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(54) **THICK STEEL PLATE HAVING EXCELLENT CRYOGENIC TOUGHNESS**

(57) This steel plate contains predetermined steel chemical compositions and has a Di value of 2.5 or more, where the Di value is defined by the steel chemical compositions. The steel plate includes a retained austenite phase (retained γ) existing at -196°C in a volume fraction

of 2.0% to 12.0% and has a retained austenite stabilization parameter of 3.1 or more, where the parameter is defined by chemical compositions contained in the retained austenite existing at -196°C.

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Description

Technical Field

[0001] The present invention relates to steel plates having excellent cryogenic toughness (toughness at cryogenic temperatures). Specifically, the present invention relates to a steel plate having good toughness [in particular, toughness in a crosswise direction (width direction; C-direction)] at cryogenic temperatures of -196°C or lower 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), in which the steel plates are exposed to the cryogenic temperatures. Such steel plates are represented by those for use in 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

[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 high toughness as to endure a cryogenic temperature of -196°C . In general, steels are known to have better hardness-toughness balance especially at low temperatures by the addition of Ni. For this reason, steel plates having a Ni content of about 9% (9% Ni steel plates) have been used as steel plates for the use. However, owing to increasing Ni cost in recent years, there are developed steel plates having excellent cryogenic toughness even though containing Ni in a lower content of less than 9%.

[0003] Typically, Nonpatent Literature 1 describes the effects of a heat treatment of 6% Ni steel in the ferrite-austenite two-phase region on low-temperature toughness. Specifically, a heat treatment (L treatment; lamellarizing) in the ferrite-austenite two-phase region (between A_{c1} and A_{c3}) is added prior to a tempering treatment of a conventional process. This allows the formation of a large amount of finely dispersed retained austenite, where the retained austenite is stable even against impact load at cryogenic temperatures. Accordingly, the resulting 6% Ni steel can ensure 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. The 6% Ni steel has excellent cryogenic toughness in the L-direction, but, unfortunately, 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). In addition, the literature fails to describe percent brittle fracture.

[0004] Techniques as in Nonpatent Literature 1 are also described in Patent Literature 1 and Patent Literature 2. Of these, Patent Literature 1 describes a method. This method uses a steel having a Ni content of 4.0% to 10% and having austenite grain size and other factors controlled within predetermined ranges. In the method, the steel is subjected to a specific treatment one or more times and tempered at a temperature equal to or lower than the A_{c1} transformation temperature. In the 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 Nonpatent Literature 1. Patent Literature 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 Patent Literature 1. The values of impact energy at -196°C (vE_{-196}) described in these methods are probably those in the L-direction, and the values as toughness in the C-direction are not found therein. In addition, the methods fail to consider the strength and to describe the percent brittle fracture.

[0005] Nonpatent Literature 2 describes development of a 6% Ni steel for LNG tanks, in which the L treatment (two-phase region quenching treatment) and a thermal-mechanical control process (TMCP) are employed 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).

[0006] In contrast, Patent Literature 3 describes a steel plate for cryogenic temperature use, where the steel plate has a reduced Ni content, and a method for producing the steel plate. The steel plate employs a Ni steel plate having a Ni content of greater than 5.0% to less than 8.0% and having a yield strength of 590 MPa or more at room temperature. Even in use environments, the steel plate has excellent safety against fracture equivalent to that of 9% Ni steels. According to the technique disclosed in Patent Literature 3, a steel ingot is heated at a low temperature for a short time in a heating process, and the heated steel ingot in a rolling process is subjected to rough rolling to such a reduction that the steel ingot upon the completion of rough rolling has a thickness 3 to 8 times as much as the thickness of the product (thickness of the steel plate after finish rolling). The technique is based on a finding that a steel plate can have better safety against fracture (namely, can have higher toughness in a low-temperature environment) when the steel plate is allowed to surely have a higher yield point in an environment at low temperatures (cryogenic temperatures), where the resulting steel plate is used in such cryogenic temperature environment. In the working examples in the literature, the workpiece (slab) is rolled from a slab thickness of 300 mm down to a finish thickness of 50 mm or less (mostly to a finish thickness of

less than 50 mm). The resulting steel plate, as surely having a relatively high rolling reduction, has both retained austenite in a certain fraction and a finely dispersed matrix phase and achieves cryogenic toughness at a level equal to the 9% Ni steels. However, the steel plate disclosed in Patent Literature 3 has a tensile strength TS at room temperature of at largest 741 MPa.

[0007] Patent Literature 3 mentions the absorbed energy in the C-direction, but fails to describe the percent brittle fracture. In addition, the steel plate disclosed in Patent Literature 3 has a tensile strength TS at room temperature of at largest about 741 MPa.

Citation List

Patent Literature

[0008]

Patent Literature 1: Japanese Unexamined Patent Application Publication (JP-A) No. Sho49(1974)-135813
Patent Literature 2: JP-A No. Sho51(1976)-13308
Patent Literature 3: JP-A No. 2011-241419

Nonpatent Literature

[0009]

Nonpatent Literature 1: Yano et al., "Effects of ferrite-austenite two-phase region heat treatment of 6% Ni steel on low-temperature toughness", Tetsu-to-hagane (in Japanese), The 59th year (1973), vol. 6, pp. 752-763

Nonpatent Literature 2: Furuya et al., "Development of 6% Ni steel for LNG tanks", CAMP-ISIJ, Vol. 23 (2010), p. 1322

Summary of Invention

Technical Problem

[0010] As is described above, on Ni steels having a Ni content of about 5.0% to about 7.5%, techniques to give Ni steels having excellent cryogenic toughness at -196°C have been proposed, but sufficient investigations on cryogenic toughness in the C-direction has not yet been made. Such steels, when allowed to have higher strengths, are advantageous typically in that they can be designed with larger margin. However, there has been provided no technique relating to a steel plate having high strengths and excellent cryogenic toughness.

[0011] In addition, none of the above-mentioned literature makes 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 having a high base metal (steel) strength and also having a percent brittle fracture meeting the condition.

[0012] The present invention has been made in consideration of these circumstances. It is an object of the present invention to provide a high-strength steel plate that includes a Ni steel having a Ni content of about 5.0% to about 7.5%, has excellent cryogenic toughness (in particular, cryogenic toughness in the C-direction) at -196°C, and achieves a percent brittle fracture of equal to or less than 10%. It is another object of the present invention to provide a method for producing the steel plate.

Solution to Problem

[0013] The present invention has achieved the objects and provides, in one embodiment (first embodiment), 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%, N in a content of 0.010% or less (excluding 0%), and 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%) with the remainder consisting of iron and inevitable impurities. The steel plate has a Di value as specified by Formula (1) of 2.5 or more. Formula (1) is defined by steel chemical compositions and is expressed as follows:

$$\text{Di value} = ([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times 1.115 \quad (1)$$

where [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], and [V] are contents (in mass percent) respectively of C, Si, Mn, Cu, Ni, Cr, Mo, and V in the steel. The steel plate includes a retained austenite phase (retained γ) existing at -196°C in a volume fraction of 2.0% to 12.0%. The steel plate has a retained austenite stabilization parameter as specified by Formula (2) of 3.1 or more. Formula (2) is defined by chemical compositions contained in the retained austenite and is expressed as follows:

$$\text{Retained austenite stabilization parameter} = (365 \times \langle C \rangle + 39 \times \langle Mn \rangle + 30 \times \langle Al \rangle + 10 \times \langle Cu \rangle + 17 \times \langle Ni \rangle + 20 \times \langle Cr \rangle + 5 \times \langle Mo \rangle + 35 \times \langle V \rangle) / 100 \quad (2)$$

where $\langle C \rangle$, $\langle Mn \rangle$, $\langle Al \rangle$, $\langle Cu \rangle$, $\langle Ni \rangle$, $\langle Cr \rangle$, $\langle Mo \rangle$, and $\langle V \rangle$ are contents (in mass percent) respectively of C, Mn, Al, Cu, Ni, Cr, Mo, and V in the retained austenite existing at -196°C .

[0014] In a preferred embodiment according to the first embodiment of the present invention, the steel plate may have a retained austenite phase volume fraction-retained austenite stabilization parameter as specified by Formula (3) of 40 or less. Formula (3) is defined by the retained austenite phase volume fraction and the retained austenite stabilization parameter and is expressed as follows:

$$\text{Retained austenite volume fraction-retained austenite stabilization parameter} = 10 / [(\text{retained austenite phase volume fraction}) \times (\text{retained austenite stabilization parameter})]^{1/2} \quad (3)$$

[0015] In a preferred embodiment of the present invention, the element contents, Di value, and retained austenite volume fraction of the steel plate may be controlled within narrower ranges (more specified ranges), and the Mn content in the retained austenite may be controlled instead of the retained austenite stabilization parameter. This steel plate can have still higher base metal strengths and can offer satisfactory cryogenic toughness.

[0016] Specifically, the present invention provides, in another embodiment (second embodiment), 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 0.6% 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%, N in a content of 0.010% or less (excluding 0%), Mo in a content of 0.30% to 1.0%, and Cr in a content of 1.20% or less (excluding 0%) with the remainder consisting of iron and inevitable impurities. The steel plate has a Di value as specified by Formula (1) of greater than 5.0. The steel plate includes a retained austenite phase (retained γ) existing at -196°C in a volume fraction of 2.0% to 5.0%. The retained austenite phase (retained γ) existing at -196°C has a Mn content of 1.05% or more. In addition, the steel has Mn and Ni contents (in mass percent) meeting a condition specified by Formula (4):

$$[Mn] \geq 0.31 \times (7.20 - [Ni]) + 0.50 \quad (4)$$

where [Mn] and [Ni] are contents (in mass percent) respectively of Mn and Ni in the steel.

[0017] In a preferred embodiment of the present invention, the steel plate may further contain Cu in a content of 1.0% or less (excluding 0%).

[0018] In a preferred embodiment of the present invention, the steel plate may further contain at least one 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%).

[0019] In a preferred embodiment of the present invention, the steel plate may further contain B in a content of 0.0050% or less (excluding 0%).

[0020] In a preferred embodiment of the present invention, the steel plate may further contain at least one selected from the group consisting of Ca in a content of 0.0030% or less (excluding 0%) and at least one rare-earth element

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

[0021] In a preferred embodiment of the present invention, the steel plate may further contain Zr in a content of 0.005% or less (excluding 0%).

[0022] The present invention also achieves the objects and further provides, in yet another embodiment (third embodiment), a method for producing the steel plate according to the first embodiment of the present invention. The method includes the steps a) and b). In the step a), a steel plate is formed from a steel and subjected to a heat treatment (L treatment) in a ferrite-austenite two-phase region (between A_{c1} and A_{c3}). The steel has such controlled chemical compositions and the L treatment is performed at such a controlled temperature (L treatment temperature) that an L parameter as specified by Formula (5) is 0.25 to 0.45 and a λ_L parameter as specified by Formula (6) is 7 or less. The step b) is performed after the L treatment, in which the steel plate is water-cooled down to room temperature and subjected to a tempering treatment (T treatment) at a temperature equal to or lower than the A_{c1} temperature for 10 to 60 minutes. Formula (5) is defined by the L treatment temperature and the A_{c1} and A_{c3} temperatures in the steel. Formula (6) is defined by the L parameter and the steel chemical compositions. Formulae (5) and (6) are expressed as follows:

$$L \text{ parameter} = ((L \text{ treatment temperature}) - A_{c1}) / (A_{c3} - A_{c1}) + 0.25 \quad (5)$$

$$\lambda_L \text{ parameter} = 9.05 \times (0.90 \times [L \text{ parameter}] + 0.14) \times [Mn] + 1.46 \times (0.37 \times [L \text{ parameter}] + 0.67) \times [Cr] - 41.5 \times (0.26 \times [L \text{ parameter}] + 0.79) \times [Mo] \quad (6)$$

where [Mn], [Cr], and [Mo] are contents (in mass percent) respectively of Mn, Cr, and Mo in the steel.

[0023] In addition, the present invention achieves the objects and provides, in still another embodiment (fourth embodiment), a method for producing the steel plate according to the second embodiment of the present invention. In the method, the L treatment temperature and the steel chemical compositions are adjusted so that an L parameter as specified by Formula (5) is 0.6 to 1.1 and a λ_L parameter as specified by Formula (6) is 0 or less.

Advantageous Effects of Invention

[0024] The present invention can provide high-strength steel plates each including a Ni steel having a Ni content of about 5.0% to about 7.5%. The steel plates have high base metal strengths, specifically, have a tensile strength TS of greater than 741 MPa and a yield strength YS of greater than 590 MPa, and preferably have a tensile strength TS of equal to or greater than 830 MPa and a yield strength YS of equal to or greater than 690 MPa. Even having such high base metal strengths, the steel plates have excellent cryogenic toughness (in particular, cryogenic toughness in the C-direction) at temperatures of -196°C or lower and have a percent brittle fracture of equal to or less than 10% at -196°C, and preferably have a percent brittle fracture of equal to or less than 50% at -233°C.

Description of Embodiments

[0025] The present inventors made investigations so as to provide a steel plate that has a Ni content of 7.5% or less and, when subjected to a Charpy impact test in the C-direction, has a percent brittle fracture of 10% or less at -196°C, a tensile strength TS of greater than 741 MPa, and a yield strength YS of greater than 590 MPa.

[0026] In particular, the present inventors made investigations while paying attention to following points.

[0027] Initially, a production method according to the present invention was designed to attain cryogenic toughness at the same level as compared with a 9% Ni steel even without strictly controlling rolling and cooling conditions after T treatment as in the techniques disclosed in Patent Literatures 1 and 3. Specifically, the chemical compositions of a material steel were designed in consideration of the case where such rolling reduction as in Patent Literature 3 is not obtained. Rolling in the present invention was designed on the assumption that the rolling reduction at a temperature of 830°C or higher is controlled to about 50% or less, and the rolling reduction at a temperature of 700°C or higher is controlled to about 85% or less; and that cooling after the tempering treatment (T treatment) is performed not by water cooling, but by air cooling. The rolling reduction (%) was calculated as: $100 \times [(\text{Thickness before rolling}) - (\text{Thickness after rolling})] / (\text{Thickness before rolling})$.

[0028] The steel (plate) was designed to have cryogenic toughness as evaluated in the C-direction, in which direction toughness is tend to be hardly ensured as compared with the L-direction. In addition, the cryogenic toughness was to be evaluated not by absorbed energy, but by percent brittle fracture so as to surely provide toughness at a certain level. The steel plate herein was also designed to have a tensile strength (TS) of greater than 741 MPa. This is because a higher tensile strength TS within specifications is better in consideration of safety in designing of pressure vessels to be

used at cryogenic temperatures.

[0029] Specifically, the present inventors made intensive investigations so as to provide a steel plate that is produced under the production conditions, has a percent brittle fracture at -196°C of equal to or less than 10% in the C-direction in a Charpy impact test, a tensile strength TS of greater than 741 MPa, and a yield strength YS of greater than 590 MPa.

[0030] As a result, the present inventors have found the controls of retained austenite morphology [control conditions (A) and (B)] and λ_L parameter [control condition (C)] as follows; and have found that the controls allow the steel plate to include stable retained austenite at a certain level and to have excellent cryogenic toughness, where the stable retained austenite does not transform into martensite, but plastically deforms during the Charpy impact test. The controls are expressed as follows:

(A) The Di value is controlled by an appropriate balance among steel chemical compositions, as specified by Formula (1). This control is performed so as to surely provide stable retained austenite (i.e., to provide better stability of retained austenite), because such stable retained austenite does not transform into martensite, but plastically deforms during the application of impact at a cryogenic temperature, and thus contributes to better toughness.

(B) Steel chemical compositions and an L treatment temperature are balanced by the L parameter as specified by Formula (5). The L treatment temperature refers to a temperature of a heat treatment (L treatment) in a ferrite-austenite two-phase region (between A_{c1} and A_{c3}). After the L treatment, the steel plate is water-cooled down to room temperature, subjected to a tempering treatment (T treatment) under predetermined conditions, and then air-cooled. Thus, the volume fraction of retained austenite (retained γ) existing at -196°C is controlled within the range of 2.0% to 12.0%; and the retained austenite stabilization parameter as specified by Formula (2) is controlled to 3.1 or more, where the retained austenite stabilization parameter is defined by chemical compositions in the retained austenite existing at -196°C. Preferably, the retained austenite volume fraction-retained austenite stabilization parameter as specified by Formula (3) is controlled to 40 or less, where the retained austenite volume fraction-retained austenite stabilization parameter is defined by the retained austenite volume fraction and the retained austenite stabilization parameter.

(C) The λ_L parameter is controlled as specified by Formula (5), where the λ_L parameter is defined by chemical compositions (Mn, Cr, and Mo) and the L treatment temperature.

[0031] Specifically, the steel plate according to the embodiment of 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%, N in a content of 0.010% or less (excluding 0%), and 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%), with the remainder consisting of iron and inevitable impurities. The steel plate has a Di value as specified by Formula (1) of 2.5 or more, a volume fraction of retained austenite phase (retained γ) existing at -196°C of 2.0% to 12.0%, and a retained austenite stabilization parameter as specified by Formula (2) of 3.1 or more. Formula (1) is defined by the steel chemical compositions. Formula (2) is defined by chemical compositions contained in the retained austenite existing at -196°C. Formulae (1) and (2) are expressed as follows:

Di value =

$$\left(\frac{[C]}{10}\right)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times 1.115 \quad (1)$$

where [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], and [V] are contents (in mass percent) respectively of C, Si, Mn, Cu, Ni, Cr, Mo, and V in the steel,

Retained austenite stabilization parameter =

$$(365 \times \langle C \rangle + 39 \times \langle Mn \rangle + 30 \times \langle Al \rangle + 10 \times \langle Cu \rangle + 17 \times \langle Ni \rangle + 20 \times \langle Cr \rangle + 5 \times \langle Mo \rangle + 35 \times \langle V \rangle) / 100 \quad (2)$$

where $\langle C \rangle$, $\langle Mn \rangle$, $\langle Al \rangle$, $\langle Cu \rangle$, $\langle Ni \rangle$, $\langle Cr \rangle$, $\langle Mo \rangle$, and $\langle V \rangle$ are contents (in mass percent) respectively of C, Mn, Al, Cu, Ni, Cr, Mo, and V in the retained austenite existing at -196°C.

1. Steel Chemical Compositions

[0032] Initially, the steel chemical compositions will be described.

Carbon (C): 0.02% to 0.10%

[0033] Carbon (C) is essential to ensure strengths and retained austenite at certain levels. To have such activities effectively, the carbon content is controlled in its lower limit to be 0.02% or more, 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 have inferior cryogenic toughness contrarily. To prevent this, the carbon content is controlled in its upper limit to be 0.10% or less, preferably 0.08% or less, and more preferably 0.06% or less.

Silicon (Si): 0.40% or less (excluding 0%)

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

Manganese (Mn): 0.50% to 2.0%

[0035] Manganese (Mn) stabilizes austenite (γ) and contributes to a larger amount of retained austenite. To have such activities effectively, the Mn content is controlled in its lower limit to be 0.50% or more, 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 desired cryogenic toughness. To prevent this, the Mn content is controlled in its upper limit to be 2.0% or less, preferably 1.5% or less, and more preferably 1.3% or less.

Phosphorus (P): 0.007% or less (excluding 0%)

[0036] Phosphorus (P) is an impurity element and causes grain boundary fracture. To ensure desired cryogenic toughness, the phosphorus content is controlled in its upper limit to be 0.007% or less, and preferably 0.005% or less. The phosphorus content is preferably minimized, but it is difficult to industrially control the phosphorus content to be 0%.

Sulfur (S): 0.007% or less (excluding 0%)

[0037] Sulfur (S) is an impurity element and causes grain boundary fracture, as with phosphorus. To ensure desired cryogenic toughness, the sulfur content is controlled in its upper limit to be 0.007% or less. As will be indicated in after-mentioned experimental examples, a steel has an increasing percent brittle fracture with an increasing sulfur content and fails to achieve desired cryogenic toughness (percent brittle fracture at -196°C of equal to or less than 10%). The sulfur content is preferably controlled in its upper limit to be 0.005% or less. The sulfur content is preferably minimized, but it is difficult to industrially control the sulfur content to be 0%.

Aluminum (Al): 0.005% to 0.050%

[0038] Aluminum (Al) accelerates desulfurization and fixes nitrogen. The steel plate, if having an insufficient Al content, may have increased contents typically of solute sulfur and solute nitrogen to thereby have inferior cryogenic toughness. To prevent this, the Al content is controlled in its lower limit to be 0.005% or more, preferably 0.010% or more, and more preferably 0.015% or more. However, Al, if added in excess, may cause oxides, nitrides, and other particles to coarsen and may also cause the steel plate to have inferior cryogenic toughness. To prevent this, the Al content is controlled in its upper limit to be 0.050% or less, preferably 0.045% or less, and more preferably 0.04% or less.

Nickel (Ni): 5.0% to 7.5%

[0039] Nickel (Ni) is essential to allow the steel plate to surely include retained austenite (retained γ) that is useful for better cryogenic toughness. To have such activities effectively, the Ni content is controlled in its lower limit to be 5.0% or more, preferably 5.2% or more, and more preferably 5.4% or more. However, Ni, if added in excess, may cause increased cost of the raw material. To prevent this, the Ni content is controlled in its upper limit to be 7.5% or less, preferably 7.0% or less, more preferably 6.5% or less, furthermore preferably 6.2% or less, and still more preferably 6.0% or less.

Nitrogen (N): 0.010% or less (excluding 0%)

[0040] Nitrogen (N) causes strain aging and causes the steel plate to have inferior cryogenic toughness. To prevent this, the nitrogen content is controlled in its upper limit to be 0.010% or less, preferably 0.006% or less, and more preferably 0.004% or less.

[0041] At least one element selected from the group consisting of chromium (Cr) in a content of 1.20% or less (excluding 0%) and molybdenum (Mo) in a content of 1.0% or less (excluding 0%)

[0042] Chromium (Cr) and molybdenum (Mo) each contribute to higher strengths. Each of these elements may be added alone or in combination. To have the activities effectively, the Cr content is controlled to be 0.05% or more, and the Mo content is controlled to be 0.01% or more. However, each of the elements, if added in excess, may cause the steel plate to have excessively high strengths and to fail to ensure desired cryogenic toughness. To prevent this, the Cr content is controlled in its upper limit to be 1.20% or less, preferably 1.1% or less, more preferably 0.9% or less, and furthermore preferably 0.5% or less; and the Mo content is controlled in its upper limit to be 1.0% or less, preferably 0.8% or less, and more preferably 0.6% or less.

[0043] The steel plate according to the present invention contains the chemical compositions as basic compositions with the remainder consisting of iron and inevitable impurities.

[0044] The steel plate according to the present invention may further contain one or more of following selective chemical compositions so as to further have one or more properties.

Copper (Cu): 1.0% or less (excluding 0%)

[0045] Copper (Cu) stabilizes austenite and contributes to an increased amount of retained austenite. To have such activities 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 high strengths and to fail to effectively have desired cryogenic toughness. To prevent this, the Cu content is preferably controlled in its upper limit to be 1.0% or less, more preferably 0.8% or less, and furthermore preferably 0.7% or less.

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

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

Boron (B): 0.0050% or less (excluding 0%)

[0048] Boron (B) element allows the steel to have better hardenability and to thereby have higher strengths. To have the activities effectively, the boron content is preferably controlled to be 0.0005% or more. However, boron, if added in excess, may cause the steel plate to have excessively high strengths and to fail to ensure desired cryogenic toughness. To prevent this, the boron content is preferably controlled in its upper limit to be 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 calcium (Ca) in a content of 0.0030% or less (excluding 0%) and at least one rare-earth element (REM) in a content of 0.0050% or less (excluding 0%)

[0050] Calcium (Ca) and rare-earth elements (REM) fix solute sulfur and make sulfides harmless. Each of these elements may be added alone or in combination. Each of these elements, if present in an insufficient content, may cause the steel plate to have a higher solute sulfur content and to have inferior toughness. To prevent this, the Ca content is preferably controlled to be 0.0005% or more; and the REM content is preferably controlled to be 0.0005% or more. The term "REM content" refers to the content of one rare-earth element when the one rare-earth element alone as selected from the rare-earth elements mentioned below is contained; and refers to the total content of two or more rare-earth elements when the two or more rare-earth elements are contained. Hereinafter this is true for the REM contents. Each of Ca and REM, if added in excess, may cause particles such as sulfides, oxides, and nitrides to coarsen and may also cause the steel plate to have inferior toughness. To prevent this, the Ca content is preferably controlled in its upper limit to be 0.0030% or less, and more preferably 0.0025% or less. Likewise, the REM content is preferably controlled in its upper limit to be 0.0050% 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 as well as Sc (scandium) and Y (yttrium). The lanthanoid elements are fifteen elements from La with atomic number 57 to Lu with atomic number 71 in the periodic table of elements. The steel may contain each of these elements alone or in combination. Among the rare-earth elements, Ce and La are preferred. The REM may be added in a form not limited. Typically, the REM may be added in the form of a misch metal or in the form of a single element such as Ce or La. The misch metal mainly contains Ce and La and may for example contain about 70% of Ce and about 20% to about 30% of La.

Zirconium (Zr): 0.005% or less (excluding 0%)

[0052] Zirconium (Zr) fixes nitrogen. The steel plate, if having an insufficient Zr content, may have an increased solute nitrogen content and have inferior toughness. To prevent this, the Zr content is preferably controlled to be 0.0005% or more. However, Zr, if added in excess, may cause particles such as oxides and nitrides to coarsen and may cause the steel plate to have inferior toughness. To prevent this, the Zr content is preferably controlled in its upper limit to be 0.005% or less, and more preferably 0.0040% or less.

[0053] The steel chemical compositions in the embodiment of the present invention have been described above.

2. Retained Austenite Phase (Retained γ) Volume Fraction

[0054] In addition, the steel plate according to the present invention contains a retained austenite phase existing at -196°C in a volume fraction of 2.0% to 12.0% (preferably 4.0% to 12.0%).

[0055] For better cryogenic toughness, it is effective to ensure retained austenite in a certain amount. This is because the retained austenite readily plastically deforms during an impact test at a cryogenic temperature. To obtain desired cryogenic toughness, the volume fraction of the retained austenite phase is controlled to 2.0% or more of the total 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 amount, may cause the steel plate to fail to have a yield strength YS at a predetermined level. To prevent this, the retained austenite phase volume fraction is controlled in its upper limit to be 12.0% or less. The retained austenite phase volume fraction is preferably 4.0% or more, and more preferably 6.0% or more in its lower limit; and is preferably 11.5% or less, and more preferably 11.0% or less in its upper limit.

[0056] Of phases existing at -196°C , the retained austenite phase is importantly controlled in its volume fraction in the steel plate according to the present invention. The other phases than the retained austenite are not limited and may be those generally present in steel plates. The other phases than retained austenite are exemplified by bainite, martensite, cementite, and other carbides.

3. Di value

[0057] The steel plate according to the present invention also has a Di value as specified by Formula (1) of 2.5 or more. Formula (1) is defined by the steel chemical compositions and is expressed as follows:

$$\text{Di value} = \frac{([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times 1.115}{(1)} \quad (1)$$

where [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], and [V] are contents (in mass percent) respectively of C, Si, Mn, Cu, Ni, Cr, Mo, and V in the steel.

[0058] Formula (1) relates to the Di value indicating hardenability and is described as Grossmann's equation in Trans. Metall. Soc. AIME, 150 (1942), p. 227. With increasing amounts of the alloy elements defining Formula (1) as the Di value, the steel plate is more readily hardened (has a higher Di value) and more readily include a finely dispersed microstructure. In addition, with an increasing Di value, the steel plate has higher strengths and more surely has strengths at desired levels. After investigations, the present inventors have found that there is a correlation between the Di value and the microstructure size after rolling; and that the Di value may be controlled to 2.5 or more so as to obtain a finely dispersed microstructure after rolling and to obtain high strengths at desired levels. Specifically, the Di value is found to be a parameter as a useful index so as to obtain a finely dispersed rolling microstructure even with a low rolling reduction in a non-crystallization region. This leads to the formation of retained austenite in a sufficient volume fraction as a result of the subsequent heat treatment and thereby ensures stable retained austenite that is useful for better cryogenic toughness. The Di value is also an effective parameter so as to ensure good properties even when a reduced process

load is applied. The process load herein is reduced by mitigating production conditions described in Patent Literature 3, such as a lowered rolling reduction at low temperatures in a non-recrystallization region, and time restriction until cooling start.

[0059] To have such activities effectively, the D_i value is controlled to be 2.5 or more. The steel plate, if having a D_i value of less than 2.5, may fail to obtain a finely dispersed microstructure after rolling and fail to obtain retained austenite in a predetermined amount. In addition, this steel plate may fail to control the after-mentioned retained austenite stabilization parameter and retained austenite volume fraction-retained austenite stabilization parameter at predetermined levels and may thereby fail to include stable retained austenite phase and to ensure desired cryogenic toughness. The D_i value is preferably 3.0 or more. In contrast, the upper limit of the D_i value is not limited from the above-mentioned viewpoints, but is preferably about 5.0 or less. This is preferred from the viewpoints typically of cost and in consideration that the current strength specification range for LNG tank steels is 830 MPa or less.

4. Retained Austenite Stabilization Parameter

[0060] The steel plate according to the present invention also has a retained austenite stabilization parameter as specified by Formula (2) controlled to be 3.1 or more. This allows the steel plate to have desired cryogenic toughness. Formula (2) is expressed as follows:

$$\text{Retained austenite stabilization parameter} = (365 \times \langle C \rangle + 39 \times \langle Mn \rangle + 30 \times \langle Al \rangle + 10 \times \langle Cu \rangle + 17 \times \langle Ni \rangle + 20 \times \langle Cr \rangle + 5 \times \langle Mo \rangle + 35 \times \langle V \rangle) / 100 \quad (2)$$

where $\langle C \rangle$, $\langle Mn \rangle$, $\langle Al \rangle$, $\langle Cu \rangle$, $\langle Ni \rangle$, $\langle Cr \rangle$, $\langle Mo \rangle$, and $\langle V \rangle$ are contents (in mass percent) respectively of C, Mn, Al, Cu, Ni, Cr, Mo, and V in the retained austenite existing at -196°C .

[0061] For better cryogenic toughness, it is effective to ensure stable retained austenite that does not transform into martensite, but plastically deforms during the impact test, as is described above. This may be achieved probably by ensuring retained austenite in a sufficient volume fraction before the impact test and by stabilizing (increasing the stability of) the retained austenite so as not to transform into martensite, but to plastically deform even upon impact receipt. The present inventors specified the retained austenite volume fraction within the range from the former viewpoint. In addition, the present inventors made experiments also from the latter viewpoint. As a result, they have found that the stability of retained austenite existing at -196°C is determined by chemical compositions in the retained austenite existing at -196°C ; and that, for better stability, it is effective to control the parameter specified by Formula (2). A steel, if having a reduced Ni content of 7.5% or less as in the present invention, generally has inferior hardenability, thereby includes a coarsened microstructure after rolling, and fails to ensure the retained austenite volume fraction obtained after the heat treatment, or fails to obtain a D_i value at a certain level. According to the present invention, however, these parameters or conditions can be appropriately controlled by appropriately controlling the retained austenite stabilization parameter, where the parameter is determined in consideration of balance among chemical compositions in the retained austenite. The retained austenite stabilization parameter is derived with reference to an equation relating to the M_s point (martensite transformation start temperature).

[0062] To ensure desired cryogenic toughness, the retained austenite stabilization parameter is controlled in its lower limit to be 3.1 or more, preferably 3.3 or more, more preferably 3.5 or more, and furthermore preferably 3.7 or more. The retained austenite stabilization parameter is not critical in its upper limit from the viewpoint of providing better cryogenic toughness.

5. Retained Austenite Volume Fraction-Retained Austenite Stabilization Parameter

[0063] The steel plate according to the present invention preferably has a retained austenite volume fraction-retained austenite stabilization parameter as specified by Formula (3) as controlled to be 40 or less so as to ensure still better cryogenic toughness. Formula (3) is expressed as follows:

$$\text{Retained austenite volume fraction-retained austenite stabilization parameter} = 10 / [(\text{Retained austenite phase volume fraction}) \times (\text{Retained austenite stabilization parameter})]^{1/2} \quad (3)$$

[0064] As specified by Formula (3), the parameter is defined by the retained austenite volume fraction and the retained austenite stabilization parameter. The present inventors have conceived that the distribution of retained austenite sig-

nificantly affects the improvement of cryogenic toughness and have defined the parameter as above, because the retained austenite plastically deforms during the impact test at a cryogenic temperature and effectively contributes to better toughness. Specifically, in a steel having a high retained austenite volume fraction and a high retained austenite stabilization parameter, retained austenite grains are present at small intervals and are finely dispersed, and these grains do not transform into martensite, but plastically deform even at cryogenic temperature. Thus, the steel plate has good cryogenic toughness.

[0065] The retained austenite volume fraction-retained austenite stabilization parameter is preferably 35 or less, and more preferably 30 or less. From the viewpoint of better cryogenic toughness, the parameter is preferably minimized. The parameter is not critical in its lower limit in relation to the cryogenic toughness, but is preferably about 10 or more in consideration of the chemical compositions specified in the present invention.

[0066] As is demonstrated in after-mentioned Experimental Example 2, the steel plate, when being controlled to have a retained austenite volume fraction-retained austenite stabilization parameter within a more appropriate range, can have a percent brittle fracture at a good level of 50% or less even at a temperature of -233°C, lower than the temperature of -196°C. Specifically, when the retained austenite volume fraction-retained austenite stabilization parameter is minimized in its upper limit (about 30 or less), the steel plate can have a percent brittle fracture at -233°C as reduced to 50% or less.

[0067] The above-described configuration according to the present invention can give a steel plate that has a percent brittle fracture at -196°C of equal to or less than 10% in the C-direction in a Charpy impact test and has a tensile strength TS of greater than 741 MPa and a yield strength YS of greater than 590 MPa. The present inventors made further investigations so as to give a steel plate that has high base metal strengths and still has satisfactory cryogenic toughness.

[0068] Specifically, the present inventors made investigations in order to provide a steel plate that has a percent brittle fracture at -196°C of 10% or less in the C-direction in a Charpy impact test, a tensile strength TS of greater than 830 MPa, and a yield strength YS of greater than 690 MPa. As a result, the present inventors have found that steel plate can have higher base metal strengths as above and still have satisfactory cryogenic toughness when the element contents, Di value, and retained austenite volume fraction in the steel plate are controlled within more specific ranges, and the Mn content in the retained austenite is controlled instead of the retained austenite stabilization parameter.

[0069] The element contents, Di value, and retained austenite volume fraction in the steel plate are controlled within the more specific ranges as follows.

- (a) The Mn content is controlled in its lower limit to be 0.6%.
 - (b) Both Cr and Mo are added as essential elements, and the Mo content is controlled in its lower limit to be 0.30%.
 - (c) The Di value is controlled to be greater than 5.0.
 - (d) The volume fraction of retained austenite existing at -196°C is controlled in its upper limit to be 5.0%.
 - (e) The balance between Mn and Ni contents in the steel as specified by Formula (4) is appropriately controlled
- Formula (4) is expressed as follows:

$$[\text{Mn}] \geq 0.31 \times (7.20 - [\text{Ni}]) + 0.50 \quad (4)$$

where [Mn] and [Ni] are contents (in mass percent) respectively of Mn and Ni in the steel.

In addition to the conditions, the steel plate, when meeting the condition (f) below, can have a percent brittle fracture at -196°C of 10% or less, a tensile strength TS of greater than 830 MPa, and a yield strength YS of greater than 690 MPa even without controlling the retained austenite stabilization parameter. The condition (f) is expressed as follows:

- (f) The Mn content in the retained austenite existing at -196°C is controlled to be 1.05% or more.

[0070] The steel plate according to the first embodiment of the present invention has a percent brittle fracture at -196°C of equal to or less than 10% in the C-direction in a Charpy impact (absorption) test, a tensile strength TS of greater than 741 MPa, and a yield strength YS of greater than 590 MPa. The steel plate (according to the second embodiment) meeting the conditions (a) to (e) (preferably further meeting the condition (f)) has a configuration different from the steel plate according to the first embodiment. The conditions (a) to (f) will be described below.

[0071]

- (a) The Mn content lower limit is controlled to be 0.6%.

The Mn content in the steel is controlled to be 0.6% or more so as to have still higher strengths of a tensile strength TS of greater than 830 MPa and a yield strength YS of greater than 690 MPa and to have a Mn content in the retained austenite at a certain level. The Mn content is preferably 0.7% or more in its lower limit.

(b) Both Cr and Mo are essentially contained, and the Mo content lower limit is controlled to be 0.30%.

(c) The Di value is controlled to be greater than 5.0.

To have still higher strengths of a tensile strength TS of greater than 830 MPa and a yield strength YS of greater than 690 MPa, both Cr and Mo are essentially added, and Mo is controlled to be contained in a content of 0.30% or more. In addition, the Di value is controlled to be greater than 5.0.

(d) The volume fraction of retained austenite existing at -196°C is controlled in its upper limit to be 5.0%.

The retained austenite phase volume fraction is preferably higher from the viewpoint of better cryogenic toughness. However, the retained austenite is relatively soft as compared with the matrix phase and, if contained in an excessively high volume fraction, may cause the steel plate to fail to surely have a yield strength YS and a tensile strength TS at the predetermined levels. To prevent this, the retained austenite volume fraction is controlled in its upper limit to be 5.0%, and preferably 4.8%. The retained austenite phase volume fraction is preferably controlled in its lower limit to be 3.0%, and more preferably 3.5%.

(e) The balance between Mn and Ni contents in the steel as specified by Formula (4) is appropriately controlled, where Formula (4) is expressed as follows:

$$[\text{Mn}] \geq 0.31 \times (7.20 - [\text{Ni}]) + 0.50 \quad (4)$$

[0072] The steel plate, when meeting this condition, can have still better stability of retained austenite. Hereinafter the condition as specified by Formula (4) is also referred to as "Ni-Mn balance in the steel" or simply referred to as "Ni-Mn balance".

[0073] The story that led up to Formula (4) will be schematically illustrated below. The present inventors intended to ensure satisfactory balance between strengths and toughness at cryogenic temperatures while controlling or reducing the Ni content to be 7.5% or less. The present inventors found that, for this purpose, it is important to effectively use Mn among steel chemical compositions, because Mn acts as an austenite-stabilizing element; and that the balance between Mn and Ni is also important because Ni is contained in a relatively high content among the steel chemical compositions. Based on these considerations, the present inventors made investigations on steel design guidelines so as to have better stability of retained austenite. Specifically, the present inventors made intensive investigations as including the Di value and a Ms temperature (martensite-start temperature) in consideration that how the reduction of Ni content affects the hardenability, how alloy elements are concentrated (enriched) upon the L treatment, and how martensite-austenite (MA) constituents formed upon impact are refined (reduced in size). As a result, the present inventors found that the size of MA constituents formed upon impact has a correlation with the size of the phase as rolled and has a correlation with the Ni and Mn contents in the steel. Based on the findings, the present inventors made further investigations and have specified Formula (4) as an index for Ni-Mn balance in the steel so as to ensure desired strength-toughness balance at cryogenic temperatures.

[0074]

(f) The Mn content in the retained austenite existing at -196°C is controlled to be 1.05% or more.

[0075] The steel plate, when meeting this condition, can have better stability of the retained austenite and achieve excellent strength-toughness balance at cryogenic temperatures.

[0076] The Mn content in the retained austenite existing at -196°C is preferably 1.40% or more, and more preferably 1.75% or more. The upper limit of the preferred Mn content in the retained austenite is not critical in relation with the activities, but is preferably about 2.50% or less in consideration typically of the Mn content range in the steel.

[0077] In a preferred embodiment, at least one of the factors (i) the retained austenite volume fraction, (ii) the Mn content in the retained austenite, and (iii) the λ_L parameter is controlled within a more appropriate range. The steel plate according to the second embodiment can have a percent brittle fracture at a good level of 50% or less even at -233°C, lower than -196°C. This was demonstrated in after-mentioned Experimental Example 4. Specifically, (i) the retained austenite volume fraction is controlled to be about 3.5% to about 4.8%, (ii) the Mn content in the retained austenite is controlled to be about 1.40% to about 2.5%, and/or (iii) the λ_L parameter is controlled to be about -10 or less. At least one of these controls allows the steel to have better toughness at -233°C. In another preferred embodiment, at least two of the conditions (i) to (iii) are controlled within the ranges, and/or (i) the Mn content in the retained austenite is further controlled to be 1.75% to 2.50%. The steel plate according to this embodiment can have still better toughness at -233°C.

[0078] The steel plates according to the embodiments of the present invention have been illustrated above.

[0079] Next, methods for producing the steel plates according to the embodiments of the present invention will be illustrated. In an embodiment (third embodiment), the method for producing the steel plate according to the first embod-

iment of the present invention includes the steps a) and b). In the step a), a steel plate is formed from a steel and is subjected to a heat treatment (L treatment) in a ferrite-austenite two-phase region (between A_{c1} and A_{c3}). The steel has such chemical compositions, and the L treatment is performed at such a temperature (L treatment temperature) that an L parameter as specified by Formula (5) is 0.25 to 0.45 and a λ_L parameter as specified by Formula (6) is 7 or less. Formula (5) is defined by the L treatment temperature and the A_{c1} and A_{c3} temperatures in the steel. Formula (6) is defined by the L parameter and the steel chemical compositions. The step b) is performed after the L treatment. In the step b), the steel plate is water-cooled down to room temperature and subjected to a tempering treatment (T treatment) at a temperature equal to or lower than the A_{c1} temperature for 10 to 60 minutes. Formulae (5) and (6) are expressed as follows:

$$L \text{ parameter} = [(L \text{ treatment temperature}) - A_{c1}] / (A_{c3} - A_{c1}) + 0.25 \quad (5)$$

$$\lambda_L \text{ parameter} = 9.05 \times (0.90 \times [L \text{ parameter}] + 0.14) \times [Mn] + 1.46 \times (0.37 \times [L \text{ parameter}] + 0.67) \times [Cr] - 41.5 \times (0.26 \times [L \text{ parameter}] + 0.79) \times [Mo] \quad (6)$$

where [Mn], [Cr], and [Mo] are contents (in mass percent) respectively of Mn, Cr, and Mo in the steel.

[0080] The individual steps will be illustrated in detail below.

[0081] The production method according to the third embodiment of the present invention appropriately controls a rolling process and a subsequent tempering treatment (T treatment) so as to produce the steel plate meeting the conditions. A steel making process herein is not limited and can be performed by a generally employed procedure.

[0082] Steps (processes) including the rolling process and subsequent processes that feature the present invention will be sequentially illustrated in detail below.

[0083] Initially, in a preferred embodiment, the heating temperature is controlled to be about 900°C to about 1100°C, the finish rolling temperature (FRT) is controlled to be about 700°C to about 900°C, and the start cooling temperature (SCT) is controlled to be about 650°C to about 800°C. In this process, the start cooling temperature (SCT) is preferably controlled within the range within 60 seconds after the finish rolling. This gives a finely dispersed microstructure after rolling and subsequent cooling, where the finely dispersed microstructure usefully contributes to better toughness.

[0084] Next, the workpiece is cooled in a temperature range from 800°C to 500°C at an average cooling rate of about 10°C/s or more. In particular, the average cooling rate in the temperature range is controlled herein so as to give a finely dispersed microstructure after cooling. The average cooling rate is not critical in its upper limit.

[0085] The cooling herein is preferably performed at an average cooling rate of about 10°C/s or more at least in the temperature range. The cooling at the average cooling rate is preferably stopped at a temperature of 200°C or lower.

This can reduce the amount of untransformed austenite and can give a finely dispersed and homogeneous microstructure.

[0086] After the hot rolling, the workpiece is heated to and held at a temperature in a ferrite (α)-austenite (γ) two-phase region between the A_{c1} and A_{c3} temperatures and then water-cooled. This process is referred to as an "L treatment", and the heating and holding temperature in this process is referred to as an "L treatment temperature". According to the embodiment of the present invention, the L treatment temperature and chemical compositions in the steel are appropriately controlled so that the L parameter specified by Formula (5) and the λ_L parameter specified by Formula (6) fall within the predetermined ranges. This control is performed so as to control the retained austenite volume fraction and the retained austenite stabilization parameter (preferably retained austenite volume fraction-retained austenite stabilization parameter) within the ranges specified herein.

[0087] Initially, the L treatment temperature after the hot rolling is preferably controlled to be within the range of A_{c1} to $(A_{c1} + A_{c3})/2$. This allows alloy elements such as Ni to concentrate in formed austenite phase, part of which becomes a metastable retained austenite phase that metastably exists at room temperature. The L treatment, if performed at a temperature of lower than the A_{c1} temperature or higher than $(A_{c1} + A_{c3})/2$, may eventually fail to allow the steel plate to have a sufficient volume fraction of retained austenite existing at -196°C and/or sufficient retained austenite stability (see Sample Nos. 29 and 30 in Table 2B of after-mentioned Experimental Example 1). The L treatment temperature is preferably from about 620°C to about 650°C.

[0088] The A_{c1} and A_{c3} temperatures herein are calculated based on formulae below (see "Koza Gendai no Kinzokugaku, Zairyo-hen 4, Tekko Zairyo" (in Japanese), The Japan Institute of Metals and Materials).

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

A_{c3} temperature = $910 - 203 \times [C]^{1/2} - 15.2 \times [Ni] + 44.7 \times [Si] + 104 \times [V] + 31.5 \times [Mo] - 30 \times [Mn] + 11 \times [Cr] + 20 \times [Cu]$ where [Mn], [Ni], [Si], [Cr], [As], [W], [C], [V], [Mo], and [Cu] are contents (in mass percent) respectively of alloy elements Mn, Ni, Si, Cr, As, W, C, V, Mo, and Cu in the steel. The steel plate according to the present invention does not contain As and W as steel chemical compositions, and the calculation according to the formula is performed while defining [As] and [W] each as 0%.

[0089] The heating at a temperature in the two-phase region is preferably performed for a time (holding time) of about 10 to about 50 minutes. The heating, if performed for a time shorter than 10 minutes, may fail to allow alloy elements to sufficiently concentrate in the austenite phase. In contrast, the heating, if performed for a time longer than 50 minutes, may cause the α phase to be annealed and cause the steel plate to have lower strengths. The heating time is preferably 30 minutes in its upper limit.

[0090] In addition, the L parameter specified by Formula (5) is herein controlled to be 0.25 to 0.45, where Formula (5) is defined by individual chemical compositions. The L parameter is defined to efficiently use the alloy element concentration during the L treatment so as to allow the steel plate to finally have a retained austenite volume fraction and retained austenite stability both at certain levels. A steel plate having an L parameter out of the range fails to have a desired retained austenite volume fraction and/or sufficient retained austenite stability, as demonstrated in after-mentioned Experimental Examples. The L parameter is preferably 0.28 to 0.42, and more preferably 0.30 to 0.40.

[0091] The λ_L parameter is herein controlled to be 7 or less. The λ_L parameter is defined by the contents of Mn, Cr, and Mo, and the L parameter, as specified by Formula (6). The λ_L parameter is defined so as to restrain adverse effects of temper embrittlement occurring in a portion where Mn and Cr are excessively concentrated, where the Mn and Cr concentration is caused typically by phosphorus segregation at prior austenite grain boundaries during the L treatment. It is difficult to directly measure the content of phosphorus segregated at prior austenite grain boundaries. Accordingly, the λ_L parameter can act as, so to speak, an alternate parameter for the content of phosphorus segregated at prior austenite grain boundaries. A steel including a smaller amount of phosphorus segregated at prior austenite grain boundaries has a lower λ_L parameter. The λ_L parameter is preferably 0.0 or less, and more preferably -10.0 or less. The λ_L parameter is not critical in its lower limit, but is preferably about -30 or more. This is preferred in synthetic consideration that the amount of Mo to be added is preferably minimized from the viewpoint of cost; and that the contents and the L parameter preferably fall within the specific ranges.

[0092] Specifically, at a temperature of -196°C in the cryogenic temperature range, adverse effects of trace impurities such as phosphorus readily become obvious, and, when phosphorus is significantly segregated at prior austenite grain boundaries (i.e., when the λ_L parameter is high), the temper embrittlement probably adversely affects the cryogenic toughness. Typically, Sample Nos. 1, 2, and 25 (all according to the present invention) in Table 1A in after-mentioned Experimental Example 1 are compared. These samples have retained austenite volume fractions and retained austenite stabilization parameters at the same levels. Specifically, Sample No. 1 has a retained austenite volume fraction of 8.0% and a retained austenite stabilization parameter of 3.7. Sample No. 2 has a retained austenite volume fraction of 9.4% and a retained austenite stabilization parameter of 3.8. Sample No. 25 has a retained austenite volume fraction of 7.9% and a retained austenite stabilization parameter of 3.7. However, these samples have significantly different λ_L parameters of -6.8 (Sample No. 1), -10.9 (Sample No. 2), and 5.2 (Sample No. 25). Accordingly, among the three samples, Sample No. 2 having the lowest λ_L parameter is most excellent in cryogenic toughness.

[0093] Next, the workpiece is water-cooled down to room temperature and subjected to a tempering treatment (T treatment).

[0094] The tempering treatment is performed at a temperature of equal to or lower than the A_{c1} temperature for 10 to 60 minutes. Such low-temperature tempering allows carbon to concentrate in the metastable retained austenite and thereby further stabilizes the metastable retained austenite phase to give a retained austenite phase that stably exists at -196°C. In addition, the low-temperature tempering helps the steel plate to have a low Ms temperature.

[0095] The tempering, if performed at a temperature higher than the A_{c1} temperature, may cause the metastable retained austenite phase to decompose into a ferrite (α) phase and a cementite phase and may cause the steel plate to fail to include the retained austenite phase existing at -196°C in a sufficient volume fraction, where the metastable retained austenite phase is formed during holding in the two-phase region. In contrast, the tempering, if performed at a temperature lower than 540°C or for a time shorter than 10 minutes, may cause carbon to fail to sufficiently concentrate into the metastable retained austenite phase and may cause the steel plate to fail to have a desired volume fraction of retained austenite existing at -196°C. The tempering, if performed for a time longer than 60 minutes, may cause excessive reduction of α phase dislocation density and may thereby cause the steel plate to fail to surely have predetermined strengths (TS and YS) (see Sample No. 33 of Table 2B in Experimental Example 1).

[0096] The tempering treatment is preferably performed at a temperature of 540°C to 560°C for a time of 15 minutes to 45 minutes (more preferably 35 minutes or shorter, and furthermore preferably 25 minutes or shorter).

[0097] After undergoing the tempering treatment as above, the workpiece is cooled down to room temperature. The cooling after the tempering is performed not by water cooling, but by air cooling. This is because carbon is concentrated into the retained austenite during air cooling, and the steel plate cooled by air cooling has a higher retained austenite

stabilization parameter as compared with a steel plate cooled by water cooling.

[0098] Next, a method for producing the steel plate according to the second embodiment of the present invention will be illustrated.

[0099] This production method according to the fourth embodiment of the present invention includes the steps a') and b). In the step a), the L treatment temperature and the steel chemical compositions are adjusted so that an L parameter as specified by Formula (5) is 0.6 to 1.1 and a λ_L parameter as specified by Formula (6) is 0 or less. Formula (6) is defined by the L parameter and the steel chemical compositions. The step b) is performed after the L treatment, in which the steel plate is water-cooled down to room temperature and subjected to a tempering treatment (T treatment) at a temperature equal to or lower than the A_{c1} temperature for 10 to 60 minutes.

[0100] The individual steps or processes will be described in detail below. However, description will be omitted for conditions the same as in the method for producing the steel plate according to the first embodiment of the present invention. The conditions are exemplified by the conditions in the rolling step, and conditions of the temperature and holding time of the L treatment.

[0101] The method for producing the steel plate according to the second embodiment of the present invention controls the L parameter specified by Formula (5) to be 0.6 to 1.1. The L parameter is defined so as to allow the final steel plate to have a sufficient retained austenite volume fraction and satisfactory retained austenite stability (in particular one determined by the Di value and the Mn content in the retained austenite). In particular, the L parameter is specified in its upper limit to be 1.1 or less from the viewpoints of the chemical compositions and desired microstructure conditions of the steel plate according to the embodiment of the present invention. The L treatment increases the retained austenite stability (namely, allows Mn to be concentrated into the retained austenite). Conversely, the L treatment causes the Mn content in the matrix (in the steel) to be reduced. Such reduced Mn content in the matrix steel may adversely affect the steel plate and may cause the steel plate to have insufficient strengths or to have a retained austenite volume fraction and retained austenite stability both at unsatisfactory levels. To prevent this, the L parameter is controlled in its lower limit (0.6 or more) in the embodiment of the present invention. The L parameter is preferably 0.7 to 1.0.

[0102] In addition, the λ_L parameter is herein controlled to be 0 or less. The λ_L parameter is defined by the L parameter and the contents of Mn, Cr, and Mo in the steel, as specified by Formula (6). The λ_L parameter is defined so as to restrain adverse effects of temper embrittlement occurring in a portion where Mn and Cr are excessively concentrated, where the Mn and Cr concentration is caused typically by phosphorus segregation at prior austenite grain boundaries during the L treatment, as is described above. It is difficult to directly measure the content of phosphorus segregated at prior austenite grain boundaries. Accordingly, the λ_L parameter can act as, so to speak, an alternate parameter for the content of phosphorus segregated at prior austenite grain boundaries. A steel including a smaller amount of phosphorus segregated at prior austenite grain boundaries has a lower λ_L parameter. The λ_L parameter is preferably -10.0 or less. The λ_L parameter is not critical in its lower limit, but is preferably about -30 or more. This is preferred in synthetic consideration that the amount of Mo to be added is preferably minimized from the viewpoint of cost; and that the contents and the L parameter preferably fall within the specific ranges.

[0103] Next, the workpiece is water-cooled down to room temperature and subjected to a tempering treatment (T treatment).

[0104] The tempering treatment is performed at a temperature of equal to or lower than the A_{c1} temperature for 10 to 60 minutes. Such low-temperature tempering allows carbon to be concentrated in the metastable retained austenite and thereby further stabilizes the metastable retained austenite phase to give a retained austenite phase that stably exists at -196°C, as is described above. In addition, the low-temperature tempering helps the steel plate to have a low Ms temperature.

[0105] The tempering, if performed at a temperature higher than the A_{c1} temperature, may cause the metastable retained austenite phase to decompose into a ferrite (α) phase and a cementite phase and may cause the steel plate to fail to include the retained austenite phase at -196°C in a sufficient volume fraction, where the metastable retained austenite phase is formed during holding in the two-phase region. In contrast, the tempering, if performed for a time shorter than 10 minutes, may cause carbon to fail to be sufficiently concentrated into the metastable retained austenite phase and may cause the steel plate to fail to have a desired volume fraction of retained austenite existing at -196°C. The tempering, if performed for a time longer than 60 minutes, may cause excessive reduction of α phase dislocation density and may thereby cause the steel plate to fail to surely have predetermined strength (TS) (see Sample No. 7 of Table 2B in after-mentioned Experimental Example 3). The tempering is preferably performed for a time of 15 minutes to 45 minutes, and more preferably 20 minutes to 35 minutes.

[0106] The tempering is performed at a temperature equal to or lower than the A_{c1} temperature, and preferably at a temperature of 510°C to 520°C.

[0107] After undergoing the tempering treatment as above, the workpiece is cooled down to room temperature. The cooling after the tempering is performed not by water cooling, but by air cooling. This is because carbon is concentrated into the retained austenite during air cooling, and the steel plate cooled by air cooling has higher stability of retained austenite as compared with a steel plate cooled by water cooling.

Experimental Examples

[0108] The present invention will be illustrated in further detail with reference to several examples (experimental 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

[0109] This experimental example relates to steel plates having a percent brittle fracture at -196°C of equal to or less than 10%, a tensile strength TS of greater than 741 MPa, and a yield strength YS of greater than 590 MPa.

[0110] Molten steels as test samples having chemical compositions given in Table 1 (with the remainder consisting of iron and inevitable impurities, in mass percent) were made using a vacuum induction furnace (150-kg VIF). The molten steels were cast, subjected to hot forging, and yielded ingots of a size of 150 mm by 150 mm by 600 mm. REM used in this experimental example was a misch metal containing about 50% of Ce and about 25% of La.

[0111] Next, the ingots were heated to 1100°C and rolled at a temperature of 830°C or higher to a thickness of 75 mm. The workpieces were rolled at a finish rolling temperature (FRT) of 700°C and water-cooled from a start cooling temperature (SCT) of 650°C within 60 seconds after the finish rolling. Thus, the workpieces were rolled down to a thickness of 25 mm with a rolling reduction of 83%. The cooling in the range from 800°C down to 500°C was performed at an average cooling rate of 19°C/s , and the cold rolling was performed to a stop temperature of 200°C or lower to give steel plates.

[0112] The above-prepared steel plates were each subjected to an L treatment by heating to and holding at an L treatment temperature given in Table 2 for 30 minutes, followed by water cooling. The steel plates were further subjected to a T treatment (tempering) at a temperature (T treatment temperature) for a time (T time) given in Table 2, and air-cooled down to room temperature.

[0113] The prepared steel plates were evaluated on the amount (volume fraction) of retained austenite phase existing at -196°C , retained austenite stabilization parameter, 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) in the following manner.

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

[0114] 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, 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".

(2) Retained Austenite Stabilization Parameter Measurement

[0115] To determine the retained austenite stabilization parameter as specified by Formula (2), the contents of chemical compositions in the retained austenite existing at -196°C to define Formula (2) were measured. Specifically, $\langle\text{C}\rangle$, $\langle\text{Mn}\rangle$, $\langle\text{Al}\rangle$, $\langle\text{Cu}\rangle$, $\langle\text{Ni}\rangle$, $\langle\text{Cr}\rangle$, $\langle\text{Mo}\rangle$, and $\langle\text{V}\rangle$ as contents (in mass percent) respectively of C, Mn, Al, Cu, Ni, Cr, Mo, and V were measured in manners as follows.

(2-1) Measurement of C content $\langle\text{C}\rangle$ in retained austenite existing at -196°C

[0116] Simultaneously with the measurement (1), calibrator silicon (Si) was applied onto each test sample steel, and a precise $\gamma\text{-Fe}$ lattice constant [a_0 (in angstrom)] was determined with angle correction with the Si peak. The carbon (C) content in the retained austenite was determined by inverse calculation from the precisely determined $\gamma\text{-Fe}$ lattice constant and the contents of following chemical compositions excluding carbon.

(2-2) Measurement of Ni content $\langle\text{Ni}\rangle$ in retained austenite existing at -196°C

[0117] Test specimens of a size of 10 mm by 10 mm by 55 mm were sampled from each steel plate at a position one-fourth the thickness, held at the liquid nitrogen temperature (-196°C) for 5 minutes, and subjected to Ni content meas-

urement using an electron probe microanalyzer (EPMA) JXA-8500F supplied by JEOL Ltd. at an acceleration voltage of 15 kV and an applied current of 50 nA with a minimum beam diameter. The measurement was performed three times per each sample (steel plate), and the maximum among the measured values was defined as the Ni content in the retained austenite.

(2-3) Measurement of Al content <Al> in retained austenite existing at -196°C

[0118] The Al content in the retained austenite was determined as zero (0) on the assumption that all Al formed oxides and/or nitrides and existed therein.

(2-4) Measurement of contents <Mn>, <Cu>, <Cr>, <Mo>, and <V> of Mn, Cu, Cr, Mo, and V in retained austenite existing at -196°C

[0119] In this experimental example, the alloy element contents <Mn>, <Cu>, <Cr>, <Mo>, and <V> after the L treatment and the subsequent T treatment were considered to be proportional to the measured Ni content <Ni> as measured by the measurement (2-2) and were calculated in a manner as follows.

[0120] The Ni content in the heat treatments, i.e., the L treatment and the T treatment may behave (vary) as specified by the formula:

$$(\text{Constant in each heat treatment}) \times (\text{Driving force of austenite reverse transformation}) \times (\text{Diffusion constant of each alloy element})$$

[0121] The term "driving force of austenite reverse transformation" in the formula was calculated based on the temperature in the heat treatment using a commercially available computational software (Thermo-Calc). The term "diffusion constant of each alloy element" in the formula was calculated based on the temperature and holding time in each heat treatment using a value found in "Diffusion in Solid Metals and Alloys", H. Mehrer, 1990.

[0122] The term "constant in each heat treatment" was experimentally determined in the following manner. The measured Ni content after the L treatment and the subsequent T treatment is specified by the formula as the product of [(Constant in L treatment) × (Driving force of austenite reverse transformation) × (Ni diffusion constant in L treatment)] and [(Constant in T treatment) × (Driving force of austenite reverse transformation) × (Ni diffusion constant in L treatment)]. Specifically, the measured Ni content after the L treatment and the subsequent T treatment includes both the terms "constant in L treatment" and "constant in T treatment", and the "constant in T treatment" varies with the "constant in L treatment". Based on these, the constants in the individual heat treatments ["constant in L treatment" and "constant in T treatment"] were recursively determined so that the product be most approximal to the measured Ni content after the L treatment and the subsequent T treatment. Using the thus-determined constants, the alloy element contents <Mn>, <Cu>, <Cr>, <Mo>, and <V> were calculated.

(3) Measurement of tensile properties (tensile strength TS and yield strength YS)

[0123] A JIS Z2241 No. 4 test specimen was sampled from each steel plate at a position one-fourth the thickness 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 of greater than 740 MPa and a yield strength YS of greater than 590 MPa was evaluated as having satisfactory base metal strengths.

(4) Measurement of cryogenic toughness (percent brittle fracture in C-direction)

[0124] 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 percents brittle fracture at -196°C (%) of the test specimens at the two positions were measured by the method prescribed in JIS Z2242 and were averaged independently. Of the two averages thus calculated, one indicating inferior properties (namely, one with a higher percent brittle fracture) was employed. A sample having an employed average of 10% or less was evaluated as having excellent cryogenic toughness in this experimental example.

[0125] Results of these measurements and evaluations are together indicated in Tables 2A and 2B.

[Table 1A]

No.	C	Si	Mn	P	S	Al	Ni	N	Cu	Cr	Mo	Ti	Nb	V	B	Ca	REM	Zr
1	0.05	0.06	0.90	<0.005	<0.0005	0.032	5.64	0.0033		0.40	0.30							
2	0.05	0.06	1.05	<0.004	0.001	0.030	5.66	0.0032		0.42	0.43							
3	0.05	0.06	0.55	<0.004	0.001	0.030	5.62	0.0034		0.82	0.43							
4	0.06	0.06	1.01	<0.004	0.001	0.032	5.61	0.0033		0.75								
5	0.05	0.06	0.79	0.005	0.001	0.033	5.88	0.0032		0.98	0.05							
6	0.04	0.09	1.28	<0.004	0.004	0.035	6.13	0.0039	0.72		0.35							
7	0.04	0.15	0.89	<0.004	0.001	0.032	5.72	0.0033		0.52	0.33							
8	0.09	0.05	0.87	<0.004	0.002	0.020	6.15	0.0031	0.21	0.36	0.05							
9	0.02	0.20	1.48	<0.004	0.001	0.030	5.33	0.0032			0.82						0.0042	
10	0.03	0.38	0.80	<0.004	0.004	0.038	7.25	0.0031			0.75		0.027				0.0023	
11	0.05	0.29	0.54	<0.004	0.001	0.033	6.24	0.0038	0.15	0.13	0.67				0.0019			
12	0.04	0.12	1.58	<0.004	0.001	0.034	5.92	0.0029		0.41	0.06							
13	0.05	0.06	0.79	0.007	0.002	0.038	7.08	0.0029			0.83		0.012					
14	0.04	0.19	1.19	<0.004	0.007	0.011	5.65	0.0045			0.52	0.012						0.0022
15	0.07	0.10	0.66	<0.004	0.003	0.047	5.88	0.0034		1.05				0.25				
16	0.04	0.02	0.66	0.005	0.002	0.041	5.09	0.0033	0.51	0.50	0.53				0.0019			
17	0.03	0.22	1.72	<0.004	0.001	0.019	5.70	0.0031			0.61			0.02				0.0046
18	0.04	0.05	0.70	<0.004	0.001	0.031	5.41	0.0075		0.71	0.22	0.016			0.0007	0.0011		
19	0.05	0.11	0.74	<0.004	0.003	0.035	5.86	0.0058	0.10	0.26	0.38							
20	0.04	0.19	0.82	<0.004	0.001	0.035	5.62	0.0033		1.15				0.05		0.0022		
21	0.04	0.15	0.54	0.01	0.005	0.029	5.90	0.0031		0.83	0.52	0.021					0.0030	
22	0.04	0.22	1.03	<0.004	0.002	0.034	6.89	0.0035	0.42		0.43		0.055					
23	0.05	0.08	0.65	<0.004	0.001	0.031	5.68	0.0032		0.96	0.05			0.38				
24	0.06	0.08	0.89	0.005	0.001	0.030	6.37	0.0032	0.15		0.50				0.0033			
25	0.04	0.13	1.13	<0.004	0.001	0.031	6.30	0.0032		0.70				0.11		0.0027		

[Table 1B]

No.	C	Si	Mn	P	S	Al	Ni	N	Cu	Cr	Mo	Ti	Nb	V	B	Ca	REM	Zr
26	0.05	0.09	0.88	<0.004	0.001	0.032	5.45	0.0035										
27	0.11	0.10	0.75	<0.004	0.004	0.027	6.21	0.0038		0.65								
28	0.05	0.08	0.89	0.008	0.001	0.033	5.75	0.0032	0.21	0.33	0.49							
29	0.07	0.15	0.80	<0.004	0.001	0.031	6.32	0.0033		0.36	0.15							
30	0.10	0.42	1.12	<0.004	0.001	0.031	6.25	0.0032		0.20	0.12				0.0021			
31	0.04	0.06	1.33	0.005	0.001	0.030	6.24	0.0032			0.45							
32	0.03	0.04	2.15	<0.004	0.002	0.029	6.33	0.0032		0.63								
33	0.05	0.06	0.96	<0.004	0.002	0.032	5.45	0.0040	0.50	0.29	0.18							
34	0.05	0.08	0.48	0.005	0.001	0.032	5.79	0.0038		0.62		0.015						
35	0.04	0.10	1.42	<0.004	0.008	0.038	6.50	0.0051		0.25	0.17							
36	0.05	0.06	0.70	<0.004	0.001	0.030	5.03	0.0030		0.50	0.30							
37	0.01	0.08	1.05	<0.004	0.001	0.052	4.80	0.0045		0.83	0.46			0.22				
38	0.08	0.12	0.88	<0.004	0.001	0.004	6.40	0.0107		0.25	0.15		0.016					
39	0.05	0.08	0.79	<0.004	0.004	0.037	6.49	0.0032	1.08	0.23	0.16					0.0032		
40	0.06	0.11	0.93	0.006	0.001	0.029	5.55	0.0029		1.25								0.0057
41	0.04	0.10	1.34	<0.004	0.001	0.045	6.25	0.0030		0.59			0.104				0.0051	
42	0.04	0.22	1.21	<0.004	0.003	0.037	5.90	0.0034		0.05	1.07							
43	0.05	0.12	1.05	<0.004	0.003	0.028	6.47	0.0036		0.66		0.027					0.0021	
44	0.05	0.32	0.82	<0.004	0.001	0.015	5.83	0.0029			0.15			0.52				
45	0.05	0.20	0.90	<0.004	0.001	0.035	6.04	0.0033		0.31	0.22				0.0052			

[Table 2A]

No.	A _{c1}	A _{c3}	(A _{c1} +A _{c3})/2	L treatment temperature (°C)	T treatment temperature (°C)	T time (min)	Cooling after tempering	L parameter	λ_L parameter	Dilution value	Retained γ (%)	Retained γ stabilization parameter	Retained γ volume fraction retained γ stabilization parameter	Cryogenic toughness	Tensile properties	
															YS	TS
1	627	769	698	640	550	30	Air cooling	0.34	-6.8	3.5	8.0%	3.7	18	3	720	775
2	625	769	697	640	550	30	Air cooling	0.35	-10.9	4.8	9.4%	3.8	17	0	753	811
3	638	789	714	640	560	30	Air cooling	0.26	-12.5	4.3	5.9%	3.9	21	0	743	799
4	632	756	694	640	550	35	Air cooling	0.32	4.7	3.1	8.8%	4.2	16	5	711	765
5	633	767	700	640	550	30	Air cooling	0.30	2.2	3.3	7.4%	4.1	18	5	715	769
6	608	767	688	620	550	20	Air cooling	0.32	-7.7	3.2	6.8%	3.6	20	3	717	771
7	630	779	704	640	550	25	Air cooling	0.32	-7.9	4.0	7.0%	3.7	20	3	734	790
8	617	741	679	620	560	20	Air cooling	0.27	1.6	3.0	8.5%	4.6	16	0	705	792
9	623	791	707	650	550	40	Air cooling	0.41	-23.7	3.4	12.0%	4.0	15	0	726	781
10	603	781	692	620	550	30	Air cooling	0.35	-24.1	3.3	2.3%	3.3	36	5	717	771
11	622	792	707	630	550	30	Air cooling	0.29	-22.0	3.5	3.7%	3.6	27	0	721	776
12	616	744	680	630	550	15	Air cooling	0.36	4.9	3.3	10.4%	3.8	16	5	726	781
13	597	763	680	610	550	15	Air cooling	0.33	-27.0	3.6	3.0%	3.4	32	5	725	779
14	620	773	697	640	550	30	Air cooling	0.38	-14.0	3.1	10.1%	3.6	16	0	710	764
15	637	789	713	640	560	30	Air cooling	0.27	3.5	4.7	8.3%	4.5	16	0	752	809
16	639	806	722	640	560	20	Air cooling	0.26	-16.1	4.1	2.1%	3.8	35	0	761	819
17	615	768	691	630	550	20	Air cooling	0.35	-15.2	4.2	9.0%	3.7	17	0	755	813
18	638	783	710	650	550	40	Air cooling	0.34	-4.4	3.0	7.5%	3.7	19	3	709	763
19	624	775	699	640	550	55	Air cooling	0.36	-10.5	3.2	9.1%	3.7	17	0	617	747
20	644	786	715	650	550	20	Air cooling	0.29	4.3	3.4	7.3%	4.0	19	5	719	774
21	636	796	716	640	550	20	Air cooling	0.28	-15.8	4.9	5.1%	3.7	23	0	775	834

(continued)

No.	A _{c1}	A _{c3}	(A _{c1} +A _{c3})/2	L treatment temperature (°C)	T treatment temperature (°C)	T time (min)	Cooling after tempering	L parameter	λ_L parameter	D value	Retained γ (%)	Retained γ stabilization parameter	Retained γ volume fraction-retained γ stabilization parameter	Cryogenic toughness Percent brittle fracture at -196 °C (%)	Tensile properties	
															YS	TS
22	602	766	684	610	550	30	Air cooling	0.30	-11.7	3.3	5.8%	3.6	22	0	716	770
23	639	814	726	640	560	20	Air cooling	0.26	1.5	4.7	6.2%	4.1	20	5	753	810
24	608	759	684	620	550	25	Air cooling	0.33	-14.7	3.1	7.7%	3.7	19	0	753	810
25	620	765	692	630	550	20	Air cooling	0.32	5.2	3.6	7.9%	3.7	18	10	723	778

[Table 2B]

No.	A _{c1}	A _{c3}	(A _{c1} +A _{c3})/2	L treatment temperature (°C)	T treatment temperature (°C)	T time (min)	Cooling after tempering	L parameter	λ_L parameter	Dilution value	Retained γ (%)	Retained γ stabilization parameter	Retained γ volume fraction-retained γ stabilization parameter	Cryogenic toughness	Tensile properties	
															YS	TS
26	624	759	692	650	550	20	Air cooling	0.44	4.3	1.0	1.8%	2.5	47	23	656	705
27	624	737	681	630	550	15	Air cooling	0.30	3.5	3.4	10.0%	8.0	11	17	850	900
28	624	777	701	640	550	20	Air cooling	0.35	-13.9	4.6	0.7%	3.0	69	21	750	807
29	618	752	685	590	550	35	Air cooling	0.04	-3.3	3.2	1.5%	1.0	82	42	713	767
30	621	742	681	770	550	30	Air cooling	1.48	9.4	4.3	0.8%	0.5	158	30	773	831
31	605	752	678	630	500	25	Air cooling	0.42	-10.6	3.0	1.5%	2.5	52	29	713	767
32	605	723	664	610	580	20	Air cooling	0.29	8.6	4.0	11.8%	4.0	15	29	709	862
33	627	775	701	630	550	65	Air cooling	0.27	-2.8	3.0	5.9%	4.4	20	10	588	712
34	633	773	703	650	550	20	Air cooling	0.37	2.8	1.6	1.2%	2.0	65	34	672	723
35	605	741	673	620	550	20	Air cooling	0.36	0.0	3.4	9.7%	3.6	17	16	723	778
36	641	785	713	680	550	20	Air cooling	0.52	-7.0	3.0	0.4%	3.3	86	17	784	825
37	647	835	741	690	550	25	Air cooling	0.48	-11.0	4.2	0.3%	0.5	258	50	623	687
38	613	742	677	620	550	40	Air cooling	0.30	-1.8	3.1	12.0%	3.1	16	35	711	766
39	611	775	693	620	550	20	Air cooling	0.30	-2.5	3.1	6.8%	3.8	20	47	803	900
40	644	767	705	650	550	15	Air cooling	0.30	4.9	4.2	9.0%	4.5	16	58	780	906
41	616	745	681	630	550	40	Air cooling	0.36	6.3	3.0	12.0%	3.9	15	55	775	907
42	618	788	703	630	550	20	Air cooling	0.32	-34.0	6.0	6.9%	3.6	20	12	816	906
43	617	747	682	620	550	15	Air cooling	0.27	4.4	3.1	6.5%	4.1	19	24	817	902
44	625	825	725	640	550	35	Air cooling	0.33	-2.2	3.1	7.7%	3.6	19	21	788	894
45	622	765	694	630	550	20	Air cooling	0.30	-4.2	3.2	6.5%	3.7	20	25	809	895

Considerations can be made from Tables 2A and 2B as follows.

[0126] Sample Nos. 1 to 25 in Table 2A are samples meeting all the conditions specified in the present invention. These samples could provide steel plates having excellent cryogenic toughness at -196°C even though having high base metal strengths. Specifically, the samples each had an average of percent brittle fracture in the C-direction of equal to or less than 10%.

[0127] In contrast, Sample Nos. 26 to 45 in Table 2B are 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 failed to have desired property or properties.

[0128] Sample No. 26 had a Di value not meeting the condition specified in the present invention. The sample failed to have a desired retained austenite volume fraction and had a low retained austenite stabilization parameter. In addition, the sample had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had a high percent brittle fracture and failed to achieve desired cryogenic toughness at -196°C. In addition, the sample had a low Di value and therefore had a low tensile strength TS.

[0129] Sample No. 27 employed Steel No. 27 in Table 1B having an excessively high carbon content and had inferior cryogenic toughness.

[0130] Sample No. 28 employed Steel No. 28 in Table 1B having an excessively high phosphorus content. The sample failed to have a desired retained austenite volume fraction and had a low retained austenite stabilization parameter. In addition, the sample had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range and, as a result, had inferior cryogenic toughness.

[0131] Sample No. 29 employed Steel No. 29 in Table 1B having chemical compositions meeting the conditions specified in the present invention, but underwent heating at a temperature lower than the two-phase region temperature (L treatment temperature), and had a low L parameter. The sample therefore contained retained austenite in an insufficient volume fraction and had a low retained austenite stabilization parameter. In addition, the sample had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had inferior cryogenic toughness.

[0132] Sample No. 30 employed Steel No. 30 in Table 1B having an excessively high Si content, underwent heating at a temperature higher than the two-phase region temperature (L treatment temperature), and had excessively high L parameter and λ_L parameter. The sample therefore contained retained austenite in an insufficient volume fraction, a low retained austenite stabilization parameter, and a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had inferior cryogenic toughness.

[0133] Sample No. 31 employed Steel No. 31 in Table 1B having chemical compositions meeting the conditions specified in the present invention, but underwent tempering (T treatment) at an excessively low temperature. The sample therefore contained retained austenite in an insufficient volume fraction and had a low retained austenite stabilization parameter. In addition, the sample had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had inferior cryogenic toughness.

[0134] Sample No. 32 employed Steel No. 32 in Table 1B having an excessively high Mn content and had an excessively high λ_L parameter. The sample therefore had inferior cryogenic toughness.

[0135] Sample No. 33 employed Steel No. 33 in Table 1B having chemical compositions meeting the conditions specified in the present invention, but underwent tempering for an excessively long time (T time). As a result, the sample had low strengths (TS and YS).

[0136] Sample No. 34 employed Steel No. 34 in Table 1B having an excessively low Mn content and had an excessively low Di value. The sample failed to have a desired retained austenite volume fraction and had a low retained austenite stabilization parameter. In addition, the sample had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had a high percent brittle fracture and failed to achieve desired cryogenic toughness at -196°C. The sample also had a low tensile strength TS due to the low Di value.

[0137] Sample No. 35 employed Steel No. 35 in Table 1B having an excessively high sulfur content. As a result, the sample had a high percent brittle fracture and failed to achieve desired cryogenic toughness.

[0138] Sample No. 36 employed Steel No. 36 in Table 1B having chemical compositions meeting the conditions specified in the present invention, but had an excessively high L parameter. The sample therefore contained retained austenite in an insufficient volume fraction and had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had inferior cryogenic toughness.

[0139] Sample No. 37 employed Steel No. 37 in Table 1B having a low carbon content, a high Al content, and a low Ni content. The sample therefore contained retained austenite in an insufficient volume fraction and had a low retained austenite stabilization parameter. In addition, the sample had a retained austenite volume fraction-retained austenite stabilization parameter of greater than the predetermined range. As a result, the sample had inferior cryogenic toughness and also had a low tensile strength TS.

[0140] Sample No. 38 employed Steel No. 38 in Table 1B having a low Al content and a high nitrogen content and

therefore had inferior cryogenic toughness.

[0141] Sample No. 39 employed Steel No. 39 in Table 1B having excessively high contents of selective compositions Cu and Ca and therefore had inferior cryogenic toughness.

[0142] Sample No. 40 employed Steel No. 40 in Table 1B having excessively high contents of selective compositions Cr and Zr and therefore had inferior cryogenic toughness.

[0143] Sample No. 41 employed Steel No. 41 in Table 1B having excessively high contents of selective compositions Nb and REM and therefore had inferior cryogenic toughness.

[0144] Sample No. 42 employed Steel No. 42 in Table 1B having an excessively high content of selective composition Mo, had a high Di value, and therefore had inferior cryogenic toughness.

[0145] Sample No. 43 employed Steel No. 43 in Table 1B having an excessively high content of selective composition Ti and therefore had inferior cryogenic toughness.

[0146] Sample No. 44 employed Steel No. 44 in Table 1B having an excessively high content of selective composition V and therefore had inferior cryogenic toughness.

[0147] Sample No. 45 employed Steel No. 45 in Table 1B having an excessively high content of selective composition boron (B) and therefore had inferior cryogenic toughness.

Experimental Example 2

[0148] In this experimental example, part of the samples according to the present invention used in Experimental Example 1 were examined and evaluated on percent brittle fracture at -233°C.

[0149] Specifically, each three test specimens were sampled from each of samples given in Table 3 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. The sample numbers in Table 3 correspond to the sample numbers (steel numbers) in Tables 1A and 2A.

[0150] In this experimental example, a sample having a percent brittle fracture equal to or less than 50% was evaluated as being excellent in percent brittle fracture at -233°C.

[0151] "Cryogenic-Temperature Impact Test of Austenitic Stainless Cast Steel", Journal of the High Pressure Gas Safety Institute of Japan, vol. 24, p. 181.

[0152] Results of these determinations and evaluations are indicated in Table 3.

[Table 3]

No.	Retained γ volume fraction-retained γ stabilization parameter	Cryogenic toughness	
		Percent brittle fracture at -196°C (%)	Percent brittle fracture at -233°C (%)
1	18	3	49
2	17	0	32
3	21	0	24
6	20	3	48
8	16	0	40
9	15	0	15
10	36	5	56
14	16	0	21
16	35	0	58
18	19	3	47
20	19	5	43

[0153] Sample Nos. 1 to 3, 6, 8, 9, 14, 18, and 20 in Table 3 have satisfactorily low percent brittle fracture not only at -196°C, but also at a lower temperature of -233°C and could achieved extremely excellent cryogenic toughness. This is probably because each of these samples had a low retained austenite volume fraction-retained austenite stabilization parameter of 21 or less.

[0154] In contrast, Sample Nos. 10 and 16 had higher retained austenite volume fraction-retained austenite stabilization

parameter of about 35 and therefore had higher percent brittle fracture at -233°C as compared with the above-mentioned samples.

[0155] The experimental results demonstrate that it is effective to minimize the retained austenite volume fraction-retained austenite stabilization parameter, particularly among the conditions specified in the present invention, so as to give steel plates that have good (low) percent brittle fracture not only at -196°C, but also at a lower temperature of -233°C.

Experimental Example 3

[0156] This experimental example relates to steel plates having a percent brittle fracture at -196°C of equal to or less than 10%, a tensile strength TS of greater than 830 MPa, and a yield strength YS of greater than 690 MPa.

[0157] Molten steels as test samples having chemical compositions given in Table 4 (with the remainder consisting of iron and inevitable impurities, in mass percent) were made using a vacuum induction furnace (150-kg VIF). The molten steels were cast, subjected to hot forging, and yielded ingots of a size of 150 mm by 150 mm by 600 mm. REM used in this experimental example was a misch metal containing about 50% of Ce and about 25% of La.

[0158] Next, the ingots were heated to 1100°C and rolled at a temperature of 830°C or higher to a thickness of 75 mm. The workpieces were rolled at a finish rolling temperature (FRT) of 700°C and water-cooled from a start cooling temperature (SCT) of 650°C within 60 seconds after the finish rolling. Thus, the workpieces were rolled to a thickness of 25 mm with a rolling reduction of 85%. The cooling in the range from 800°C down to 500°C was performed at an average cooling rate of 19°C/s, and the cold rolling was performed to a stop temperature of 200°C or lower to give steel plates.

[0159] The above-prepared steel plates were each subjected to an L treatment by heating to and holding at an L treatment temperature given in Table 5 for 30 minutes, followed by water cooling. The steel plates were further subjected to a T treatment (tempering) at a temperature (T treatment temperature) for a time (T time) given in Table 2, and air-cooled down to room temperature.

[0160] The above-prepared steel plates were examined and evaluated on the amount (volume fraction) of retained austenite phase existing at -196°C, Mn content in the retained austenite phase, 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).

[0161] The amount (volume fraction) of 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) were measured by the procedure of Experimental Example 1. How the Mn content in the retained austenite phase existing at -196°C was measured will be described below.

[0162] An average Mn content in the retained austenite phase was measured by transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDX) and calculated by a procedure as follows. The calculation was performed assuming that the retained austenite phase includes Fe, Mn, and Ni as chemical compositions. An actual retained austenite phase may include other elements such as C and Si, in addition to Fe, Mn, and Ni. However, these elements are present in small amounts and are approximately trivial in this experimental example.

[0163] 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, held at the liquid nitrogen temperature (-196°C) for 5 minutes, cut to a size of 10 mm by 10 mm by 2 mm, mechanically polished to reduce the thickness "t" from 2 mm to 0.1 mm, blanked into a disc having a size of 3 mm in diameter, electrically polished, and yielded a thin-film specimen. The above-prepared thin-film specimen was analyzed using a transmission electron microscope H-800 supplied by Hitachi, Ltd, based on which an austenite phase was identified using a transition image and a reciprocal lattice, and the Mn content in the austenite phase was measured using an EDX analyzer F.MAX7000 supplied by HORIBA, Ltd. The measurement using the EDX was performed at an acceleration voltage of 200 kV and a 75000-fold observation magnification on five points per sample. The measured values at the five points were averaged, and the average was defined as the Mn content in the retained austenite.

[0164] In Experimental Example 3, a sample having a tensile strength TS of greater than 830 MPa and a yield strength YS of greater than 690 MPa was evaluated as having excellent base metal strengths, differing from Experimental Example 1.

[0165] Results of these measurements and evaluations are together indicated in Tables 5A and 5B.

[Table 4A]

No.	C	Si	Mn	P	S	Al	Ni	Mo	Cr	N	Cu	Ti	Nb	V	B	Ca	REM	Zr
1	0.05	0.06	1.27	<0.004	0.001	0.032	5.66	0.43	0.42	0.0032								
2	0.05	0.06	1.27	<0.004	0.001	0.030	5.62	0.43	0.82	0.0034								
3	0.05	0.06	1.10	<0.004	0.001	0.030	5.84	0.30	0.62	0.0033								
4	0.09	0.05	0.87	<0.004	0.002	0.020	6.15	0.38	0.36	0.0031	0.21							
5	0.02	0.20	1.48	<0.004	0.001	0.030	5.33	0.82	0.55	0.0032							0.0042	
6	0.03	0.38	0.90	<0.004	0.004	0.038	7.25	0.75	0.33	0.0031			0.027				0.0023	
7	0.05	0.29	0.82	<0.004	0.001	0.033	6.24	0.67	0.55	0.0038	0.15							
8	0.04	0.12	1.58	<0.004	0.001	0.034	5.92	0.33	0.35	0.0029						0.0019		
9	0.05	0.06	1.06	0.007	0.002	0.038	7.08	0.83	0.38	0.0029			0.012					
10	0.04	0.19	1.19	<0.004	0.007	0.011	5.65	0.52	0.33	0.0045		0.012						0.0022
11	0.07	0.10	1.10	<0.004	0.003	0.047	5.88	0.30	0.30	0.0034				0.25				
12	0.04	0.02	1.15	0.005	0.002	0.041	5.09	0.53	0.69	0.0033	0.51				0.0019			
13	0.03	0.22	1.72	<0.004	0.001	0.019	5.70	0.61	0.33	0.0031				0.02				0.0046
14	0.04	0.05	1.09	<0.004	0.001	0.031	5.41	0.45	0.58	0.0075		0.016			0.0007	0.0011		
15	0.05	0.11	1.06	<0.004	0.003	0.035	5.86	0.38	0.45	0.0058	0.10							
16	0.04	0.19	1.06	<0.004	0.001	0.035	5.62	0.30	1.15	0.0033				0.05		0.0022		
17	0.04	0.15	1.07	0.006	0.005	0.029	5.90	0.52	0.83	0.0031		0.021					0.0030	
18	0.04	0.22	1.07	<0.004	0.002	0.034	6.89	0.43	0.32	0.0035	0.42		0.055					
19	0.05	0.08	1.10	<0.004	0.001	0.031	5.68	0.30	0.64	0.0032				0.38				
20	0.06	0.08	1.07	0.005	0.001	0.030	6.37	0.35	0.52	0.0032	0.15				0.0033			
21	0.04	0.13	1.02	<0.004	0.001	0.031	6.30	0.38	0.70	0.0032				0.11		0.0027		

[Table 4B]

No.	C	Si	Mn	P	S	Al	Ni	Mo	Cr	N	Cu	Ti	Nb	V	B	Ca	REM	Zr
1	0.05	0.09	1.00	<0.004	0.001	0.032	5.45	0.53	0.30	0.0035								
2	0.11	0.10	1.01	<0.004	0.004	0.027	6.21	0.24	0.65	0.0038								
3	0.05	0.08	1.12	0.008	0.001	0.033	5.75	0.49	0.33	0.0032	0.21							
4	0.07	0.15	1.08	<0.004	0.001	0.031	6.32	0.34	0.36	0.0033								
5	0.10	0.42	1.03	<0.004	0.001	0.031	6.25	0.30	0.20	0.0032					0.0021			
6	0.03	0.04	2.15	<0.004	0.002	0.029	8.33	0.22	0.49	0.0032								
7	0.05	0.06	0.96	<0.004	0.002	0.032	5.45	0.36	0.55	0.0040	0.50							
8	0.05	0.08	0.51	0.005	0.001	0.032	5.20	0.58	0.86	0.0038		0.015						
9	0.04	0.10	1.42	<0.004	0.008	0.038	6.50	0.35	0.34	0.0051								
10	0.01	0.08	1.18	<0.004	0.001	0.052	4.80	0.82	0.55	0.0045				0.22				
11	0.08	0.12	1.01	<0.004	0.001	0.004	6.40	0.20	0.57	0.0107			0.016					
12	0.05	0.08	1.01	<0.004	0.004	0.037	6.49	0.32	0.33	0.0032	1.08					0.0032		
13	0.06	0.11	1.05	0.006	0.001	0.029	5.55	0.21	1.25	0.0029								0.0057
14	0.04	0.10	1.34	<0.004	0.001	0.045	6.25	0.36	0.47	0.0030			0.104				0.0051	
15	0.04	0.22	1.21	<0.004	0.003	0.037	5.90	1.07	0.10	0.0034								
16	0.05	0.12	1.02	<0.004	0.003	0.028	6.47	0.38	0.47	0.0036		0.027					0.0021	
17	0.05	0.32	1.02	<0.004	0.001	0.015	5.83	0.31	0.36	0.0029				0.52				
18	0.05	0.20	1.07	<0.004	0.001	0.035	6.04	0.37	0.52	0.0033					0.0052			
19	0.05	0.17	0.95	<0.004	0.001	0.032	5.70	0.42	0.50	0.0027								
20	0.05	0.24	0.75	<0.004	0.001	0.029	5.65	0.39	0.67	0.0030								
21	0.05	0.05	1.98	<0.004	0.001	0.035	5.10	0.25	0.30	0.0034								

[Table 5A]

No.	Divalue	Mn content in retained γ (%)	[Mn]-[0.31*(7.20- [Ni])]+ 0.50]	A _{c1} (°C)	A _{c3} (°C)	(A _{c1} +A _{c3}) /2 (°C)	L treatment tempera- ture (°C)	T treatment tempera- ture (°C)	T time (min)	Cooling af- ter tem- pering	L paramete- r	λ _L param- eter	Retained γ (%)	Cryogenic toughness	Tensile proper- ties	
															Percent brittle frac- ture at -196°C (%)	YS (MPa)
1	5.5	1.66	0.29	623	763	693	700	520	30	Air cooling	0.80	-7.3	2.1%	3%	825	860
2	8.0	1.66	0.27	630	768	699	690	510	30	Air cooling	0.69	-7.5	3.0%	3%	850	882
3	5.1	1.44	0.11	628	766	697	700	520	30	Air cooling	0.77	-3.2	2.5%	3%	814	852
4	5.6	1.14	0.04	617	752	885	700	510	20	Air cooling	0.86	-8.3	2.6%	7%	827	862
5	7.4	1.93	0.39	632	797	714	730	520	40	Air cooling	0.84	-21.5	4.5%	0%	845	878
6	6.2	1.17	0.42	607	782	695	710	520	30	Air cooling	0.84	23.6	4.6%	1%	836	869
7	7.9	1.07	0.02	626	788	707	720	520	30	Air cooling	0.83	-20.6	2.7%	5%	849	881
8	5.2	2.06	0.68	615	751	683	700	510	15	Air cooling	0.87	0.0	4.3%	0%	818	854
9	8.2	1.39	0.53	600	759	680	700	520	15	Air cooling	0.88	-25.6	4.7%	1%	853	884
10	5.3	1.55	0.20	626	776	701	720	520	30	Air cooling	0.88	-11.5	2.7%	1%	820	857
11	6.6	1.44	0.19	620	777	699	710	510	30	Air cooling	0.82	-3.3	2.2%	3%	839	873
12	7.4	1.50	0.00	637	793	715	730	520	20	Air cooling	0.85	-11.8	2.2%	1%	845	878
13	7.3	2.24	0.75	620	771	696	710	510	20	Air cooling	0.84	-11.1	4.6%	0%	844	877
14	5.3	1.42	0.03	631	777	704	720	510	40	Air cooling	0.86	-9.1	2.0%	3%	819	856
15	5.2	1.38	0.14	624	768	696	710	510	55	Air cooling	0.85	-6.6	2.9%	7%	789	835
16	7.9	1.39	0.07	642	788	715	730	510	20	Air cooling	0.85	-2.2	2.7%	7%	849	881
17	7.9	1.39	0.16	630	780	705	720	510	20	Air cooling	0.85	-11.9	2.7%	5%	849	881
18	5.7	1.40	0.48	607	768	687	700	510	30	Air cooling	0.83	-8.9	4.7%	3%	829	864
19	8.9	1.44	0.12	628	805	717	730	510	20	Air cooling	0.83	-2.8	2.0%	3%	865	892
20	6.3	1.40	0.31	615	755	685	700	520	25	Air cooling	0.86	-4.9	4.1%	3%	836	870
21	7.1	1.33	0.23	621	780	701	720	520	20	Air cooling	0.87	-6.5	3.3%	7%	843	876

[Table 5B]

No.	Divalue	Mncontent in retained γ (%)	$[Mn]-[0.31*(7.20-[Ni])]+0.50]$	A_{c1} (°C)	A_{c3} (°C)	$(A_{c1}+A_{c3})$ /2 (°C)	L treatment tempera- ture (°C)	T treatment tempera- ture (°C)	T time (min)	Cooling af- ter tem- pering	L param- eter	λ_L param- eter	Retained γ (%)	Cryogenic toughness	Tensile proper- ties	
															YS (MPa)	TS (MPa)
1	4.6	1.31	-0.05	628	776	702	720	520	20	Air cooling	0.87	-13.5	1.7%	15%	798	840
2	7.4	1.32	0.20	621	737	679	690	510	15	Air cooling	0.84	-1.1	2.6%	25%	895	928
3	5.5	1.46	0.16	622	770	696	710	510	20	Air cooling	0.84	-10.9	2.0%	63%	825	860
4	5.6	1.41	0.30	615	749	682	590	520	35	Air cooling	0.06	-9.1	0.5%	55%	826	861
5	5.6	1.35	0.24	622	750	686	790	510	30	Air cooling	1.56	0.2	1.8%	20%	828	862
6	5.7	2.81	1.38	602	728	665	680	580	20	Air cooling	0.87	9.6	13.2%	70%	829	863
7	5.4	1.25	-0.09	632	783	707	720	510	65	Air cooling	0.83	-6.5	4.5%	13%	765	823
8	5.1	0.67	-0.62	647	802	724	740	510	20	Air cooling	0.85	-18.9	1.5%	27%	814	851
9	5.1	1.85	0.70	607	747	677	690	510	20	Air cooling	0.84	-2.6	4.7%	55%	816	853
10	5.3	1.54	-0.07	641	840	740	760	510	25	Air cooling	0.85	-23.9	1.1%	25%	770	806
11	5.5	1.31	0.25	617	743	680	690	520	40	Air cooling	0.83	0.4	4.0%	23%	826	861
12	5.6	1.32	0.29	610	774	692	710	510	20	Air cooling	0.86	-4.7	4.0%	19%	877	912
13	7.6	1.38	0.04	642	770	706	720	520	15	Air cooling	0.86	1.7	2.9%	17%	896	929
14	5.6	1.75	0.54	614	755	684	700	510	40	Air cooling	0.86	-3.2	4.9%	18%	877	912
15	6.5	1.58	0.30	618	788	703	720	520	20	Air cooling	0.85	-34.8	2.5%	12%	889	923
16	5.4	1.34	0.29	614	758	686	700	510	15	Air cooling	0.85	-6.9	2.9%	20%	873	908
17	8.6	1.33	0.09	629	827	728	750	520	35	Air cooling	0.86	-4.0	2.1%	19%	908	937
18	5.8	1.39	0.20	624	767	696	710	520	20	Air cooling	0.85	-6.1	2.6%	17%	880	915
19	5.3	1.01	-0.02	630	776	703	790	520	20	Air cooling	1.35	-7.4	1.3%	14%	870	906
20	5.2	0.98	-0.24	638	787	712	730	640	20	Air cooling	0.87	-9.2	12.3%	12%	688	774
21	5.1	2.58	0.82	622	741	682	730	520	20	Air cooling	1.16	10.3	4.8%	64%	864	902

Considerations can be made from Tables 5A and 5B as follows.

[0166] Sample Nos. 1 to 21 in Table 5A respectively employed Steel Nos. 1 to 21 in Table 4A having chemical compositions meeting the conditions specified in the present invention and were prepared under the production conditions specified in the present invention. These samples could provide steel plates having excellent cryogenic toughness at -196°C even though having high base metal strengths. Specifically, the samples each had an average percent brittle fracture in the C-direction of equal to or less than 10%.

[0167] In contrast, Sample Nos. 1 to 21 in Table 5B are comparative examples not meeting one or more of the conditions specified in the present invention, including the steel chemical compositions and production conditions, and failed to have desired properties.

[0168] Sample No. 1 in Table 5B employed Steel No. 1 in Table 4B having chemical compositions meeting the conditions specified in the present invention, but had a Di value not meeting the condition specified in the present invention. The sample failed to have a desired retained austenite volume fraction. As a result, the sample had a high percent brittle fracture and failed to achieve desired cryogenic toughness at -196°C.

[0169] Sample No. 2 in Table 5B employed Steel No. 2 in Table 4B having a high carbon content and a low Mo content and had inferior cryogenic toughness.

[0170] Sample No. 3 in Table 5B employed Steel No. 3 in Table 4B having an excessively high phosphorus content and had inferior cryogenic toughness.

[0171] Sample No. 4 in Table 5B employed Steel No. 4 in Table 4B having chemical compositions meeting the conditions specified in the present invention, but underwent heating at a temperature lower than the two-phase region temperature (L treatment temperature), and had a low L parameter. The sample therefore contained retained austenite in an insufficient volume fraction and had inferior cryogenic toughness.

[0172] Sample No. 5 in Table 5B employed Steel No. 5 in Table 4B having excessively high Si and Mo contents, underwent heating at a temperature higher than the two-phase region temperature (L treatment temperature), and had excessively high L parameter and λ_L parameter. The sample therefore contained retained austenite in an insufficient volume fraction and had inferior cryogenic toughness.

[0173] Sample No. 6 in Table 5B employed Steel No. 6 in Table 4B having a high Mn content and a low Mo content, underwent tempering at an excessively high temperature (T treatment temperature), had an excessively high λ_L parameter, and failed to have a desired retained austenite volume fraction. As a result, the sample had inferior cryogenic toughness.

[0174] Sample No. 7 in Table 5B employed Steel No. 7 in Table 4B having chemical compositions meeting the conditions specified in the present invention, but underwent tempering for an excessively long time (T time). The sample had a Ni-Mn balance as specified by Formula (2) lower than the preferred range. As a result, the sample had inferior low-temperature toughness (cryogenic toughness) and also had a low strength (TS).

[0175] Sample No. 8 in Table 5B employed Steel No. 8 in Table 4B having an excessively low Mn content. The sample had a Ni-Mn balance as specified by Formula (2) lower than the preferred range, had a low Mn content in the retained austenite, and contained retained austenite in an insufficient volume fraction. As a result, the sample had inferior cryogenic toughness.

[0176] Sample No. 9 in Table 5B employed Steel No. 9 in Table 4B having an excessively high sulfur content. As a result, the sample had a high percent brittle fracture and failed to achieve desired cryogenic toughness.

[0177] Sample No. 10 in Table 5B employed Steel No. 10 in Table 4B having an excessively low carbon content, an excessively high Al content, and an excessively low Ni content and having a Ni-Mn balance specified by Formula (2) lower than the preferred range. The sample contained retained austenite in a low volume fraction because of excessively low contents of C and Ni that are useful for ensuring retained austenite in a sufficient volume fraction. As a result, the sample had inferior cryogenic toughness, although having a yield strength YS at good level. However, the steel had a low tensile strength TS because of excessively low contents of C and Ni that are effective for higher strength.

[0178] Sample No. 11 in Table 5B employed Steel No. 11 in Table 4B having excessively low Al and Mo contents and an excessively high nitrogen content and had an excessively high λ_L parameter. The sample therefore had inferior cryogenic toughness.

[0179] Sample No. 12 in Table 5B employed Steel No. 12 in Table 4B having excessively high contents of selective compositions Cu and Ca. The sample therefore had inferior cryogenic toughness.

[0180] Sample No. 13 in Table 5B employed Steel No. 13 in Table 4B having an excessively low content of Mo and excessively high contents of Cr and Zr each added as selective compositions and had an excessively high λ_L parameter. The sample therefore had inferior cryogenic toughness.

[0181] Sample No. 14 in Table 5B employed Steel No. 14 in Table 4B having excessively high contents of selective compositions Nb and REM. The sample therefore had inferior cryogenic toughness.

[0182] Sample No. 15 in Table 5B employed Steel No. 15 in Table 4B having an excessively high content of selective composition Mo. The sample therefore had inferior cryogenic toughness.

[0183] Sample No. 16 in Table 5B employed Steel No. 16 in Table 4B having an excessively high content of elective

composition Ti. The sample therefore had inferior cryogenic toughness.

[0184] Sample No. 17 in Table 5B employed Steel No. 17 in Table 4B having an excessively high content of selective composition vanadium (V). The sample therefore had inferior cryogenic toughness.

[0185] Sample No. 18 in Table 5B employed Steel No. 18 in Table 4B having an excessively high content of selective composition boron (B). The sample therefore had inferior cryogenic toughness.

[0186] Sample No. 19 in Table 5B employed Steel No. 19 in Table 4B having chemical compositions meeting the conditions specified in the present invention, but had an excessively high L parameter, and underwent an L treatment at an excessively high temperature. The sample therefore had an excessively low Mn content in the retained austenite, contained the retained austenite in an insufficient volume fraction, and had inferior cryogenic toughness.

[0187] Sample No. 20 in Table 5B employed Sample No. 20 in Table 5B having chemical compositions meeting the conditions specified in the present invention, but underwent tempering at an excessively high temperature (T treatment temperature), and had a Ni-Mn balance specified by Formula (2) lower than the preferred range. The sample failed to have a desired retained austenite volume fraction and had a low Mn content in the retained austenite. As a result, the sample had a high percent brittle fracture, failed to achieve desired cryogenic toughness at -196°C, and was inferior in yield strength YS and tensile strength TS.

[0188] Sample No. 21 in Table 5B employed Steel No. 21 in Table 4B having an excessively low Mo content and had an excessively high L parameter and an excessively high λ_L parameter. As a result, the sample had a high percent brittle fracture and failed to achieve desired cryogenic toughness at -196°C.

Experimental Example 4

[0189] In this experimental example, the samples according to the present invention in Table 5A used in Experimental Example 3 were further examined and evaluated on percent brittle fracture at -233°C.

[0190] Specifically, each three test specimens were sampled from each of samples given in Table 6 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 described below, and an average of measured percent brittle fracture values was calculated and evaluated. The sample numbers in Table 6 correspond to the sample numbers (steel numbers) in Tables 4A and 5A. In this experimental example, a sample having a percent brittle fracture equal to or less than 50% was evaluated as being excellent in percent brittle fracture at -233°C. "Cryogenic-Temperature Impact Test of Austenitic Stainless Cast Steel", Journal of the High Pressure Gas Safety Institute of Japan, vol. 24, p. 181.

[0191] Results of the measurements and evaluations are indicated in Table 6. For reference, Table 6 also indicates data of the (i) retained austenite volume fraction, (ii) Mn content in retained austenite, and (iii) λ_L parameter as abstracted from Table 5A. Details of them are as follows.

[Table 6]

No.	Retained γ (%)	Mn content in retained γ (%)	λ_L parameter	Cryogenic toughness	
				Percent brittle fracture at -196°C (%)	Percent brittle fracture at -233°C (%)
1	2.1%	1.66	-7.3	3%	50%
2	3.0%	1.66	-7.5	3%	50%
3	2.5%	1.44	-3.2	3%	50%
4	2.6%	1.14	-8.3	7%	60%
5	4.5%	1.93	-21.5	0%	15%
6	4.6%	1.17	-23.6	1%	40%
7	2.7%	1.07	-20.6	5%	50%
8	4.3%	2.06	0.0	0%	25%
9	4.7%	1.39	-25.6	1%	40%
10	2.7%	1.55	-11.5	1%	40%
11	2.2%	1.44	-3.3	3%	50%
12	2.2%	1.50	-11.8	1%	40%
13	4.6%	2.24	-11.1	0%	15%

(continued)

No.	Retained γ (%)	Mn content in retained γ (%)	λ_L parameter	Cryogenic toughness	
				Percent brittle fracture at -196°C (%)	Percent brittle fracture at -233°C (%)
14	2.0%	1.42	-9.1	3%	50%
15	2.9%	1.38	-6.6	7%	60%
16	2.7%	1.39	-2.2	7%	60%
17	2.7%	1.39	-11.9	5%	50%
18	4.7%	1.40	-8.9	3%	50%
19	2.0%	1.44	-2.8	3%	50%
20	4.1%	1.40	-4.9	3%	50%
21	3.3%	1.33	-6.5	7%	60%

[0192] Sample No. 1 to 3, 5 to 14, and 17 to 20 in Table 6 respectively employed Steel Nos. 1 to 3, 5 to 14, and 17 to 20 in Table 5A meeting at least one of the preferred conditions (i) to (iii). The samples each had a good percent brittle fracture at -233°C of 50% or less. In contrast, Sample Nos. 4, 15, 16, and 21 in Table 6 respectively employed Steel Nos. 4, 15, 16, and 21 in Table 5A meeting none of the preferred conditions (i) to (iii). The samples failed to have desired toughness at -233°C.

[0193] Specifically, Sample Nos. 1 to 3 in Table 6 respectively employed Steel Nos. 1 to 3 in Table 5A and had a good percent brittle fracture at -233°C of 50%.

[0194] In contrast, Sample No. 4 in Table 6 employed Steel No. 4 in Table 5A meeting none of the preferred conditions (i) to (iii) and failed to have desired toughness at -233°C.

[0195] Sample No. 5 in Table 6 employed Steel No. 5 in Table 5A meeting all the preferred conditions (i) to (iii) and having a Mn content in the retained austenite controlled within the more preferred range of 1.75% to 2.50% in the condition (ii). The sample could have still better toughness (lower percent of brittle fracture) at -233°C of 15%.

[0196] Sample No. 6 in Table 6 employed Steel No. 6 in Table 5A meeting the preferred conditions (i) and (iii). The sample could have still better toughness (lower percent of brittle fracture) at -233°C of 40%.

[0197] Sample No. 7 in Table 6 employed Steel No. 7 in Table 5A meeting the preferred condition (iii) and had a good percent brittle fracture at -233°C of 50%.

[0198] Sample No. 8 in Table 6 employed Steel No. 8 in Table 5A meeting the preferred conditions (i) and (ii) and having a Mn content in the retained austenite controlled within the more preferred range of 1.75% to 2.50% in the condition (ii). The sample could have still better toughness (lower percent of brittle fracture) at -233°C of 25%.

[0199] Sample No. 9 in Table 6 employed Steel No. 9 in Table 5A meeting the preferred conditions (i) and (iii) and could have still better toughness (lower percent of brittle fracture) at -233°C of 40%.

[0200] Sample No. 10 in Table 6 employed Steel No. 10 in Table 5A meeting the preferred conditions (ii) and (iii) and could have still better toughness (lower percent of brittle fracture) at -233°C of 40%.

[0201] Sample No. 11 in Table 6 employed Steel No. 11 in Table 5A meeting the preferred condition (ii) and had a good percent brittle fracture at -233°C of 50%.

[0202] Sample No. 12 in Table 6 employed Steel No. 12 in Table 5A meeting the preferred conditions (ii) and (iii) and could have still better toughness (lower percent of brittle fracture) at -233°C of 40%.

[0203] Sample No. 13 in Table 6 employed Steel No. 13 in Table 5A meeting all the preferred conditions (i) to (iii) and having a Mn content in the retained austenite controlled within the more preferred range of 1.75% to 2.50% in the condition (ii). The sample could have still better toughness (lower percent of brittle fracture) at -233°C of 15%.

[0204] Sample No. 14 in Table 6 employed Steel No. 14 in Table 5A meeting the preferred condition (ii) and had a good percent brittle fracture at -233°C of 50%.

[0205] In contrast, Sample Nos. 15 and 16 in Table 6 respectively employed Steel Nos. 15 and 16 in Table 5A meeting none of the preferred conditions (i) to (iii) and failed to have desired toughness at -233°C.

[0206] In contrast, Sample No. 17 in Table 6 employed Steel No. 17 in Table 5A meeting the preferred condition (iii) and had a good percent brittle fracture at -233°C of 50%.

[0207] Sample No. 18 in Table 6 employed Steel No. 18 in Table 5A meeting the preferred condition (i) and had a good percent brittle fracture at -233°C of 50%.

[0208] Sample No. 19 in Table 6 employed Steel No. 19 in Table 5A meeting the preferred condition (ii) and had a good percent brittle fracture at -233°C of 50%.

[0209] Sample No. 20 in Table 6 employed Steel No. 20 in Table 5A meeting the preferred condition (i) and had a good percent brittle fracture at -233°C of 50%.

[0210] In contrast, Sample No. 21 in Table 6 employed Steel No. 21 in Table 5A meeting none of the preferred conditions (i) to (iii) and failed to have desired toughness at -233°C.

[0211] 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.

[0212] The present application claims priority to Japanese Patent Application No. 2012-272184 filed on December 13, 2012 and Japanese Patent Application No. 2012-285916 filed on December 27, 2012, the entire contents of which are incorporated herein by reference.

Industrial Applicability

[0213] The steel plates according to the present invention are useful as steel plates that are in contact with substances at cryogenic temperatures, such as in liquefied natural gas storage tanks.

Claims

1. A steel plate having excellent cryogenic toughness, 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%;

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

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%),

with the remainder consisting of iron and inevitable impurities,

the steel plate having a D_i value as specified by Formula (1) of 2.5 or more, Formula (1) defined by the steel chemical compositions and expressed as follows:

D_i value =

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times 1.115 \quad (1)$$

where [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], and [V] are contents (in mass percent) respectively of C, Si, Mn, Cu, Ni, Cr, Mo, and V in the steel,

the steel plate comprising a retained austenite phase (retained γ) existing at -196°C in a volume fraction of 2.0% to 12.0%,

the steel plate having a retained austenite stabilization parameter as specified by Formula (2) of 3.1 or more, Formula (2) defined by chemical components contained in the retained austenite and expressed as follows:

Retained austenite stabilization parameter =

$$(365 \times \langle C \rangle + 39 \times \langle Mn \rangle + 30 \times \langle Al \rangle + 10 \times \langle Cu \rangle + 17 \times \langle Ni \rangle + 20 \times \langle Cr \rangle + 5 \times \langle Mo \rangle + 35 \times \langle V \rangle) / 100 \quad (2)$$

where <C>, <Mn>, <Al>, <Cu>, <Ni>, <Cr>, <Mo>, and <V> are contents (in mass percent) respectively of C, Mn, Al, Cu, Ni, Cr, Mo, and V in the retained austenite existing at -196°C.

2. The steel plate according to claim 1,
wherein the steel plate has a retained austenite phase volume fraction-retained austenite stabilization parameter as specified by Formula (3) of 40 or less, Formula (3) defined by the retained austenite phase volume fraction and the retained austenite stabilization parameter and expressed as follows:

$$\text{Retained austenite volume fraction-retained austenite stabilization parameter} = 10/[(\text{retained austenite phase volume fraction}) \times (\text{retained austenite stabilization parameter})]^{1/2} \quad (3)$$

3. A steel plate having excellent cryogenic toughness, 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 0.6% 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%;

N in a content of 0.010% or less (excluding 0%) Mo in a content of 0.30% to 1.0%;

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

with the remainder consisting of iron and inevitable impurities,

the steel plate having a Di value of greater than 5.0, the Di value specified based on steel chemical compositions by Formula (1):

$$\text{Di value} = ([C]/10)^{0.5} \times (1+0.7 \times [Si]) \times (1+3.33 \times [Mn]) \times (1+0.35 \times [Cu]) \times (1+0.36 \times [Ni]) \times (1+2.16 \times [Cr]) \times (1+3 \times [Mo]) \times (1+1.75 \times [V]) \times 1.115 \quad (1)$$

where [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], and [V] are contents (in mass percent) respectively of C, Si, Mn, Cu, Ni, Cr, Mo, and V in the steel,

the steel plate comprising a retained austenite phase (retained γ) existing at -196°C in a volume fraction of 2.0% to 5.0%,

the retained austenite phase (retained γ) existing at -196°C having a Mn content of 1.05% or more, and

the steel plate having Mn and Ni contents (in mass percent) meeting a condition specified by Formula (4):

$$[Mn] \geq 0.31 \times (7.20 - [Ni]) + 0.50 \quad (4)$$

where [Mn] and [Ni] are contents (in mass percent) respectively of Mn and Ni in the steel.

4. The steel plate according to any one of claims 1 to 3, further comprising at least one group of element selected from the group consisting of:

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

(b) 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%);

- (c) B in a content of 0.0050% or less (excluding 0%);
 (d) at least one element selected from the group consisting of Ca in a content of 0.0030% or less (excluding 0%); and at least one rare earth element (REM) in a content of 0.0050% or less (excluding 0%); and
 (e) Zr in a content of 0.005% or less (excluding 0%).

5 5. A method for producing the steel plate according to one of claims 1 and 2, the method comprising the steps of

- 10 a) forming a steel plate from a steel and performing a heat treatment (L treatment) of the steel plate in a ferrite-austenite two-phase region (between A_{c1} and A_{c3}), the steel having such controlled chemical compositions and the L treatment performed at such a controlled temperature (L treatment temperature) that an L parameter as specified by Formula (5) is 0.25 to 0.45 and a λ_L parameter as specified by Formula (6) is 7 or less; and
 15 b) water-cooling the steel plate after the L treatment down to room temperature and subjecting the steel plate to a tempering treatment (T treatment) at a temperature equal to or lower than the A_{c1} temperature for 10 to 60 minutes, Formula (5) defined by the L treatment temperature and the A_{c1} and A_{c3} temperatures in the steel, Formula (6) defined by the L parameter and the steel chemical compositions, Formulae (5) and (6) expressed as follows:

$$20 \quad L \text{ parameter} = [(L \text{ treatment temperature}) - A_{c1}] / (A_{c3} - A_{c1}) + 0.25 \quad (5)$$

$$25 \quad \lambda_L \text{ parameter} = 9.05 \times (0.90 \times [L \text{ parameter}] + 0.14) \times [Mn] + 1.46 \times (0.37 \times [L \text{ parameter}] + 0.67) \times [Cr] - 41.5 \times (0.26 \times [L \text{ parameter}] + 0.79) \times [Mo] \quad (6)$$

where [Mn], [Cr], and [Mo] are contents (in mass percent) respectively of Mn, Cr, and Mo in the steel.

6. A method for producing the steel plate according to claim 3, the method comprising the steps of:

- 30 a) forming a steel plate from a steel and performing a heat treatment (L treatment) of the steel plate in a ferrite-austenite two-phase region (between A_{c1} and A_{c3}), the steel having such controlled chemical compositions and the L treatment performed at such a controlled temperature (L treatment temperature) that an L parameter as specified by Formula (5) is 0.6 to 1.1 and a λ_L parameter as specified by Formula (6) is 0 or less,
 35 Formula (5) defined by the L treatment temperature and the A_{c1} and A_{c3} temperatures in the steel, Formula (6) defined by the L parameter and the steel chemical compositions, Formulae (5) and (6) expressed as follows:

$$40 \quad L \text{ parameter} = [(L \text{ treatment temperature}) - A_{c1}] / (A_{c3} - A_{c1}) + 0.25 \quad (5)$$

$$45 \quad \lambda_L \text{ parameter} = 9.05 \times (0.90 \times [L \text{ parameter}] + 0.14) \times [Mn] + 1.46 \times (0.37 \times [L \text{ parameter}] + 0.67) \times [Cr] - 41.5 \times (0.26 \times [L \text{ parameter}] + 0.79) \times [Mo] \quad (6)$$

where [Mn], [Cr], and [Mo] are contents (in mass percent) respectively of Mn, Cr, and Mo in the steel.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/083239

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D6/00(2006.01)i, C22C38/58(2006.01)i, 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, C21D6/00, C22C38/58, C21D8/02

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.
P, A	JP 2013-234381 A (Kobe Steel, Ltd.), 21 November 2013 (21.11.2013), entire text (Family: none)	1-6
P, A	JP 2013-213273 A (Kobe Steel, Ltd.), 17 October 2013 (17.10.2013), entire text (Family: none)	1-6
P, A	JP 2013-014812 A (Nippon Steel & Sumitomo Metal Corp.), 24 January 2013 (24.01.2013), entire text (Family: none)	1-6

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

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
28 January, 2014 (28.01.14)Date of mailing of the international search report
04 February, 2014 (04.02.14)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/083239

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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