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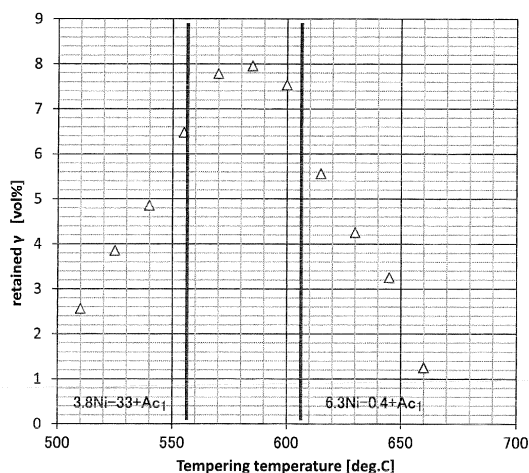
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(54) **STEEL MATERIAL, PROCESS FOR PRODUCING SAME, AND LNG TANK**

(57) A steel is provided in which a lower limit of an amount of retained γ at a $(1/4)t$ location regarding a plate thickness t of the steel is 4.0 volume%, the retained γ has a form in which an upper limit of an average of an aspect ratio thereof is 2.5 and an upper limit of an average of a major axis thereof is $0.85\ \mu\text{m}$, and an average Mn concentration in the retained γ and an average Ni concentration in the retained γ satisfy relationships of $[\text{Mn}]_{\text{retained } \gamma} > [\text{Mn}]_{\alpha} \times 1.4$, and $[\text{Ni}]_{\text{retained } \gamma} > [\text{Ni}]_{\alpha} \times 1.4$.

FIG. 1



Description

[Technical Field of the Invention]

[0001] The present invention relates to a steel for very low-temperature use which is excellent in toughness, a method for manufacturing the steel, and an LNG tank to which the steel is applied. In addition, the term "for very-low temperature use" represents use of a liquefied petroleum gas (LPG), a liquefied natural gas (LNG), and the like at a temperature region in which the LPG, LNG, and the like exist in a liquid state, that is, use in a very low-temperature environment of -60°C or lower. Particularly, in the invention, use in the vicinity of -165°C, which is a temperature environment in which the LNG is stored in a liquid state, is set as a main target.

[Related Art]

[0002] A steel which is used to manufacture a very-low-temperature storage tank that stores a liquefied gas such as LPG and LNG is demanded to have excellent fracture toughness from the viewpoint of securement of stability.

[0003] For example, brittle crack propagation arrest characteristics (hereinafter, referred to as "arrest characteristics") of a base metal and a welded joint in the vicinity of -165°C, which is an LNG temperature environment and the like are demanded for 9% Ni steel that is used in an LNG tank (in the specification, "%" represents "mass%" unless otherwise stated). Particularly, to prevent the entirety of a structure from collapsing when a brittle crack occurs, the arrest characteristics are demanded as important characteristics without limitation to the LNG tank. In addition, with regard to base metal characteristics, an improvement has been made by control according to various methods such as a decrease in impurities including P and S, a decrease in C, and a three-stage heat treatment method (quenching (Q), two-phase region quenching(lamellarizing) (L), and tempering (T)).

[0004] On the other hand, when assuming construction of a ground type LNG tank in an earthquake-prone country such as Japan, it is demanded that the tank has no problems under earthquake conditions. An LNG ground type storage guideline (JGA-guideline-108-02, Investigation committee of technical standards for gas construction and the like, The Japan Gas Association) describes that as a target performance of an inner tank, liquid-tightness and air-tightness are demanded to be maintained when receiving an earthquake vibration of Level 2. That is, in a case where the inner tank member receives the earthquake vibration of Level 2, residue of deformation is permitted in the inner tank member, but a fracture that penetrates through the plate thickness of the inner tank member is not permitted. However, when a large external force similar to the earthquake vibration of Level 2 is applied, it can be assumed that the inner tank member is subject to large plastic deformation. Accordingly, it can be said that a fracture-resistant performance is a very high level characteristic. Examples of steel corresponding to the demand include 9% Ni steel.

[0005] When the 9% Ni steel is subjected to the above-described three-stage heat treatment method (quenching (Q), two-phase region quenching(lamellarizing) (L), and tempering (T)), the 9% Ni steel can have the target performance. However, the 9% Ni steel, in which a large amount of an expensive alloy element such as Ni is added, is expensive, and thus there is an economical problem. Accordingly, to suppress the cost of a steel, a steel in which an amount of Ni is suppressed has been developed.

[0006] With regard to low-Ni type steel for very low-temperature use, Patent Document 1 discloses a steel in which the amount of Ni is decreased to less than 8%. Here, Patent Document 1 discloses a finding that the brittle crack propagation arrest characteristics of a steel plate are improved by increasing an amount of retained γ . Accordingly, the present inventors have performed various fracture toughness tests with respect to steel plates with satisfactory V-notch Charpy absorbed energy $\sqrt{E_{196}}$, which are disclosed in Patent Document 1 (particularly, Test Nos. 1-a to 1-h, 4-12, and 22 to 35 described in Patent Document 1). As a result, it was proved that in any sample, a dynamic tear (DT) energy (a fracture characteristic evaluation parameter obtained by a DT test) at -196°C does not satisfy 1500 J, or absorption energy at -196°C, which is obtained by a pre-crack Charpy test with respect to a test specimen having a plate thickness of less than 15 mm, does not satisfy 100 J/cm². According to the subsequent advance of research, the present inventors have obtained a finding that an effect of improving the brittle crack propagation arrest characteristics are limited only with a simple increase in the amount of retained γ , and in a case where the increased retained γ is not stable, martensite after transformation may become a cause of deterioration in the brittle crack propagation arrest characteristics. The present inventors have found that to improve the brittle crack propagation arrest characteristics, it is important to secure an amount of γ capable of stably and continuously existing even when being subjected to slight plastic deformation at a very low temperature. Patent Document 1 does not disclose a necessity for stabilization of the retained γ , and also does not disclose a method of stabilizing the retained γ . When the retained γ is not stabilized, it is considered that the brittle crack propagation arrest characteristics are not sufficiently improved.

[0007] Patent Document 2 discloses a technology of securing a large amount of retained γ (retained austenite) with high stability by performing rolling with a defined cumulative reduction, and by performing an off-line quenching and tempering (QT) or direct-quenching and tempering (DQT) treatment. However, to stabilize the retained γ , it is necessary

for Ni or Mn in the retained γ to be concentrated in comparison to a structure at the periphery of the retained γ . In addition, when cooling after tempering is gradually performed, fracture-resistance characteristics of steel are damaged. Patent Document 2 does not disclose these findings at all. In addition, the majority of examples disclosed in Patent Document 2 contain 9% or more Ni in terms of mass%, but there are only two examples in which the retained γ is secured in an amount of 4% or more that are defined in the present invention. The two examples include an example that is manufactured by DQT, but a heating temperature during DQT is as high as 1200°C, and thus it is recognized that the example is different from the invention from the viewpoint of a process. This implies that the invention disclosed in Patent Document 2 does not have high fracture-resistant characteristics due to the reason to be described later.

[0008] Patent Document 3 discloses processes of so-called controlled rolling, direct-quenching, and tempering (CR-DQT) or controlled rolling, direct-quenching, lamellarizing, and tempering (CR-DQLT) in which low-temperature reduction is performed after low-temperature heating, water cooling is performed to a temperature of 200°C or lower immediately after the low-temperature reduction, and a heat treatment is performed. These processes themselves are the same as those in the invention. However, in the invention disclosed in Patent Document 3, a cumulative reduction is small, and thus the invention disclosed in Patent Document 3 does not include an example in which the cumulative reduction is 50% or larger that is defined in the present example. In a case where the cumulative reduction is small, the above-described concentration of Ni or Mn is not sufficiently provided, and thus it is considered that retained γ is not stabilized. In addition, Patent Document 3 does not disclose a cooling rate after tempering and a concentration of Ni or Mn in the retained γ which greatly relate to characteristics of a steel. This implies that the invention disclosed in Patent Document 3 does not have high fracture-resistant characteristics.

[0009] The invention disclosed in Patent Document 4 has paid attention to a segregation ratio of Ni, but in Patent Document 4, it is necessary to perform a crack diffusion treatment so as to decrease the segregation ratio. This is not preferable from the viewpoints of economic efficiency or lead time. In addition, as is the case with Patent Document 3, Patent Document 4 relates to the processes of so-called CR-DQT or CR-DQLT. These processes themselves are the same as those in the invention. However, Patent Document 4 does not disclose a cooling rate after tempering at all, and does not define a concentration of Ni or Mn in the retained γ . Accordingly, it can be said that the technology disclosed in Patent Document 4 is not a technology capable of stably satisfying very high fracture-resistant characteristics.

[Prior Art Document]

[Patent Document]

[0010]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2011-241419

[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. H6-184630

[Patent Document 3] Pamphlet of PGT International Publication No. WO2007/034576

[Patent Document 4] Pamphlet of PCT International Publication No. WO2012/005330

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0011] The invention has been made in consideration of the above-described circumstances, and an object thereof is to provide a steel excellent in economic efficiency and fracture-resistant characteristics by realizing compatibility between provision of very high fracture-resistant characteristics and suppression of the cost of the steel, a method for manufacturing the steel, and an LNG tank.

[Means for Solving the Problem]

[0012] To solve the above-described problems, the present inventors have employed steel in which an amount of Ni, which is effective to secure low-temperature toughness, is in a range of 6.6% to 8.0% in terms of mass%, and have performed various experimental tests in the above-described range to examine correspondence with characteristics. As a result, the present inventors have obtained the following findings (a) to (h).

(a) Fracture-resistant characteristics, which are necessary for a material for a low-temperature storage tank so as to maintain liquid-tightness and gas-tightness when receiving a force due to an earthquake, are brittle fracture initiation characteristics, and brittle crack propagation arrest characteristics (arrest characteristics) which is capable of arresting propagation of a crack caused by a brittle fracture if the fracture occurs.

(b) To improve these characteristics, it is necessary for the amount of Ni to be in a chemical component range of 6.6% to 8.0% in terms of mass%, and it is necessary to secure retained austenite (retained γ). In addition, even when being subjected to plastic deformation, it is necessary to secure an absolute amount of the retained γ .

(c) The retained γ is a structure having a very high brittle crack propagation arrest function, and when the structure is finely distributed, arrest characteristics of the material significantly increase. Here, it is possible to evaluate an amount of the retained γ in accordance with an X-ray diffraction method. With regard to a grain size of the retained γ , when an average major axis is 0.85 μm or less, a steel exhibits satisfactory arrest characteristics. Here, the major axis of the retained γ represents the length of the retained γ along the longest direction of the retained γ when observing a cross-section. In addition, the retained γ may be measured by collecting a sample at a $(1/4)t$ location regarding the plate thickness t of the steel.

(d) Here, the retained γ is in a metastable state, and thus when the steel is subjected to plastic deformation, a martensite transformation tends to occur. In order for the steel not to lose a lot of retained γ even when being subjected to the plastic deformation, it is preferable that the geometrical configuration of the retained γ be close to a spherical shape. Specifically, when being defined in terms of a number, it is preferable that the upper limit of an average aspect ratio of the retained γ be 2.5. Here, the aspect ratio of the retained γ represents a ratio between the major axis (L) of the retained γ , that is, the longest diameter of the retained γ , and the minor axis (W) of the retained γ , that is, the shortest diameter of the retained γ , that is, L/W . As is clear from the definition, the lower limit of the aspect ratio is 1.

(e) In addition, to minimize the amount of retained γ that is lost when being subjected to plastic deformation, it is necessary for Ni and Mn in the retained γ to be concentrated to a certain extent in comparison to a peripheral structure of the retained γ . Specifically, it is necessary for an average concentration of Ni and an average concentration of Mn in the retained γ to exceed 1.4 times an average concentration of Ni and an average concentration of Mn in ferrite (α phase).

(f) With regard to a manufacturing method to accomplish the objects, it is possible to realize compatibility between fracture-resistant characteristics and economic efficiency by controlling heating conditions or rolling conditions in detail, but this is not defined as a particularly essential condition. In addition, if heat treatment conditions are defined in detail, even when performing only a tempering treatment without performing an L treatment (in which a steel is heated in a temperature range of a two-phase region including ferrite and austenite, and then a water cooling treatment is performed) which has been frequently used with respect to 9% Ni steel in the related art, it is possible to obtain a steel exhibiting sufficient characteristics. However, even when performing the L treatment, the performance of the steel is not damaged. Accordingly, to further improve toughness by making a structure fine and by generating stable austenite, the L treatment, in which the steel is heated in a temperature range of 620°C to 720°C and a water cooling treatment is performed, may be performed as necessary. Regardless of the presence or absence of the L treatment, after performing a tempering treatment, it is necessary to set the lower limit of a cooling rate until a surface temperature of the steel reaches 300°C or lower to 0.5 °C/s so as to obtain satisfactory characteristics. When the cooling rate is made to be large with water cooling and the like after tempering, it is possible to generate austenite in which a Ni concentration is high and which is more stable without being affected by tempering embrittlement, and thus it is possible to secure high toughness. It is necessary for details to be examined, but a part of γ generated during tempering is subjected to martensite transformation between tempering and cooling. When the lower limit of the cooling rate is set to 0.5 °C/s, it is possible to suppress a decrease in a density of dislocation in martensite which occurs due to the martensite transformation, and a dynamic restriction effect is added to the retained γ adjacent to the martensite, and thus it can be assumed that stability of the retained γ can be improved.

(g) The steel excellent in low-temperature toughness has high fracture stability, and thus the steel can be applied to an inner tank member of the LNG tank.

(h) In the ground type LNG tank, as a portion to which large plastic deformation is applied during a very severe earthquake, an annular plate may be exemplified. The steel excelling in low-temperature toughness has high fracture stability, and thus the steel can be applied to the annular plate of the LNG tank.

[0013] The invention has been completed on the basis of the above-described findings, and the gist of the invention relates to a steel in (1) to (4) to be described below, a method for manufacturing a steel in (5) to (8) to be described below, and an LNG tank to which the steel is applied in (9) to (10).

(1) A steel according to an aspect of the invention has a chemical composition including, in terms of mass%, C: 0.01% to 0.12%, Si: 0.01% to 0.30%, Mn: 0.4% to 2.0%, Ni: 6.6% to 8.0%, Al: 0.002 to 0.08%, N: 0.0050% or less, P: 0.05% or less, S: 0.008% or less, Cu: 0% to 1.0%, Cr: 0% to 1.0%, Mo: 0% to 0.5%, V: 0% to 0.10%, B: 0% to 0.0050%, Nb: 0% to 0.10%, Ti: 0% to 0.10%, Sn: 0% to 0.50%, Ca: 0% to 0.004%, Mg: 0% to 0.0020%, REM: 0% to 0.0020%, and remainder: Fe and impurities. A lower limit of an amount of retained γ at a $(1/4)t$ location regarding a plate thickness t of the steel is 4.0 volume%. The retained γ has a form in which an upper limit of an average of

an aspect ratio thereof is 2.5 and an upper limit of an average of a major axis thereof is 0.85 μm . An average Mn concentration in the retained γ and an average Ni concentration in the retained γ satisfy Expression (A) and Expression (B), respectively.

$$[\text{Mn}]_{\text{retained } \gamma} > [\text{Mn}]_{\alpha} \times 1.4 \dots (\text{A})$$

$$[\text{Ni}]_{\text{retained } \gamma} > [\text{Ni}]_{\alpha} \times 1.4 \dots (\text{B})$$

Here, the $[\text{Mn}]_{\text{retained } \gamma}$ indicates the average Mn concentration in the retained γ , the $[\text{Mn}]_{\alpha}$ indicates an average Mn concentration in ferrite, the $[\text{Ni}]_{\text{retained } \gamma}$ indicates the average Ni concentration in the retained γ , and the $[\text{Ni}]_{\alpha}$ indicates an average Ni concentration in the ferrite.

(2) In the steel according to (1), the chemical composition may further include, in terms of mass%, C: 0.02% to 0.07%, Si: 0.01% to 0.10%, Mn: 0.6% to 1.0%, Ni: 7.0 to 7.8%, Cu: 0% to 0.30%, Cr: 0% to 0.80%, Mo: 0% to 0.20%, V: 0 to 0.05%, B: 0 to 0.0005%, Nb: 0 to 0.02%, Ti: 0 to 0.02%, and Sn: 0 to 0.01%.

(3) In the steel according to (1) or (2), the chemical composition may further include, in terms of mass%, Cr: 0.30% to 0.60%, and Mo: 0.05% to 0.15%.

(4) The steel according to any one of (1) to (3) may be a steel plate of which a plate thickness is 3 mm to 100 mm, a lower limit of a yield stress is 585 MPa, and a tensile strength is 690 MPa to 885 MPa.

(5) In an LNG tank according to another aspect of the invention, the steel according to any one of (1) to (4) is applied to a member of an inner tank.

(6) In an LNG tank according to still another aspect of the invention, the steel according to any one of (1) to (4) is applied to a member of an annular plate.

[Effects of the Invention]

[0014] It is possible to provide a low-Ni steel in which an amount of Ni is 6.6% to 8.0% in terms of mass% and which is excellent in economic efficiency and fracture-resistant characteristics, a method of manufacturing the steel, and an LNG tank.

[Brief Description of the Drawings]

[0015]

FIG. 1 is a graph illustrating a relationship between a tempering temperature and an amount of retained γ .

FIG. 2 is a graph illustrating a relationship between a cumulative reduction at 850°C or lower, and concentration rates of Ni and Mn.

FIG. 3 is a graph illustrating a relationship between the concentration rates of Ni and Mn, and dynamic tear (DT) energy that is a representative fracture characteristic evaluation parameter.

[Embodiment of the Invention]

[0016] Hereinafter, a steel according to this embodiment will be described in detail for each requirement thereof. Here, "%" relating to an amount represents "mass%" unless otherwise stated.

(A) With Regard to Chemical Composition

C: 0.01% to 0.12%

[0017] C is an element that is necessary to secure strength of a base metal. When an amount of C is less than 0.01%, it is difficult to secure necessary strength, and formation of lath martensite in a fusion line (FL) becomes insufficient during welding, and thus toughness of a heat-affected zone (HAZ) in the vicinity of FL also decreases. Accordingly, it is necessary for the lower limit of the amount of C to be set to 0.01%. On the other hand, when the amount of C exceeds 0.12%, deterioration in toughness of the HAZ, particularly, the HAZ in the vicinity of FL becomes significant. Accordingly, the amount of C is set to 0.01% to 0.12%. To reliably secure the strength, the lower limit of the amount of C may be set to 0.02%, 0.03%, or 0.04%. To improve the toughness of the HAZ, the upper limit of the amount of C may be set to

0.10%, 0.08%, 0.07%, or 0.06%.

Si: 0.01% to 0.30%

5 **[0018]** Si is an element that is necessary as a deoxidizing agent. To attain a deoxidation effect, it is necessary for the lower limit of an amount of Si to be set to 0.01%. On the other hand, in the case of the steel according to this embodiment, Si and a tempering of as-quenched martensite are greatly relevant to each other, and thus when the amount of Si exceeds 0.30%, Si suppresses a decomposition precipitation reaction of C with respect to cementite from martensite, in which C is solid-dissolved in a supersaturated state, during a weld cooling. Due to the suppression of the decomposition precipitation reaction of C, self-tempering is delayed, and thus toughness of a welded portion decreases. Alternatively, Si contained in an amount of more than 0.30% increases martensite-austenite constituent, thereby decreasing the toughness of the welded portion. Accordingly, the amount of Si is set to 0.01% to 0.30%. In addition, it is preferable that the amount of Si be as small as possible from the viewpoint of an improvement in the toughness of the welded portion, and the upper limit of the amount of Si may be set to 0.20%, 0.15%, or 0.10% so as to improve the toughness of the welded portion. The lower limit of the amount of Si may be set to 0.02%, 0.03%, or 0.04% so as to reliably perform deoxidation.

Mn: 0.4% to 2.0%

20 **[0019]** Mn is a deoxidizing agent, and is an element that is necessary to secure the strength and the toughness of the base metal, and the hardenability of the HAZ. When an amount of Mn is less than 0.4%, these effects are not obtained, and a ferrite side plate is generated in the HAZ, and thus formation of the lath martensite becomes insufficient. Therefore, the toughness of the welded portion decreases, and thus the lower limit of the amount of Mn is set to 0.4%. On the other hand, when the amount of Mn exceeds 2.0%, uniformity in base metal characteristics may be caused in a plate thickness direction due to central segregation of Mn. Accordingly, the amount of Mn is set to 0.4% to 2.0%. The lower limit of the amount of Mn may be set to 0.50%, 0.60%, or 0.70% so as to secure hardenability and improve the toughness of the welded portion. The upper limit of the amount of Mn may be set to 1.5%, 1.2%, 1.0%, or 0.9% so as to prevent uniformity in the base metal characteristics in the plate thickness direction.

30 P: 0.05% or less

[0020] P exists in steel as an impurity. In addition, P segregates at a grain boundary, and thus P becomes a cause of decreasing toughness. When an amount of P exceeds 0.05%, high-temperature cracks may be caused during welding, and thus the amount of P is limited to 0.05% or less. In addition, it is preferable that the amount of P be as small as possible to improve toughness, and the upper limit of the amount of P may be set to 0.03%, 0.02%, 0.01%, 0.008%, or 0.006%. It is not necessary to particularly define the lower limit of the amount of P, and the lower limit thereof is 0%. However, a decrease in P more than necessary leads to an increase in the cost during refining, and thus the lower limit of the amount of P may be set to 0.0001% or 0.0005%.

40 S: 0.008% or less

[0021] S exists in steel as an impurity. S that excessively exists promotes central segregation, or becomes a cause of generating a large amount of MnS having a stretched shape that becomes a cause of a brittle fracture. When an amount of S exceeds 0.008%, mechanical properties of the base metal and the HAZ deteriorate. Accordingly, the amount of S is set to 0.008% or less. The upper limit of the amount of S may be set to 0.006%, 0.004%, 0.003%, or 0.002% to improve the mechanical properties of the base metal and the HAZ. It is preferable that the amount of S be as small as possible, and thus it is not necessary to define the lower limit of the amount of S, and the lower limit is 0%. The lower limit of the amount of S may be set to 0.0001% or 0.0003% from the viewpoint of the refining cost.

50 Ni: 6.6% to 8.0%

[0022] Ni is the most basic element that is necessary to secure toughness for a steel for low-temperature use. It is necessary for Ni to be contained in an amount of 6.6% or more so as to secure the toughness for the steel for low-temperature use. The more an amount of Ni increases, the higher low-temperature toughness is obtained. However, the more the amount of Ni increases, the more the cost increases, and thus the upper limit of the amount of Ni is set to 8.0%. Accordingly, a target of the amount of Ni is 6.6% to 8.0%. It is preferable that the amount of Ni be 6.7% or more from the viewpoint of securing low-temperature toughness, and the lower limit of the amount of Ni may be set to 6.8%, 6.9%, or 7.0% as necessary. In addition, the upper limit of the amount of Ni may be set to 7.8%, 7.6%, or 7.4% from the

viewpoint of suppressing an increase in the cost. However, even when the amount of Ni exceeds 8.0%, characteristics demanded for the steel for low-temperature use are obtained.

Al: 0.002% to 0.080%

[0023] Al is an element that is typically contained as a deoxidizing agent. However, in the case of the steel according to this embodiment, as is the case with Si, Al has a function of delaying self-tempering of martensite. Accordingly, it is preferable that an amount of Al be as small as possible. When the amount of Al exceeds 0.080% and becomes excessive, as is the case with the above-described Si, Al suppresses the decomposition precipitation reaction of C with respect to cementite from martensite, in which C is solid-dissolved in a supersaturated state, during a weld cooling. Accordingly, Al may decrease the toughness of the welded portion. However, when the amount of Al is less than 0.002%, it is difficult to obtain a sufficient deoxidizing effect. Accordingly, the amount of Al is set to 0.002% to 0.080%. The lower limit of the amount of Al may be set to 0.005%, 0.010%, 0.015%, or 0.020% so as to reliably perform deoxidization. The upper limit of the amount of Al may be set to 0.060%, 0.050%, or 0.040% so as to improve the toughness of the welded portion.

N: 0.0050% or less

[0024] N exists in steel as an impurity, and becomes a cause of deterioration in the toughness of the HAZ through an increase in solid-dissolved N or generation of a precipitate, and thus it is preferable that an amount of N be small so as to secure the toughness of the HAZ. When the amount of N exceeds 0.0050%, deterioration in the toughness of the HAZ may be significant, and thus the amount of N is set to 0.0050% or less. The upper limit of the amount of N may be set to 0.0045% or 0.0040% to improve the toughness of the HAZ. It is not necessary to define the lower limit of the amount of N, and the lower limit is 0%. However, the lower limit of the amount of N may be set to 0.0001% or 0.0010% from the viewpoint of the cost during refining.

[0025] The steel according to this embodiment includes the above-described components, and remainder includes Fe and impurities. Here, the impurities represent ore or scrap as a raw material when the steel is industrially manufactured, or a component that is unavoidably mixed in due to various factors of a manufacturing, and the impurities are permitted in a range having no effect on the invention.

[0026] The steel according to this embodiment may contain one or more kinds of elements selected from Cu, Cr, Mo, V, B, Nb, Ti, Sn, Ca, Mg, and REM in addition to the above-described components. It is not necessary to particularly define the lower limit of the amount of these components, and the lower limit is 0%. In addition, even though these alloy elements are intentionally added to the steel according to this embodiment, or even when these alloy elements are mixed-in to the steel as impurities, if the amount of these alloy elements is in a defined range, it is interpreted that the steel is within the claims of the invention.

Cu: 0% to 1.00%

[0027] Cu may be contained as necessary. When Cu is contained, it is possible to improve the strength of the base metal. However, when an amount of Cu exceeds 1.00%, the toughness of the HAZ that is heated to a temperature of A_{c3} point or lower may deteriorate, and thus the upper limit of the amount of Cu is set to 1.00%. It is preferable that the upper limit of the amount of Cu be 0.80% or 0.60%, and more preferably 0.30%. In addition, in the case of desiring to obtain the effect of improving the strength of the base metal due to Cu, the lower limit of the amount of Cu may be set to 0.10%.

Cr: 0% to 1.00%

[0028] Cr may be contained as necessary. When Cr is contained, carbon dioxide gas corrosion resistance is improved, and hardenability is improved. As a result, strength can be improved. However, when an amount of Cr exceeds 1.00%, it is difficult to suppress hardening of the HAZ, and the effect of improving the carbon dioxide gas corrosion resistance becomes saturated, and thus the upper limit of the amount of Cr is set to 1.00%. The upper limit of the amount of Cr may be set to 0.80%, 0.60%, or 0.50% so as to suppress hardening of the HAZ. It is not necessary to define the lower limit of the amount of Cr, and the lower limit is 0%. In the case of desiring to obtain the effect of improving the carbon dioxide gas corrosion resistance and the hardenability due to Cr, the lower limit of the amount of Cr may be set to 0.05%. The lower limit of the amount of Cr may be set to 0.10% so as to reliably obtain the effect of improving the hardenability. More preferably, the lower limit of the amount of Cr is 0.20%. The lower limit of the amount of Cr may be set to 0.30% to 0.40% as necessary.

Mo: 0% to 0.50%

[0029] Mo may be contained as necessary. When Mo is contained, it is possible to obtain an effect of improving the strength and the toughness of the base metal. However, when an amount of Mo exceeds 0.50%, hardness of the HAZ increases, and thus toughness and SSC resistance may be damaged. Accordingly, the upper limit of the amount of Mo is set to 0.50%, and preferably 0.30%. The upper limit of the amount of Mo may be set to 0.20%, 0.15%, or 0.12% so as to improve the toughness and the SSC resistance. It is not necessary to define the lower limit of the amount of Mo, and the lower limit is 0%. In the case of desiring to obtain the effect of improving the strength and the toughness of the base metal due to Mo, it is preferable that the lower limit of the amount of Mo be set to 0.05%. The lower limit of the amount of Mo may be set to 0.06% or 0.07% as necessary.

V: 0% to 0.10%

[0030] V may be contained as necessary. When V is contained, it is possible to obtain an effect of improving the strength of the base metal mainly due to precipitation of carbonitrides during tempering. However, when an amount of V exceeds 0.10%, the effect of improving the strength of the base metal may be saturated, and deterioration in toughness may be caused, and thus the upper limit of the amount of V is set to 0.10%. It is not necessary to define the lower limit of the amount of V, and the lower limit is 0%. The upper limit of the amount of V may be set to 0.08%, 0.06%, or 0.04% so as to improve the toughness. In addition, in the case of desiring to obtain the effect of improving the strength of the base metal due to V, the lower limit of the amount of V may be set to 0.015% or 0.02%.

B: 0% to 0.0050%

[0031] B may be contained as necessary. When B is contained, it is possible to obtain an effect of improving the strength of the base metal. However, when an amount of B exceeds 0.0050%, precipitation of coarse boron compounds is caused, and thus the toughness may deteriorate, and thus the upper limit of the amount of B is set to 0.0050%. The upper limit of the amount of B may be set to 0.0040%, 0.0030%, or 0.0020% so as to prevent deterioration in the toughness. It is not necessary to define the lower limit of the amount of B, and the lower limit is 0%. In addition, in the case of desiring to obtain the effect of improving the strength of the base metal due to B, it is preferable that the lower limit of the amount of B be set to 0.0003%, and more preferably 0.0005% or 0.0010%. In a case where it is not necessary to obtain the effect of improving the strength of the base metal due to B, the upper limit of the amount of B may be set to 0.0010%, 0.0005%, 0.0003%, or 0.0002%.

Nb: 0% to 0.10%

[0032] Nb may be contained as necessary. When Nb is contained, a structure is made fine, and thus it is possible to obtain an effect of improving low-temperature toughness. However, when an amount of Nb exceeds 0.10%, coarse carbides or nitrides may be formed, and thus the toughness may deteriorate. Accordingly, the upper limit of the amount of Nb is set to 0.10%. It is not necessary to define the lower limit of the amount of Nb, and the lower limit is 0%. The upper limit of the amount of Nb may be set to 0.08%, 0.06%, or 0.04% so as to prevent a decrease in the toughness. In addition, in the case of desiring to obtain the effect of improving the low-temperature toughness due to Nb, the lower limit of the amount of Nb may be set to 0.01% or 0.02%.

Ti: 0% to 0.10%

[0033] Ti may be contained as necessary. Ti is mainly used as a deoxidizing element, and also forms an oxide phase including Al, Ti, and Mn, and thus Ti has an effect of making a structure fine. However, when an amount of Ti exceeds 0.10%, an oxide that is formed becomes a Ti oxide or a Ti-Al oxide, and thus a dispersion density decreases. Particularly, an effect of making a structure of a heat-affected zone of a small-heat-input welded portion fine may be lost. Accordingly, the upper limit of the amount of Ti is set to 0.10%, and preferably 0.07% or 0.05%. It is not necessary to define the lower limit of the amount of Ti, and the lower limit is 0%. In addition, in the case of desiring to obtain the effect of making a structure fine due to Ti, the lower limit of the amount of Ti may be set to 0.02% or 0.03%.

Sn: 0% to 0.50%

[0034] Sn may be contained as necessary. When Sn is contained, Sn is converted into Sn^{2+} , and is dissolved in a material that adheres to a surface of the steel, and has an effect of suppressing corrosion due to an inhibitor effect in an acidic chloride solution. In addition, Sn rapidly reduces Fe^{3+} , and has an effect of decreasing a concentration of Fe^{3+} .

as an oxidizing agent. Accordingly, Sn suppresses a corrosion-promoting effect of Fe^{3+} , and thus weather resistance in a high floating salinity environment is improved. However, when an amount of Sn exceeds 0.50%, the above-described effects are saturated, and thus the upper limit of the amount of Sn is set to 0.50%, and preferably 0.20%. The upper limit of the amount of Sn may be limited to 0.10%, 0.05%, or 0.01% to decrease the cost of an alloy. It is not necessary to define the lower limit of the amount of Sn, and the lower limit is 0%. In addition, in the case of desiring to obtain the effect of corrosion resistance and weather resistance due to Sn, the lower limit of the amount of Sn may be set to 0.03% or 0.05%.

Ca: 0% to 0.004%

[0035] Ca may be contained as necessary. When Ca is contained, Ca reacts with S in steel to form an oxysulfide in molten steel. When being subjected to rolling, the oxysulfide does not extend in a rolling direction by rolling differently from MnS, and thus the oxysulfide has a spherical shape even after rolling. The spherical oxysulfide has an effect of suppressing a welding crack or a hydrogen-induced crack in which a front end and the like of a stretched inclusion serve as a crack origin. However, when an amount of Ca exceeds 0.004%, deterioration in toughness may be caused, and thus the upper limit of the amount of Ca is set to 0.004%. The upper limit of the amount of Ca may be set to 0.003% so as to reliably avoid a decrease in toughness. It is not necessary to define the lower limit of the amount of Ca, and the lower limit is 0%. In addition, in the case of desiring to obtain the effect of suppressing the welding crack or the hydrogen-induced crack due to Ca, the lower limit of the amount of Ca may be set to 0.0003% or 0.0005%.

Mg: 0% to 0.0020%

[0036] Mg may be contained as necessary. When Mg is contained, a fine Mg-containing oxide is generated, and thus Mg is effective for miniaturization of a grain size of γ . However, when an amount of Mg exceeds 0.0020%, an amount of oxides may excessively increase, and thus a decrease in ductility may be caused. Accordingly, the upper limit of the amount of Mg is set to 0.0020%, and preferably 0.0010%. It is not necessary to define the lower limit of the amount of Mg, and the lower limit is 0%. In addition, in the case of desiring to obtain the effect of miniaturizing the grain size of γ due to Mg, it is preferable that the lower limit of the amount of Mg be set to 0.0002%, and more preferably 0.0004%.

REM: 0% to 0.0020%

[0037] REM (rare-earth element) may be contained as necessary. When REM is contained in steel, REM makes a structure of a welding heat-affected zone fine, and is coupled to S, thereby obtaining an effect of fixing S. When REM is excessively contained, an inclusion is formed, and thus cleanliness of a welded portion may decrease. However, the inclusion formed when REM is contained has a relatively little effect on deterioration in toughness, and thus when the amount of REM is 0.0020% or less, a decrease in the toughness of the base metal when REM is contained is permissible. Accordingly, the upper limit of the amount of REM is set to 0.0020%, and more preferably 0.0010%. It is not necessary to define the lower limit of the amount of REM, and the lower limit is 0%. In addition, in the case of desiring to obtain the effect of making the structure of the welding heat affect zone fine and the effect of fixing S due to REM, it is preferable that the lower limit of the amount of REM be set to 0.0002%, and more preferably 0.0003%.

[0038] Here, REM is a general term of a total of 17 elements including 15 elements of lanthanoid, Y, and Sc, and one or more kinds of these elements may be contained. In addition, the term of the amount of REM represents a total amount of these elements.

[0039] The steel according to this embodiment contains the above-described components, and remainder includes iron and impurities. However, in addition to the above-described components, a weld steel according to this embodiment may contain the following alloy elements to further improve strength, toughness, and the like of the steel itself, or as impurities from an auxiliary raw material such as scrap.

[0040] Sb damages the toughness of the HAZ, and thus the upper limit of an amount of Sb may be set to 0.03%. The upper limit of the amount of Sb may be set to 0.01 %, 0.005%, 0.003%, or 0.001% so as to improve the toughness of the HAZ.

[0041] As damages the toughness of the HAZ, and an upper limit of an amount of As may be set to 0.02%. The upper limit of the amount of As may be set to 0.005%, 0.003, or 0.001% as necessary.

[0042] In addition, the upper limit of an amount of each of Pb, Zr, Zn, and W may be set to 0.1 %, 0.01%, or 0.005% so as to improve the strength and the toughness. It is not necessary to particularly determine the lower limit of the amount of these elements, and the lower limit is 0%.

[0043] Co may be contained in Ni as an impurity. Co damages the toughness of the HAZ, and thus the upper limit of an amount of Co may be set to 0.5%, 0.3%, 0.1%, or 0.05%. It is not necessary to particularly determine the lower limit of the amount of Co, and the lower limit is 0%.

(B) With Regard to Structure

(B-1) The lower limit of an amount of the retained γ at a $(1/4)t$ location regarding a plate thickness t is set to 4.0 vol%.

[0044] The retained γ in a steel contributes to an improvement in brittle crack propagation arrest characteristics of the steel. As a result, it is possible to expect an effect of improving toughness under a low-temperature environment. To obtain this effect, it is necessary for the lower limit of the amount of the retained γ at the $(1/4)t$ location regarding the plate thickness t of the steel to be 4.0 vol%. The lower limit of the amount of retained γ may be set to 4.5 vol%, 5.0 vol%, 5.5 vol%, 6.0 vol%, or 6.5 vol% so as to improve the toughness. The upper limit of the amount of retained γ is not particularly defined, but when the retained γ excessively exists, there is a concern that a yield strength may decrease. Accordingly, the upper limit of the amount of the retained γ may be set to 20.0 vol% or 15.0 vol%. Here, evaluation of the amount of the retained γ at the $(1/4)t$ location regarding the plate thickness t is performed for evaluation at a mean location over the entire region in a plate thickness direction.

[0045] Here, when a tempering temperature $T(^{\circ}\text{C})$ satisfies the following Expression (3), it is possible to set the lower limit of the amount of the retained γ at the $(1/4)t$ location regarding the plate thickness t to 4.0 vol%.

$$3.8 \times \text{Ni} - 33 + \text{Ac}_1 \leq T \leq 6.3 \times \text{Ni} - 0.4 + \text{Ac}_1 \quad \dots (3)$$

Here, Ac_1 is defined by the following Expression (4).

$$\text{Ac}_1 = 712 + 20.1 \times \text{Si} - 17.8 \times \text{Mn} - 19.1 \times \text{Ni} + 11.9 \times \text{Cr} - 9.8 \times \text{Mo} \quad \dots (4)$$

Here, a symbol of an element in Expression represents an amount (mass%) of each element in a steel.

[0046] FIG. 1 is a graph illustrating a relationship between the tempering temperature and the amount of the retained γ in various steels manufactured by heating a slab having a chemical composition of Steel No. 1 described in Table 1 at 950°C , performing rolling of attaining a cumulative reduction of 70% at 850°C or lower, performing water cooling to room temperature immediately after the rolling, performing tempering at various temperatures, and performing water cooling. Here, the cumulative reduction represents a percentage $((t_1 - t_2)/t_1 \times 100)$ of a value obtained by dividing a difference between a plate thickness t_1 at the time of initiating rolling and a plate thickness t_2 at the time of completing the rolling by the plate thickness t_1 at the time of initiating the rolling. As shown in FIG. 1, when the tempering temperature is too low, a region in which reverse transformation to γ occurs is too small, and thus the amount of the retained γ is small. In contrast, when the tempering temperature is too high, γ that is generated becomes unstable, and is subjected to martensite transformation during cooling, and thus the amount of the retained γ decreases. Accordingly, when Expression (3) is satisfied, it can be seen that a lot of retained γ can be secured.

(B-2) The upper limit of an average value of an aspect ratio of the retained γ is 2.5, and the upper limit of an average value of the major axis is $0.85 \mu\text{m}$.

[0047] Typically, the retained γ in an α structure (ferrite structure) is in a metastable state, and when the retained γ is subjected to plastic deformation, martensite transformation tends to occur. It is necessary for the retained γ to be dispersed so as to improve brittle fracture initiation characteristics or brittle fracture propagation arrest characteristics. If the retained γ is lost when an earthquake occurs, desired fracture-resistant characteristics are not exhibited. Even when an applied amount of macro plastic deformation is constant, deformation that is applied to retained γ grains greatly varies in accordance with a distribution type of the retained γ . The more the retained γ grains are relatively fine and are close to a spherical shape, the more a deformation distribution rate decreases. Accordingly, it is necessary for the upper limit of the average value of the aspect ratio of the retained γ , which is obtained with observation of a cross-section, to be set to 2.5, and it is necessary for the upper limit of the average value of the major axis of the retained γ grains, which is obtained with observation of a cross-section, to be set to $0.85 \mu\text{m}$. The less the average aspect ratio of the retained γ grains is, the further the toughness is improved. Accordingly, the upper limit of the average value of the aspect ratio may be set to 2.3 or 2.0. In addition, the smaller the average value of the major axis is, the further the toughness is improved. Accordingly, the upper limit of the average value of the major axis may be set to $0.80 \mu\text{m}$ or $0.75 \mu\text{m}$. It is not necessary to define the lower limit of the average value of the major axis, but the lower limit is typically $0.05 \mu\text{m}$.

(B-3) An average concentration of Mn and an average concentration of Ni in the retained γ satisfy the following Expression (1) and (2).

[0048]

$$[\text{Mn}]_{\text{retained } \gamma} > [\text{Mn}]_{\alpha} \times 1.4 \dots (1)$$

$$[\text{Ni}]_{\text{retained } \gamma} > [\text{Ni}]_{\alpha} \times 1.4 \dots (2)$$

[0049] Here, the $[\text{Mn}]_{\text{retained } \gamma}$ indicates the average Mn concentration in the retained γ , the $[\text{Mn}]_{\alpha}$ indicates an average Mn concentration in ferrite, the $[\text{Ni}]_{\text{retained } \gamma}$ indicates the average Ni concentration in the retained γ , and the $[\text{Ni}]_{\alpha}$ indicates an average Ni concentration in ferrite.

[0050] Ni and Mn, which are austenite stabilization elements, are elements that lower a transformation point of γ to α , and it is known that Ni and Mn have an effect of stabilizing the retained γ . To secure a large amount of retained γ after being subjected to plastic deformation, it is very important to set the lower limit of the concentration of Mn and the lower limit of the concentration of Ni in individual retained γ to 1.4 times the concentration of Mn and the concentration of Ni in ferrite, respectively.

[0051] To satisfy the above-described Expression (1) and Expression (2), it is necessary set the lower limit of a cumulative reduction at 850°C or lower during a hot-rolling to 50%, and it is necessary to set a cooling rate after tempering to be larger than 0.5 °C/s. FIG. 2 is a graph illustrating a relationship between a cumulative reduction at 850°C or lower and concentration rates ($[\text{Mn}]_{\gamma}/[\text{Mn}]_{\alpha}$) of Ni and Mn in various steels manufactured by heating a slab having a chemical composition of Steel No. 1 described in Table 1 at 960°C, performing rolling with various cumulative reductions, performing water cooling to room temperature immediately after the rolling, and performing tempering at 570°C (with water cooling after tempering). Here, the concentration rates of Ni and Mn represent values that are obtained by dividing $[\text{Mn}]_{\text{retained } \gamma}$ and $[\text{Ni}]_{\text{retained } \gamma}$ by $[\text{Mn}]_{\alpha}$ and $[\text{Ni}]_{\alpha}$, respectively. From FIG. 2, it can be seen that particularly, when the lower limit of the cumulative reduction is set to 50%, a concentration ratio of 1.4 or more is obtained, and thus Expression (1) and Expression (2) can be satisfied.

[0052] FIG. 3 illustrates a relationship between the concentration rates of Ni and Mn and dynamic tear (DT) energy that is a representative fracture characteristic evaluation parameter. In a case where the DT energy is high, it is determined that the arrest characteristics are good. In a steel used to manufacture a very-low-temperature storage tank that stores a liquefied gas such as LPG and LNG, it is preferable that the DT energy is more than 1500 J. From FIG. 3, it can be seen that when the lower limits of the concentrations rates of Ni and Mn are set to 1.4, the DT energy is more than 1500 J. In a case where the lower limits of the concentration rates are set to 1.5 or 1.6, higher DT energy is obtained, and thus this case is preferable.

[0053] It is not necessary to particularly define the upper limits of the concentration rates of Ni and Mn. However, the concentration rates of Ni and Mn hardly exceed 10 or 5, and thus the upper limits may be set to 10 or 5.

(C) With Regard to Manufacturing Method

[0054] The steel according to this embodiment can be manufactured through the following. However, there is no limitation to the following manufacturing methods.

[0055] With regard to a slab, casting conditions thereof are not particularly defined. A slab obtained through ingot-making and blooming may be used, or a continuously cast slab may be used. From the viewpoints of manufacturing efficiency, yield rate, and energy saving, it is preferable to use the continuously cast slab. In addition, the plate thickness of the steel that is manufactured is set to 3 mm to 100 mm, and mainly 6 mm to 50 mm. The steel that is manufactured may be referred to as a steel plate.

(C-1) Slab Heating

[0056] In the heating, a slab heating temperature is controlled to 920°C to 980°C. It is preferable that the lower limit of the slab heating temperature be set to 920°C so as to obtain desired fracture-resistant characteristics by allowing solid-dissolution of AlN to progress to suppress coarsening of crystal grains during the subsequent heat treatment. In addition, the upper limit of the slab heating temperature is set to 970°C in order for γ grains not to be excessively coarsened and in order for the fracture-resistant characteristics not to be damaged.

(C-2) Rolling

[0057] In a hot-rolling, a heated slab is rolled. Specifically, rolling may be performed by dividing the rolling into rough rolling and finish rolling.

[0058] In the rough rolling with respect to the heated slab, it is preferable that reduction be performed until a slab thickness at the time of terminating the rough rolling becomes 3 times to 8 times a product thickness (steel thickness). When reduction is performed in order for the slab thickness after termination of the rough rolling to be 3 or more times the plate thickness of the product, it is possible to perform sufficient reduction in the subsequent finish rolling. As a result, it is possible to improve the toughness of the steel that is a product. On the other hand, when reduction is performed in order for the slab thickness after termination of the rough rolling to be 8 or less times the plate thickness of the product, it is easy to control a finish rolling temperature (a temperature when the finish rolling is terminated) in the subsequent finish rolling to 700°C or higher.

[0059] In the finish rolling, reduction is continuously performed with respect to the slab subjected to the rough rolling as described above without performing cooling, thereby obtaining a production having a predetermined plate thickness. In the finish rolling, the lower limit of the cumulative reduction at 850°C or lower is set to 50%. In a case where the reduction at a relatively low temperature is set to be large, introduction of a deformation band is positively performed, and thus the retained γ that is finally formed remains in a large amount. In addition, this case is effective to make the average aspect ratio of the retained γ small. This is because when the reduction is large, the retained γ that is stretched is divided. In addition, for positive introduction of the deformation band, it is preferable that a finish rolling initiation temperature be set as low as possible in order for the final rolling temperature (finish rolling temperature) during the finish rolling to be 700°C to 730°C.

(C-3) Cooling

[0060] In a cooling, it is preferable that the steel after the finish rolling be subjected to accelerated cooling. Particularly, as the plate thickness increases, it is difficult to secure the toughness of the steel. Accordingly, in a steel having a large plate thickness, it is preferable that the cooling rate in the accelerated cooling after the rolling be fast. Specifically, in a case where the plate thickness is 15 mm or less, the lower limit of the cooling rate at the central portion of the plate thickness t of the steel, that is, at a $(1/2)t$ location regarding the plate thickness t is set to 3 °C/s. In a case where the plate thickness exceeds 15 mm, the lower limit of the cooling rate is set to 10 °C/s. According to this setting, coarsening of an effective grain size of a final structure which is caused by deterioration of the cooling rate during the accelerated cooling after the rolling is prevented. The upper limit of the cooling rate at the $(1/2)t$ location regarding the plate thickness t is not particularly defined, but may be set to 50 °C/s in consideration of facility capacity. When performing the accelerated cooling, the lower limit of a cooling initiation temperature is set to 660°C so as to convert a structure of the steel into a sufficiently quenched structure, and to obtain a concentration ratio of 1.4 or more with fine retained γ by the subsequent tempering treatment and the like.

[0061] In a case where the steel after the finish rolling is cooled with air without performing accelerated cooling, a grain size is coarsened, and thus this case is not preferable.

[0062] It is preferable that the accelerated cooling be performed until a surface temperature of the steel reaches 250°C or lower. In a case where a cooling stop temperature is higher than 250°C, transformation into a martensite structure becomes incomplete, or a phenomenon in which dislocation in the martensite structure is recovered due to auto-tempering effect occurs. As a result, fine retained γ is not effectively generated at the subsequent heat treatment, and thus a possibility of deficiency in strength increases. It is preferable that the upper limit of the cooling stop temperature be set to 200°C or 150°C. The lower limit of the cooling stop temperature is not particularly defined, but may be set to 50°C or room temperature in consideration of facility capacity.

[0063] To form fine retained γ in a large amount, it is preferable to perform a direct-quenching and tempering (DQT) or a direct-quenching, lamellarizing, and tempering (DQLT). In the off-line QT or the off-line QLT of the related art, a steel is heated at a heating temperature higher than A_{c3} point before quenching, and thus a lattice defect introduced during rolling basically does not remain in the steel. Accordingly, γ before quenching enters a state in which a lattice defect density is low. In the case of performing quenching in this state, a size of packet, block, and lass of martensite increases. Therefore, in a heat treatment configured to increase an amount of γ , a generation site of γ fails, and thus the amount of γ does not increase sufficiently. On the other hand, when performing the DQT or the DQLT, work strain, which is introduced to γ during rolling, is maintained before quenching, and thus it is possible to very finely adjust a martensite structure after quenching. γ , which is generated from the fine martensite structure during the subsequent heat treatment, is fine and exists in a large amount.

(C-4) L Treatment

[0064] In a case where a sufficient quenched structure is obtained, in this embodiment, it is not necessary to perform an L treatment (i.e. heating a steel in a temperature range of a two-phase region of ferrite and austenite, and then water-cooling) which has been frequently used with respect to 9% Ni steel in the related art, and it is possible to obtain a steel having sufficient characteristics by performing only a tempering treatment. However, when the steel is heated at a temperature of a two-phase region of ferrite and austenite, toughness can be improved due to miniaturization of a structure and generation of stable austenite, and thus the L treatment, in which heating is performed in a temperature range of 620°C to 720°C and then a water cooling treatment is performed, may be performed as necessary. When the lower limit of the heating temperature is set to 620°C, an increase in the retained γ can be expected. When the upper limit of the heating temperature is set to 720°C, coarsening of a structure can be prevented. A preferable heating temperature range in the L treatment is 640°C to 700°C.

(C-5) Tempering

[0065] The tempering is very important to realize the invention, and is essential in which detailed control is necessary. In a case where a tempering temperature is too low, an amount of the retained γ generated becomes deficient, and thus the amount of the retained γ itself becomes small. In addition, when the tempering temperature is too low, there is a possibility that tempering embrittlement occurs, and as a result, fracture-resistant characteristics are damaged. In contrast, when the tempering temperature is too high, the amount of γ during heating increases, but the concentration of Ni and Mn in the retained γ decreases. In this case, the retained γ is mostly transformed during the subsequent cooling, or even when transformation does not occur during cooling, the retained γ is transformed only when being exposed to a very low temperature and is lost. A tempering temperature range depends on a thermodynamic equilibrium behavior and varies in accordance with a chemical composition of a steel. Specifically, it is necessary to set the lower limit and the upper limit of the tempering temperature T to $3.8 \times \text{Ni} - 33 + \text{Ac}_1$ and $6.3 \times \text{Ni} - 0.4 + \text{Ac}_1$, respectively. That is, it is necessary to satisfy the following Expression (3). Here, coefficients described in Expression (3) are obtained by multiple regression of experiment results. It is preferable that the tempering temperature be set to be higher than Ac_1 .

[0066] In addition, in a case where a cooling rate after heating in the tempering is slow, the fracture-resistant characteristics are damaged by progress of partial bainite transformation due to diffusion migration of carbon, and the like. In addition, in a case where a cooling rate in the tempering is slow, it is considered that a reaction of expelling partial carbon as cementite from γ generated during tempering progresses, and thus γ becomes unstable, and after cooling to room temperature, a total amount of the retained γ tends to decrease. In addition, a part of the retained γ generated during tempering is subjected to martensite transformation between tempering and cooling. When the lower limit of the cooling rate is set to 0.5 °C/s, a density of dislocation in martensite which occurs due to the martensite transformation can be increased, and a dynamic restriction effect is added to the retained γ adjacent to the martensite, and thus it can be assumed that stability of the retained γ can be improved. Accordingly, after performing heating in the tempering, it is necessary to set the lower limit of the cooling rate at the central portion in a plate thickness direction to 0.5 °C/s until a surface temperature reaches 300°C or lower. The upper limit of the cooling rate after the heating in the tempering is not particularly defined, but may be set to 50 °C/s in consideration of the maximum facility capacity. The lower limit of the cooling stop temperature is not particularly defined, but may be set to 50°C or room temperature in consideration of facility capacity.

$$3.8 \times \text{Ni} - 33 + \text{Ac}_1 \leq T \leq 6.3 \times \text{Ni} - 0.4 + \text{Ac}_1 \quad \dots (3)$$

Here, Ac_1 is defined by the following Expression (4).

$$\text{Ac}_1 = 712 + 20.1 \times \text{Si} - 17.8 \times \text{Mn} - 19.1 \times \text{Ni} + 11.9 \times \text{Cr} - 9.8 \times \text{Mo} \quad \dots (4)$$

[0067] Here, a symbol of an element in Expression represents an amount (mass%) of each element in a steel.

[0068] In Patent Document 1, the reason why the DT test and pre-crack Charpy test were not satisfactory in steel plates (particularly, Test Nos. 1-a to 1-h, 4-12, and 22-35) with satisfactory V-notch Charpy absorbed energy $\sqrt{E_{196}}$ and the like is that the accelerated cooling was not performed with respect to all of the steel plates after tempering, or the cooling rate was set to less than 0.5 °C/s.

Examples

[0069] Slabs of 56 types of steel having chemical compositions illustrated in Table 1 were prepared with a plate thickness of 300 mm, and heating, rolling, accelerated cooling, and the like were performed under conditions illustrated in Table 2, and then a heat treatment was performed as necessary. The plate thickness of each of steels which were obtained was 6 mm to 50 mm. To evaluate room-temperature strength, a tensile test specimen of No. 10, a tensile test specimen of No. 5, or a tensile test specimen of No. 4, which are defined in JIS Z 2241, were collected from the steels which were obtained. The tensile test specimen of No. 4 was collected at a $(1/4)t$ location regarding a plate thickness t . A collection direction was perpendicular to a rolling direction. In addition, a V-notch test specimen (a full-size test specimen) defined in JIS Z 2242 was collected along the rolling direction. With regard to steel types having a plate thickness of less than 10 mm, it was impossible to collect the V-notch test specimen having a width of 10 mm and a plate thickness of 10 mm, and thus a sub-size test specimen was collected.

TABLE 1

5	STEEL No.	CHEMICAL COMPOSITION (mass%, REMAINDER: Fe AND IMPURITIES)																			Ac ₁
		C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	Nb	Ti	B	Sn	Al	N	Ca	Mg	REM	
	1	0.064	0.090	0.81	0.012	0.001	-	7.24	-	-	-	-	-	-	-	0.025	0.0027	-	-	-	561
	2	0.046	0.082	0.61	0.013	0.001	-	*9.30	-	-	-	-	-	-	-	0.006	0.0023	-	-	-	525
	3	0.041	0.112	0.61	0.009	0.002	-	7.24	-	-	-	-	-	-	-	0.019	0.0019	-	-	-	565
	4	0.053	0.098	0.61	0.009	0.001	0.31	7.62	0.164	0.080	0.033	-	-	-	-	0.023	0.0015	-	-	-	559
10	5	0.044	0.068	0.77	0.007	0.001	-	6.82	-	-	-	-	-	-	0.040	0.020	0.0021	-	-	-	573
	6	0.053	0.083	0.65	0.009	0.001	0.66	7.62	0.164	0.105	0.033	-	-	-	-	0.020	0.0015	-	-	-	558
	7	0.046	0.108	0.76	0.008	0.001	0.38	6.87	-	0.124	0.021	0.009	0.009	-	-	0.012	0.0025	-	-	-	568
	8	0.046	0.108	0.76	0.009	0.001	-	6.78	0.069	-	-	0.009	-	-	-	0.022	0.0021	-	-	-	572
	9	0.049	0.108	0.76	0.009	0.001	0.44	6.77	-	0.124	-	-	-	0.0008	-	0.022	0.0025	-	-	-	570
	10	0.049	0.108	0.64	0.008	0.001	0.51	7.48	0.244	0.147	-	0.011	-	-	0.180	0.009	0.0019	-	0.001	0.001	561
15	11	0.052	0.081	0.76	0.010	0.001	0.64	6.84	0.331	-	0.043	-	0.009	-	-	0.019	0.0023	0.001	-	-	573
	12	0.041	0.122	0.68	0.009	0.001	-	6.91	-	0.078	-	-	0.009	0.0007	-	0.019	0.0021	-	0.001	-	570
	13	0.049	0.053	0.61	0.010	0.001	0.64	7.16	-	-	-	-	-	-	-	0.012	0.0025	0.001	-	-	566
	14	0.010	0.108	0.64	0.009	0.001	-	6.84	-	0.147	0.043	0.009	-	-	-	0.009	0.0015	0.001	-	0.001	571
	15	0.049	0.010	0.72	0.009	0.001	0.38	6.69	-	0.170	0.032	-	0.010	-	0.080	0.015	0.0019	-	-	-	570
	16	0.049	0.122	0.40	0.010	0.001	0.51	7.01	-	-	0.043	-	0.012	0.0010	-	0.022	0.0017	0.001	0.001	0.001	573
20	17	0.041	0.081	0.64	0.005	0.001	0.64	7.48	-	-	0.043	0.010	-	0.0006	-	0.015	0.0021	-	-	0.001	559
	18	0.046	0.094	0.68	0.007	0.001	-	6.87	-	0.078	-	-	-	0.0010	-	0.012	0.0021	0.001	-	0.001	570
	19	0.049	0.053	0.64	0.010	0.001	0.38	7.05	0.156	-	-	0.008	0.008	-	-	0.015	0.0023	-	-	-	569
	20	0.052	0.122	0.64	0.007	0.001	0.31	6.84	-	-	0.027	-	0.014	-	-	0.015	0.0015	-	-	-	572
	21	0.054	0.122	0.61	0.009	0.001	0.31	6.87	-	0.147	0.027	-	-	0.0009	-	0.015	0.0021	-	-	-	571
	22	0.043	0.122	0.76	0.007	0.001	-	6.87	0.156	-	-	0.010	0.012	0.0006	-	0.002	0.0021	-	-	-	572
25	23	0.046	0.094	0.79	0.011	0.001	-	6.84	0.506	-	0.027	0.009	0.013	-	-	0.009	0.0015	0.001	-	0.001	575
	24	0.120	0.053	0.72	0.008	0.001	0.64	6.84	0.069	0.147	-	0.011	-	0.0009	0.150	0.019	0.0021	-	-	-	569
	25	0.049	0.300	0.68	0.009	0.001	-	7.16	-	0.101	-	-	-	0.0009	-	0.009	0.0021	-	-	-	568
	26	0.052	0.053	1.99	0.008	0.001	-	7.16	0.244	-	0.043	0.011	-	-	-	0.019	0.0015	-	0.001	-	544
	27	0.052	0.108	0.61	0.049	0.001	0.64	6.69	0.156	-	0.027	-	0.014	-	-	0.006	0.0017	-	-	0.001	577
	28	0.054	0.053	0.72	0.011	0.007	0.38	6.69	0.156	-	0.036	-	-	-	0.130	0.006	0.0015	0.000	-	-	574
	29	0.052	0.053	0.72	0.007	0.001	-	*9.48	-	0.078	0.049	0.009	0.009	0.0006	-	0.012	0.0023	-	-	-	518
30	30	0.054	0.122	0.79	0.010	0.001	-	6.69	0.419	-	-	0.098	-	0.0009	-	0.009	0.0023	0.001	0.001	-	578
	31	0.052	0.081	0.76	0.009	0.001	0.31	6.61	-	0.055	0.049	0.009	0.098	0.0008	0.120	0.012	0.0021	-	-	-	573
	32	0.041	0.094	0.61	0.007	0.001	-	6.87	0.419	0.147	0.043	-	0.014	-	-	0.050	0.0015	0.001	0.001	-	575
	33	0.052	0.094	0.61	0.009	0.001	-	6.84	0.506	-	-	0.009	-	-	-	0.022	0.0040	-	-	0.001	579
	34	*0.130	0.080	0.84	0.015	0.002	-	6.70	-	-	0.044	-	0.010	0.0005	0.090	0.012	0.0031	0.001	-	0.001	571
	35	0.052	*0.310	0.68	0.013	0.001	1.00	7.90	0.240	-	-	-	-	-	-	0.019	0.0035	-	0.002	0.001	558
35	36	0.046	0.140	*2.20	0.007	0.002	-	7.52	1.000	-	0.080	-	0.008	0.0009	0.080	0.012	0.0031	-	-	-	523
	37	0.052	0.140	1.00	0.009	0.002	-	*6.44	-	0.300	-	-	-	0.0011	-	0.026	0.0031	0.001	-	0.001	602
	38	0.058	0.140	0.84	0.007	0.001	-	7.88	0.050	0.050	-	0.012	-	0.0009	-	*0.082	0.0019	-	-	-	549
	39	0.052	0.170	0.76	0.010	0.002	0.72	6.80	0.620	0.050	0.020	0.012	0.018	0.0015	-	0.019	*0.0052	0.001	-	0.001	579
	40	*0.008	0.090	0.99	0.008	0.001	-	7.21	-	0.440	-	-	-	-	-	0.028	0.0028	-	-	-	554
	41	0.064	*0.008	0.88	0.013	0.001	-	7.33	-	-	-	-	-	-	-	0.029	0.0031	-	-	-	556
40	42	0.057	0.112	*0.38	0.008	0.003	-	7.12	-	-	-	-	-	-	-	0.022	0.0036	-	-	-	571
	43	0.066	0.149	0.87	0.007	0.002	-	7.32	-	-	-	-	-	-	-	*0.001	0.0030	-	-	-	560
	44	0.060	0.118	0.98	*0.052	0.002	-	7.50	-	-	-	-	-	-	-	0.024	0.0038	-	-	-	554
	45	0.062	0.107	0.83	0.008	*0.010	-	7.46	-	-	-	-	-	-	-	0.023	0.0033	-	-	-	557
	46	0.059	0.103	0.91	0.007	0.002	*1.10	7.06	-	-	-	-	-	-	-	0.026	0.0030	-	-	-	563
	47	0.063	0.149	1.00	0.009	0.002	-	7.49	*1.520	-	-	-	-	-	-	0.025	0.0036	-	-	-	572
45	48	0.066	0.141	0.88	0.008	0.002	-	7.39	-	*0.520	-	-	-	-	-	0.027	0.0035	-	-	-	553
	49	0.056	0.109	0.84	0.006	0.003	-	7.71	-	-	*0.120	-	-	-	-	0.030	0.0030	-	-	-	552
	50	0.053	0.145	0.95	0.009	0.003	-	7.71	-	-	-	*0.105	-	-	-	0.022	0.0037	-	-	-	551
	51	0.056	0.123	0.97	0.008	0.003	-	7.23	-	-	-	-	*0.105	-	-	0.021	0.0038	-	-	-	559
	52	0.067	0.101	0.98	0.008	0.002	-	7.07	-	-	-	-	-	*0.0052	-	0.029	0.0031	-	-	-	561
	53	0.059	0.141	0.98	0.009	0.002	-	7.21	-	-	-	-	-	-	*0.520	0.029	0.0033	-	-	-	560
	54	0.063	0.150	0.87	0.008	0.003	-	7.62	-	-	-	-	-	-	-	*0.082	0.0031	-	-	-	554
50	55	0.052	0.104	0.90	0.008	0.003	-	7.79	-	-	-	-	-	-	-	0.030	0.0038	-	*0.003	-	549
	56	0.058	0.118	0.81	0.008	0.002	-	7.27	-	-	-	-	-	-	-	0.025	0.0036	-	-	*0.003	561

THE VALUE WITH SYMBOL "*" IS OUT OF THE RANGE OF THE PRESENT INVENTION.

TABLE 2

	Test No.	STEEL No.	AMOUNT OF N (%)	HEATING TEMPERATURE (°C)	PLATE THICKNESS AFTER ROUGH ROLLING (mm)	PLATE THICKNESS AFTER ROUGH ROLLING / PLATE THICKNESS OF PRODUCT	CUMULATIVE REDUCTION AT 850°C OR LOWER (%)	FINISH ROLLING TEMPERATURE (°C)	PLATE THICKNESS (mm)	REMARK
5	1-a	1	7.24	950	164	6.5	81	720	25	EXAMPLE
	1-b	1	7.24	940	125	3.1	*40	710	40	COMPARATIVE EXAMPLE
	1-c	1	7.24	950	181	4.5	77	710	40	
	1-d	1	7.24	980	132	3.3	62	720	40	
	1-e	1	7.24	940	185	3.7	72	720	50	
10	1-f	1	7.24	930	66	6.6	63	720	10	EXAMPLE
	1-g	1	7.24	930	65	6.5	82	730	10	
	1-h	1	7.24	970	109	4.4	68	710	25	
	1-i	1	7.24	*990	120	3.0	65	720	40	
	1-j	1	7.24	*900	145	5.8	71	700	25	
15	1-k	1	7.24	940	70	*2.8	52	725	25	COMPARATIVE EXAMPLE
	1-l	1	7.24	940	210	*6.4	72	*645	25	
	1-m	1	7.24	940	120	4.8	72	720	25	
	1-n	1	7.24	930	128	5.1	74	730	25	
	1-o	1	7.24	960	160	6.4	-	710	25	
20	1-p	1	7.24	950	150	6.0	-	710	25	REFERENCE EXAMPLE
	2	2	*9.30	980	115	7.7	82	720	15	EXAMPLE
	3	3	7.24	920	55	3.6	69	730	15	
	4	4	7.62	960	125	4.2	62	730	30	
	5	5	6.62	950	73	7.3	84	720	10	
25	6	6	7.62	930	374	7.5	85	710	50	COMPARATIVE EXAMPLE
	7	7	6.87	960	67	6.7	69	720	10	
	8	8	6.78	960	42	7.0	82	730	6	
	9	9	6.77	930	235	5.9	83	700	40	
	10	10	7.48	960	129	3.2	57	720	40	
30	11	11	6.84	970	133	3.3	54	710	40	EXAMPLE
	12	12	6.91	980	163	4.1	65	710	40	
	13	13	7.16	940	161	4.0	74	710	40	
	14	14	6.84	930	121	3.0	56	720	40	
	15	15	6.69	970	195	4.9	79	710	40	
35	16	16	7.01	950	135	3.4	52	730	40	EXAMPLE
	17	17	7.48	980	145	3.6	60	710	40	
	18	18	6.87	930	132	3.3	-	720	40	
	19	19	7.05	980	128	3.2	63	720	40	
	20	20	6.84	960	221	5.5	78	730	40	
40	21	21	6.87	950	135	3.4	53	720	40	EXAMPLE
	22	22	6.87	970	173	4.3	69	720	40	
	23	23	6.84	960	121	3.0	65	720	40	
	24	24	6.84	980	244	6.1	81	730	40	
	25	25	7.16	950	134	3.4	68	710	40	
45	26	26	7.16	950	143	3.6	62	720	40	EXAMPLE
	27	27	6.69	940	174	4.3	76	730	40	
	28	28	6.69	950	144	3.6	59	720	40	
	29	29	*9.48	950	123	3.1	63	720	40	
	30	30	6.69	980	161	4.0	70	730	40	
50	31	31	6.61	950	174	4.3	76	710	40	EXAMPLE
	32	32	6.87	940	147	3.7	63	720	40	
	33	33	6.84	950	220	5.5	81	730	40	
	34	34	6.70	960	153	3.8	67	730	40	
	35	35	7.90	930	228	5.7	82	720	40	
55	36	36	7.52	970	124	3.1	55	720	40	COMPARATIVE EXAMPLE
	37	37	*6.44	930	240	6.0	83	700	40	
	38	38	7.88	920	177	4.4	72	720	40	
	39	39	6.80	940	135	3.4	55	720	40	
	40	40	7.21	960	150	6.0	73	710	25	
55	41	41	7.33	950	101	4.0	71	710	25	COMPARATIVE EXAMPLE
	42	42	7.12	930	129	5.2	77	720	25	
	43	43	7.32	930	116	4.6	72	720	25	
	44	44	7.50	980	126	5.1	70	730	25	
	45	45	7.46	960	97	3.9	80	730	25	
55	46	46	7.06	960	114	4.5	70	710	25	COMPARATIVE EXAMPLE
	47	47	7.49	930	120	4.8	78	710	25	
	48	48	7.39	980	138	5.5	76	720	25	
	49	49	7.71	970	131	5.2	78	720	25	
	50	50	7.71	960	125	5.0	71	720	25	
55	51	51	7.23	960	95	3.8	78	730	25	COMPARATIVE EXAMPLE
	52	52	7.07	960	143	5.7	79	700	25	
	53	53	7.21	930	126	5.0	74	710	25	
	54	54	7.62	970	135	5.4	74	720	25	
	55	55	7.79	960	126	5.0	76	720	25	
55	56	56	7.27	970	134	5.4	72	710	25	

THE VALUE WITH SYMBOL "*" IS OUT OF THE RANGE OF THE PRESENT INVENTION.

TABLE 3

Test No.	STEEL No.	WATER COOLING START TEMPERATURE (°C)	WATER COOLING STOP TEMPERATURE (°C)	COOLING RATE AFTER ROLLING (°C/s)	Ac ₁ (°C)	Q TREATMENT TEMPERATURE (°C)	T TREATMENT TEMPERATURE (°C)	3.8Ni -33+Ac ₁ (°C)	6.3Ni -0.4+Ac ₁ (°C)	TEMPERING TEMPERATURE (°C)	COOLING RATE AFTER TEMPERING (°C/s)	REMARK
1-a	1	679	ROOM TEMPERATURE	20	561	-	-	556	606	570	>30	EXAMPLE
1-b	1	665	150	12	561	-	-	556	606	570	>30	COMPARATIVE EXAMPLE
1-c	1	675	150	*8	561	-	-	556	606	580	23	
1-d	1	667	*280	12	561	-	-	556	606	570	15	
1-e	1	675	ROOM TEMPERATURE	11	561	-	-	556	606	565	*0.4	
1-f	1	663	150	30	561	-	-	556	606	*500	>30	
1-g	1	665	150	30	561	-	680	556	606	575	>30	EXAMPLE
1-h	1	677	ROOM TEMPERATURE	24	561	-	*730	556	606	570	25	COMPARATIVE EXAMPLE
1-i	1	670	150	12	561	-	-	556	606	580	23	
1-j	1	672	ROOM TEMPERATURE	20	561	-	-	556	606	580	>30	
1-k	1	679	ROOM TEMPERATURE	20	561	-	-	556	606	580	>30	
1-l	1	665	ROOM TEMPERATURE	20	561	-	-	556	606	580	>30	
1-m	1	672	ROOM TEMPERATURE	20	561	-	-	556	606	*615	>30	COMPARATIVE EXAMPLE
1-n	1	673	ROOM TEMPERATURE	20	561	-	*610	556	606	580	>30	
1-o	1	-	-	*0.8	561	810	-	556	606	580	>30	
1-p	1	-	-	*0.8	561	810	680	556	606	590	>30	REFERENCE EXAMPLE
2	2	674	200	>30	525	-	-	528	583	535	>30	EXAMPLE
3	3	664	200	30	565	-	-	560	610	592	>30	
4	4	685	200	18	559	-	-	555	606	581	14	
5	5	663	200	30	573	-	-	565	615	605	>30	
6	6	676	150	10	558	-	-	553	605	579	12	COMPARATIVE EXAMPLE
7	7	-	-	*1.6	568	-	-	561	611	585	>30	
8	8	-	-	*2.5	572	-	-	565	614	570	>30	
9	9	668	150	15	570	-	-	563	612	599	1	EXAMPLE
10	10	663	150	15	561	-	-	557	608	557	14	
11	11	672	ROOM TEMPERATURE	15	573	-	-	566	616	589	14	
12	12	677	ROOM TEMPERATURE	15	570	-	-	563	613	572	14	
13	13	670	150	15	566	-	-	560	610	583	14	
14	14	682	150	15	571	-	-	564	613	572	14	
15	15	678	ROOM TEMPERATURE	15	570	-	-	562	612	583	14	
16	16	681	ROOM TEMPERATURE	15	573	-	-	567	617	603	14	
17	17	671	ROOM TEMPERATURE	15	559	-	-	555	606	596	14	
18	18	676	ROOM TEMPERATURE	15	570	-	-	563	613	564	14	
19	19	667	150	15	569	-	-	563	613	563	14	
20	20	673	150	15	572	-	-	565	615	577	14	REFERENCE EXAMPLE
21	21	668	ROOM TEMPERATURE	15	571	-	-	564	614	567	14	
22	22	669	150	15	572	-	-	565	615	570	14	
23	23	678	150	15	575	-	-	568	618	591	14	
24	24	686	ROOM TEMPERATURE	15	569	-	-	562	612	611	14	
25	25	692	ROOM TEMPERATURE	15	568	-	-	562	613	603	14	
26	26	685	150	15	544	-	-	538	589	578	14	
27	27	679	150	15	577	-	-	570	619	589	14	
28	28	668	ROOM TEMPERATURE	15	574	-	-	567	616	603	14	
29	29	672	ROOM TEMPERATURE	15	518	-	-	521	578	555	14	
30	30	675	ROOM TEMPERATURE	15	578	-	-	570	619	604	14	EXAMPLE
31	31	677	ROOM TEMPERATURE	15	573	-	-	566	615	587	14	
32	32	665	150	15	575	-	-	569	618	593	14	
33	33	682	150	15	579	-	-	572	621	600	14	
34	34	672	ROOM TEMPERATURE	15	571	-	-	563	612	568	14	
35	35	670	ROOM TEMPERATURE	15	558	-	-	555	607	601	14	COMPARATIVE EXAMPLE
36	36	674	ROOM TEMPERATURE	15	523	-	-	519	570	543	14	
37	37	679	150	15	602	-	-	593	642	602	14	
38	38	671	150	15	549	-	-	546	599	567	14	
39	39	666	ROOM TEMPERATURE	15	579	-	-	572	621	578	14	
40	40	681	ROOM TEMPERATURE	20	554	-	-	549	599	571	>30	COMPARATIVE EXAMPLE
41	41	672	ROOM TEMPERATURE	20	556	-	-	551	602	602	>30	
42	42	676	ROOM TEMPERATURE	20	571	-	-	565	616	595	>30	
43	43	671	ROOM TEMPERATURE	20	560	-	-	555	605	566	>30	
44	44	664	ROOM TEMPERATURE	20	554	-	-	549	600	585	>30	
45	45	669	ROOM TEMPERATURE	20	557	-	-	552	603	597	>30	
46	46	677	ROOM TEMPERATURE	20	563	-	-	557	607	606	>30	
47	47	672	ROOM TEMPERATURE	20	572	-	-	568	619	601	>30	
48	48	669	ROOM TEMPERATURE	20	553	-	-	548	599	592	>30	
49	49	670	ROOM TEMPERATURE	20	552	-	-	548	600	557	>30	
50	50	685	ROOM TEMPERATURE	20	551	-	-	547	599	588	>30	COMPARATIVE EXAMPLE
51	51	688	ROOM TEMPERATURE	20	559	-	-	554	604	565	>30	
52	52	664	ROOM TEMPERATURE	20	561	-	-	555	606	588	>30	
53	53	679	ROOM TEMPERATURE	20	560	-	-	554	605	566	>30	
54	54	674	ROOM TEMPERATURE	20	554	-	-	550	602	575	>30	
55	55	679	ROOM TEMPERATURE	20	549	-	-	546	598	565	>30	
56	56	673	ROOM TEMPERATURE	20	561	-	-	556	606	579	>30	

THE VALUE WITH SYMBOL "*" IS OUT OF THE RANGE OF THE PRESENT INVENTION.

[0070] A tensile test at room temperature and a Charpy impact test at -196°C were performed to examine a tensile strength TS (MPa), a yield strength YS (MPa), and V-notch Charpy absorbed energy $\sqrt{E_{-196}}$ (J) (an average value of three values). Absorbed energy was converted into absorbed energy per 1 cm² for easy comparison between a sub-size test specimen and a full-size test specimen. In addition, to evaluate brittle crack propagation characteristics, a dynamic tear (DT) test defined in ASTM E604 was performed at -196°C, and the absorbed energy DT₋₁₉₆ (J) was evaluated. In addition, with regard to criteria for determination of good or bad characteristics, YS: 585 MPa or higher, TS: 690 MPa or higher, V-notch Charpy absorbed energy value $\sqrt{E_{-196}}$ per unit area: 150 J/cm² or more, and absorbed energy DT₋₁₉₆ (J) in a DT test: 1500 J or more were determined as "passing". In addition, the DT test could not be performed to evaluate a material having a plate thickness less than 15 mm, and thus a pre-crack Charpy test was performed with respect to a test specimen having a plate thickness of less than 15 mm. Similar to typical V-notch Charpy, the test specimen for pre-crack Charpy test has a crack depth of 2 mm with respect to a test specimen width of 10 mm. but a V-notch depth in the crack depth was limited to 1 mm, and a fatigue crack was introduced as the remaining 1 mm. In the test specimen for pre-crack Charpy test, a crack easily occurred. According to this, pre-crack Charpy test results and brittle crack propagation arrest characteristics had a satisfactory correlation. A criterion for determination of good or bad brittle crack propagation characteristics with the pre-crack Charpy test was absorbed energy at -196°C similar to the V-notch Charpy, and a test specimen in which absorbed energy per 1 cm² was 100 J/cm² or more was determined as "passing".

[0071] A method of evaluating the amount of the retained γ was as follows. A test specimen for measurement of the retained γ was collected from a (1/4)t location regarding the plate thickness t of the steel, and the amount (vol%) of the retained γ was measured with X-ray diffraction. A cross-section that was measured was set to an L cross-section (plane that is parallel with a rolling direction and is perpendicular to a surface of a steel plate). In addition, a shape of the retained γ was evaluated by thin film observation with a transmission electron microscope. Twenty or more of retained γ grains were observed, and an average aspect ratio and an average value of the major axis of the grain samples were measured, and an average value in the sample was calculated. In addition, concentration rates of Mn and Ni in the retained γ were evaluated by the following method. An average Mn concentration and an average Ni concentration in the retained γ were measured with energy dispersive X-ray spectrometry (EDX) quantitative analysis, and the average concentrations were compared with an average Mn concentration and an average Ni concentration in ferrite, respectively, and then evaluation of whether or not the following Expression (1) and Expression (2) were satisfied was performed. In addition, the average Mn concentration and the average Ni concentration in ferrite were set to a bulk value (chemical analysis result) of a corresponding steel.

$$[\text{Mn}]_{\text{retained } \gamma} > [\text{Mn}]_{\alpha} \times 1.4 \dots (1)$$

$$[\text{Ni}]_{\text{retained } \gamma} > [\text{Ni}]_{\alpha} \times 1.4 \dots (2)$$

[0072] Here, the $[\text{Mn}]_{\text{retained } \gamma}$ indicates the average Mn concentration in the retained γ , the $[\text{Mn}]_{\alpha}$ indicates the average Mn concentration in ferrite, the $[\text{Ni}]_{\text{retained } \gamma}$ indicates the average Ni concentration in the retained γ , and the $[\text{Ni}]_{\alpha}$ indicates the average Ni concentration in ferrite.

[0073] Results of the above-described tests are shown in Table 4.

TABLE 4

	Test No.	STEEL No.	PLATE THICKNESS (mm)	AMOUNT OF RETAINED γ (volume%)	AVERAGE ASPECT RATIO OF RETAINED γ	AVERAGE MAJOR AXIS OF RETAINED γ	[Ni] _{retained γ} / [Ni] _{α}	[Mn] _{retained γ} / [Mn] _{α}	MECHANICAL PROPERTIES					PASSING STATUS	REMARK
									YS MPa	TS MPa	vE-196 J/cm ²	DT-196 J	PRE-CRACK (J/cm ²)		
5	1-a	1	25	8.0	2.2	0.39	1.5	1.9	630	720	312	1958	-	G	EXAMPLE
	1-b	1	40	*3.7	*2.6	*0.90	1.8	*1.3	681	741	224	*1320	-	B	COMPARATIVE EXAMPLE
	1-c	1	40	*3.0	2.0	*1.10	*1.3	1.5	*550	*675	*120	*958	-	B	
	1-d	1	40	*2.8	*2.6	0.72	2.1	1.8	*575	*658	*105	*1025	-	B	
	1-e	1	50	*1.2	1.6	0.74	*1.3	2.0	*552	*677	*89	*856	-	B	
1-f	1	10	*0.2	2.1	0.62	1.7	2.1	681	752	*102	-	*24	B	EXAMPLE	
1-g	1	10	12.0	2.0	0.47	1.5	1.7	588	713	248	-	157	G		
1-h	1	25	*3.5	2.0	0.39	2.0	1.6	688	756	*58	*548	-	B		COMPARATIVE EXAMPLE
1-i	1	40	*2.6	*3.5	*1.20	1.7	1.5	595	720	*122	*985	-	B		
1-j	1	25	4.2	*2.8	*1.10	*1.3	*1.3	*545	*675	*102	1520	-	B		
1-k	1	25	*2.3	*3.2	*1.20	*1.3	*1.2	597	711	*88	*977	-	B		
1-l	1	25	4.1	*2.7	*1.05	*1.2	*1.2	*554	*674	*100	*1453	-	B	COMPARATIVE EXAMPLE	
1-m	1	25	5.2	2.0	0.75	*1.2	*1.2	595	735	*86	*875	-	B		
1-n	1	25	*2.5	2.1	0.67	1.5	1.6	605	744	*78	*955	-	B		
1-o	1	25	*0.8	*4.5	*1.85	*1.2	*1.3	603	735	*78	*1023	-	B		
1-p	1	25	*1.2	*5.2	*1.66	*1.2	*1.2	612	732	*73	*1235	-	B		REFERENCE EXAMPLE
2	2	15	9.1	2.5	0.71	2.0	2.3	625	732	293	1777	-	G		
3	3	15	8.0	2.1	0.72	2.3	1.5	626	725	239	1776	-	G	EXAMPLE	
4	4	30	7.5	1.5	0.36	2.0	1.8	621	715	221	1902	-	G		
5	5	10	8.4	1.7	0.81	1.7	1.4	606	713	297	-	143	G		
6	6	50	6.4	1.7	0.84	1.5	2.2	638	738	293	1708	-	G		COMPARATIVE EXAMPLE
7	7	10	8.3	1.9	0.36	2.0	2.3	617	728	*115	-	*80	B		
8	8	6	4.3	2.4	0.61	1.9	1.7	652	740	*128	-	*85	B		
9	9	40	11.6	1.9	0.39	1.9	2.4	611	706	201	1716	-	G	EXAMPLE	
10	10	40	5.8	1.7	0.69	1.8	1.7	616	730	307	1722	-	G		
11	11	40	9.7	1.6	0.73	1.9	2.2	606	709	333	1575	-	G		
12	12	40	4.1	2.3	0.60	2.3	2.0	606	717	303	1902	-	G		
13	13	40	13.6	2.0	0.63	1.5	2.4	656	733	328	1624	-	G		COMPARATIVE EXAMPLE
14	14	40	7.1	1.5	0.67	1.7	2.1	605	695	268	1631	-	G		
15	15	40	5.1	1.6	0.85	1.6	2.1	593	696	284	1741	-	G		
16	16	40	4.2	1.6	0.70	1.7	2.0	633	738	301	1825	-	G		
17	17	40	9.4	2.3	0.56	1.7	2.1	609	717	212	1620	-	G	EXAMPLE	
18	18	40	4.8	1.7	0.72	2.1	1.9	605	699	215	1879	-	G		
19	19	40	6.9	1.7	0.76	1.6	1.8	615	720	301	1911	-	G		
20	20	40	5.9	1.7	0.54	1.5	1.5	595	701	253	1611	-	G		
21	21	40	9.3	2.4	0.50	2.3	1.4	598	690	283	1766	-	G		COMPARATIVE EXAMPLE
22	22	40	5.9	2.1	0.81	1.7	1.8	618	724	218	1571	-	G		
23	23	40	13.9	1.8	0.37	2.0	2.2	618	716	252	1969	-	G		
24	24	40	7.3	2.0	0.47	2.2	2.1	596	693	252	1838	-	G		
25	25	40	12.0	1.7	0.37	2.1	1.8	602	716	281	1665	-	G	REFERENCE EXAMPLE	
26	26	40	12.9	1.6	0.59	2.4	2.0	593	692	304	1667	-	G		
27	27	40	5.9	1.7	0.39	2.4	1.6	604	717	259	1894	-	G		
28	28	40	8.4	2.0	0.83	1.5	1.8	617	718	339	1622	-	G		
29	29	40	4.7	2.5	0.43	2.3	1.7	605	700	200	1700	-	G		EXAMPLE
30	30	40	7.5	1.7	0.55	2.0	1.9	683	756	287	1535	-	G		
31	31	40	9.5	1.7	0.69	2.0	2.0	654	702	289	1870	-	G		
32	32	40	10.8	1.6	0.74	2.2	2.3	593	710	285	2011	-	G		
33	33	40	4.2	2.1	0.51	2.1	1.4	695	732	316	1978	-	G	COMPARATIVE EXAMPLE	
34	34	40	4.6	1.7	0.59	1.8	1.6	640	758	*133	*853	-	B		
35	35	40	6.9	2.4	0.36	1.9	2.3	636	702	*59	*489	-	B		
36	36	40	7.7	1.8	0.78	2.0	2.3	631	696	*55	*468	-	B		
37	37	40	*2.5	2.4	0.48	*1.3	*1.3	627	*690	*69	*675	-	B		EXAMPLE
38	38	40	*2.5	2.0	0.36	1.9	2.2	622	*683	*66	*239	-	B		
39	39	40	*2.6	2.2	0.68	1.8	1.8	618	*677	*49	*345	-	B		
40	40	25	*2.2	*2.6	0.66	1.7	1.9	*501	*623	*45	*501	-	B		
41	41	25	7.6	2.5	0.76	2.1	2.1	639	728	*99	*847	-	B	COMPARATIVE EXAMPLE	
42	42	25	*3.4	2.2	0.70	1.8	1.9	*565	*685	*73	*988	-	B		
43	43	25	6.8	2.0	0.70	2.1	2.1	633	756	*74	*913	-	B		
44	44	25	7.6	2.2	0.76	1.9	1.9	649	780	*89	*929	-	B		
45	45	25	7.0	2.1	0.81	2.0	2.1	647	785	*70	*909	-	B		COMPARATIVE EXAMPLE
46	46	25	7.3	2.3	0.79	1.9	1.9	624	752	*95	*1113	-	B		
47	47	25	*2.3	2.4	0.63	2.1	2.1	656	801	*85	*886	-	B		
48	48	25	*2.2	2.2	0.64	1.9	2.0	633	821	*92	*1047	-	B		
49	49	25	7.5	2.4	0.72	1.9	1.9	645	785	*95	*927	-	B	COMPARATIVE EXAMPLE	
50	50	25	7.5	2.3	0.75	1.8	1.8	655	775	*91	*870	-	B		
51	51	25	6.3	2.2	0.68	1.8	1.8	631	765	*96	*1021	-	B		
52	52	25	4.5	2.2	0.81	2.0	2.1	628	750	*97	*1186	-	B		
53	53	25	6.8	2.4	0.62	1.9	1.9	636	775	*72	*1041	-	B		COMPARATIVE EXAMPLE
54	54	25	6.5	2.4	0.81	2.0	2.1	639	768	*86	*1090	-	B		
55	55	25	6.5	2.1	0.78	1.8	1.9	638	764	*97	*1183	-	B		
56	56	25	7.7	2.2	0.72	2.0	2.0	620	743	*87	*844	-	B		

THE VALUE WITH SYMBOL "*" IS OUT OF THE RANGE OF THE PRESENT INVENTION.

[0074] As can be seen from characteristic evaluation results shown in Table 4, in all steels of Test No. 1-a, Test No. 1-g, Test Nos. 3 to 6, Test Nos. 9 to 28, and Test Nos. 30 to 33 in which the amount of retained γ and the shape thereof were adjusted in ranges defined in the invention by performing rolling and heat treatment with respect to steel of Steel No. 1, Steel Nos. 3 to 6, Steel Nos. 9 to 28, and Steel Nos. 30 to 33 having chemical composition in the range defined in the invention with an appropriate method, the strength (the yield strength YS, the tensile strength TS), the brittle crack initiation characteristics (V-notch Charpy absorbed energy $\sqrt{E_{-196}}$ per unit area), and the arrest characteristics (absorbed energy DT₋₁₉₆ of DT) reached target passing ranges. In addition, in steel of Steel No. 2 and Steel No. 29, the amount of Ni exceeded the range defined in the invention, but reached the passing range similar to steel of the invention because Ni does not have an adverse effect on the fracture-resistance characteristics of steel.

[0075] In contrast, in a steel of Test No. 1-c in which the cooling rate after rolling was lower than the defined range, a steel of Test No. 1-d in which the water cooling stop temperature after rolling was higher than the defined range, a steel of Test No. 1-e in which the cooling rate after tempering was slower than the defined range, a steel of Test No. 1-j in which the heating temperature was lower than the defined range, and a steel of Test No. 1-l in which the slab thickness after termination of rough rolling with respect to the plate thickness of a product having a product thickness exceeded the defined range and thus the finish rolling temperature was lowered, the strength (the yield strength YS, the tensile strength TS) was deficient.

[0076] In a steel of Test No. 1-c, a steel of Test No. 1-d, a steel of Test No. 1-e, a steel of Test No. 1-f in which the tempering temperature was lower than the defined range, a steel of Test No. 1-h in which the L treatment temperature was higher than the defined range, a steel of Test No. 1-i in which the heating temperature was higher than the defined range, a steel of Test No. 1-j, a steel of Test No. 1-k in which the slab thickness after rough rolling termination with respect to the plate thickness of a product having a product thickness is less than the defined range, a steel of Test No. 1-l, a steel of Test No. 1-m in which the tempering temperature was higher than the defined range, a steel of Test No. 1-n in which the L treatment temperature was lower than the defined range, a steel of Test No. 1-o that was subjected to the off-line QT, and a steel of Test No. 1-p that was subjected to the off-line QLT, the brittle crack initiation characteristics (V-notch Charpy absorbed energy $\sqrt{E_{-196}}$ per unit area) were deficient.

[0077] In a steel of Test No. 1-b in which the cumulative reduction at 850°C or lower was less than the defined range, and steels of Test Nos. 1-c to 1-f, Test No. 1-h, Test No. 1-i, and Test Nos. 1-k to 1-p, the arrest characteristics (absorbed energy of DT: DT₋₁₉₆, or absorbed energy at -196°C which was obtained with the pre-crack Charpy test) were deficient.

[0078] In a steel of Test No. 34 formed from steel of Steel No. 34, the amount of C was excessive. In a steel of Test No. 35 formed from steel of Steel No. 35, the amount of Si was excessive. In a steel of Test No. 36 formed from steel of Steel No. 36, the amount of Mn was excessive. Therefore, even though the strength characteristics (the yield strength and the tensile strength) were not problematic, the fracture characteristics (the brittle crack initiation characteristics and the arrest characteristics) were deficient. In addition, in a steel of Test No. 37 formed from steel of Steel No. 37, the amount of Ni was too small, and thus the tensile strength was deficient, and the retained γ could not be secured sufficiently. Accordingly, the fracture characteristics were deficient. In addition, in a steel of Test No. 38 formed from steel of Steel No. 38, the amount of Al was excessive. In a steel of Test No. 39 formed from steel of Steel No. 39, the amount of N was excessive. Therefore, the tensile strength was deficient, and the retained γ was not sufficient, and thus the fracture characteristics were deficient. In a steel of Test No. 40 formed from steel of Steel No. 40 in which the amount of C was less than the defined value, and a steel of Test No. 42 formed from steel of Steel No. 42 in which the amount of Mn was less than the defined value, both of the strength characteristics and the fracture characteristics were deficient. A steel of Test No. 41 formed from steel of Steel No. 41 in which the amount of Si was less than the defined value, and a steel of Test No. 43 formed from steel of Steel No. 43 in which the amount of Al was less than the defined value, the fracture characteristics were deficient. In Steel No. 44 to Steel No. 56, any one of the amounts of, P, S, Cu, Cr, Mo, V, Nb, Ti, B, Sn, Al, Mg, and REM exceeded the defined value, but in steels of Test No. 44 to Test No. 56 formed from steel of Steel No. 44 to steel of Steel No. 56, the fracture characteristics decreased.

[Industrial Applicability]

[0079] The steel according to the invention in which the amount of Ni is 6.6% to 8.0% on terms of mass% is excellent in economic efficiency and fracture-resistant characteristics. This steel is suitable for use in an inner tank member or an annular plate of an LNG tank.

Claims

1. A steel having a chemical composition comprising, in terms of mass%:

C: 0.01% to 0.12%;

Si: 0.01% to 0.30%;

Mn: 0.4% to 2.0%;

Ni: 6.6% to 8.0%;

Al: 0.002 to 0.08%

N: 0.0050% or less;

P: 0.05% or less;

S: 0.008% or less;

Cu: 0% to 1.00%;

Cr: 0% to 1.00%;

Mo: 0% to 0.50%;

V: 0% to 0.10%;

B: 0% to 0.0050%;

Nb: 0% to 0.10%;

Ti: 0% to 0.10%;

Sn: 0% to 0.50%;

Ca: 0% to 0.004%;

Mg: 0% to 0.0020%;

REM: 0% to 0.0020%; and

remainder: Fe and impurities, wherein

a lower limit of an amount of retained γ at a $(1/4)t$ location regarding a plate thickness t of the steel is 4.0 volume%, the retained γ has a form in which an upper limit of an average of an aspect ratio thereof is 2.5 and an upper limit of an average of a major axis thereof is $0.85\ \mu\text{m}$, and

an average Mn concentration in the retained γ and an average Ni concentration in the retained γ satisfy Expression 1 and Expression 2, respectively,

$$[\text{Mn}]_{\text{retained } \gamma} > [\text{Mn}]_{\alpha} \times 1.4 \quad \text{:Expression 1,}$$

$$[\text{Ni}]_{\text{retained } \gamma} > [\text{Ni}]_{\alpha} \times 1.4 \quad \text{:Expression 2,}$$

and

the $[\text{Mn}]_{\text{retained } \gamma}$ indicates the average Mn concentration in the retained γ , the $[\text{Mn}]_{\alpha}$ indicates an average Mn concentration in ferrite, the $[\text{Ni}]_{\text{retained } \gamma}$ indicates the average Ni concentration in the retained γ , and the $[\text{Ni}]_{\alpha}$ indicates an average Ni concentration in the ferrite.

2. The steel according to Claim 1, wherein

the chemical composition further comprises, in terms of mass%,

C: 0.02% to 0.07%,

Si: 0.01% to 0.10%,

Mn: 0.6% to 1.0%,

Ni: 7.0 to 7.8%,

Cu: 0% to 0.30%,

Cr: 0% to 0.80%,

Mo: 0% to 0.20%,

V: 0 to 0.05%,

B: 0 to 0.0005%,

Nb: 0 to 0.02%,

Ti: 0 to 0.02%, and

Sn: 0 to 0.01 %.

3. The steel according to Claim 1 or 2, wherein

the chemical composition further comprises, in terms of mass%,

Cr: 0.30% to 0.60%, and

Mo: 0.05% to 0.15%.

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4. The steel according to any one of Claims 1 to 3, wherein the steel is a steel plate of which a plate thickness is 3 mm to 100 mm, a lower limit of a yield strength is 585 MPa, and a tensile strength is 690 MPa to 885 MPa.

- 5 5. An LNG tank, wherein the steel according to any one of Claims 1 to 4 is applied to a member of an inner tank.

6. An LNG tank, wherein the steel according to any one of Claims 1 to 4 is applied to a member of an annular plate.

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FIG. 1

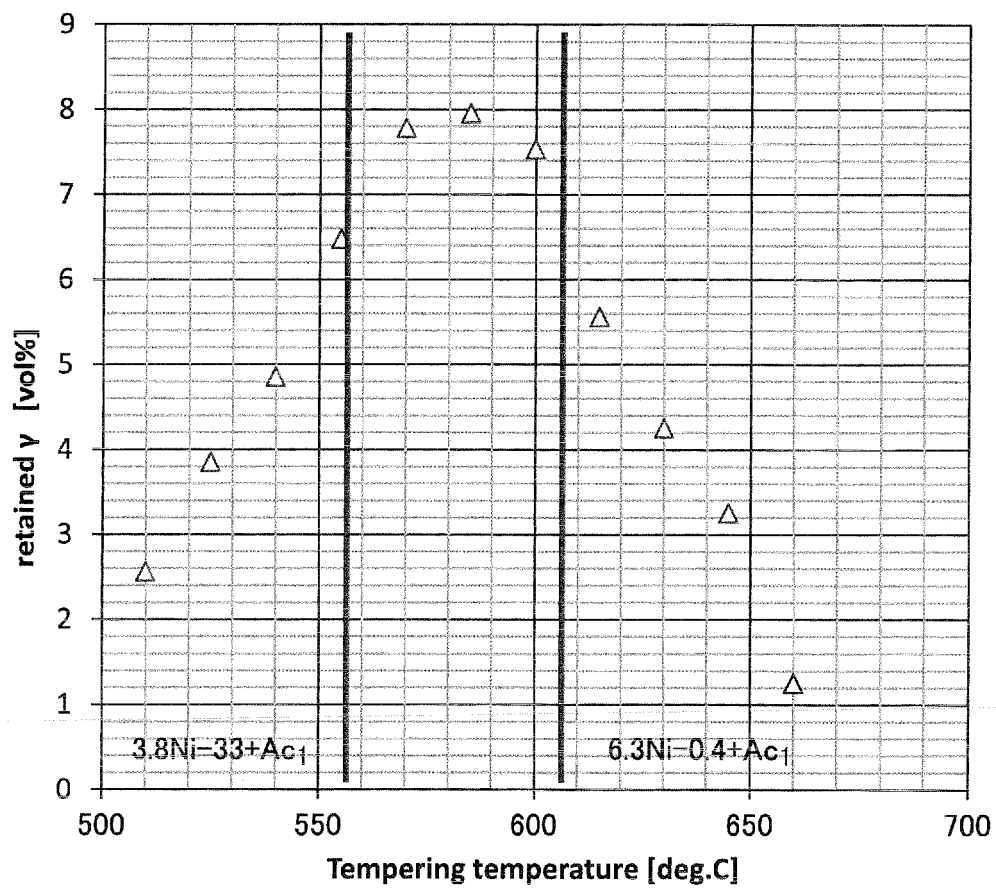


FIG. 2

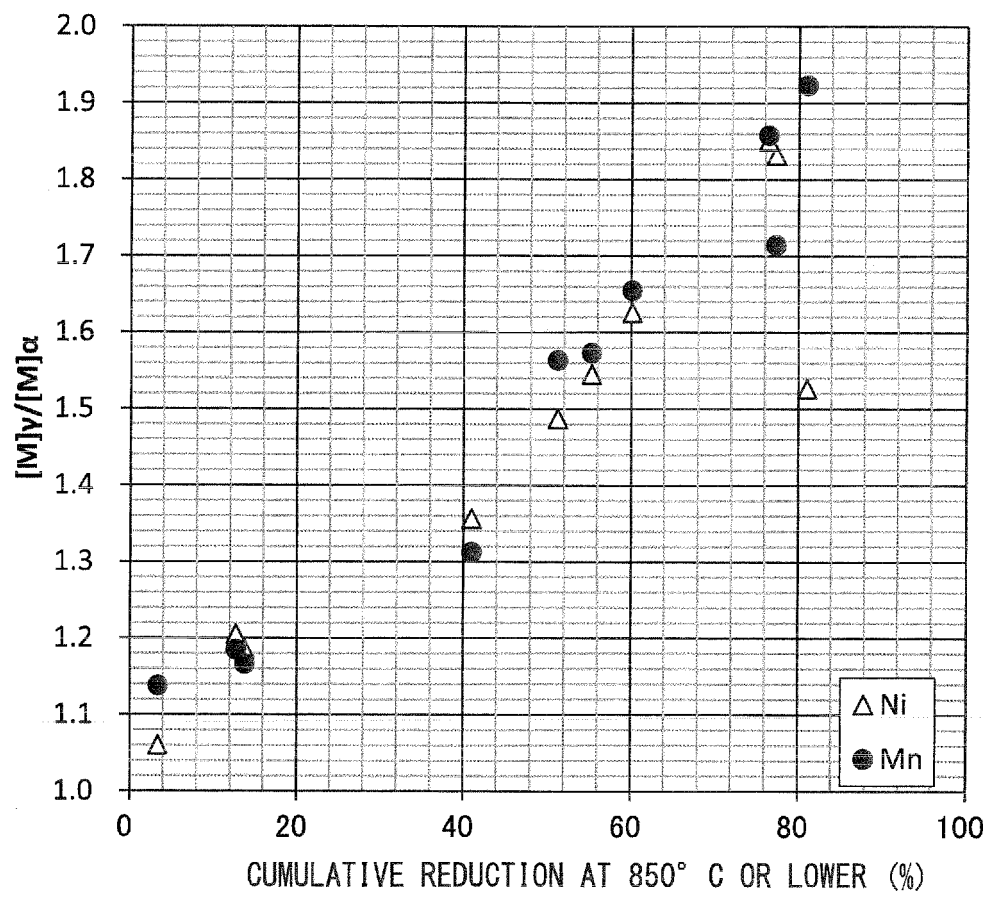
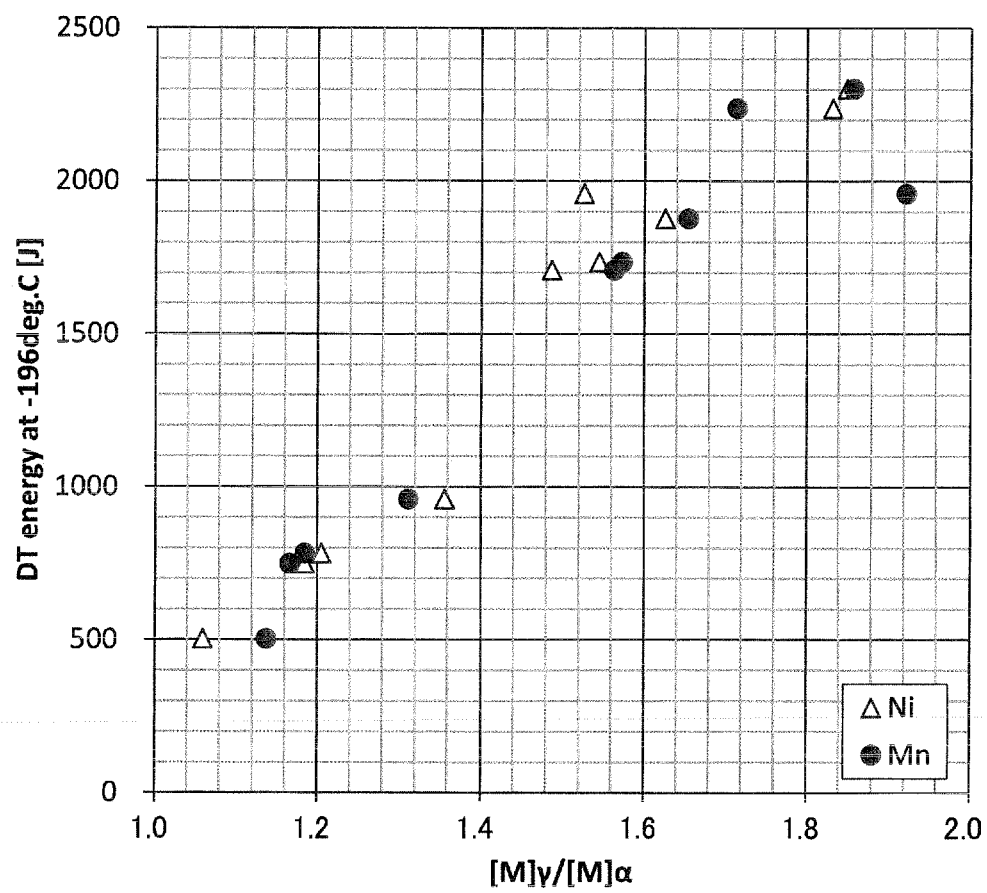


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/066825

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(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, 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 1996-2013

Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-14811 A (Nippon Steel & Sumitomo Metal Corp.), 24 January 2013 (24.01.2013), claims 1 to 12; paragraphs [0077] to [0092] (Family: none)	1-6
A	WO 2007/034576 A1 (Sumitomo Metal Industries, Ltd.), 29 March 2007 (29.03.2007), claims 1 to 6; paragraphs [0056] to [0063] & JP 4872917 B & EP 1942203 A1 & KR 10-2008-0038226 A & KR 10-0984413 B1	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
02 September, 2013 (02.09.13)Date of mailing of the international search report
10 September, 2013 (10.09.13)Name and mailing address of the ISA/
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/066825

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-21243 A (Sumitomo Metal Industries, Ltd.), 03 February 2011 (03.02.2011), claims 1 to 5; paragraphs [0090] to [0104] (Family: none)	1-6
A	WO 2013/046357 A1 (Nippon Steel & Sumitomo Metal Corp.), 04 April 2013 (04.04.2013), claims 1 to 8; paragraphs [0052], [0058] to [0078] & JP 5059244 B	1-6
A	WO 2012/005330 A1 (Nippon Steel Corp.), 12 January 2012 (12.01.2012), claims 1 to 9; paragraphs [0059], [0066] to [0082] & JP 4975888 B & US 2013/0098514 A1 & EP 2592166 A1 & CN 102985576 A & KR 10-2013-0014069 A	1-6
A	JP 7-316654 A (Kawasaki Steel Corp.), 05 December 1995 (05.12.1995), claims 1 to 3; paragraphs [0027] to [0031] (Family: none)	1-6

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

REFERENCES CITED IN THE DESCRIPTION

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- WO 2012005330 A [0010]