpy impact absorption test is decreased, too. Therefore, an appropriate range of the Di value that is an indicator of hardenability during quenching is set to 2.5 or more and 5.0 or less.

(The sol. N parameter is 20 ppm or less)

[0021] In order to reduce the low-temperature YS to improve the toughness without increasing the addition amount of main additive elements, it is effective to fix an interstitial element that locks on dislocation to impair dislocation motion. In the present invention, an attention has been paid particularly to fixation of solute N.

[0022] Examples of the element fixing solute N may include Al, B, Nb, Ti, and the like. However, since HAZ is influenced by the heat cycle, even when N fixation is made on the base metal, an N compound that is thermally instable is dissolved during the heat cycle in HAZ. In order to achieve N fixation even after the heat cycle in HAZ, it is effective to add Ti capable of forming a thermally stable N compound.

[0023] In view of the facts that measurement from the N compound is difficult according to current measurement accuracy; and that other elements than Ti simultaneously form other compounds, such as oxides, sulfides, etc., and are hardly measured, in the present invention, the Ti compound is used as an indicator of the N fixation. An appropriate range of the sol. N parameter that can be determined according to the following formula is 20 ppm or less in terms of a mass ratio. Though a lower limit value of the sol. N parameter is not particularly prescribed, it is preferably set to -40 ppm or more because there is a concern that when Ti is excessive relative to N, reduction of the toughness following an increase of the hardness is brought.

$$\text{sol. N parameter} = \text{N fixed to all N-Ti} = [\text{all N} - (14/48) \times (\text{compound type Ti})]$$

[0024] Here, the "compound type Ti" refers to a Ti content contained in the Ti compound.

[0025] The mass (unit: ppm) of the compound type Ti can be determined by measuring a Ti concentration (insol. Ti amount) at which the compound is formed by means of electrolytic extraction from a t/4 position of the thick steel plate (t: plate thickness). For example, the extraction may be performed by the iodine methanol method, and the mass of the compound type Ti can be determined by filtering an electrolytic solution after extraction with a filter having a pore size of 0.1 μm and quantitating the Ti amount in the extraction residue remained on the filter by inductively coupled plasma (ICP) emission spectrum analysis.

(The Ni-Ti balance is satisfied with a relationship: $\{0.0024 \times ([Ni] - 7.5)^2 + 0.010 - [Ti]\} \geq 0$)

[0026] By increasing the content of Ni in the steel, it is possible to reduce the low-temperature YS. However, as described previously, in view of the fact that Ni is an expensive element, it is desirable to decrease the content of Ni as far as possible. For such a reason, in the present invention, the Ni-Ti balance at which the above-described effect by the addition of Ti can be obtained was determined through experiments. It may be considered that the effect by the addition of Ti mainly relies upon the above-described sol. N fixation. However, besides, it may also be considered that the refinement of microstructure size by the Ti compound and the like may be considered to be effective, and apart from a Ti-N balance, it is also necessary to control the Ni-Ti balance.

[0027] Specifically, it is necessary to set the Ni-Ti balance so as to satisfy a relationship: $\{0.0024 \times ([Ni] - 7.5)^2 + 0.010 - [Ti]\} \geq 0$. In the present invention, though an upper limit value by this formula is not particularly prescribed, a desired upper value thereof is, for example, 0.0180.

(The grain size after heating at 700°C for 5 seconds and cooling from 700°C to 500°C over 19 seconds is 4.0 μm or less)

[0028] By making the grain size of HAZ fine, the low-temperature toughness of HAZ is improved. However, the grain size of HAZ is influenced by some factors, such as a strain within the microstructure, etc., in addition to the base metal microstructure and the grain size of the base metal, and therefore, it is insufficient to prescribe the grain size of HAZ only by the base metal microstructure. Accordingly, in the present invention, the grain size after a heat cycle of heating at 700°C for 5 seconds and further cooling from 700°C to 500°C over 19 seconds is prescribed. The microstructure after such a heat cycle may be said to be a microstructure of an HAZ-corresponding part. By regulating the grain size after the heat cycle to 4.0 μm or less, it is possible to prepare a thick steel plate having excellent HAZ toughness at cryogenic temperatures as intended in the present invention.

[0029] In the present invention, in addition to the above-described Di value, sol. N parameter, Ni-Ti balance, and grain size after heat cycle, the component composition of the thick steel plate is prescribed. The component composition is described in detail. The content of each of elements (chemical components) is hereunder described merely in terms of %, but all of them are mass %.

(Component Composition)

C: 0.02 to 0.10%

[0030] C is effective for lowering an Ms point to obtain a microstructure of a fine size. In order to effectively exhibit such an action, C must be contained in an amount of at least 0.02% or more. A lower limit of the content of C is preferably 0.03%, and more preferably 0.04%. However, when C is excessively added, the cryogenic-temperature toughness is reduced due to an excessive increase of strength, and therefore, an upper limit thereof is controlled to 0.10%. The upper limit of the content of C is preferably 0.08%, and more preferably 0.06%.

Si: 0.40% or less (not including 0%)

[0031] Si is a useful element as a deoxidizer. Si has an action to prevent Ti from consumption for deoxidation and assist the N fixation. However, when Si is excessively added, a hard martensite island is promoted, leading to reduction of the cryogenic-temperature toughness. Thus, an upper limit thereof is controlled to 0.40%. The upper limit of the content of Si is preferably 0.35%, and more preferably 0.20%. Though a lower limit of the content of Si is not particularly prescribed, it is preferably 0.01%.

Mn: 0.5 to 2.0%

[0032] Mn is effective for lowering an Ms point to obtain a microstructure of a fine size. In order to effectively exhibit such an action, Mn must be contained in an amount of at least 0.5% or more. A lower limit of the content of Mn is preferably 0.6%, and more preferably 0.7%. However, when Mn is excessively added, temper brittleness is brought, whereby the desired cryogenic-temperature toughness cannot be ensured. Thus, an upper limit thereof is controlled to 2.0%. The upper limit of the content of Mn is preferably 1.5%, and more preferably 1.3%.

P: 0.007% or less (not including 0%)

[0033] P is an impurity element causing reduction of the toughness, and therefore, its content is preferably low as far as possible. From the viewpoint of ensuring the desired cryogenic-temperature toughness, the content of P is needed to be controlled to 0.007% or less and is preferably controlled to 0.005% or less. Though it is desirable that the content of P is low as far as possible, it is industrially difficult to decrease the content of P in the steel to 0%.

S: 0.007% or less (not including 0%)

[0034] Similar to P, S is an impurity element causing reduction of the toughness, and therefore, its content is preferably low as far as possible. From the viewpoint of ensuring the desired cryogenic-temperature toughness, the content of S is needed to be controlled to 0.007% or less and is preferably controlled to 0.005% or less. Though it is desirable that the content of S is low as far as possible, it is industrially difficult to decrease the content of S in the steel to 0%.

Al: 0.005 to 0.05%

[0035] Al is a useful element as a deoxidizer. Al has an action to prevent Ti from consumption for deoxidation and assist the N fixation. In addition, Al promotes desulfurization. When the content of Al is insufficient, the concentrations of solute sulfur, solute nitrogen, and so on increase, and the cryogenic-temperature toughness is reduced. Thus, a lower limit thereof is controlled to 0.005%. The lower limit of the content of Al is preferably 0.010%, and more preferably 0.015%. However, when Al is excessively added, oxides, nitrides, and so on are coarsened, and the cryogenic-temperature toughness is reduced, too. Thus, an upper limit thereof is controlled to 0.05%. The upper limit of the content of Al is preferably 0.045%, and more preferably 0.04%.

Ni: 5.0 to 7.5%

[0036] Ni is an effective element for improving the cryogenic-temperature toughness. In order to effectively exhibit such an action, Ni must be contained in an amount of at least 5.0% or more. A lower limit of the content of Ni is preferably 5.2%, and more preferably 5.4%. However, when Ni that is an expensive element is excessively added, an increase of costs of raw material is brought. Thus, an upper limit thereof is controlled to 7.5%. The upper limit of the content of Ni is preferably 6.5%, more preferably 6.2%, and still more preferably 6.0%.

Ti: 0.025% or less (not including 0%)

[0037] Ti is an effective element for fixation of solute N. A lower limit thereof is preferably 0.003%, and more preferably 0.005%. On the other hand, when Ti is excessively added, coarse inclusions are formed to reduce the toughness. Thus, a preferred upper limit of the content of Ti is controlled to 0.025%. The upper limit of the content of Ti is more preferably 0.018%, and still more preferably 0.015%.

N: 0.010% or less (not including 0%)

[0038] When a large quantity of N is present as solute N, the HAZ toughness is reduced. Even if the solute N could be fixed by some method, from the viewpoint of solubility product, all of N activities are preferably small. Thus, an upper limit thereof is controlled to 0.010%. The upper limit of the content of N is preferably 0.006%, and more preferably 0.004%. Though it is desirable that the content of N is low as far as possible, it is industrially difficult to decrease the content of N in the steel to 0%.

[0039] The foregoing are elements contained necessary as prescribed in the present invention, with the remainder being iron and inevitable impurities. In addition, the following tolerable components can be added so long as the actions of the present invention are not impaired.

One or two or more of Cu: 1.0% or less (not including 0%), Cr: 1.2% or less (not including 0%), and Mo: 1.0% or less (not including 0%)

[0040] Cu, Cr, and Mo are each an effective element for lowering an Ms point to obtain a microstructure of a fine size. These elements may be added singly or in combination of two or more thereof. In order to effectively exhibit the above-described action, in the case of adding Cu, its content is preferably 0.05% or more; in the case of adding Cr, its content is preferably 0.05% or more, and in the case of adding Mo, its content is preferably 0.01% or more. However, when each element is excessively added, an excessive improvement of strength is brought, so that the desired cryogenic-temperature toughness cannot be ensured. Thus, in the case of adding Cu, its content is needed to be controlled to 1.0% or less, preferably 0.8% or less, and more preferably 0.7% or less. In addition, in the case of adding Cr, its content is needed to be controlled to 1.2% or less, preferably 1.1 % or less, and more preferably 0.9% or less. In addition, in the case of adding Mo, its content is needed to be controlled to 1.0% or less, preferably 0.8% or less, and more preferably 0.6% or less.

One or two or more of Nb: 0.1% or less (not including 0%), V: 0.5% or less (not including 0%), B: 0.005% or less (not including 0%), and Zr: 0.005% or less (not including 0%)

[0041] Nb, V, B, and Zr, although not comparable to Ti, are each an effective element for fixation of solute N. These elements may be added singly or in combination of two or more thereof. In order to effectively exhibit the above-described action, in the case of adding Nb, its content is preferably 0.005% or more; in the case of adding V, its content is preferably 0.005% or more; in the case of adding B, its content is 0.0005% or more; and in the case of adding Zr, its content is 0.0005% or more. However, when each element is excessively added, an excessive improvement of strength is brought, or coarse inclusions are formed to reduce the toughness. Thus, in the case of adding Nb, its content is needed to be controlled to 0.1% or less, preferably 0.05% or less, and more preferably 0.02% or less. In addition, in the case of adding V, its content is needed to be controlled to 0.5% or less, preferably 0.3% or less, and more preferably 0.2% or less. In addition, in the case of adding B, its content is needed to be controlled to 0.005% or less, preferably 0.003% or less, and more preferably 0.002% or less. In addition, in the case of adding Zr, its content is needed to be controlled to 0.005% or less and preferably 0.004% or less.

One or two of Ca: 0.003% or less (not including 0%) and REM (rare earth element): 0.005% or less (not including 0%)

[0042] Ca and REM are each an element that fixes solute sulfur and further makes sulfides harmless. These elements may be added singly or in combination of two or more thereof. When the content of each of these elements is insufficient, the concentration of solute sulfur in the steel increases, and the toughness is reduced. Thus, in the case of adding Ca, its content is preferably controlled to 0.0005% or more, and in the case of adding REM, its content is preferably controlled to 0.0005% or more. However, when each element is excessively added, sulfides, oxides, nitrides, and so on are coarsened, so that the toughness is reduced, too. Thus, in the case of adding Ca, its content is needed to be controlled to 0.003% or less and preferably 0.0025% or less. In addition, in the case of adding REM, its content is needed to be controlled to 0.005% or less and preferably 0.004% or less.

[0043] The REM (rare earth element) as referred to herein means a group of elements including Sc (scandium) and Y (yttrium) in addition to lanthanide elements (15 elements of from La (atomic No. 57) to Lu (atomic No. 71) in the periodic table), and these elements can be used singly or in combination of two or more thereof. In addition, the content of REM means a content of a sole element in the case where only one REM is contained or a total content in the case where two or more REMs are contained.

[0044] However, Sc and Y are low in an atomic weight as compared with other REMs. Typically, an inexpensive misch metal containing plural lanthanide elements is used, but Sc and Y may also be used. In order to suppress the formation of coarse sulfides, oxides, and nitrides of REM, in the case of adding Sc and Y, they are added so as to satisfy the following formula.

$$(2/3) \times (1/88) \times (226) \times (1/4.8) \times [\text{REM (Sc, Y)}] + (2/3) \times (1/140) \times (327) \times (1/7) \times [\text{REM (others)}] \leq 0.0015$$

[0045] In the foregoing formula, [REM (Sc, Y)] represents an addition amount (mass %) of Sc and Y; and [REM (others)] represents an addition amount (mass %) of REMs other than Sc and Y.

[0046] In addition, among REMs, Ce and La are a preferred element. In addition, the addition form of REM is not particularly limited, REM may be added in a form of misch metal mainly containing Ce and La (for example, Ce: about 70% and La: about 20 to 30%), or may be added in a form of a simple substance of Ce or La, or the like.

(Manufacturing Requirements)

[0047] The thick steel plate of the present invention can be obtained through steps of melting steel satisfying the above-described component composition by a usual melting method to prepare a slab, followed by performing usual heating, hot rolling (rough rolling and finish rolling), and cooling. However, by carrying out the heat treatment of the base metal under the following condition, the thick steel plate capable of surely satisfying the requirements of the present invention can be manufactured.

[0048] Namely, the heat treatment of the base metal is carried out in a temperature region of 630°C to Ac3 (two-phase region). By carrying out the heat treatment under such a condition, the microstructure of the HAZ part after welding can be subjected to grain refining. That is, in the present invention, the grain size after a heat cycle of heating at 700°C for 5 seconds and cooling from 700°C to 500°C over 19 seconds can be regulated to 4.0 μm or less. In the case of carrying out the heat treatment under a condition exceeding Ac3, the grain size after the above-described heat cycle becomes coarse, so that the predetermined toughness cannot be satisfied.

EXAMPLES

[0049] Although the invention is now described in detail with some Examples, the invention should not be limited thereto, and modifications or alternations may be made within the scope without departing from the gist described before and later, all of which are included in the technical scope of the invention.

(Example 1)

[0050] Thick steel plates having respective component compositions shown in Tables 1 and 2 were used, and from a t/4 position (t: plate thickness) of each of those thick steel plates, a small specimen having a size of 12.5t × 55W ×

33L in parallel to the plate width direction was taken. Thereafter, from the small specimen to which a heat treatment described in each of Tables 3 and 4 had been applied, every two Charpy impact test specimens (JIS Z2242 V-notch test specimens) were taken and measured for absorption energy at -196°C according to the essentials described in JIS Z2242. As for the heat cycle condition, heating in correspondence to a heat input of 4.2 kJ/mm is performed at 700°C for 5 seconds, and cooling is then performed from 700°C to 500°C over 19 seconds. As a result of the measurement, the case where an average value of the absorption energy at -196°C is 41 J or more, namely a relationship of ($vE_{-196} \geq 41$ J) is satisfied was evaluated to be excellent in the cryogenic temperature toughness. Test results are shown in Tables 3 and 4.

[0051] As described previously, the sol. N parameter can be determined according to the following numeral formula:

$$\text{sol. N parameter} = \text{N fixed to all N-Ti} = [\text{all N} - (14/48) \times (\text{compound type Ti})]$$

[0052] In addition, the grain size was measured as follows. That is, in the microstructure just beneath the fractured surface photographed by an optical microscope, with respect to the range of 150 μm substantially in the notch vertical direction and 200 μm in the notch horizontal direction, a site divided by a segment of black contrast having a width of 0.5 μm or less was defined as a microstructure unit, 50 or more structure units were measured by the segment method relative to the notch horizontal direction, and an average thereof was defined as the grain size.

[Table 1]

No.	Classification	C	Si	Mn	P	S	Al	Ni	N
1	Invention Example	0.05	0.06	0.85	<0.005	<0.0005	0.032	5.64	0.0040
2	Invention Example	0.05	0.06	0.90	<0.004	0.001	0.030	5.64	0.0040
3	Invention Example	0.05	0.06	1.25	<0.004	0.001	0.030	5.62	0.0034
4	Invention Example	0.09	0.05	0.87	<0.004	0.002	0.020	6.15	0.0031
5	Invention Example	0.02	0.20	1.48	<0.004	0.001	0.030	5.33	0.0032
6	Invention Example	0.03	0.38	0.80	<0.004	0.004	0.038	7.25	0.0020
7	Invention Example	0.05	0.29	0.54	<0.004	0.001	0.033	6.24	0.0038
8	Invention Example	0.04	0.12	1.58	<0.004	0.001	0.034	5.92	0.0029
9	Invention Example	0.05	0.06	0.79	0.007	0.002	0.038	7.08	0.0029
10	Invention Example	0.04	0.19	1.19	<0.004	0.007	0.011	5.65	0.0045
11	Invention Example	0.07	0.10	0.66	<0.004	0.003	0.047	5.88	0.0034
12	Invention Example	0.04	0.02	0.86	0.005	0.002	0.041	5.09	0.0033
13	Invention Example	0.03	0.22	1.72	<0.004	0.001	0.019	5.70	0.0031
14	Invention Example	0.04	0.05	0.90	<0.004	0.001	0.031	5.05	0.0075
15	Invention Example	0.05	0.11	0.74	<0.004	0.003	0.035	5.86	0.0058
16	Invention Example	0.04	0.19	0.82	<0.004	0.001	0.035	5.62	0.0033
17	Invention Example	0.04	0.15	0.54	0.006	0.005	0.029	5.15	0.0031
18	Invention Example	0.04	0.22	1.03	<0.004	0.002	0.034	6.89	0.0035
19	Invention Example	0.05	0.08	0.65	<0.004	0.001	0.031	5.68	0.0032
20	Invention Example	0.06	0.08	0.89	0.005	0.001	0.030	6.27	0.0032
21	Invention Example	0.04	0.13	1.13	<0.004	0.001	0.031	6.20	0.0032

[Table 1 continued]

No.	Classification	Cu	Cr	Mo	Ti	Nb	V	B	Ca	REM	Zr
1	Invention Example	-	0.40	0.15	0.012	-	-	-	-	-	-
2	Invention Example	-	0.40	0.30	0.012	-	-	-	-	-	-
3	Invention Example	-	0.70	0.20	0.006	-	-	-	-	-	-
4	Invention Example	0.21	0.36	0.05	0.009	-	-	-	-	-	-
5	Invention Example	-	-	0.82	0.006	-	-	-	-	0.0042	-
6	Invention Example	-	-	0.75	0.001	0.027	-	-	-	0.0023	-
7	Invention Example	0.15	0.13	0.67	0.007	-	-	-	-	-	-
8	Invention Example	-	0.41	0.06	0.008	-	-	-	0.0019	-	-
9	Invention Example	-	-	0.83	0.008	0.012	-	-	-	-	-
10	Invention Example	-	-	0.52	0.010	-	-	-	-	-	0.0022
11	Invention Example	-	1.05	-	0.010	-	0.25	-	-	-	-
12	Invention Example	0.51	0.50	0.53	0.005	-	-	0.0019	-	-	-
13	Invention Example	-	-	0.61	0.010	-	0.02	-	-	-	0.0046
14	Invention Example	-	0.71	0.22	0.024	-	-	0.0007	0.0011	-	-
15	Invention Example	0.10	0.26	0.38	0.016	-	-	-	-	-	-
16	Invention Example	-	1.15	-	0.006	-	0.05	-	0.0022	-	-
17	Invention Example	-	0.83	0.52	0.023	-	-	-	-	0.0030	-
18	Invention Example	0.42	-	0.43	0.010	0.055	-	-	-	-	-
19	Invention Example	-	0.96	0.05	0.008	-	0.38	-	-	-	-
20	Invention Example	0.15	-	0.50	0.006	-	-	0.0033	-	-	-
21	Invention Example	-	0.70	-	0.009	-	0.11	-	0.0027	-	-

[Table 2]

No.	Classification	C	Si	Mn	P	S	Al	Ni	N
22	Comparative Example	0.08	0.05	1.20	<0.004	0.002	0.020	6.15	0.0031
23	Comparative Example	0.08	0.05	1.20	<0.004	0.002	0.020	6.15	0.0045
24	Comparative Example	0.11	0.10	0.75	<0.004	0.004	0.027	6.21	0.0038
25	Comparative Example	0.05	0.08	0.89	0.008	0.001	0.033	5.75	0.0032
26	Comparative Example	0.10	0.42	1.12	<0.004	0.001	0.031	6.25	0.0032
27	Comparative Example	0.03	0.04	2.15	<0.004	0.002	0.029	6.33	0.0032
28	Comparative Example	0.05	0.08	0.48	0.005	0.001	0.032	5.79	0.0038
29	Comparative Example	0.04	0.10	1.42	<0.004	0.008	0.038	6.50	0.0051
30	Comparative Example	0.01	0.08	1.05	<0.004	0.001	0.052	4.80	0.0045
31	Comparative Example	0.08	0.12	0.88	<0.004	0.001	0.004	6.40	0.0107
32	Comparative Example	0.05	0.08	0.79	<0.004	0.004	0.037	6.49	0.0032
33	Comparative Example	0.06	0.11	0.93	0.006	0.001	0.029	5.55	0.0029
34	Comparative Example	0.04	0.10	1.34	<0.004	0.001	0.045	6.25	0.0030
35	Comparative Example	0.04	0.22	1.21	<0.004	0.003	0.037	5.90	0.0034
36	Comparative Example	0.05	0.12	1.05	<0.004	0.003	0.028	6.47	0.0036
37	Comparative Example	0.05	0.32	0.82	<0.004	0.001	0.015	5.83	0.0029
38	Comparative Example	0.05	0.20	0.90	<0.004	0.001	0.035	6.04	0.0033
39	Comparative Example	0.05	0.06	0.85	<0.005	<0.0005	0.032	5.64	0.0040

Note 1) The underline falls outside the scope of the present invention.

[Table 2 continued]

No.	Classification	Cu	Cr	Mo	Ti	Nb	V	B	Ca	REM	Zr
22	Comparative Example	0.21	0.50	0.13	0.007	-	-	-	-	-	-
23	Comparative Example	0.21	0.36	0.05	0.007	-	-	-	-	-	-
24	Comparative Example	-	0.65	-	0.008	-	-	-	-	-	-
25	Comparative Example	0.21	0.33	0.49	0.007	-	-	-	-	-	-
26	Comparative Example	-	0.20	0.12	0.007	-	-	0.0021	-	-	-
27	Comparative Example	-	0.63	-	0.007	-	-	-	-	-	-
28	Comparative Example	-	0.62	-	0.007	-	-	-	-	-	-
29	Comparative Example	-	0.25	0.17	0.012	-	-	-	-	-	-
30	Comparative Example	-	0.83	0.46	0.013	-	0.22	-	-	-	-
31	Comparative Example	-	0.25	0.15	0.024	0.016	-	-	-	-	-
32	Comparative Example	1.08	0.23	0.16	0.005	-	-	-	0.0032	-	-
33	Comparative Example	-	1.25	-	0.009	-	-	-	-	-	0.0057
34	Comparative Example	-	0.59	-	0.009	0.104	-	-	-	0.0051	-
35	Comparative Example	-	0.05	1.07	0.006	-	-	-	-	-	-
36	Comparative Example	-	0.66	-	0.027	-	-	-	-	0.0021	-
37	Comparative Example	-	-	0.15	0.008	-	0.52	-	-	-	-
38	Comparative Example	-	0.31	0.22	0.008	-	-	0.0052	-	-	-
39	Comparative Example	-	0.40	0.15	0.012	-	-	-	-	-	-

Note 1) The underline falls outside the scope of the present invention.

[Table 3]

No.	Classification	sol. N	Ni-Ti balance	Di value	Finish plate thickness (mm)	Ac3 temperature (°C)	L treatment temperature (°C)
1	Invention Example	0.0005	0.0063	2.5	25	766	660
2	Invention Example	0.0005	0.0063	3.4	25	770	660
3	Invention Example	0.0017	0.0128	5.0	25	760	660
4	Invention Example	0.0004	0.0051	3.0	25	733	650
5	Invention Example	0.0015	0.0155	3.4	25	791	660
6	Invention Example	0.0017	0.0092	3.3	25	781	650
7	Invention Example	0.0018	0.0068	3.5	25	786	660
8	Invention Example	0.0006	0.0080	3.3	25	744	650
9	Invention Example	0.0005	0.0022	3.6	25	763	640
10	Invention Example	0.0016	0.0082	3.1	25	773	660
11	Invention Example	0.0006	0.0066	4.65	25	789	680
12	Invention Example	0.0018	0.0189	5.0	25	779	670
13	Invention Example	0.0002	0.0078	4.2	25	768	650
14	Invention Example	0.0005	0.0004	3.5	25	777	670
15	Invention Example	0.0011	0.0005	3.2	25	771	660
16	Invention Example	0.0017	0.0129	3.4	25	786	680
17	Invention Example	-0.0030	0.0003	4.5	25	799	680
18	Invention Example	0.0007	0.0013	3.3	25	749	640
19	Invention Example	0.0008	0.0099	4.72	25	814	680
20	Invention Example	0.0013	0.0072	3.1	25	755	650
21	Invention Example	0.0005	0.0050	3.5	25	766	660

Note 1) The unit of [sol. N] is “%”.

[Table 3 continued]

No.	Classification	vE_{-196} (J)	Grain size (μm)	Joint toughness (FL + 3-mm notch)
1	Invention Example	62	2.9	Crack passes through the base metal side from CG-HAZ.
2	Invention Example	59	3.2	Crack passes through the base metal side from CG-HAZ.
3	Invention Example	45	2.1	Crack does not pass through the base metal side from CG-HAZ.
4	Invention Example	65	3.1	Crack passes through the base metal side from CG-HAZ.
5	Invention Example	47	3.0	Crack passes through the base metal side from CG-HAZ.
6	Invention Example	48	3.8	Crack passes through the base metal side from CG-HAZ.
7	Invention Example	42	3.1	Crack passes through the base metal side from CG-HAZ.
8	Invention Example	68	2.6	Crack passes through the base metal side from CG-HAZ.
9	Invention Example	62	2.9	Crack passes through the base metal side from CG-HAZ.
10	Invention Example	47	3.3	Crack passes through the base metal side from CG-HAZ.
11	Invention Example	59	2.9	Crack passes through the base metal side from CG-HAZ.
12	Invention Example	42	2.9	Crack does not pass through the base metal side from CG-HAZ.
13	Invention Example	70	2.7	Crack passes through the base metal side from CG-HAZ.
14	Invention Example	63	2.4	Crack passes through the base metal side from CG-HAZ.
15	Invention Example	50	3.2	Crack passes through the base metal side from CG-HAZ.
16	Invention Example	48	3.0	Crack passes through the base metal side from CG-HAZ.
17	Invention Example	70	2.1	Crack passes through the base metal side from CG-HAZ.
18	Invention Example	57	2.6	Crack passes through the base metal side from CG-HAZ.
19	Invention Example	55	2.8	Crack does not pass through the base metal side from CG-HAZ.
20	Invention Example	49	3.1	Crack passes through the base metal side from CG-HAZ.
21	Invention Example	62	3.2	Crack passes through the base metal side from CG-HAZ.

Note 1) The unit of [sol. N] is "%".

[Table 4]

No.	Classification	sol. N	Ni-Ti balance	Di value	Finish plate thickness (mm)	Ac3 temperature (°C)	L treatment temperature (°C)	vE_{-196} (J)	Grain size (μm)
22	Comp. Ex.	0.0011	0.0070	5.1	25	731	640	Less than 41	2.7
23	Comp. Ex.	0.0025	0.0070	3.6	25	727	640	Less than 41	2.7
24	Comp. Ex.	0.0015	0.0060	3.4	25	737	650	Less than 41	2.8
25	Comp. Ex.	0.0012	0.0100	4.6	25	769	660	Less than 41	2.6
26	Comp. Ex.	0.0012	0.0064	4.3	25	742	650	Less than 41	3.1
27	Comp. Ex.	0.0012	0.0063	4.0	25	723	630	Less than 41	3.1
28	Comp. Ex.	0.0018	0.0100	1.6	25	773	670	Less than 41	3.6
29	Comp. Ex.	0.0016	0.0004	3.4	25	741	640	Less than 41	2.4
30	Comp. Ex.	0.0007	0.0145	4.2	25	835	690	Less than 41	3.1
31	Comp. Ex.	0.0037	-0.0111	3.1	25	742	650	Less than 41	2.8
32	Comp. Ex.	0.0017	0.0070	3.1	25	732	640	Less than 41	2.9
33	Comp. Ex.	0.0003	0.0099	4.2	25	767	670	Less than 41	2.3
34	Comp. Ex.	0.0004	0.0044	3.0	25	745	650	Less than 41	2.6
35	Comp. Ex.	0.0017	0.0102	6.0	25	788	660	Less than 41	1.9
36	Comp. Ex.	-0.0043	-0.0145	3.1	25	747	650	Less than 41	2.7
37	Comp. Ex.	0.0006	0.0090	3.1	25	825	670	Less than 41	2.5
38	Comp. Ex.	0.0010	0.0067	3.2	25	765	660	Less than 41	3.1
39	Comp. Ex.	0.0005	0.0063	2.5	50	766	820	Less than 41	6.5

Note 1) The underline falls outside the scope of the present invention.
Note 2) The unit of [sol. N] is "%".

[0053] Nos. 1 to 21 are concerned with an invention example satisfying the requirements of the present invention; and in Nos. 1 to 21, all of the average values of the absorption energy at -196°C were 41 J or more, and the relationship of

($vE_{-196} \geq 41$ J) was satisfied. From these test results, it can be said that all of the invention examples of Nos. 1 to 21 satisfying the requirements of the present invention are a thick steel plate having excellent HAZ toughness at cryogenic temperatures.

[0054] On the other hand, Nos. 22 to 39 are concerned with a comparison example not satisfying any one of the requirements of the present invention; and in Nos. 22 to 39, all of the average values of the absorption energy at -196°C were less than 41 J, and the relationship of ($vE_{-196} \geq 41$ J) could not be satisfied, and thus, the thorough HAZ toughness at cryogenic temperatures could not be ensured.

(Example 2)

[0055] With respect to the invention examples in which in the above-described tests, favorable results that the average value of the absorption energy at -196°C is 41 J or more could be obtained, every three joints were fabricated and examined for the toughness.

[0056] Specifically, a single bevel groove (root gap: 6 mm, groove angle: 30°) was applied, and a joint was fabricated under the following condition. In a practical structure, the design is performed in such a manner that by applying a multi-pass X groove, a low-toughness HAZ is not substantially included, and from the standpoint of shape, a crack develops only in the low-toughness HAZ part. However, in order to confirm that the joint is free from an adverse influence of CG-HAZ, the single bevel groove was applied.

[0057]

- Direction of travel: Vertical upward welding direction relative to the L direction of steel plate
- Welding material: NIC-70S (KOBE)
- Pass number: BP: 5 to 6/FP: 3
- Heat input: 35 kJ/cm in average in a range of from 24.5 to 41.4 kJ/cm
- Between passes: Lower than 100°C

[0058] In the joint under the above-described heat input condition, CG-HAZ having relatively low toughness is formed in the vicinity extremely near a fusion line (FL). A condition under which the joint toughness is not reduced without causing development of a crack only in this CG-HAZ was determined.

[0059] With respect to the joint fabricated using the thick steel plate of the invention example in which the favorable HAZ toughness was obtained in the above-described test, a V-notch was introduced into each of the positions of 1 mm and 3 mm from the fusion line, and the Charpy impact absorption test was performed. With respect to all of the steel materials, in th case of (FL + 1 mm) notch, the crack traversed without passing through only the CG-HAZ, to reach a molten metal and thereafter, developed in the molten metal. 80% or more of the whole length of the crack developed in the molten metal, and in all of the cases, the metal was ductilely fractured, so that the toughness was favorable.

[0060] On the other hand, in the case of (FL + 3 mm) notch, there were found the case where the crack went to the molten metal side and the case where the crack went to the base metal side. In all of the cases, though the vE_{-196} thoroughly exceeded 41 J, the case where the crack passes through the base metal side from the CG-HAZ is desirable.

[0061] In the Charpy impact absorption test in which the notch position is (FL + 3 mm), all of the three joints passing through the base metal side from the CG-HAZ are a joint using the thick steel plate having the Di value of 4.7 or less, and it can be said that Nos. 1, 2, 4 to 11, 13 to 18, 20, and 21 satisfying this requirement are excellent in the joint toughness.

[0062] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[0063] It is to be noted that the present application is based on Japanese Patent Application No. 2014-079378 filed on April 8, 2014, and the contents are incorporated herein by reference.

INDUSTRIAL APPLICABILITY

[0064] The thick steel plate of the present invention has excellent HAZ toughness at cryogenic temperatures and is useful as a structural member requiring cryogenic-temperature properties, for an LNG storage tank and so on.

Claims

1. A thick steel plate having HAZ toughness at a cryogenic temperature, comprising, in terms of mass %, 0.02 to 0.10% of C, 0.40% or less (not including 0%) of Si, 0.5 to 2.0% of Mn, 0.007% or less (not including 0%) of P, 0.007% or less (not including 0%) of S, 0.005 to 0.05% of Al, 5.0 to 7.5% ofNi, 0.025% or less (not including 0%) of Ti, and

0.010% or less (not including 0%) of N, with the remainder being iron and inevitable impurities, wherein a Di value determined according to the following formula is 2.5 or more and 5.0 or less:

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times (1.7 - 0.09 \times 6.5),$$

a sol. N parameter is 20 ppm or less,
an Ni-Ti balance is $\{0.0024 \times ([Ni] - 7.5)^2 + 0.010 - [Ti,]\} >\_ 0$, and
a grain size after heating at 700°C for 5 seconds and cooling from 700°C to 500°C over 19 seconds is 4.0 μm or less, provided that in each of the formulae, [ ] expresses mass %.

2. The thick steel plate having HAZ toughness at a cryogenic temperature according to claim 1, further comprising at least one of the following (a) to (c):

(a) one or two or more of 1.0% or less (not including 0%) of Cu, 1.2% or less (not including 0%) of Cr, and 1.0% or less (not including 0%) of Mo in terms of mass %;
(b) one or two or more of 0.1% or less (not including 0%) of Nb, 0.5% or less (not including 0%) of V, 0.005% or less (not including 0%) of B, and 0.005% or less (not including 0%) of Zr in terms of mass %; and
(c) one or two of 0.003% or less (not including 0%) of Ca and 0.005% or less (not including 0%) of REM in terms of mass %.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/060285

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/14*(2006.01)i, *C22C38/58*(2006.01)i, *C21D6/00*(2006.01)n

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)
C22C38/00-38/60, C21D6/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-219296 A (Kobe Steel, Ltd.), 12 November 2012 (12.11.2012), entire text (Family: none)	1,2
A	JP 2008-150670 A (Nippon Steel Corp.), 03 July 2008 (03.07.2008), entire text (Family: none)	1,2
A	JP 57-207155 A (Nippon Steel Corp.), 18 December 1982 (18.12.1982), entire text (Family: none)	1,2

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 June 2015 (24.06.15)	07 July 2015 (07.07.15)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/060285

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2005-029842 A (Nippon Steel Corp.), 03 February 2005 (03.02.2005), entire text (Family: none)	1,2
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REFERENCES CITED IN THE DESCRIPTION

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- Improvement of Toughness of 51/2% Ni Steel-Welded Portion (Development VI of Nickel Steels for Low Temperature. **KAORU KIMURA et al.** Iron and Steel. The Iron and Steel Institute of Japan, 1972, vol. 58, 228 **[0008]**
- Development of 7% Ni-TMCP Steel Plates for LNG Tank (Second Report). **YUKITO OGIWARA et al.** Proceedings of Welding Structure Symposium 2011, Japan Welding Society, Welding Structure Research Committee. 2011, 459 **[0008]**