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(54) **THICK STEEL PLATE HAVING EXCELLENT ULTRALOW-TEMPERATURE TOUGHNESS**

(57) Disclosed is a steel plate that contains predetermined steel chemical compositions. The content of Mn-containing inclusions each having a largest dimension greater than 0.1 μm in the steel is from 0.001 to 0.07 mass percent. The fraction of a retained austenite phase existing at -196°C is from 2.0 to 12.0 volume percent.

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Description

Technical Field

5 **[0001]** The present invention relates to steel plates having excellent cryogenic toughness (ultralow-temperature toughness). Specifically, the present invention relates to a steel plate having good toughness [in particular, good toughness in a crosswise direction (width direction; C-direction)] at cryogenic temperatures equal to or lower than -196°C even when having a reduced Ni content of about 5.0% to about 7.5%. Hereinafter descriptions will be made while centering on steel plates for liquefied natural gas (LNG) use, in which the steel plates are exposed to the cryogenic temperatures. 10 Such steel plates are representatively exemplified by those for use in LNG storage tanks and transport ships. It should be noted, however, that the present invention is not limited to steel plates of this type and is applicable to all steel plates for use in applications where the steel plates are exposed to cryogenic temperatures of -196°C or lower.

Background Art

15 **[0002]** LNG tank-use steel plates are to be used in liquefied natural gas (LNG) storage tanks and require not only high strengths, but also such good toughness as to endure a cryogenic temperature of -196°C . Steel plates having a Ni content of about 9% (9% Ni steel plates) have been used as steel plates for this use. However, owing to increasing Ni cost in recent years, there are increasingly developed steel plates having excellent cryogenic toughness even though 20 containing Ni in a lower content of less than 9%.

[0003] Typically, Nonpatent Literature (NPL) 1 describes the effects of a heat treatment of 6% Ni steel in the ferrite-austenite two-phase region on low-temperature toughness. Specifically, the literature describes that a heat treatment (lamellarizing; L treatment) in the ferrite-austenite two-phase region (between A_{c1} and A_{c3}) is performed before tempering treatment, and this imparts, to the resulting 6% Ni steel, cryogenic toughness at -196°C of equal to or better than the cryogenic toughness of a 9% Ni steel that has undergone regular quenching and tempering treatments; that this heat treatment allows a crosswise direction (C-direction) test specimen to have better toughness; and that these effects are obtained by the presence of a large amount of finely dispersed retained austenite that is stable even against impact load at cryogenic temperatures. Unfortunately, however, the steel according to the technique tends to generally have inferior cryogenic toughness in a crosswise direction (C-direction) as compared with the cryogenic toughness in a rolling direction (longitudinal direction; L-direction), although it has excellent cryogenic toughness in the L-direction. In addition, the literature lacks the description about percent brittle fracture. 25 30

[0004] Techniques similar to the technique in NPL 1 are described in Patent Literature (PTL) 1 and PTL 2. Of these, PTL 1 describes a method as follows. This method employs a steel having a Ni content of 4.0% to 10% and having an austenite grain size and other factors controlled within predetermined ranges. The method subjects the steel to a specific treatment one or more times and then to tempering at a temperature equal to or lower than the A_{c1} transformation temperature. In the specific treatment, the steel is hot-rolled, heated to a temperature between A_{c1} and A_{c3} , and then cooled. This treatment corresponds to the L treatment in NPL 1. PTL 2 describes another method. This method employs a steel having a Ni content of 4.0% to 10% and having a particle size of AlN particles before hot rolling of 1 μm or less. The method subjects the steel to heat treatments (L treatment and subsequent tempering treatment) as in PTL 1. The values of impact energy at -196°C (vE_{-196}) described in these techniques are probably those in the L-direction, and values as toughness in the C-direction are not found therein. In addition, the techniques fail to consider the strengths and fail to describe the percent brittle fracture. 35 40

[0005] NPL 2 describes a technique relating to the development of a 6% Ni steel for LNG tanks. The technique employ the L treatment (two-phase region quenching treatment) and a thermal-mechanical control process (TMCP) in combination. This literature describes that the resulting steel has a satisfactory value of toughness in the rolling direction (L-direction), but fails to describe the toughness value in the crosswise direction (C-direction). 45

[0006] PTL 3 describes a high-toughness and high-tensile-strength steel having a tensile strength on the order of 570 MPa or more and having excellent weld bead toughness. The steel contains 0.3% to 10% of Ni and a predetermined amount of Mg and includes Mg-containing oxide particles each having a predetermined particle size and being dispersed appropriately. PTL 3 describes as follows. The control of Mg-containing oxides allows austenite grains after heating to undergo refinement (to have smaller grain sizes) and thereby allows the base plate and the heat affected zone (HAZ) to have better toughness. For this purpose, an O (oxygen) content before addition of deoxidizing elements and the order of additions of Mg and other deoxidizing elements are important. Specifically, the steel according to the technique may be prepared by adding Mg, Ti, and Al simultaneously to a molten steel having a dissolved oxygen content of 0.001% to 0.02% and casting the resulting molten steel to give slabs; or by adding Al lastly among the additions of Mg, Ti, and Al to the molten steel and casting the resulting molten steel to give slabs. PTL 3 also describes, in working examples, toughness values (fracture appearance transition temperatures $vTrs$) in the C-direction. The disclosed 9% Ni steel has a toughness value at a good level (fracture appearance transition temperature $vTrs$ of equal to or lower than -196°C); 50 55

but a steel having a Ni content near to 5% has a toughness value (fracture appearance transition temperature $vTrs$) of $-140^{\circ}C$. Steels of this type are still susceptible to further improvements.

Citation List

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Patent Literature

[0007]

- 10 PTL1: Japanese Unexamined Patent Application Publication (JP-A) No. Sho49(1974)-135813
 PTL2: JP-A No. Sho51(1976) -13308
 PTL 3: JP-A No. 2001-123245

Nonpatent Literature

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[0008]

- 20 NPL1: Yano et al., "Effect of Heat Treatment in the Ferrite-Austenite Region on Notch Toughness of 6% Nickel Steel", Tetsu-to-Hagane (in Japanese), Vol 59 (1973), No. 6, pp. 752-763
 NPL 2: Furuya et al, "Development of 6% Ni Steel for LNG Storage Tanks", CAMP-ISIJ, 23 (2010),1322

Summary of Invention

Technical Problem

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[0009] As is described above, there have been proposed techniques to provide Ni steels having a Ni content of about 5.0% to about 7.5% and still having excellent cryogenic toughness at $-196^{\circ}C$. However, the techniques lack sufficient investigations on cryogenic toughness in the C-direction. In particular, strong demands are made to provide still better cryogenic toughness (better cryogenic toughness in the C-direction at high strengths of the base plate (base metal), specifically, at a tensile strength TS greater than 690 MPa and a yield strength YS greater than 590 MPa.

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[0010] In addition, all the above-mentioned literature lacks investigations on percent brittle fracture. The percent brittle fracture refers to a percentage of brittle fracture occurring upon the application of a load in a Charpy impact test. In a region where brittle fracture occurs, energy to be absorbed by the steel until the fracture occurs is remarkably lowered, and this causes the fracture to easily proceed. To prevent this and to provide better cryogenic toughness, the steel should very importantly have not only a better general Charpy impact value (vE_{-196}), but also a percent brittle fracture of 10% or less. However, there has not yet been proposed a technique relating to a high-strength steel plate that has high base plate strengths as described above and still has a percent brittle fracture meeting the condition.

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[0011] The present invention has been made in view of these circumstances and has an object to provide a high-strength steel plate that is based on a Ni steel having a Ni content of about 5.0% to about 7.5%, has excellent cryogenic toughness (in particular, excellent cryogenic toughness in the C-direction) at $-196^{\circ}C$, and achieves a percent brittle fracture of equal to or less than 10%.

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Solution to Problem

[0012] The present invention can achieve the object and provides a steel plate having excellent cryogenic toughness. The steel plate contains, in mass percent, C in a content of 0.02% to 0.10%, Si in a content of 0.40% or less (excluding 0%), Mn in a content of 0.50% to 2.0%, P in a content of 0.007% or less (excluding 0%), S in a content of 0.007% or less (excluding 0%), Al in a content of 0.005% to 0.050%, Ni in a content of 5.0% to 7.5%, and N in a content of 0.010% or less (excluding 0%), with the remainder being iron and inevitable impurities. The content of Mn-containing inclusions each having a largest dimension greater than $0.1 \mu m$ in the steel is 0.001 to 0.07 mass percent. The fraction of a retained austenite phase existing at $-196^{\circ}C$ is 2.0 to 12.0 volume percent.

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[0013] According to a preferred embodiment of the present invention, the steel plate may further contain Cu in a content of 1.0% or less (excluding 0%).

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[0014] According to another preferred embodiment of the present invention, the steel plate may further contain at least one element selected from the group consisting of Cr in a content of 1.20% or less (excluding 0%) and Mo in a content of 1.0% or less (excluding 0%).

[0015] According to another preferred embodiment of the present invention, the steel plate may further contain at least one element selected from the group consisting of Ti in a content of 0.025% or less (excluding 0%), Nb in a content of

0.100% or less (excluding 0%), and V in a content of 0.50% or less (excluding 0%).

[0016] According to another preferred embodiment of the present invention, the steel plate may further contain B in a content of 0.0050% or less (excluding 0%).

[0017] According to another preferred embodiment of the present invention, the steel plate may further contain at least one element selected from the group consisting of Ca in a content of 0.0030% or less (excluding 0%), at least one rare-earth element (REM) in a content of 0.0050% or less (excluding 0%), and Zr in a content of 0.005% or less (excluding 0%).

[0018] According to another preferred embodiment of the present invention, the steel plate may have a C-value as specified by V/W of 150 or more, where V represents the fraction (in volume percent) of the retained austenite phase existing at -196°C; and W represents the content (in mass percent) of the Mn-containing inclusions each having a largest dimension greater than 0.1 μm.

Advantageous Effects of Invention

[0019] The present invention can provide a high-strength steel plate including a Ni steel having a Ni content of about 5.0% to about 7.5%, where the steel plate has excellent cryogenic toughness (in particular, excellent cryogenic toughness in the C-direction) at -196°C or lower and has a percent brittle fracture at -196°C of equal to or less than 10% (preferably has a percent brittle fracture at -233°C of equal to or less than 50%) even at high base plate strengths, specifically, at a tensile strength TS greater than 690 MPa and a yield strength YS greater than 590 MPa.

Description of Embodiments

[0020] The steel plate according to the present invention is based a Ni steel having a Ni content of about 5.0% to about 7.5% and has following features (I) and (II) so as to have still better cryogenic toughness in the C-direction. Specifically, (I) the fraction of a retained austenite phase (retained γ phase) existing at -196°C is controlled to 2.0 to 12.0 volume percent; and (II) the content of Mn-containing inclusions each having a largest dimension greater than 0.1 μm present in the steel is controlled to 0.001 to 0.07 mass percent. The "Mn-containing inclusions each having a largest dimension greater than 0.1 μm" are hereinafter also simply referred to as "Mn-containing inclusions". In particular, the present inventors found that the appropriate control (II) of the Mn-containing inclusions achieves fixation of solute sulfur that impairs toughness, reduces the content of the solute sulfur to such a range not adversely affecting the toughness, and thereby achieves very excellent cryogenic toughness.

[0021] The story behind the present invention will be illustrated below.

[0022] The present inventors made intensive investigations to give a steel plate that is based on a Ni steel having a Ni content of 7.5% or less and has excellent cryogenic toughness at -196°C or lower. Specifically, the present invention has been made so as to provide a high-strength steel plate that has excellent cryogenic toughness and meets all conditions: a percent brittle fracture at -196°C in the C-direction of equal to or less than 10%, a tensile strength TS greater than 690 MPa, and a yield strength YS greater than 590 MPa. From this viewpoint, the techniques taught in the literature in the related art were initially examined.

[0023] The literature teaches that the stabilization of retained austenite (retained γ) existing at -196°C is important to provide better cryogenic toughness in a 5% Ni steel. In synthetic consideration of the production method, the literature recommends a production process as follows. Specifically, in the ingot making step, the dissolved oxygen content in a molten steel before the addition of deoxidizing elements is controlled; the controlled molten steel is combined with the deoxidizing elements while Al is lastly added, and then cast; a heat treatment (L-treatment) in the ferrite-austenite two-phase region (between A_{c1} and A_{c3}) is performed, and then tempering is performed at a temperature equal to or lower than the A_{c1} transformation temperature. The literature teaches that this process provides better cryogenic toughness. As a result of the investigations, however, the present inventors found that the technique fails to allow the resulting steel plate to have sufficient cryogenic toughness in the C-direction and fails to achieve the target level in the present invention (a percent brittle fracture at -196°C in the C-direction of equal to or less than 10%), although the technique allows the steel plate to have better cryogenic toughness in the L-direction.

[0024] Based on the finding, the present inventors made further investigations and found that, while basically following the technique, one or more conditions are necessarily specified (added) in a steel plate and a method for producing the steel plate, so as to obtain a desired steel plate having excellent cryogenic toughness. Specifically, the present inventors found that (i) it is effective for a steel plate to control not only the fraction of a retained austenite phase existing at -196°C within the range of 2.0 to 12.0 volume percent, but also the content of Mn-containing inclusions each having a largest dimension greater than 0.1 μm within the range of 0.001 to 0.07 mass percent; and that the control is effective to restrain coarse inclusions and to fix solute sulfur (namely, to reduce the amount of solute sulfur), where the coarse inclusions and solute sulfur adversely affect the toughness.

[0025] The present inventors also found that (ii) (ii-1) further control in the ingot making step and (ii-2) control of the temperature of heating before rolling are also effective in production of the steel plate as above, in addition to the control

of the dissolved oxygen content (free oxygen content) before Al addition in the ingot making step; and sequential performing of the heat treatment (L-treatment) at a temperature between the A_{c1} and A_{c3} temperatures and the tempering within the predetermined temperature range. Specifically, the present inventors found that it is effective that (ii-1) the free oxygen content before Al addition is controlled to 100 ppm or less, and the cooling time (t_2) from 1500°C down to 1450°C upon casting is controlled to 300 seconds or shorter in the ingot making step; and (ii-2) the heating temperature in the heating step before rolling is controlled (lowered) to 1060°C or lower.

[0026] The present inventors further found that (iii) a C-value as specified by V/W is preferably controlled to 150 or more, where V represents the fraction (in volume percent) of the retained austenite phase existing at -196°C; and W represents the content (in mass percent) of the Mn-containing inclusions each having a largest dimension greater than 0.1 μm as specified in the condition (i); and that this control allows the steel plate to maintain a percent brittle fracture at a good level of 50% or less even at a temperature of -233°C lower than the temperature -196°C. The present invention has been made based on these findings.

[0027] As used herein the term (one having) "excellent cryogenic toughness" refers to one having a percent brittle fracture at -196°C of equal to or less than 10%, where the percent brittle fracture is measured in a Charpy impact test in the C-direction (crosswise direction) by a method described in after-mentioned experimental example. The percent brittle fracture in the L-direction (rolling direction) is not measured in the experimental example. This is based on an empirical rule that a steel plate having a percent brittle fracture in the C-direction of 10% or less essentially has a percent brittle fracture in the L-direction of 10% or less.

[0028] As used herein the term "steel plate" refers to a steel plate having a thickness of about 6 to about 50 mm.

[0029] The present invention may be applied to high-strength steel plates each having a tensile strength TS greater than 690 MPa and a yield strength YS greater than 590 MPa.

[0030] The steel plate according to the present invention will be illustrated in detail below.

[0031] As described above, the steel plate according to the present invention contains, in mass percent, C in a content of 0.02% to 0.10%, Si in a content of 0.40% or less (excluding 0%), Mn in a content of 0.50% to 2.0%, P in a content of 0.007% or less (excluding 0%), S in a content of 0.007% or less (excluding 0%), Al in a content of 0.005% to 0.050%, Ni in a content of 5.0% to 7.5%, and N in a content of 0.010% or less (excluding 0%) with the remainder being iron and inevitable impurities. In the steel plate, the fraction of the retained austenite phase existing at -196°C is 2.0 to 12.0 volume percent, and the content of the Mn-containing inclusions each having a largest dimension greater than 0.1 μm is 0.001 to 0.07 mass percent.

[0032] Initially, steel chemical compositions will be illustrated.

C in a content of 0.02% to 0.10%

[0033] Carbon (C) is essential for ensuring strength and retained austenite. To have such actions effectively, the carbon content in terms of lower limit may be controlled to 0.02% or more. The carbon content in terms of lower limit is preferably 0.03% or more, and more preferably 0.04% or more. However, carbon, if added in excess, may cause the steel plate to have excessively high strengths and to thereby have lower cryogenic toughness. To prevent this, the carbon content in terms of upper limit may be controlled to 0.10% or less. The carbon content in terms of upper limit is preferably 0.08% or less, and more preferably 0.06% or less.

Si in a content of 0.40% or less (excluding 0%)

[0034] Silicon (Si) is useful as a deoxidizing element. However, Si, if added in excess, may accelerate the formation of hard martensite islands and thereby cause the steel plate to have lower cryogenic toughness. To prevent this, the Si content in terms of upper limit may be controlled to 0.40% or less. The Si content in terms of upper limit is preferably 0.35% or less, and more preferably 0.20% or less.

Manganese (Mn) in a content of 0.50% to 2.0%

[0035] Manganese (Mn) stabilizes austenite (γ) and contributes to a larger amount of retained austenite. To have such actions effectively, the Mn content in terms of lower limit may be controlled to 0.50% or more. The Mn content in terms of lower limit is preferably 0.6% or more, and more preferably 0.7% or more. However, Mn, if added in excess, may cause temper embrittlement and cause the steel plate to fail to surely have the desired cryogenic toughness. To prevent this, the Mn content in terms of upper limit may be controlled to 2.0% or less. The Mn content in terms of upper limit is preferably 1.5% or less, and more preferably 1.3% or less.

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P in a content of 0.007% or less (excluding 0%)

5 **[0036]** Phosphorus (P) is an impurity element that causes grain boundary fracture. To surely have the desired cryogenic toughness, the phosphorus content in terms of upper limit may be controlled to 0.007% or less. The phosphorus content in terms of upper limit is preferably 0.005% or less. The lower the phosphorus content is, the better. However, it is industrially difficult to control the phosphorus content to 0%.

S in a content of 0.007% or less (excluding 0%)

10 **[0037]** Sulfur (S) is also an impurity element that causes grain boundary fracture, as with phosphorus. To surely have the desired cryogenic toughness, the sulfur content in terms of upper limit may be controlled to 0.007% or less. With an increasing sulfur content, the steel plate has an increasing percent brittle fracture and may fail to have the desired cryogenic toughness (percent brittle fracture at -196°C of equal to or less than 10%), as indicated in the experimental example. In addition, the content of desired Mn-containing inclusions excessively increases at an excessively high sulfur content, and this may still cause the steel plate to have lower cryogenic toughness. The sulfur content in terms of upper limit is preferably 0.005% or less. The lower the sulfur content is, the better. However, it is industrially difficult to control the sulfur content to 0%.

Al in a content of 0.005% to 0.050%

20 **[0038]** Al acts as a deoxidizing element. The steel, if having an insufficient Al content, may have an increased oxygen content and suffer from a larger amount of coarse Al-containing inclusions, and this may adversely affect the control of the content of desired Mn-containing inclusions (this will be illustrated in detail later). To prevent this, the Al content in terms of lower limit may be controlled to 0.005% or more. The Al content in terms of lower limit is preferably 0.010% or more, and more preferably 0.015% or more. However, Al, if added in excess, may accelerate the aggregation and/or coalescence of Al-containing inclusions and may still adversely affect the control of amount of desired Mn-containing inclusions. To prevent this, the Al content in terms of upper limit may be controlled to 0.050% or less. The Al content in terms of upper limit is preferably 0.045% or less, and more preferably 0.04% or less.

30 Ni in a content of 5.0% to 7.5%

35 **[0039]** Nickel (Ni) is essential for ensuring retained austenite (retained γ) that is useful for better cryogenic toughness. To have such actions effectively, the Ni content in terms of lower limit may be controlled to 5.0% or more. The Ni content in terms of lower limit is preferably 5.2% or more, and more preferably 5.4% or more. However, Ni, if added in excess, may cause higher material cost. To prevent this, the Ni content in terms of upper limit may be controlled to 7.5% or less. The Ni content in terms of upper limit is preferably 7.0% or less, more preferably 6.5% or less, and furthermore preferably 6.0% or less.

40 N in a content of 0.010% or less (excluding 0%)

[0040] Nitrogen (N) causes the steel plate to undergo strain aging (strain age hardening) and to have lower cryogenic toughness. To prevent this, the nitrogen content in terms of upper limit may be controlled to 0.010% or less. The nitrogen content in terms of upper limit is preferably 0.006% or less, and more preferably 0.004% or less.

45 **[0041]** The steel plate according to the present invention contains the elements as basic chemical compositions, with the remainder being iron and inevitable impurities.

[0042] The steel plate according to the present invention may further contain any of selective elements as follows, so as to further have one or more characteristic properties.

Cu in a content of 1.0% or less (excluding 0%)

50 **[0043]** Copper (Cu) stabilizes austenite and contributes to a larger amount of retained austenite. To have such actions effectively, Cu is preferably contained in a content of 0.05% or more. However, Cu, if added in excess, may cause the steel plate to have excessively higher strengths and to fail to have desired cryogenic toughness improvement effects. To prevent this, the Cu content in terms of upper limit is preferably controlled to 1.0% or less. The Cu content in terms of upper limit is more preferably 0.8% or less, and furthermore preferably 0.7% or less.

55 **[0044]** At least one element selected from the group consisting of Cr in a content of 1.20% or less (excluding 0%) and Mo in a content of 1.0% or less (excluding 0%)

[0045] Both chromium (Cr) and molybdenum (Mo) contribute to higher strengths. Each of these elements may be

added alone or in combination. To have such actions effectively, the Cr content is preferably 0.05% or more, and the Mo content is preferably 0.01% or more. However, these elements, if added in excess, may cause the steel plate to have excessively higher strengths and to fail to surely have the desired cryogenic toughness. To prevent this, the Cr content in terms of upper limit is preferably 1.20% or less, more preferably 1.1% or less, furthermore preferably 0.9% or less, and still more preferably 0.5% or less; and the Mo content in terms of upper limit is preferably 1.0% or less, more preferably 0.8% or less, and furthermore preferably 0.6% or less.

[0046] At least one element selected from the group consisting of Ti in a content of 0.025% or less (excluding 0%), Nb in a content of 0.100% or less (excluding 0%), and V in a content of 0.50% or less (excluding 0%)

[0047] Titanium (Ti), niobium (Nb), and vanadium (V) each precipitate as carbonitrides and contribute to higher strengths. Each of these elements may be added alone or in combination. To have such actions effectively, the Ti content is preferably 0.005% or more, the Nb content is preferably 0.005% or more, and the V content is preferably 0.005% or more. However, these elements, if added in excess, may cause the steel plate to have excessively higher strengths and to fail to surely have the desired cryogenic toughness. To prevent this, the Ti content in terms of upper limit is preferably 0.025% or less, more preferably 0.018% or less, and furthermore preferably 0.015% or less; the Nb content in terms of upper limit is preferably 0.100% or less, more preferably 0.05% or less, and furthermore preferably 0.02% or less; and the V content in terms of upper limit is preferably 0.50% or less, more preferably 0.3% or less, and furthermore preferably 0.2% or less.

B in a content of 0.0050% or less (excluding 0%)

[0048] Boron (B) improves the hardenability and contributes to higher strengths. To have such actions effectively, the boron content is preferably 0.0005% or more. However, boron, if added in excess, may cause the steel plate to have excessively higher strengths and to fail to surely have the desired cryogenic toughness. To prevent this, the boron content in terms of upper limit is preferably 0.0050% or less, more preferably 0.0030% or less, and furthermore preferably 0.0020% or less.

[0049] At least one element selected from the group consisting of Ca in a content of 0.0030% or less (excluding 0%), REM in a content of 0.0050% or less (excluding 0%), and Zr in a content of 0.005% or less (excluding 0%)

[0050] Calcium (Ca), rare-earth elements (REM), and zirconium (Zr) act as strong deoxidizing elements and, when added, allow the steel to have a lower oxygen content and to include a smaller amount of coarse inclusions as compared with a steel containing Si and Al alone as deoxidizing elements. Each of these elements may be added alone or in combination. To have such actions effectively, the Ca content is preferably 0.0005% or more, the REM content is preferably 0.0005% or more, and the Zr content is preferably 0.0005% or more. The REM content refers to the content of a single rare-earth element when it is contained alone; and refers to the total content of two or more rare-earth elements when they are contained in combination. Hereinafter the same is true for the REM content. However, these elements, if added in excess, may cause inclusions to coarsen contrarily and may cause the steel plate to have lower cryogenic toughness. To prevent this, the Ca content in terms of upper limit is preferably 0.0030% or less, and more preferably 0.0025% or less; the REM content in terms of upper limit is preferably 0.0050% or less, and more preferably 0.0040% or less; and the Zr content in terms of upper limit is preferably 0.005% or less, and more preferably 0.0040% or less.

[0051] As used herein the term "REM" (rare-earth element) refers to the group of elements including lanthanoid elements (fifteen elements ranging from the atomic number 57 La to the atomic number 71 Lu in the periodic table), as well as Sc (scandium) and Y (yttrium). Each of these elements may be added alone or in combination. Of the rare-earth elements, preferred are Ce and La. The REM may be added in any form not limited, and may be added as a misch metal mainly containing Ce and La (e.g., containing about 50% of Ce and about 20% to about 30% of La), or added as a single element such as Ce or La.

[0052] The chemical compositions in the steel for use in the present invention have been described.

[0053] The steel plate according to the present invention has a fraction of a retained austenite phase existing at -196°C of 2.0 to 12.0 volume percent (preferably 4.0 to 12.0 volume percent).

[0054] The retained austenite existing at -196°C is known to contribute to better cryogenic toughness. To have such actions effectively, the fraction (volume fraction) of the retained austenite phase is controlled to 2.0 volume percent or more based on the entire microstructure (all phases) existing at -196°C. However, the retained austenite is relatively soft as compared with the matrix phase and, if present in an excessively large fraction, may cause the steel plate to fail to have a predetermined level of the yield strength YS. To prevent this, the fraction in terms of upper limit may be controlled to 12.0 volume percent or less. The volume fraction of the retained austenite phase in terms of lower limit is preferably 4.0 volume percent or more, and more preferably 6.0 volume percent or more; and the volume fraction in terms of upper limit is preferably 11.5 volume percent or less, and more preferably 11.0 volume percent or less.

[0055] In the steel plate according to the present invention, it is important to control the volume fraction of the retained austenite phase, among phases existing at -196°C. The other phases than the retained austenite phase are not limited herein and have only to be phases generally existing in a steel plate. The other phases than the retained austenite phase

are exemplified by bainite, martensite, and carbides such as cementite.

[0056] In addition, the steel plate according to the present invention has a content of Mn-containing inclusions each having a largest dimension greater than $0.1\ \mu\text{m}$ in the steel of 0.001 to 0.07 mass percent. As compared with the related art, the steel plate according to the present invention is mostly featured by the control of the content of the Mn-containing inclusions within the predetermined range.

[0057] Specifically, the amount of inclusions that can act as initiation sites of cracks should be reduced so as to improve the percent brittle fracture at a cryogenic temperature while surely providing high strengths. The present inventors made intensive investigations while particularly focusing attention on, among inclusions, Mn-containing inclusions. As a result, they found that Mn-containing inclusions each having a largest dimension greater than $0.1\ \mu\text{m}$, if present in the steel in a content greater than 0.07 mass percent, may cause the steel plate to fail to surely have the desired percent brittle fracture (see Sample Nos. 29 and 39 in Table 2B in the experimental example). In contrast, they also found as follows. Assume that the content of Mn-containing inclusions is less than 0.001 mass percent. In this case, the solute sulfur that impairs toughness is not fixed in the Mn-containing inclusions, but present in a high content in the steel, because the Mn-containing inclusions include sulfur as MnS. This also causes the steel plate to fail to surely have the desired percent brittle fracture (see Sample No. 40 in Table 2B in the experimental example). The content of the Mn-containing inclusions is preferably from 0.007 mass percent to 0.065 mass percent, and more preferably from 0.015 mass percent to 0.06 mass percent.

[0058] A measuring method for the Mn-containing inclusions will be illustrated in detail in the experimental example.

[0059] The "Mn-containing inclusions" herein may have any chemical compositions not limited, as long as containing Mn. The "Mn-containing inclusions" may include inclusions of any type not limited. For example, the "Mn-containing inclusions" are exemplified by particles of a single manganese compound such as an oxide, sulfide, nitride, or oxynitride of manganese; composite substances each including two or more different types of particles of the single manganese compound; and composite particles each including any of the particles of single manganese compound combined with another element. The composite substances are exemplified by composite inclusions of an Al-containing oxide and a Mn-containing sulfide. Among them, MnS and other sulfides of manganese are particularly preferably used from the viewpoint of more effectively offering actions of the Mn-containing inclusions, such as the solute sulfur fixing action.

[0060] When viewed only from the point of inclusion control, PTL 3 discloses a similar technique. However, this technique significantly differs from the present invention in the way to control inclusions. Specifically, the technique disclosed in PTL 3 focuses particularly on magnesium (Mg), allows Mg-containing oxide particles having a size of $2\ \mu\text{m}$ or less to be dispersed in a large number, thereby restrains coarsening of austenite grains at high temperatures, and improves toughness. In contrast, the present invention focuses on manganese (Mn) useful for the fixation of solute sulfur that impairs toughness, so as to fix and reduce the solute sulfur that lowers the toughness. The two techniques differ from each other in chemical compositions of inclusions to be controlled and in way to control the inclusions.

[0061] In addition, the C-value as specified by V/W is preferably controlled to 150 or more, where V represents the volume fraction (in volume percent) of the retained austenite phase existing at -196°C ; and W represents the content (in mass percent) of the Mn-containing inclusions each having a largest dimension greater than $0.1\ \mu\text{m}$. This is preferred so as to obtain still better cryogenic toughness (specifically, to maintain the percent brittle fracture at -233°C at a level of 50% or less). The C-value is more preferably 300 or more, and furthermore preferably 1000 or more. The C-value in terms of upper limit is not critical from the viewpoint of obtaining better properties, but may be controlled to 12000 or less in consideration of the ranges of the parameters V and W.

[0062] Next, a method for producing the steel plate according to the present invention will be illustrated.

[0063] First, one of the features of the present invention is the control of the volume fraction (V) of the retained austenite phase existing at -196°C within the predetermined range. For this control, it is effective to subject the workpiece after hot rolling to heating and holding in a temperature range of from the A_{c1} temperature to the A_{c3} temperature and then to tempering in a temperature range of from 520°C to the A_{c1} temperature for 10 to 60 minutes.

[0064] Another one of the features of the present invention is the control of the content (W) of the coarse Mn-containing inclusions within the predetermined range. For this control, it is effective to control the ingot making step and to control the temperature of heating before rolling as described below.

[0065] Specifically, in the ingot making step, it is effective to control the free oxygen content [O] before Al addition to 100 ppm or less and to control the cooling time (t_2) in the temperature range from 1500°C down to 1450°C upon casting to 300 seconds or shorter. The "temperature" relating to the cooling time t_2 refers to a temperature measured at a position one-half the thickness t of the slab. It is also effective to control the temperature of heating before rolling to 1060°C or lower.

[0066] This point will be illustrated in detail below. First, Mn-containing inclusions are formed during casting on surfaces of high-melting inclusions acting as nuclei, where the "high-melting inclusions" refer to other inclusions that have higher melting points as compared with the Mn-containing inclusions and mainly include, for example, Al-containing inclusions. This requires the control of the surface area of the high-melting inclusions, where the surface area is specified (determined) by the product of the size and the number of the inclusions. If the high-melting inclusions have a small surface area, the Mn-containing inclusions formed on the surfaces of the high-melting inclusions coarsen rapidly, and this may cause Mn-

containing inclusions each having a largest dimension greater than 0.1 μm to be in the steel in a content greater than 0.07 mass percent. Of such high-melting inclusions, Al-containing inclusions formed in the molten steel tend to undergo aggregation/coalescence and to thereby have a smaller surface area. However, the present inventors found that the control of the cooling time in the temperature range from 1500°C down to 1450°C upon casting can restrain the behavior of the Al-containing inclusions and enables appropriate control of the content of the Mn-containing inclusions. As is demonstrated in the experimental example, if the cooling time (t_2 in Tables 2A and 2B) in the temperature range from 1500°C down to 1450°C upon casting is longer than 300 seconds, Mn-containing inclusions are acceleratedly formed and grow on Al-containing inclusions by the mechanism to form composite inclusions. Finally, the resulting steel plate has a content of the Mn-containing inclusions greater than 0.07 mass percent and has inferior cryogenic toughness (see Sample No. 39 in Table 2B).

[0067] The Mn-containing inclusions formed upon casting may include MnS. At some temperatures of heating before rolling, part of MnS may be dissolved to form solute sulfur that causes toughness deterioration. According to the present invention, however, the temperature of heating before rolling is controlled to 1060°C or lower, and this restrains the dissolution of the Mn-containing inclusions in the heating step before rolling and restrains the coarsening of matrix prior austenite grains. This provides reprecipitation sites for the partially dissolved Mn-containing inclusions and accelerates the reprecipitation of Mn-containing inclusions. The heating before rolling, if performed at a temperature higher than 1060°C, failed to effectively exhibit the actions and caused the steel plate to have a content of Mn-containing inclusions each having a largest dimension of greater than 0.1 μm of less than 0.001 mass percent (see Sample No. 40 in Table 2B).

[0068] The control of the free oxygen content [O] to 60 ppm or less is effective for the control of the C-value (V/W) to 150 or more among the conditions in the production method.

[0069] The steps in the production method will be described in detail below.

Ingot Making Step

[0070] The present invention pays particular attention to the way to add Al so as to prevent coarse Al-containing inclusions from forming. This is based on the viewpoint that Al-containing inclusions are liable to coarsen by aggregation/coalescence and to form coarse inclusions that act as initiation sites of cracks.

[0071] Initially, the free oxygen content is controlled to 100 ppm or less before the addition of Al, acting as a deoxidizing element, to the molten steel, where the "free oxygen content" refers to a dissolved oxygen content and is also abbreviated to "[O] content". This is because, if the [O] content is greater than 100 ppm, inclusions formed upon Al addition may have larger sizes (may coarsen), and this may impair the appropriate control of the Mn-containing inclusions and cause the steel plate to fail to have the desired cryogenic toughness. The lower the [O] content is, the better. The [O] content is therefore preferably 80 ppm or less, and more preferably 50 ppm or less. The [O] content in terms of lower limit is not particularly limited from the viewpoint of refinement of the coarse inclusions.

[0072] The way to control the [O] content as above is exemplified by the addition of deoxidizing elements Mn and Si to the molten steel to deoxidize the steel. The [O] content can also be controlled by the addition of deoxidizing elements such as Ti, Ca, REM, and Zr, where one or more of such deoxidizing elements may be added as selective elements in addition to the above-mentioned deoxidizing elements (Mn and Si).

[0073] It is important to control the [O] content before Al addition so as to control the Al-containing inclusions. The order of addition operations of Al and other deoxidizing elements is not critical. However, Al, if added to a molten steel at a high [O] content, may undergo an oxidation reaction and cause the molten steel to have a higher temperature, thus causing operational hazard. To prevent this, Si and Mn are preferably added before Al addition. The selective element(s) such as Ti is preferably added to the molten steel after Al addition.

[0074] Next, casting is started. The temperature range during casting is about 1650°C or lower. Among such temperatures during casting, it is important in the present invention to control the cooling time (t_2) in the temperature range from 1500°C down to 1450°C to 300 seconds or shorter. The present inventors found that this control contributes to appropriate refinement of Mn-containing inclusions to be controlled in the present invention and gives an appropriate amount of such Mn-containing inclusions. The cooling in the specific temperature range, if performed for a cooling time t_2 of longer than 300 seconds, may cause secondary inclusions to form compositely on the Al-containing inclusions acting as nuclei and may thereby cause the formation of larger amounts of large-sized (coarse) Mn-containing inclusions. This may cause the steel plate to fail to have the desired cryogenic toughness (see Sample No. 39 in Table 2B). From this viewpoint, the cooling time t_2 is preferably minimized and is preferably 290 seconds or shorter, and more preferably 280 seconds or shorter. The cooling time t_2 in terms of lower limit is not critical from the viewpoint, but is preferably about 100 seconds or longer in consideration typically of actual operation.

[0075] The present invention pays particular attention to, of temperature ranges during casting, the temperature range from 1500°C down to 1450°C. This is because, in the temperature range, solidification upon casting proceeds, thereby inclusions are increasingly segregated and acceleratedly grow in the molten steel.

[0076] The "temperature" in the temperature range from 1500°C down to 1450°C refers to a temperature of the central

part ($t/2$) in the thickness direction of the slab, where t represents the slab thickness. The slab thickness is about 150 to about 250 mm, and the surface temperature tends to be lower than the central part temperature by about 200°C to about 1000°C. In addition, the surface temperature has large variations. For these reasons, the temperature of the central part with small variations is defined as the "temperature" in the temperature range. The "central part" refers to the vicinity of a position one-half the thickness t . The temperature of the central part of the slab in the thickness direction can be measured with a thermocouple inserted into a mold.

[0077] The cooling time (t_2) in the temperature range from 1500°C down to 1450°C has only to be controlled to 300 seconds or shorter, and the way to control the cooling time is not limited in the present invention. Typically, cooling in the temperature range may be performed at a constant cooling rate with an average cooling rate of about 0.17°C/second or less or may be performed at a varying cooling rate, each so as to allow the cooling rate in the temperature range to be 300 seconds or shorter.

[0078] The cooling in other temperature ranges than the specific temperature range upon casting in the present invention can be performed by any technique not limited, where the technique is exemplified by common techniques such as air cooling and water cooling.

[0079] The workpiece (slab) after casting in the above manner is sequentially subjected to heating, hot rolling, and heat treatment.

[0080] The temperature of heating before hot rolling may be controlled to 1080°C or lower in the present invention. This can control the content of the Mn-containing inclusions within an appropriate range. The heating before hot rolling, if performed at a temperature higher than 1080°C, may cause the Mn-containing inclusions to be in a low content and cause the steel plate to fail to have the desired cryogenic toughness (see Sample No. 40 in Table 2B described later).

[0081] The heating temperature is preferably 1070°C or lower, and more preferably 1060°C or lower. In contrast, the heating, if performed at an excessively low temperature, may cause the rolling to be performed at a low temperature and may require a larger rolling load, thus causing inferior productivity. In consideration of this, the heating temperature in terms of lower limit is preferably 900°C or higher, and more preferably 950°C or higher.

[0082] The heating in the heating temperature range is preferably performed for a heating time of about 0.5 to about 5 hours. Disadvantageously, the heating, if performed for a heating time of shorter than 0.5 hour, may fail to sufficiently heat the slab central part. In contrast, the heating, if performed for a heating time longer than 5 hours, may cause lower productivity. In consideration of these, the heating time is more preferably from 0.75 hours to 4 hours.

[0083] Next, the workpiece is subjected to hot rolling. The hot rolling technique is not limited and can be selected from common techniques so as to give a predetermined plate thickness, in which one or more conditions such as the (finish rolling) temperature and rolling reduction may be adjusted.

[0084] The workpiece after the hot rolling is heated to, and held at a temperature (T_L) in the temperature range from the A_{c1} temperature to the A_{c3} temperature, and then water-cooled. This treatment corresponds to the L-treatment described in the related art and surely gives retained austenite stably existing at -196°C in an amount (fraction) within the predetermined range.

[0085] Specifically, the workpiece is heated to a temperature (T_L) in the ferrite (α)-austenite (γ) two-phase region ranging from the A_{c1} temperature to the A_{c3} temperature. The heating to the temperature range allows alloy elements such as Ni to concentrate in a formed austenite phase to give a metastable retained austenite phase that exists metastably at room temperature. The heating, if performed to a temperature lower than the A_{c1} temperature or higher than the A_{c3} temperature, may cause the resulting steel plate to fail to include a sufficient amount of the retained austenite phase existing at -196°C. The heating temperature is preferably from about 660°C to about 710°C.

[0086] The heating (holding) at the two-phase region temperature is preferably performed for a heating time (holding time, t_L) of about 10 to about 50 minutes. The heating (holding), if performed for a time shorter than 10 minutes, may fail to sufficiently proceed the concentration of the alloy elements in the austenite phase; and, in contrast, if performed for a time longer than 50 minutes, may cause the ferrite (α) phase to be annealed, thus resulting in lower strengths. The heating time in terms of upper limit is preferably 30 minutes or shorter.

[0087] In a preferred embodiment, the heating is performed for a heating time of 15 minutes or longer. This may allow the retained austenite phase to exist at -196°C surely in a volume fraction of 4.0 volume percent or more, and may allow the steel plate to have a percent brittle fracture at -233°C of 50% or less and to surely offer good toughness even at still lower cryogenic temperatures. To have such effects more effectively, the volume fraction in terms of lower limit is more preferably 5.0 volume percent or more. In this case, the preferred lower limit of the heating time is the same as above (30 minutes or shorter).

[0088] Next, the workpiece is subjected sequentially to water cooling down to room temperature and tempering. The tempering may be performed at a temperature (T_3) equal to or lower than the A_{c1} temperature for a time (t_3) of 10 to 60 minutes. This may allow carbon to be concentrated in the metastable retained austenite during tempering and to stabilize the metastable retained austenite phase, thus giving a retained austenite phase that stably exists even at -196°C. The tempering, if performed for a tempering temperature T_3 higher than the A_{c1} temperature, or if performed for a tempering time t_3 shorter than 10 minutes, may fail to allow the carbon concentration in the metastable retained

austenite phase to proceed sufficiently and may fail to allow the steel plate to have a desired amount (volume fraction) of the retained austenite existing at -196°C [see Sample No. 26 (sample with an excessively high tempering temperature T3) in Table 2B]. In contrast, the tempering, if performed for a tempering time t3 longer than 60 minutes, may cause the retained austenite phase at -196°C to be formed excessively and may fail to allow the steel plate to have predetermined strengths [see Sample No. 27 (sample with an excessively long tempering time t3) in Table 2B].

[0089] The tempering temperature T3 in terms of lower limit is not particularly limited from the above viewpoint, but is preferably about 400°C or higher so as typically to sufficiently accelerate the diffusion of elements in the steel and to reduce the dislocation density.

[0090] Under preferred conditions, the tempering may be performed at a tempering temperature T3 of 570°C to 620°C for a tempering time t3 of from 15 minutes to 45 minutes (more preferably 35 minutes or shorter, and furthermore preferably 25 minutes or shorter).

[0091] The workpiece after the tempering as above is cooled down to room temperature. The cooling may be performed by any technique not limited, such as either of air cooling and water cooling.

[0092] The A_{c1} and A_{c3} temperatures in the present description are calculated based on formulae below (see "Koza Gendai no Kinzoku-gaku, Zairyo-hen 4, Tekko Zairyo" (in Japanese), The Japan Institute of Metals and Materials).

$$A_{c1} \text{ temperature} = 723 - 10.7[\text{Mn}] - 16.9[\text{Ni}] + 29.1[\text{Si}] + 16.9[\text{Cr}] + 290[\text{As}] + 6.38[\text{W}]$$

$$A_{c3} \text{ temperature} = 910 - 203[\text{C}]^{1/2} - 15.2[\text{Ni}] + 44.7[\text{Si}] + 104[\text{V}] + 31.5[\text{Mo}] + 13.1[\text{W}]$$

[0093] In the formulae, values in the brackets are contents (in mass percent) of the specified alloy elements in the steel. The steel plate according to the present invention does not contain As and W as steel chemical compositions, and the calculations according to the formulae are performed while defining [As] and [W] each as 0%. Examples

[0094] The present invention will be illustrated in further detail with reference to an experimental example (including several working examples) below. It should be noted, however, that the examples are by no means intended to limit the scope of the invention; that various changes and modifications can naturally be made therein without deviating from the spirit and scope of the invention as described herein; and all such changes and modifications should be considered to be within the scope of the invention.

Experimental Example 1

[0095] Under ingot making conditions given in Tables 2A and 2B, molten test sample steels having chemical compositions (in mass percent, with the remainder being iron and inevitable impurities) given in Tables 1A and 1B were made using a vacuum induction furnace (150-kg VIF), sequentially subjected to casting and hot forging, and thereby yielded steel ingots of a size of 150 mm by 150 mm by 600 mm. This experimental example employed a misch metal containing about 50% of Ce and about 25% of La as REM. Deoxidizing elements were added in the following orders. When the deoxidizing elements included no selective element, Si and Mn were added simultaneously before Al addition; whereas, when the deoxidizing elements included one or more selective elements, Si and Mn were added simultaneously before Al addition, and the selective elements such as REM, Zr, and/or Ca were added simultaneously after Al addition. In Tables 2A and 2B, [O] represents the dissolved oxygen content (ppm) before Al addition; and t2 represents the cooling time (second) in the temperature range from 1500°C down to 1450°C upon casting. The cooling in the temperature range from 1500°C down to 1450°C was controlled by air cooling or water cooling so as to be performed for the given cooling time.

[0096] Next, the steel ingots were each heated to a "temperature of heating before rolling" given in Tables 2A and 2B, subjected to rolling at a temperature of 830°C or higher to a thickness of 75 mm, in which final rolling was performed at a final rolling temperature of 780°C. The workpieces were water-cooled and thereby yielded steel plates each having a thickness of 25 mm. The steel plates obtained as above were each heated up to a temperature as given in Tables 2A and 2B (TL in Tables 2A and 2B), held with heating at that temperature for 5 to 60 minutes (tL in Tables 2A and 2B), and water-cooled down to room temperature. Next, the workpieces were subjected to tempering at a tempering temperature of T3 for a tempering time of t3 as given in Tables 2A and 2B, and cooled down to room temperature by air cooling or water cooling.

[0097] The steel plates obtained as above were examined in the following manner to evaluate the content (indicated as "W" in Tables 2A and 2B) of Mn-containing inclusions each having a largest dimension greater than 0.1 μm; the volume fraction (indicated as "V" in Tables 2A and 2B) of a retained austenite phase existing at -196°C; tensile properties (tensile strength TS and yield strength YS); and cryogenic toughness (percent brittle fracture in the C-direction at -196°C or -233°C).

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(1) Measurement of Content of Mn-Containing Inclusions Each Having Largest Dimension Greater Than 0.1 μm

5 [0098] The content of Mn-containing inclusions each having a largest dimension greater than 0.1 μm in each steel plate was determined in the following manner. A specimen having a section of several millimeters (about 10 mm by about 10 mm by about 5 mm) was sampled at a position immediately below the fracture surface of a residual sample after a Charpy impact test, where the sample had been sampled at a position one-fourth the thickness t of the steel plate. The specimen was examined to measure the content of compound-form Mn that forms a compound (insol. Mn content) by electrolytic extraction (iodine-methanol method).

10 [0099] Specifically, the specimen was immersed in an AA electrolyte (acetylacetone-tetramethylammonium chloride-methanol solution) and subjected to constant-current electrolysis at 20 mA/cm² or less. After the completion of electrolysis, the specimen was transferred into a 14% iodine methanol solution in a beaker and stirred with a magnetic stirrer, followed by ultrasonic separation of an extract from the specimen surface. The 14% iodine methanol solution was a solution prepared by dissolving 140 g of iodine in dehydrated methanol up to 1 liter. Next, the resulting ultrasonically separated liquid and the electrolyte after the electrolysis were combined, filtered with suction, and precipitates were collected on a filter. The filter used herein was a polycarbonate membrane filter having a pore size of 0.1 μm . The residue (precipitates) remained on the filter was transferred together with the filter into a platinum crucible, heated with a gas burner, and thereby ashed. Subsequently, a flux (a mixture of sodium carbonate and sodium tetraborate) was placed in the platinum crucible, followed by heating again with the gas burner to melt the residue. Next, the resulting melt was combined with an acid (hydrochloric acid) and water to be dissolved, transferred into a volumetric flask, further combined with water up to a constant volume (50 mL), and this was defined as an assay liquid. The assay liquid was examined to measure the amount of Mn using an inductively-coupled plasma (ICP) emission spectrometer. The value measured as above was defined as the compound-form Mn amount (1) (g) as detected by ICP technique.

20 [0100] Next, the difference in the weight (g) of the specimen between before and after the electrolysis was calculated and defined as a value (2). Based on the compound-form Mn amount (1) measured as above by ICP technique and the value (2), the content of compound-form Mn in the specimen was calculated according to the formula:

$$\text{Content (\% of compound-form Mn in the specimen)} = \left[\frac{\text{Amount (1) of compound-form Mn measured by ICP technique}}{\text{Difference (2) in weight of specimen between before and after electrolysis}} \right] \times 100$$

(2) Measurement of Amount (Volume Fraction) of Retained Austenite Phase Existing at -196°C

35 [0101] A test specimen of a size of 10 mm by 10 mm by 55 mm was sampled from each steel plate at a position one-fourth the thickness t , held at the liquid nitrogen temperature (-196°C) for 5 minutes, and subjected to X-ray diffractometry using a two-dimensional micro-diffraction X-ray diffractometer (RINT-RAPID II) supplied by Rigaku Corporation. Next, integrated intensity ratios of peaks of (111), (200), (220), and (311) planes of the retained austenite phase to peaks of (110), (200), (211), and (220) planes of the ferrite phase were respectively determined, based on which the (111), (200), (220), and (311) volume fractions of the retained austenite phase were calculated and averaged, and the average was defined as a "retained austenite volume fraction".

(3) Measurement of Tensile Properties (Tensile Strength TS and Yield Strength YS)

45 [0102] A Japanese Industrial Standard (JIS) Z 2241 No. 4 test specimen was sampled from each steel plate at a position one-fourth the thickness t in a direction parallel to the C-direction and subjected to a tensile test by the method prescribed in JIS Z 2241 to measure the tensile strength TS and yield strength YS. In this experimental example, a sample having a tensile strength TS greater than 690 MPa and a yield strength YS greater than 590 MPa was evaluated as having satisfactory base plate strengths.

(4) Measurement of Cryogenic Toughness (Percent Brittle Fracture in C-direction)

(4-1) Measurement of Percent Brittle Fracture at -196°C

55 [0103] Three Charpy impact test specimens (V-notched test specimens according to JIS Z 2242) were sampled from each steel plate in a direction parallel to the C-direction each at a position one-fourth the plate thickness and one-fourth the plate width and at a position one-fourth the plate thickness and half the plate width. The percent brittle fracture (%) at -196°C of the test specimens sampled from the two positions was measured by the method prescribed in JIS Z 2242

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and were averaged independently. Of the two averages thus calculated, one indicating inferior properties (namely, one with a higher percent brittle fracture) was employed. In this experimental example, a sample having an employed average of 10% or less was evaluated as having excellent cryogenic toughness.

5 (4-2) Measurement of Percent Brittle Fracture at -233°C

[0104] Some of the samples (samples each according to the present invention) were further examined to evaluate the percent brittle fracture at -233°C.

10 **[0105]** Specifically, each three test specimens were sampled from each steel plate at a position one-fourth the plate thickness and one-fourth the plate width, subjected to a Charpy impact test at -233°C by a method mentioned below, an average of measured percent brittle fracture values was calculated and evaluated. In this experimental example, a sample having a percent brittle fracture equal to or less than 50% was evaluated as having excellent percent brittle fracture at -233°C.

15 "Cryogenic Impact Test of Cast Austenitic Stainless Steel", Journal of the High Pressure Gas Safety Institute of Japan, vol. 24, p. 181.

[0106] Results of these measurements and evaluations are also indicated in Tables 2A and 2B. For reference purposes, the A_{c1} temperature and A_{c3} temperature are also indicated in Tables 1A, 1B, 2A, and 2B.

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[Table 1A]

| No. | C | Si | Mn | P | S | Al | Ni | N | Cu | Cr | Mo | Ti | Nb | V | B | Ca | REM | Zr | A ₅₁ | A ₅₃ |
|-----|------|------|------|--------|-------|-------|------|--------|------|------|------|-------|-------|--------|--------|--------|--------|-----|-----------------|-----------------|
| 1 | 0.05 | 0.06 | 0.90 | <0.004 | 0.001 | 0.033 | 5.62 | 0.0034 | | 0.40 | 0.30 | | | | | | | | 627 | 769 |
| 2 | 0.05 | 0.07 | 1.04 | <0.004 | 0.005 | 0.031 | 5.67 | 0.0037 | | 0.40 | 0.05 | | | | | | | | 625 | 756 |
| 3 | 0.04 | 0.06 | 0.88 | <0.004 | 0.001 | 0.030 | 5.76 | 0.0035 | | 0.32 | 0.14 | | | | | | | | 623 | 766 |
| 4 | 0.09 | 0.05 | 0.67 | <0.004 | 0.002 | 0.020 | 6.02 | 0.0033 | 0.22 | 0.18 | 0.19 | | | | | | | | 619 | 755 |
| 5 | 0.02 | 0.20 | 1.25 | <0.004 | 0.001 | 0.031 | 5.44 | 0.0029 | | 0.27 | 0.41 | | | | | 0.0047 | | | 628 | 786 |
| 6 | 0.03 | 0.38 | 0.69 | <0.004 | 0.004 | 0.037 | 7.23 | 0.0029 | | | 0.03 | | 0.026 | | | 0.0019 | | | 604 | 762 |
| 7 | 0.04 | 0.28 | 0.55 | <0.004 | 0.001 | 0.033 | 6.30 | 0.0041 | 0.11 | 0.27 | 0.34 | | | | | | | 623 | 786 | |
| 8 | 0.04 | 0.13 | 1.60 | <0.004 | 0.003 | 0.034 | 5.98 | 0.0026 | | | 0.25 | | | | 0.0017 | | | 609 | 744 | |
| 9 | 0.05 | 0.05 | 0.85 | 0.007 | 0.002 | 0.039 | 6.98 | 0.0029 | | 0.20 | 0.41 | | 0.013 | | | | | 601 | 750 | |
| 10 | 0.05 | 0.19 | 0.98 | <0.004 | 0.007 | 0.010 | 5.51 | 0.0042 | | 0.17 | 0.26 | 0.011 | | | | | 0.0019 | 628 | 770 | |
| 11 | 0.07 | 0.10 | 0.89 | <0.004 | 0.003 | 0.048 | 5.75 | 0.0031 | | 0.15 | | | 0.24 | | | | | 622 | 774 | |
| 12 | 0.04 | 0.02 | 0.94 | 0.006 | 0.002 | 0.040 | 5.05 | 0.0033 | 0.49 | 0.35 | 0.28 | | | 0.0018 | | | | 634 | 788 | |
| 13 | 0.03 | 0.22 | 1.75 | <0.004 | 0.001 | 0.020 | 5.73 | 0.0032 | | | 0.20 | | 0.03 | | | | | 614 | 753 | |
| 14 | 0.04 | 0.05 | 0.88 | <0.004 | 0.005 | 0.030 | 5.40 | 0.0071 | | 0.29 | 0.24 | 0.017 | | 0.0005 | 0.0010 | | | 629 | 774 | |
| 15 | 0.05 | 0.11 | 0.84 | <0.004 | 0.003 | 0.034 | 5.90 | 0.0057 | 0.10 | 0.22 | 0.20 | | | | | | | 621 | 765 | |
| 16 | 0.04 | 0.20 | 0.84 | <0.004 | 0.001 | 0.035 | 5.75 | 0.0031 | | 0.59 | 0.16 | | | 0.01 | | 0.0023 | | 633 | 782 | |
| 17 | 0.04 | 0.15 | 0.84 | 0.007 | 0.005 | 0.028 | 5.81 | 0.0034 | | 0.42 | 0.27 | 0.022 | | | | 0.0035 | | 627 | 776 | |
| 18 | 0.04 | 0.23 | 0.84 | 0.005 | 0.002 | 0.034 | 6.81 | 0.0037 | 0.38 | 0.16 | 0.05 | | | | | | | 608 | 763 | |
| 19 | 0.04 | 0.08 | 0.90 | <0.004 | 0.001 | 0.031 | 5.78 | 0.0027 | | 0.32 | 0.15 | | 0.38 | | | | | 623 | 806 | |
| 20 | 0.07 | 0.08 | 0.85 | 0.005 | 0.001 | 0.029 | 6.22 | 0.0028 | 0.18 | 0.25 | 0.16 | | | 0.0033 | | | | 615 | 751 | |
| 21 | 0.04 | 0.13 | 0.81 | <0.004 | 0.004 | 0.030 | 6.25 | 0.0030 | | 0.35 | 0.20 | | 0.10 | | | 0.0027 | | 618 | 778 | |
| 22 | 0.05 | 0.09 | 0.79 | <0.004 | 0.001 | 0.032 | 5.60 | 0.0038 | | 0.14 | 0.27 | | | | | | | 625 | 770 | |

[Table 1B]

| No. | C | Si | Mn | P | S | Al | Ni | N | Cu | Cr | Mo | Ti | Nb | V | B | Ca | REM | Zr | A ₀₁ | A ₀₃ |
|-----|------|------|------|--------|-------|-------|------|--------|------|------|------|-------|------|--------|--------|----|--------|----|-----------------|-----------------|
| 23 | 0.11 | 0.09 | 0.81 | <0.004 | 0.004 | 0.027 | 6.08 | 0.0038 | | 0.32 | 0.13 | | | | | | | | 620 | 738 |
| 24 | 0.05 | 0.09 | 0.92 | 0.008 | 0.001 | 0.034 | 5.81 | 0.0028 | 0.20 | 0.17 | 0.24 | | | | | | | | 620 | 766 |
| 25 | 0.10 | 0.43 | 0.81 | <0.004 | 0.001 | 0.030 | 6.20 | 0.0029 | | 0.11 | 0.16 | | | 0.0190 | | | | | 624 | 753 |
| 26 | 0.03 | 0.04 | 1.93 | <0.004 | 0.002 | 0.029 | 6.45 | 0.0028 | | 0.25 | 0.10 | | | | | | | | 599 | 727 |
| 27 | 0.05 | 0.07 | 0.74 | <0.004 | 0.005 | 0.032 | 5.50 | 0.0041 | 0.48 | 0.29 | 0.17 | | | | | | | | 629 | 780 |
| 28 | 0.05 | 0.08 | 0.40 | 0.005 | 0.001 | 0.032 | 5.33 | 0.0038 | | 0.42 | 0.28 | 0.014 | | | | | | | 638 | 789 |
| 29 | 0.04 | 0.11 | 1.20 | <0.004 | 0.008 | 0.037 | 6.43 | 0.0048 | | 0.16 | 0.17 | | | | | | | | 607 | 748 |
| 30 | 0.01 | 0.08 | 0.97 | <0.004 | 0.001 | 0.052 | 4.91 | 0.0048 | | 0.27 | 0.40 | | 0.26 | | | | | | 637 | 828 |
| 31 | 0.08 | 0.13 | 0.79 | <0.004 | 0.001 | 0.004 | 6.28 | 0.0107 | | 0.28 | 0.11 | 0.018 | | | | | | | 617 | 746 |
| 32 | 0.05 | 0.07 | 0.79 | <0.004 | 0.004 | 0.037 | 6.41 | 0.0032 | 1.08 | 0.15 | 0.16 | | | | 0.0032 | | | | 611 | 775 |
| 33 | 0.05 | 0.10 | 0.84 | 0.006 | 0.001 | 0.028 | 5.49 | 0.0032 | | 1.24 | 0.11 | | | | | | 0.0057 | | 635 | 771 |
| 34 | 0.03 | 0.09 | 1.14 | <0.004 | 0.007 | 0.044 | 6.39 | 0.0029 | | 0.22 | 0.17 | 0.104 | | | | | 0.0051 | | 609 | 755 |
| 35 | 0.04 | 0.22 | 0.98 | <0.004 | 0.003 | 0.037 | 6.02 | 0.0030 | | 0.04 | 1.05 | | | | | | | | 618 | 775 |
| 36 | 0.05 | 0.13 | 0.82 | <0.004 | 0.003 | 0.028 | 6.54 | 0.0037 | | 0.23 | 0.19 | 0.027 | | | | | 0.0018 | | 611 | 755 |
| 37 | 0.06 | 0.32 | 0.82 | <0.004 | 0.001 | 0.014 | 5.76 | 0.0029 | | 0.17 | 0.16 | | 0.52 | | | | | | 629 | 823 |
| 38 | 0.05 | 0.20 | 0.84 | <0.004 | 0.001 | 0.035 | 5.92 | 0.0032 | | 0.26 | 0.18 | | | 0.0052 | | | | | 624 | 767 |
| 39 | 0.05 | 0.17 | 0.72 | <0.004 | 0.001 | 0.031 | 5.84 | 0.0030 | | 0.26 | 0.22 | | | | | | | | 626 | 772 |
| 40 | 0.05 | 0.24 | 0.53 | <0.004 | 0.001 | 0.028 | 5.66 | 0.0025 | | 0.35 | 0.19 | | | | | | | | 635 | 783 |
| 41 | 0.05 | 0.06 | 0.90 | <0.004 | 0.001 | 0.033 | 5.62 | 0.0034 | | 0.25 | 0.18 | | | | | | | | 624 | 763 |
| 42 | 0.04 | 0.06 | 0.78 | <0.004 | 0.001 | 0.030 | 5.76 | 0.0035 | | 0.12 | 0.05 | | | | | | | | 621 | 764 |

[Table 2A]

| No. | Al addition to casting to hot rolling to tempering | | | | | | | | | | Cryogenic toughness | | Tensile properties | | | | |
|-----|--|--------|---------------------------------------|---------|----------|-----------------|-----------------|---------|----------------------|-------------------------|---------------------|--------|--------------------|--|--|-----|-----|
| | [O] (ppm) | t2 (s) | Temperature of heating before rolling | TL (°C) | tL (min) | A _{c1} | A _{c3} | T3 (°C) | t ₃ (min) | Cooling after tempering | V | W | V/W | Percent brittle fracture (% at -196°C) | Percent brittle fracture (% at -233°C) | YS | TS |
| 1 | 37 | 190 | 1,020 | 630 | 20 | 627 | 769 | 510 | 30 | Air cooling | 9.9% | 0.055% | 180 | 0% | 15% | 750 | 796 |
| 2 | 42 | 250 | 1,060 | 650 | 20 | 625 | 756 | 530 | 35 | Air cooling | 8.3% | 0.017% | 485 | 0% | 15% | 687 | 743 |
| 3 | 47 | 200 | 1,030 | 650 | 15 | 623 | 766 | 530 | 30 | Air cooling | 6.1% | 0.009% | 708 | 6% | 32% | 683 | 735 |
| 4 | 65 | 190 | 1,050 | 700 | 15 | 619 | 755 | 500 | 25 | Air cooling | 3.2% | 0.034% | 93 | 5% | 57% | 723 | 745 |
| 5 | 46 | 260 | 1,040 | 690 | 15 | 628 | 786 | 530 | 40 | Air cooling | 6.3% | 0.003% | 1,848 | 9% | 42% | 702 | 760 |
| 6 | 34 | 220 | 1,050 | 690 | 10 | 604 | 762 | 550 | 30 | Air cooling | 7.1% | 0.440% | 17% | 2% | 15% | 65% | 705 |
| 7 | 45 | 250 | 1,040 | 650 | 15 | 623 | 785 | 500 | 25 | Air cooling | 3.3% | 0.005% | 704 | 8% | 43% | 715 | 749 |
| 8 | 45 | 280 | 1,050 | 660 | 10 | 609 | 744 | 530 | 15 | Air cooling | 7.7% | 0.005% | 1,665 | 8% | 42% | 680 | 750 |
| 9 | 35 | 180 | 1,040 | 650 | 15 | 601 | 750 | 540 | 15 | Air cooling | 7.8% | 0.040% | 196 | 2% | 15% | 705 | 772 |
| 10 | 62 | 240 | 1,040 | 690 | 15 | 628 | 770 | 530 | 20 | Air cooling | 2.2% | 0.044% | 51 | 6% | 58% | 722 | 752 |
| 11 | 47 | 260 | 1,020 | 650 | 15 | 622 | 774 | 500 | 30 | Air cooling | 2.5% | 0.010% | 245 | 8% | 42% | 708 | 740 |
| 12 | 32 | 250 | 1,010 | 740 | 10 | 634 | 788 | 530 | 20 | Air cooling | 2.3% | 0.009% | 245 | 8% | 42% | 738 | 763 |
| 13 | 31 | 250 | 1,020 | 690 | 15 | 614 | 753 | 530 | 20 | Air cooling | 7.3% | 0.005% | 1,541 | 9% | 42% | 685 | 744 |
| 14 | 82 | 200 | 1,020 | 700 | 15 | 629 | 774 | 540 | 45 | Air cooling | 5.3% | 0.068% | 78 | 8% | 58% | 706 | 742 |
| 15 | 74 | 190 | 1,000 | 700 | 15 | 621 | 774 | 550 | 55 | Air cooling | 5.3% | 0.051% | 103 | 3% | 45% | 691 | 744 |
| 16 | 39 | 290 | 1,050 | 690 | 50 | 633 | 782 | 550 | 25 | Air cooling | 7.4% | 0.002% | 3,703 | 7% | 42% | 719 | 770 |
| 17 | 77 | 220 | 1,040 | 680 | 25 | 627 | 776 | 550 | 20 | Air cooling | 4.1% | 0.049% | 539 | 6% | 58% | 717 | 763 |
| 18 | 30 | 240 | 1,040 | 660 | 15 | 608 | 763 | 510 | 30 | Air cooling | 6.7% | 0.012% | 539 | 5% | 32% | 673 | 729 |
| 19 | 42 | 260 | 1,050 | 700 | 15 | 623 | 806 | 510 | 15 | Air cooling | 3.0% | 0.003% | 876 | 8% | 43% | 748 | 779 |

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(continued)

| No. | Al addition to casting to hot rolling to tempering | | | | | | | | | | Cryogenic toughness | | Tensile properties | | | | |
|-----|--|--------|---|------------|-------------|-----------------|-----------------|------------|-------------------------|----------------------------|---------------------|--------|--------------------|--|--|-----|-----|
| | [O] (ppm) | t2 (s) | Temperature of heating before rolling | TL (°C) | tL (min) | A _{c1} | A _{c3} | T3 (°C) | t ₃ (min) | Cooling after tempering | V | W | V/W | Percent brittle fracture (%) at -196°C | Percent brittle fracture (%) at -233°C | YS | TS |
| 20 | 45 | 300 | 1,040 | 720 | 15 | 615 | 751 | 520 | 25 | Air cooling | 2.6% | 0.002% | 1,246 | 8% | 43% | 724 | 757 |
| 21 | 32 | 290 | 1,020 | 690 | 15 | 618 | 778 | 530 | 15 | Air cooling | 4.5% | 0.004% | 1,185 | 9% | 42% | 722 | 761 |
| 22 | 46 | 270 | 1,060 | 650 | 15 | 625 | 770 | 520 | 20 | Air cooling | 5.0% | 0.002% | 2,091 | 9% | 43% | 714 | 736 |

[Table 2B]

| No. | A) addition to casting to hot rolling to tempering | | | | | | | | | | Cryogenic toughness | | Tensile properties | | | | |
|-----|--|--------|---|------------|-------------|-----------------|-----------------|------------|-------------|----------------------------|---------------------|---------|--------------------|--|--|-----|-----|
| | [O] (ppm) | t2 (g) | Temperature of heating before rolling | TL (°C) | tL (min) | A _{c1} | A _{c3} | T3 (°C) | t3 (min) | Cooling after tempering | V | W | V/W | Percent brittle fracture (%) at -196°C | Percent brittle fracture (%) at -233°C | YS | TS |
| 23 | 45 | 290 | 1,060 | 670 | 15 | 620 | 738 | 510 | 15 | Air cooling | 6.6% | 0.004% | 1,747 | 50% | - | 787 | 35 |
| 24 | 32 | 260 | 1,000 | 710 | 15 | 620 | 766 | 510 | 20 | Air cooling | 3.6% | 0.003% | 1,049 | 83% | - | 723 | 749 |
| 25 | 40 | 210 | 1,050 | 760 | 15 | 624 | 753 | 520 | 30 | Air cooling | 1.0% | 0.012% | 83 | 67% | - | 739 | 763 |
| 26 | 38 | 270 | 1,020 | 670 | 15 | 599 | 727 | 630 | 25 | Air cooling | 1.8% | 0.005% | 379 | 42% | - | 779 | 849 |
| 27 | 39 | 240 | 1,040 | 670 | 15 | 629 | 780 | 600 | 65 | Air cooling | 12.3% | 0.031% | 396 | 6% | - | 585 | 724 |
| 28 | 43 | 220 | 1,040 | 740 | 15 | 638 | 789 | 530 | 20 | Air cooling | 1.1% | 0.010% | 111 | 23% | - | 633 | 670 |
| 29 | 103 | 180 | 1,050 | 650 | 15 | 607 | 748 | 510 | 15 | Air cooling | 5.4% | 0.160% | 34 | 65% | - | 691 | 747 |
| 30 | 40 | 240 | 1,030 | 770 | 20 | 637 | 828 | 510 | 25 | Air cooling | 1.3% | 0.006% | 209 | 43% | - | 587 | 50 |
| 31 | 41 | 200 | 1,050 | 680 | 15 | 617 | 746 | 540 | 40 | Air cooling | 4.8% | 0.014% | 319 | 57% | - | 743 | 752 |
| 32 | 33 | 210 | 1,030 | 650 | 15 | 611 | 775 | 520 | 30 | Air cooling | 7.3% | 0.046% | 152 | 38% | - | 855 | 883 |
| 33 | 46 | 190 | 1,000 | 690 | 15 | 635 | 771 | 550 | 15 | Air cooling | 3.2% | 0.017% | 186 | 33% | - | 856 | 891 |
| 34 | 45 | 250 | 1,020 | 650 | 15 | 609 | 755 - | 540 | 40 | Air cooling | 10.3% | 0.033% | 312 | 19% | - | 649 | 740 |
| 35 | 35 | 210 | 1,000 | 660 | 15 | 618 | 775 | 500 | 25 | Air cooling | 3.6% | 0.036% | 99 | 12% | - | 856 | 882 |
| 36 | 30 | 290 | 1,010 | 650 | 15 | 611 | 755 | 550 | 15 | Air cooling | 6.5% | 0.003% | 2,297 | 13% | - | 683 | 746 |
| 37 | 41 | 180 | 1,030 | 690 | 15 | 629 | 823 | 510 | 35 | Air cooling | 2.5% | 0.020% | 125 | 17% | - | 774 | 804 |
| 38 | 46 | 200 | 1,060 | 650 | 15 | 624 | 767 | 550 | 25 | Air cooling | 7.5% | 0.014% | 521 | 29% | - | 676 | 747 |
| 39 | 43 | 327 | 1,010 | 700 | 15 | 626 | 772 | 540 | 20 | Air cooling | 2.2% | 0.103% | 21 | 52% | - | 716 | 743 |
| 40 | 39 | 220 | 1,100 | 720 | 15 | 635 | 783 | 540 | 20 | Air cooling | 2.0% | <0.001% | | 62% | - | 719 | 735 |
| 41 | 44 | 260 | 1,020 | 590 | 15 | 628 | 786 | 530 | 30 | Air cooling | 1.2% | 0.003% | 350 | 45% | - | 668 | 741 |

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(continued)

| No. | Al addition to casting to hot rolling to tempering | | | | | | | | V | W | V/W | Cryogenic toughness | | Tensile properties | | | |
|-----|--|--------|---------------------------------------|---------|----------|-----------------|-----------------|---------|----|-------------|------|---------------------|-------------------------|--|--|-----|-----|
| | [O] (ppm) | t2 (g) | Temperature of heating before rolling | TL (°C) | tL (min) | A _{c1} | A _{c3} | T3 (°C) | | | | t3 (min) | Cooling after tempering | Percent brittle fracture (%) at -196°C | Percent brittle fracture (%) at -233°C | YS | TS |
| 42 | 45 | 250 | 1,040 | 720 | 60 | 623 | 786 | 600 | 25 | Air cooling | 5.2% | 0.005% | 1.104 | 8% | - | 575 | 670 |

[0107] Tables 2A and 2B give considerations as follows.

[0108] Sample Nos. 1 to 22 in Table 2A were samples respectively employing steels of Steel Nos. 1 to 22 in Table 1A and meeting all the conditions specified in the present invention. As indicated in Table 2A, these samples according to the present invention could provide steel plates having high base plate strengths and still having excellent cryogenic toughness at -196°C. Specifically, these samples had an average percent brittle fracture in the C-direction of equal to or less than 10%.

[0109] In contrast, Sample Nos. 23 to 42 in Table 2B were comparative examples not meeting one or more of the conditions specified in the present invention, because the samples did not meet either one of the steel chemical compositions and the preferred production conditions specified in the present invention. The samples therefore failed to have desired property or properties.

[0110] Specifically, Sample No. 23 employed Steel No. 23 in Table 1B having an excessively high carbon content, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0111] Sample No. 24 employed Steel No. 24 in Table 1B having an excessively high phosphorus content, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0112] Sample No. 25 employed Steel No. 25 in Table 1B having an excessively high Si content and underwent heating at a temperature (TL) higher than the two-phase region temperatures, and included an insufficient amount of retained austenite. The sample thereby suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness.

[0113] Sample No. 26 employed Steel No. 26 in Table 1B having steel chemical compositions meeting the conditions specified in the present invention, but underwent tempering at an excessively high tempering temperature (T3), and included an insufficient amount of retained austenite. The sample thereby suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness.

[0114] Sample No. 27 employed Steel No. 27 in Table 1B having steel chemical compositions meeting the conditions specified in the present invention, but underwent tempering for an excessively long tempering time (t3), and thereby included an excessively large amount of retained austenite. The sample thus failed to surely have the desired base plate strengths.

[0115] Sample No. 28 employed Steel No. 28 in Table 1B having an excessively low Mn content and included an insufficient amount of retained austenite. The sample thereby suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness.

[0116] Sample No. 29 employed Steel No. 29 in Table 1B having an excessively high sulfur content. The sample thereby included an excessively large amount of Mn-containing inclusions, although the temperature of heating before hot rolling was controlled within the preferred range (1060°C or lower) in the present invention. The sample suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness.

[0117] Sample No. 30 employed Steel No. 30 in Table 1B having an excessively low carbon content, an excessively high Al content, and an excessively low Ni content, and included an insufficient amount of retained austenite. The sample thereby suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness. In addition, the sample had a low tensile strength TS and a low yield strength YS.

[0118] Sample No. 31 employed Steel No. 31 in Table 1B having an excessively low Al content and an excessively high N content, thereby suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0119] Sample No. 32 employed Steel No. 32 in Table 1B having excessively high contents of Cu and Ca as selective elements, thereby had excessively high strengths, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0120] Sample No. 33 employed Steel No. 33 in Table 1B having excessively high contents of Cr and Zr as selective elements, thereby had excessively high strengths, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0121] Sample No. 34 employed Steel No. 34 in Table 1B having excessively high contents of Nb and REM as selective elements, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0122] Sample No. 35 employed Steel No. 35 in Table 1B having an excessively high content of Mo as a selective element, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0123] Sample No. 36 employed Steel No. 36 in Table 1B having an excessively high content of Ti as a selective element, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0124] Sample No. 37 employed Steel No. 37 in Table 1B having an excessively high content of vanadium (V) as a selective element, thereby had excessively high strengths, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0125] Sample No. 38 employed Steel No. 38 in Table 1B having an excessively high content of boron (B) as a selective element, thereby suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness.

[0126] Sample No. 39 employed Steel No. 39 in Table 1B having steel chemical compositions meeting the conditions specified in the present invention, but underwent cooling from 1500°C down to 1450°C upon casting for an excessively

long cooling time (t₂) and included an excessively high content of desired Mn-containing inclusions. The sample thereby suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness.

[0127] Sample No. 40 employed Steel No. 40 in Table 1B having steel chemical compositions meeting the conditions specified in the present invention, but underwent heating before rolling at an excessively high temperature. The sample thereby included Mn-containing inclusions in a content of less than 0.001 mass percent, suffered from a high percent brittle fracture, and failed to achieve the desired cryogenic toughness. In Table 2B, "V/W" of Sample No. 40 could not be calculated because of having W (content of Mn-containing inclusions) of less than 0.001 mass percent and is left blank.

[0128] Sample No. 41 employed Steel No. 41 in Table 1B having steel chemical compositions meeting the conditions specified in the present invention, but underwent heating at a temperature (TL) lower than the two-phase region temperatures, and included an insufficient amount of retained austenite. The sample thereby suffered from a high percent brittle fracture and failed to achieve the desired cryogenic toughness.

[0129] Sample No. 42 employed Steel No. 42 in Table 1B having steel chemical compositions meeting the conditions specified in the present invention, but underwent heating at a temperature in the two-phase region for a time (tL) longer than the desired heating time, and thereby had lower strengths.

[0130] Of the samples according to the present invention (Sample Nos. 1 to 22) in Table 2A, those excluding Sample Nos. 4, 10, 14, 15, and 17 had a percent brittle fracture at -233°C also at good level, because the free oxygen content [O] before Al addition was controlled to 60 ppm or less to adjust the C-value to 150 or more.

[0131] While the present invention has been particularly described with reference to specific embodiments thereof it is obvious to those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the present invention.

[0132] The present application is based on Japanese Patent Application No. 2013-086852 filed on April 17, 2013, the entire contents of which are incorporated herein by reference.

Industrial Applicability

[0133] The steel plate according to the present invention is useful typically for LNG storage tanks and transport ships.

Claims

1. A steel plate having excellent cryogenic toughness, the steel plate comprising:

in mass percent,

C in a content of 0.02% to 0.10%;

Si in a content of 0.40% or less (excluding 0%);

Mn in a content of 0.50% to 2.0%;

P in a content of 0.007% or less (excluding 0%);

S in a content of 0.007% or less (excluding 0%);

Al in a content of 0.005% to 0.050%;

Ni in a content of 5.0% to 7.5%); and

N in a content of 0.010% or less (excluding 0%),

with the remainder being iron and inevitable impurities,

wherein a content of Mn-containing inclusions each having a largest dimension greater than 0.1 μm in the steel is 0.001 to 0.07 mass percent, and

wherein a fraction of a retained austenite phase existing at -196°C is 2.0 to 12.0 volume percent.

2. The steel plate according to claim 1, further comprising at least one selected from groups (a) to (e):

(a) Cu in a content of 1.0% or less (excluding 0%);

(b) at least one element selected from the group consisting of

Cr in a content of 1.20% or less (excluding 0%); and

Mo in a content of 1.0% or less (excluding 0%);

(c) at least one element selected from the group consisting of

Ti in a content of 0.025% or less (excluding 0%);

Nb in a content of 0.100% or less (excluding 0%); and

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V in a content of 0.50% or less (excluding 0%);

(d) B in a content of 0.0050% or less (excluding 0%); and

(e) at least one element selected from the group consisting of

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Ca in a content of 0.0030% or less (excluding 0%);

at least one rare-earth element (REM) in a content of 0.0050% or less (excluding 0%); and

Zr in a content of 0.005% or less (excluding 0%).

- 10 **3.** The steel plate according to one of claims 1 and 2,
wherein a C-value as specified by V/W is 150 or more, where V represents the fraction (in volume percent) of the
retained austenite phase existing at -196°C ; and W represents the content (in mass percent) of the Mn-containing
inclusions each having a largest dimension greater than $0.1\ \mu\text{m}$.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/060200

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C22C38/40(2006.01)i, C22C38/58(2006.01)i, B22D11/124
(2006.01)n, C21D8/02(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, C21D8/00-8/10, B22D11/124

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 1996-2014
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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | WO 2012/005330 A1 (Nippon Steel Corp.), 12 January 2012 (12.01.2012), claims 1, 2; paragraph [0050] & US 2013/0098514 A1 & EP 2592166 A1 & CN 102985576 A & KR 10-2013-0014069 A | 1-3 |
| A | JP 1-228643 A (Nippon Steel Corp.), 12 September 1989 (12.09.1989), claim 1; page 2, upper right column, line 16 to page 3, lower left column, line 17 & US 4979558 A & EP 337114 A1 & DE 68907251 D1 | 1-3 |

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

| | |
|---|--|
| * Special categories of cited documents: | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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Date of the actual completion of the international search
25 June, 2014 (25.06.14)

Date of mailing of the international search report
08 July, 2014 (08.07.14)

Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/060200

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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