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(54) **NI-CONTAINING STEEL PLATE**

(57) An object of the present invention is to provide an Ni-containing steel plate which is low in cost and has excellent low-temperature toughness. In view of the object, the Ni-containing steel plate of the present invention has a chemical composition containing by mass% C: 0.01 % to 0.15 %, Si: 0.02 % to 0.20 %, Mn: 0.45 % to 2.00 %, P: 0.020 % or less, S: 0.005 % or less, Al: 0.005 % to 0.100 %, Ni: 5.0 % to 8.0 %, and the balance being

Fe and incidental impurities, and has a microstructure containing less than 1.7 % by volume fraction of retained austenite when cooled to liquid nitrogen temperature, and having an average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more of 5 μm or less by equivalent circle diameter.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to an Ni-containing steel plate with excellent low-temperature toughness, in particular to a steel plate which is suitable for use as members such as storage tanks for liquefied natural gas.

BACKGROUND ART

10 **[0002]** Conventionally, for members such as overland storage tanks for liquefied natural gas (hereinafter, referred to as LNG), high Ni-containing steel plates which are excellent in mechanical properties at low temperatures have been commonly used. In particular, steel plates composed of high Ni-containing steel which contains Ni by 9 mass% (hereinafter, referred to as 9 % Ni steel) have been commonly used, and they have actually been applied in many cases.

15 **[0003]** Regarding 9 % Ni steel, considerations on various properties such as mechanical properties and weldability have been made. For example, Steel and Iron by Furukimi Osamu, Suzuki Shigeharu, Nakano Yoshifumi, 69(1982)5, S492 (NPL 1) discloses that low-temperature toughness is improved by reducing the amount of impurity elements such as P and S. Further, Handbook of Metal, 4th revised edition, edited by The Japan Institute of Metals and Materials, Maruzen, p801 (NPL 2) discloses that low-temperature toughness is improved by stabilizing retained austenite. However, since Ni is an expensive metal, it is desired to reduce Ni content.

20 **[0004]** Techniques for obtaining steel plates which can be made to have an Ni content smaller than that of 9 % Ni steel and has good low temperature toughness are disclosed in for example, WO2007/034576 (PTL 1), WO2007/080645 (PTL 2), JP2011-214099A (PTL 3). PTL 1 discloses that mechanical properties of a steel plate can be improved by predetermining the chemical composition of the steel plate, defining the amount, aspect ratio, and average equivalent circular diameter of austenite contained in the steel plate, and manufacturing the steel plate with a method to satisfy
25 such definitions. Further, PTL 2 discloses that toughness of the heat-affected zone of a steel plate can be improved when the steel plate has a predetermined chemical composition and the Fe content obtained by an extraction residue method after a heat-cycle simulation test is more than a predetermined value. Further, PTL 3 discloses that a brittle crack-arrest property of steel can be improved when the steel has a predetermined chemical composition, with certain textures developed.

CITATION LIST

Patent Literature

35 **[0005]**

PTL 1: WO2007/034576

PTL 2: WO2007/080645

40 PTL 3: JP2011-214099A

Non-patent Literature

45 **[0006]**

NPL 1: Steel and Iron by Furukimi Osamu, Suzuki Shigeharu, Nakano Yoshifumi, 69(1982)5, S492

NPL 2: Handbook of Metal, 4th revised edition, edited by The Japan Institute of Metals and Materials, Maruzen, p800-802

SUMMARY OF INVENTION

(Technical Problem)

55 **[0007]** However, the techniques disclosed in PTL 1, 2 and 3 do not include definitions regarding the amount of austenite at around -165 °C where the LNG tanks are actually used, and consideration regarding low-temperature toughness when the techniques are applied to actual structures were not made. Further, there were no specific disclosures regarding the manufacturing method of the steel plates.

[0008] The present invention has been developed in view of such situation, and an object thereof is to provide an Ni-containing steel plate which is low in cost and has excellent low-temperature toughness.

(Solution to Problem)

[0009] The inventors of the present invention, as a result of intense investigation for providing an Ni-containing steel plate with excellent low-temperature toughness, discovered that by containing C, Si, Mn, P, S, Al, and Ni as essential elements of a steel, and setting the amount of retained austenite contained in the steel after performing sub-zero treatment where cooling is performed until reaching liquid nitrogen temperature to be less than 1.7 %, and setting the average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more to 5 μm or less by equivalent circle diameter, excellent low-temperature toughness can be achieved even when the Ni content is reduced compared to conventional 9 % Ni steel.

[0010] If the Ni content in steel is reduced to be smaller than that of 9 % Ni steel, even if retained austenite is stable at room temperature, it will be unstable at -165 °C where LNG tanks are used. Further, it is considered that toughness decreases when retained austenite exists at -165 °C, because the retained austenite is transformed into martensite phase due to deformation induced transformation, at the tip of a crack formed in the steel material when the LNG tank fractures. Under the situation, by reducing the amount of retained austenite remaining after sub-zero treatment corresponding to -165 °C where LNG tanks are used, and forming a fine microstructure as described above, it is assumed that low-temperature toughness can be improved even if the Ni content in steel is reduced to be smaller than that of conventional 9 % Ni steel.

[0011] The present invention is based on the above discoveries and it provides the following (1) to (4).

(1) An Ni-containing steel plate having a chemical composition containing by mass% C: 0.01 % to 0.15 %, Si: 0.02 % to 0.20 %, Mn: 0.45 % to 2.00 %, P: 0.020 % or less, S: 0.005 % or less, Al: 0.005 % to 0.100 %, Ni: 5.0 % to 8.0 %, and the balance being Fe and incidental impurities, wherein the steel plate has a microstructure containing less than 1.7 % by volume fraction of retained austenite when cooled to liquid nitrogen temperature, and having an average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more of 5 μm or less by equivalent circle diameter.

(2) The Ni-containing steel plate according to aspect (1), wherein the chemical composition further contains by mass% at least one element selected from Cr: 1.00 % or less and Mo: 1.000 % or less.

(3) The Ni-containing steel plate according to aspect (1) or (2), wherein the chemical composition further contains by mass% at least one element selected from Cu: 1.00 % or less, V: 0.100 % or less, Nb: 0.100 % or less, Ti: 0.100 % or less, and B: 0.0030 % or less.

(4) The Ni-containing steel plate according to any one of aspects (1) to (3), wherein the chemical composition further contains by mass% at least one element selected from Ca: 0.0050 % or less and REM: 0.0050 % or less.

(Advantageous Effect of Invention)

[0012] According to the present invention, an Ni-containing steel plate containing less Ni content compared to 9 % Ni steel but having low-temperature toughness equivalent to that of 9 % Ni steel can be easily manufactured, and an industrially remarkable effect is provided.

DESCRIPTION OF EMBODIMENTS

[0013] Hereinafter, the Ni-containing steel plate according to the present invention will be explained in detail and separately based on chemical composition, microstructure, and manufacturing method.

[0014] Unless otherwise specified, the indication of "%" regarding composition shall stand for "mass%".

(1) Chemical Composition

[0015] First, the chemical composition will be described.

C: 0.01 % to 0.15 %

[0016] C is an important element for solid solution strengthening of steel. If C content is less than 0.01 %, sufficient strength cannot be obtained. On the other hand, adding C in an amount exceeding 0.15 % would cause deterioration of weldability and workability. Therefore, C content is set to be in the range of 0.01 % to 0.15 %. Preferably, the range is from 0.03 % to 0.10 %.

Si: 0.02 % to 0.20 %

[0017] Si is an effective element as a deoxidizer in molten steel and an effective element for solid solution strengthening. If Si content is less than 0.02 %, deoxidizing effect cannot be sufficiently obtained. On the other hand, adding Si in an amount exceeding 0.20 % would cause problems such as reduction in ductility and toughness, and an increase of inclusions. Therefore, Si content is set to be in the range of 0.02 % to 0.20 %, and preferably in the range of 0.03 % to 0.10 %.

Mn: 0.45 % to 2.00 %

[0018] Mn is an effective element from the viewpoint of ensuring quench hardenability and enhancing strength. If Mn content is less than 0.45 %, the effect thereof cannot be sufficiently obtained. On the other hand, adding Mn in an amount exceeding 2.00 % would cause deterioration of weldability. Therefore, Mn content is set to be in the range of 0.45 % to 2.00 %, and preferably in the range of 0.55 % to 1.00 %.

P: 0.020 % or less

[0019] Although high P content in steel leads to deterioration of low temperature toughness, the content thereof of 0.020 % or less would be acceptable. Therefore, the upper limit of P content is set to be 0.020 %.

S: 0.005 % or less

[0020] High S content in steel causes precipitation as MnS, and this, as an inclusion, becomes the fracture generation origin of high tensile strength steel and leads to deterioration of toughness. However, if the content thereof is 0.005 % or less, it would cause no problem. Therefore, the upper limit of S content is set to be 0.005 %.

Al: 0.005 % to 0.100 %

[0021] Al is an effective element as a deoxidizer in molten steel and an effective element for improving low-temperature toughness. If Al content is less than 0.005 %, these effects cannot be sufficiently obtained. On the other hand, if the content thereof exceeds 0.100 %, weldability will decrease. Therefore, Al content is set to be in the range of 0.005 % to 0.100 %, and preferably in the range of 0.020 % to 0.050 %.

Ni: 5.0 % to 8.0 %

[0022] Ni is an important element for the present invention, and it is an element that enhances quench hardenability and improves toughness of ferrite matrix. If Ni content is less than 5.0 %, these effects cannot be sufficiently exhibited. On the other hand, if the content thereof exceeds 8.0 %, costs will increase. Therefore, Ni content is set to be in a range of 5.0 % to 8.0 %. In addition, from the viewpoint of further reducing costs, it is desirable for Ni content to be in the range of 5.0 % to 7.5 %.

[0023] In addition to the above basic chemical compositions, it is possible to contain at least one element selected from Cr and Mo, as a first group of selected components, if necessary, in the following ranges.

Cr: 1.00 % or less

[0024] Cr enhances quench hardenability and provides an effect of improving low-temperature toughness by refining martensite phase. However, if the content thereof exceeds 1.00 %, it would cause deterioration of weldability and an increase in manufacturing costs. Therefore, when containing Cr, the content thereof is set to be in the range of 1.00 % or less. In order to effectively exhibit the above effect, it is preferable for the Cr content to be 0.05 % or more, and more preferably in the range of 0.10 % to 0.75 %.

Mo: 1.000 % or less

[0025] Mo enhances quench hardenability and provides an effect of improving low-temperature toughness by refining martensite phase. However, if the content thereof exceeds 1.000 %, it would cause deterioration of weldability and an increase in manufacturing costs. Therefore, when containing Mo, the content thereof is set to be in the range of 1.000 % or less. In order to effectively exhibit the above effects, it is preferable for the content thereof to be 0.005 % or more, and more preferably in the range of 0.010 % to 0.500 %.

[0026] Further, in the present invention, it is possible to contain at least one element selected from Cu, V, Nb, Ti, and

B as a second group of selected components, if necessary, in the following ranges.

Cu: 1.00 % or less

5 **[0027]** Cu is an element that enhances quench hardenability. However, if the content thereof exceeds 1.00 %, it would cause reduction of hot workability and an increase in costs. Therefore, when containing Cu, the content thereof is set to be in the range of 1.00 % or less. In order to effectively exhibit the above effect, it is preferable for the content thereof to be 0.05 % or more.

10 V: 0.100 % or less

[0028] V is an element that precipitates as carbonitride, has an effect of refining microstructures, and is useful for improving toughness. However, if the content thereof exceeds 0.100 %, it would cause deterioration of weldability. Therefore, when containing V, the content thereof is set to be in the range of 0.100 % or less. In order to effectively exhibit the above effects, it is preferable for the content thereof to be 0.005 % or more.

Nb: 0.100 % or less

20 **[0029]** Nb is an element that precipitates as carbonitride, has an effect of refining microstructures, and is useful for improving toughness. However, if the content thereof exceeds 0.100 %, it would cause deterioration of weldability. Therefore, when containing Nb, the content thereof is set to be in the range of 0.100 % or less. In order to effectively exhibit the above effects, it is preferable for the content thereof to be 0.005 % or more.

Ti: 0.100 % or less

25 **[0030]** Ti has an effect of improving toughness by fixing solute N, which is harmful to toughness, as TiN. However, if the content thereof exceeds 0.100 %, it would cause precipitation of a coarse carbonitride, and deteriorate toughness. Therefore, when containing Ti, the content thereof is set to be in the range of 0.100 % or less. In order to effectively exhibit the above effect, it is preferable for the content thereof to be 0.005 % or more, and more preferably in the range of 0.010 % to 0.050 %.

B: 0.0030 % or less

35 **[0031]** B is an element that enhances quench hardenability when added to steel by a small amount. However, if the content thereof exceeds 0.0030 %, it would cause deterioration of toughness. Therefore, when containing B, the content thereof is set to be in the range of 0.0030 % or less. In order to effectively exhibit the above effect, it is preferable for the content thereof to be 0.0003 % or more.

[0032] Further, in the present invention, it is possible to contain at least one element selected from Ca and REM as a third group of selected components, if necessary, in the following ranges.

40 Ca: 0.0050 % or less

[0033] Ca is an element that fixes S and inhibits generation of MnS which becomes the cause of reduction in toughness. However, if the content thereof exceeds 0.0050 %, it would cause an increase in the amount of inclusions existing in steel and lead to deterioration of toughness rather than providing the above effect. Therefore, when containing Ca, the content thereof is set to be in the range of 0.0050 % or less. In order to effectively exhibit the above effect, it is preferable for the content thereof to be 0.0005 % or more.

50 REM: 0.0050 % or less

[0034] REM (Rare Earth Metal) is an element that fixes S and inhibits generation of MnS which becomes the cause of reduction in toughness. However, if the content thereof exceeds 0.0050 %, it would cause an increase in the amount of inclusions existing in steel and lead to deterioration of toughness rather than providing the above effect. Therefore, when containing REM, the content thereof is set to be in the range of 0.0050 % or less. In order to effectively exhibit the above effect, it is preferable for the content thereof to be 0.0005 % or more.

[0035] The balance other than the components described above includes Fe and incidental impurities.

(2) Microstructure

[0036] Next, the microstructure will be described.

[0037] The Ni-containing steel plate of the present invention has the above chemical composition, and also has a microstructure containing less than 1.7 % of retained austenite when cooled to liquid nitrogen temperature, and having an average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more of 5 μm or less by equivalent circle diameter.

[0038] Since the steel plate of the present invention is used mainly in storage tanks for LNG, the microstructure at -165 °C where LNG tanks are used is important. Therefore, the microstructure after sub-zero treatment where the steel plate is held at liquid nitrogen temperature, is defined. If the amount of retained austenite remaining after sub-zero treatment is 1.7 % or more by volume fraction, sufficient low-temperature toughness cannot be obtained. Some reports have been made that retained austenite improves low temperature toughness. However, for the Ni-containing steel plate of the present invention, retained austenite has a harmful effect on toughness. It is considered that this is due to the fact that, since in Ni-containing steel plate of the present invention, the Ni content is smaller than the Ni content in conventional 9 % Ni steel, even if retained austenite exists at -165 °C, it is unstable, and if the steel structure undergoes plastic deformation at the tip of a crack, the retained austenite transforms into martensite by plasticity-induced martensite phase transformation. Therefore, the amount of retained austenite when the steel plate is cooled to liquid nitrogen temperature is set to be less than 1.7 % by volume fraction. This amount is preferably 1.0 % or less, and more preferably 0.5 % or less.

[0039] Further, if the average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more exceeds 5 μm by equivalent circle diameter, sufficient low-temperature toughness cannot be obtained. Therefore, the average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more is set to be 5 μm or less by equivalent circle diameter, and preferably 3 μm or less by equivalent circle diameter.

(3) Manufacturing Condition

[0040] Next, a preferable manufacturing condition for manufacturing the steel plate of the present invention having the above described chemical composition and the above microstructure will be described. The following manufacturing condition is merely an example of a condition for manufacturing the Ni-containing steel plate of the present invention, and as long as the Ni-containing steel plate of the present invention can be obtained, manufacturing condition for the present invention is not limited to the following manufacturing condition.

[0041] In the present invention, it is preferable to heat a slab or a steel billet having the above described chemical composition at a temperature range of 900 °C to 1100 °C for 10 hours or less, and then to subject it to hot rolling at a temperature range of 870 °C or lower so that the cumulative rolling reduction ratio is 40 % or more and 70 % or less and the finisher delivery temperature is between 700 °C and 820 °C, and then to subject the obtained hot rolled steel plate to direct quenching treatment where quenching is immediately performed until reaching a temperature of 200 °C or lower at a cooling rate of 5 °C/s or more, and then to heat the steel plate to a temperature range of 500 °C to 650 °C at a heating rate of 0.05 °C/s to 1.0 °C/s, and then to subject the steel plate to tempering by holding the temperature at the same temperature range for 10 minutes or more and 60 minutes or less.

Heating Temperature: 900 °C to 1100 °C, Heating duration: 10 hours or less

[0042] In a case where the heating temperature is lower than 900 °C, coarse AlN which precipitates during the stage of casting of the steel slab does not dissolve, and toughness decreases. Further, the following rolling conditions cannot be substantially satisfied. If the heating temperature exceeds 1100 °C, austenite becomes coarse grains and toughness will decrease. If the heating duration exceeds 10 hours, austenite grains become coarse and toughness decreases. Therefore, the heating temperature is set to be between 900 °C and 1100 °C, and the heating duration is 10 hours or less.

Rolling Reduction Ratio: Cumulative Rolling Reduction Ratio of 40 % or more and 70 % or less at 870 °C or lower

[0043] If the cumulative rolling reduction ratio in the non-recrystallized region of austenite at 870 °C or lower is less than 40 %, refinement of martensite phase will not be sufficient, and toughness decreases. On the other hand, in a case where the cumulative rolling reduction ratio exceeds 70 %, it is difficult to substantially perform rolling at the following finisher delivery temperature. Therefore, the rolling reduction ratio is set to be 40 % or more and 70 % or less at 870 °C or lower.

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Finisher delivery temperature: 700 °C to 820 °C

[0044] If the finisher delivery temperature is lower than 700 °C, it results in α - γ dual phase rolling so that bainite phase forms, and therefore a desired strength cannot be satisfied. On the other hand, if the finisher delivery temperature exceeds 820 °C, it becomes substantially difficult to perform sufficient rolling reduction in the non-recrystallized region of austenite, a fine microstructure cannot be obtained, and toughness decreases. Therefore, the finisher delivery temperature is set to be in the range of 700 °C to 820 °C.

Cooling (Direct Quenching): Start immediately after rolling

[0045] Cooling (direct quenching) is started immediately after rolling is finished. If cooling is not immediately started, bainite phase will generate, and therefore a desired strength cannot be satisfied. Therefore, cooling is started immediately after rolling is finished. Here, "immediately" refers to a point in time within 120 seconds after the completion of rolling.

Cooling Rate: 5 °C/s or more

[0046] In a case where the cooling rate is less than 5 °C/s, transformation to martensite phase will not occur, and a desirable strength and toughness cannot be obtained. Therefore, the cooling rate is set to be 5 °C/s or more. Preferably, the cooling rate is 10 °C/s or more.

Cooling Stop Temperature: 200 °C or lower

[0047] In a case where the cooling stop temperature exceeds 200 °C, transformation to martensite phase will not occur uniformly in the steel plate, and a desirable strength and toughness cannot be obtained. Therefore, the cooling stop temperature is set to be 200 °C or lower.

Tempering Heating Rate: 0.05 °C/s to 1.0 °C/s

[0048] In a case where the tempering heating rate is less than 0.05 °C/s, the precipitated carbide would become coarse, and toughness will decrease. On the other hand, in order to perform rapid short time heating where the tempering heating rate exceeds 1.0 °C/s, induction heating facilities and the like will be required, and costs will increase. Therefore, the tempering heating rate is set to be in the range of 0.05 °C/s to 1.0 °C/s.

Tempering temperature: 500 °C to 650 °C

[0049] In a case where the tempering temperature is lower than 500 °C, toughness improving effect caused by precipitation of fine carbides such as cementite cannot be sufficiently obtained. On the other hand, in a case where the tempering temperature exceeds 650 °C, coarse carbide precipitates, and toughness decreases. Therefore, the tempering temperature is set to be in the range of 500 °C to 650 °C.

Tempering Holding Time: 10 minutes or more and 60 minutes or less

[0050] In a case where the tempering holding time is less than 10 minutes, toughness improving effect caused by precipitation of fine carbides such as cementite cannot be sufficiently obtained. On the other hand, in a case where the tempering holding time exceeds 60 minutes, toughness will decrease due to reasons such as precipitation of a coarse carbide. Further, manufacturing costs will increase. Therefore, the tempering holding time is set to be 10 minutes or more and 60 minutes or less. Cooling after tempering may be performed by either water cooling or air cooling. However, if the cooling rate is too fast, the temperature difference between the surface and the inside of the steel plate becomes large and causes formation of strains inside the steel plate and low temperature toughness decreases. Therefore, the cooling rate is preferably 5 °C/s or less.

[0051] In the aforementioned manufacturing condition, after direct quenching, dual phase heat treatment where the steel plate is heated to a temperature range from 650 °C to 800 °C at a heating rate of 0.1 °C/s to 1.5 °C/s, held at the same temperature range for 10 minutes or more and 60 minutes or less, and then subjected to quenching until reaching a temperature of 200 °C or lower at a cooling rate of 5 °C/s or more, may be performed.

Dual Phase Heat Treatment Heating Rate: 0.1 °C/s to 1.5 °C/s

[0052] By performing dual phase heat treatment, part of the microstructure transforms into austenite, and as crystal

grains become fine, tempering proceeds and thereby improves toughness. However, in a case where the dual phase heat treatment heating rate is less than 0.1 °C/s, austenite grains become coarse and toughness decreases. Further, since the microstructure generated after cooling also becomes coarse, toughness decreases. On the other hand, in a case where the heating rate exceeds 1.5 °C/s, induction heating facilities and the like are required, and costs increase.

Dual Phase Heat Treatment Temperature: 650 °C to 800 °C

[0053] In a case where the dual phase heat treatment temperature is lower than 650 °C, sufficient austenite reverse transformation does not occur, and refining effect of the microstructure cannot be obtained, and therefore a toughness improving effect cannot be obtained. Further, since the amount of austenite reverse transformation is small, C easily concentrates in austenite, and retained austenite increases. On the other hand, if the dual phase heat treatment temperature exceeds 800 °C, reverse transformation austenite becomes coarse and toughness decreases. Further, since the microstructure after cooling becomes coarse, toughness decreases. Further, manufacturing costs increase. Therefore, the dual phase heat treatment temperature is set to be in the range of 650 °C to 800 °C. In a case where the dual phase heat treatment temperature is high, the amount of reverse transformation austenite increases and the amount of concentration of C in reverse transformation austenite decreases compared to a case where the dual phase heat treatment temperature is low, and therefore the amount of martensite transformation caused by cooling after dual phase heat treatment increases, and the amount of retained austenite decreases. Therefore, the dual phase heat treatment temperature is preferably in the range of 720 °C to 780 °C.

Dual Phase Heat Treatment Holding Time: 10 minutes or more and 60 minutes or less

[0054] If the dual phase heat treatment holding time is less than 10 minutes, sufficient austenite reverse transformation does not occur and toughness improving effect caused by refinement of the microstructure cannot be sufficiently obtained. On the other hand, in a case where the dual phase heat treatment holding time exceeds 60 minutes, austenite grains become coarse and toughness decreases. Further, since the microstructure generated after cooling also becomes coarse, toughness decreases. Since C concentrates in austenite, retained austenite increases. Manufacturing costs increase as well. Therefore, the dual phase heat treatment holding time is set to be 10 minutes or more and 60 minutes or less.

Cooling Rate after Dual Phase Heat Treatment: 5 °C/s or more

[0055] In a case where the cooling rate is less than 5 °C/s, transformation from austenite to martensite phase will not occur, and a desirable strength and toughness cannot be obtained. Further, if the cooling rate is slow, the amount of solute C in ferrite decreases as the temperature is lowered, and therefore C moves to austenite from the ferrite surrounding the reverse transformed austenite, and C concentrates in the austenite and the austenite tends to remain as retained austenite. Therefore, the cooling rate is set to be 5 °C/s or more. Preferably, the cooling rate is 10 °C/s or more.

Cooling Stop Temperature after Dual Phase Heat Treatment: 200 °C or lower

[0056] In a case where the cooling stop temperature exceeds 200 °C, transformation to martensite phase will not occur uniformly in the steel plate, and a desirable strength and toughness cannot be obtained. Further, C concentrates in austenite and tends to remain as retained austenite. Therefore, the cooling stop temperature is set to be 200 °C or lower.

[0057] After performing the dual phase heat treatment and cooling until reaching 200 °C or lower, tempering is conducted in the manner previously described. That is, the steel plate is heated to a temperature range of 500 °C to 650 °C at a heating rate of 0.05 °C/s to 1.0 °C/s, and then subjected to tempering by holding the temperature at the same temperature range for 10 minutes or more and 60 minutes or less.

EXAMPLES

[0058] Next, Examples of the present invention will be described.

[0059] Molten steels with the chemical compositions shown in table 1 were obtained by steelmaking in a vacuum melting furnace and made into small-sized steel ingots (150 kg). These steels were heated in the conditions shown in table 2, subjected to hot rolling until reaching a plate thickness of 7 mm to 50 mm, and then subjected to quenching just after the rolling. Some of the steel plates were then subjected to tempering treatment. Regarding the rest of the steel plates, after quenching, they were subjected to dual phase heat treatment and then to tempering treatment. The obtained steel plates were each subjected to a tensile test, a Charpy impact test, a measurement of austenite volume fraction,

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and a measurement of grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more, in the manner described below.

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Table 1

Steel No.	Chemical Composition (mass%)															Remarks	
	C	Si	Mn	P	S	Al	Ni	Cr	Mo	Cu	V	Nb	Ti	B	Ca		REM
A	0.06	0.06	1.21	0.005	0.0011	0.035	5.7	-	-	-	-	-	-	-	-	-	Inventive Example
B	0.07	0.09	0.95	0.010	0.0009	0.033	7.2	-	-	-	-	-	-	-	-	-	Inventive Example
C	0.05	0.04	0.67	0.003	0.0012	0.029	7.8	-	-	0.12	-	-	-	-	-	-	Inventive Example
D	0.09	0.03	1.06	0.009	0.0010	0.028	6.9	0.12	-	-	0.043	-	-	-	0.0023	-	Inventive Example
E	0.03	0.05	0.88	0.004	0.0012	0.033	7.4	0.72	-	-	-	-	-	-	-	-	Inventive Example
F	0.02	0.06	1.36	0.008	0.0011	0.036	7.6	-	0.03	-	-	-	-	-	-	-	Inventive Example
G	0.05	0.08	0.63	0.006	0.0008	0.024	6.8	-	0.41	-	-	0.014	-	-	-	-	Inventive Example
H	0.04	0.07	0.97	0.011	0.0008	0.031	7.3	-	-	0.23	-	-	0.015	0.0012	-	0.0018	Inventive Example
I	0.06	0.05	1.02	0.005	0.0009	0.030	<u>4.9</u>	-	-	-	-	-	-	-	-	-	Comparative Example
The underlined values are outside the scope of the invention.																	

the rolling direction, a tensile test specimen having a parallel portion length of 30 mm, GL of 24 mm, a parallel portion diameter of 6ϕ was collected and subjected to a tensile test at room temperature. From the obtained stress-strain curve, tensile strength (TS) and yield strength (YS) were calculated. TS of 690 MPa or more and YS of 590 MPa or more are each considered as excellent TS and YS.

[Charpy Impact Test]

[0060] From each steel plate, at a position of a half the plate thickness, and in a direction orthogonal to the rolling direction, V-notch test specimens were collected in accordance with JIS Z2202 (1998) standard, and subjected to a Charpy impact test with 3 specimens per each temperature for each steel plate in accordance with JIS Z2242 (1998) standard, and absorbed energy at -196°C was measured to evaluate base material toughness. Steel plates with an average value of absorbed energy (vE_{-196}) of 3 specimens of 150 J or more are considered as having excellent base material toughness.

[Austenite Volume Fraction]

[0061] Samples collected from each steel plate at a position of a half the plate thickness in a direction orthogonal to the rolling direction were subjected to sub-zero treatment for 10 minutes in liquid nitrogen, and then the austenite volume fraction was measured by X-ray diffraction.

[Measurement of Grain Size of Crystal Grains]

[0062] Samples collected from each steel plate at a position of a half the plate thickness in a direction orthogonal to the rolling direction were polished and mirror finished, and subjected to EBSD analysis. Among the obtained data, a high-angle grain boundary where the orientation difference between two crystal grains contacting the grain boundary is 15° or more was selected and the average grain size by equivalent circle diameter of the region surrounded by the high-angle grain boundary was obtained.

[0063] The obtained results are shown in Table 2.

[0064] As shown in table 2, it has been confirmed that the inventive examples have excellent low-temperature toughness whereas the comparative examples outside the scope of the present invention have reduced low-temperature toughness.

[0065] [Table 2]

Table 2-1

Steel Plate No.	Steel No.	Plate Thickness (mm)	Heating Temp. (°C)	Rolling Reduction Ratio* (%)	Finisher Delivery Temp. (°C)	Start of Cooling** (s)	Temp. of Starting Cooling (°C)	Cooling Rate (°C/s)	Cooling Stop Temp. (°C)	Dual Phase Heat Treatment Rate (°C/s)	Dual Phase Heat Treatment Temp. (°C)	Dual Phase Heat Treatment Holding Time (min)	Cooling Rate after Dual Phase Heat Treatment (°C/s)	Cooling Stop Temp. after Dual Phase Heat Treatment (°C)	Tempering Heating Rate (°C)	Tempering Temp. (°C)	Tempering Holding Time (min)	Cooling Rate after Tempering (°C/s)	TS (MPa)	YS (MPa)	vE-196 (J)	Austenite Volume Fraction (%)	Ave. Grain Size by Equivalent Circle Diameter (μm)	Remarks
1	A	25	1050	50	780	34	760	25	150	0.34	750	20	22	100	0.18	570	20	0.4	698	642	225	0.2	2.3	Inventive Example
2	A	25	1050	60	750	35	730	25	150	0.37	640	20	22	150	0.19	580	20	0.4	711	682	121	2.0	5.6	Comparative Example
3	A	25	1050	55	730	38	710	25	150	-	-	-	-	-	0.17	560	15	0.4	701	650	156	0.3	3.9	Inventive Example
4	B	25	1050	0	900	30	880	25	150	0.33	740	30	22	75	0.18	570	15	0.4	722	699	120	0.2	5.8	Comparative Example
5	B	25	1050	55	800	34	780	25	150	0.33	740	20	22	125	0.19	580	20	0.4	740	715	235	0.2	1.9	Inventive Example
6	B	25	1050	55	800	34	780	25	150	0.33	630	30	22	125	0.19	580	20	0.4	810	785	56	2.6	3.6	Comparative Example
7	B	25	1050	55	800	34	780	25	150	0.33	740	120	22	125	0.19	580	20	0.4	822	765	98	1.8	5.1	Comparative Example
8	B	25	1050	55	800	34	780	25	150	0.33	740	30	2	100	0.19	580	20	0.4	752	722	110	1.9	3.2	Comparative Example
9	B	25	1050	55	800	34	780	25	150	0.33	700	30	20	350	0.19	580	20	0.4	720	735	103	1.9	2.5	Comparative Example
10	B	25	1000	60	750	36	730	25	150	0.31	730	20	22	100	0.19	580	25	0.4	731	685	220	0.3	1.4	Inventive Example
11	B	25	1000	55	740	37	720	25	150	0.29	720	15	22	150	0.19	580	20	0.4	705	615	245	0.3	1.1	Inventive Example
12	B	25	1000	50	800	33	780	25	100	-	-	-	-	-	0.18	570	40	0.4	715	682	160	0.1	4.3	Inventive Example
13	B	25	1050	60	740	37	720	25	150	-	-	-	-	-	0.20	590	15	0.4	735	719	152	0.1	4.0	Inventive Example
14	B	25	1000	55	910	39	870	25	100	-	-	-	-	100	0.19	580	20	0.4	730	705	116	0.3	7.3	Comparative Example
15	B	7	1000	65	800	18	780	40	100	0.64	740	10	37	150	0.53	590	20	1.2	745	719	225	0.2	1.3	Inventive Example

The underlined values are outside the scope of the invention.

*: Cumulative rolling reduction ratio at 870 °C or lower

**: Time from when finishing rolling is completed to when cooling is started

Table 2-2

Steel Plate No.	Steel No.	Plate Thickness (mm)	Heating Temp. (°C)	Rolling Reduction Ratio* (%)	Finisher Delivery Temp. (°C)	Start of Cooling** (s)	Temp. of Starting Cooling (°C)	Cooling Rate (°C/s)	Cooling Stop Temp. (°C)	Dual Phase Heat Treatment Heating Rate (°C/s)	Dual Phase Heat Treatment Temp. (°C)	Dual Phase Heat Treatment Holding Time (min)	Cooling Rate after Dual Phase Heat Treatment (°C/s)	Cooling Stop Temp. after Dual Phase Heat Treatment (°C)	Tempering Heating Rate (°C)	Tempering Temp. (°C)	Tempering Holding Time (min)	Cooling Rate after Tempering (°C/s)	TS (MPa)	YS (MPa)	VE-196 (J)	Austenite Volume Fraction (%)	Ave. Grain Size by Equivalent Circle Diameter (μm)	Remarks
16	B	50	1000	50	780	60	760	12	150	0.19	720	20	9	100	0.13	600	15	0.2	721	674	167	1.4	2.5	Inventive Example
17	C	25	1050	60	780	34	760	25	150	0.31	730	20	22	100	0.19	580	20	0.4	749	713	234	0.2	1.4	Inventive Example
18	C	25	1050	55	800	33	780	25	150	-	-	-	-	-	0.2	590	30	0.4	720	687	174	0.3	4.1	Inventive Example
19	C	25	1050	55	810	32	790	25	150	-	-	-	-	-	0.14	520	20	0.4	736	701	151	0.1	4.6	Inventive Example
20	C	50	1050	60	800	32	780	12	100	0.20	720	20	9	100	0.11	560	15	0.2	732	699	173	1.1	2.0	Inventive Example
21	D	25	1050	65	750	36	730	25	150	0.35	780	50	22	150	0.19	580	20	0.4	726	694	219	0.1	2.0	Inventive Example
22	E	25	1200	50	800	33	780	25	100	0.34	750	20	22	75	0.17	560	15	0.4	713	689	88	0.5	6.7	Comparative Example
23	E	25	950	55	790	33	770	25	150	0.33	740	20	22	100	0.18	570	20	0.4	720	692	239	0.2	1.2	Inventive Example
24	F	25	1050	60	770	35	750	25	150	0.31	730	30	22	100	0.2	590	20	0.4	721	675	215	0.1	1.5	Inventive Example
25	F	25	1050	30	800	33	780	25	150	0.19	720	20	22	100	0.19	580	30	0.4	712	653	102	0.3	5.7	Comparative Example
26	G	25	1050	65	730	37	710	25	100	0.18	730	20	22	150	0.13	600	25	0.4	716	665	258	0.2	1.0	Inventive Example
27	H	25	1050	55	750	36	730	25	100	0.29	700	20	22	150	0.19	580	20	0.4	721	653	182	1.2	1.4	Inventive Example
28	H	25	1050	60	780	34	760	25	150	-	-	-	-	-	0.23	630	20	0.4	702	643	176	0.2	4.1	Inventive Example
29	I	25	1050	60	800	33	780	25	150	0.34	760	20	22	100	0.16	540	20	0.4	675	621	76	0.1	1.9	Comparative Example

The underlined values are outside the scope of the invention.

*: Cumulative rolling reduction ratio at 870 °C or lower

**: Time from when finishing rolling is completed to when cooling is started

Table 2-2

Steel Plate No.	Steel No.	Plate Thickness (mm)	Heating Temp. (°C)	Rolling Reduction Ratio* (%)	Finisher Delivery Temp. (°C)	Start of Cooling** (s)	Temp. of Starting Cooling (°C)	Cooling Rate (°C/s)	Cooling Stop Temp. (°C)	Dual Phase Heat Treatment Heating Rate (°C/s)	Dual Phase Heat Treatment Temp. (°C)	Dual Phase Heat Treatment Holding Time (min)	Cooling Rate after Dual Phase Heat Treatment (°C/s)	Cooling Stop Temp. after Dual Phase Heat Treatment (°C)	Tempering Heating Rate (°C)	Tempering Temp. (°C)	Tempering Holding Time (min)	Cooling Rate after Tempering (°C/s)	TS (MPa)	YS (MPa)	vE-196 (J)	Austenite Volume Fraction (%)	Ave. Grain Size by Equivalent Circle Diameter (μm)	Remarks
16	B	50	1000	50	780	60	760	12	150	0.19	720	20	9	100	0.13	600	15	0.2	721	674	167	1.4	2.5	Inventive Example
17	C	25	1050	60	780	34	760	25	150	0.31	730	20	22	100	0.19	580	20	0.4	749	713	234	0.2	1.4	Inventive Example
18	C	25	1050	55	800	33	780	25	150	-	-	-	-	-	0.2	590	30	0.4	720	687	174	0.3	4.1	Inventive Example
19	C	25	1050	55	810	32	790	25	150	-	-	-	-	-	0.14	520	20	0.4	736	701	151	0.1	4.6	Inventive Example
20	C	50	1050	60	800	32	780	12	100	0.20	720	20	9	100	0.11	560	15	0.2	732	699	173	1.1	2.0	Inventive Example
21	D	25	1050	65	750	36	730	25	150	0.35	780	50	22	150	0.19	580	20	0.4	726	694	219	0.1	2.0	Inventive Example
22	E	25	1200	50	800	33	780	25	100	0.34	750	20	22	75	0.17	560	15	0.4	713	689	88	0.5	6.7	Comparative Example
23	E	25	950	55	790	33	770	25	150	0.33	740	20	22	100	0.18	570	20	0.4	720	692	239	0.2	1.2	Inventive Example
24	F	25	1050	60	770	35	750	25	150	0.31	730	30	22	100	0.2	590	20	0.4	721	675	215	0.1	1.5	Inventive Example
25	F	25	1050	30	800	33	780	25	150	0.19	720	20	22	100	0.19	580	30	0.4	712	653	102	0.3	5.7	Comparative Example
26	G	25	1050	65	730	37	710	25	100	0.18	730	20	22	150	0.13	600	25	0.4	716	665	258	0.2	1.0	Inventive Example
27	H	25	1050	55	750	36	730	25	100	0.29	700	20	22	150	0.19	580	20	0.4	721	653	182	1.2	1.4	Inventive Example
28	H	25	1050	60	780	34	760	25	150	-	-	-	-	-	0.23	630	20	0.4	702	643	176	0.2	4.1	Inventive Example
29	I	25	1050	60	800	33	780	25	150	0.34	760	20	22	100	0.16	540	20	0.4	675	621	76	0.1	1.9	Comparative Example

The underlined values are outside the scope of the invention.

*: Cumulative rolling reduction ratio at 870 °C or lower

**: Time from when finishing rolling is completed to when cooling is started

Claims

1. An Ni-containing steel plate having a chemical composition containing by mass% C: 0.01 % to 0.15 %, Si: 0.02 % to 0.20 %, Mn: 0.45 % to 2.00 %, P: 0.020 % or less, S: 0.005 % or less, Al: 0.005 % to 0.100 %, Ni: 5.0 % to 8.0 %, and the balance being Fe and incidental impurities, wherein the steel plate has a microstructure containing less than 1.7 % by volume fraction of retained austenite when cooled to liquid nitrogen temperature, and having an average grain size of crystal grains surrounded by high-angle grain boundaries with an orientation difference of 15° or more of 5 μm or less by equivalent circle diameter.
2. The Ni-containing steel plate according to Claim 1, wherein the chemical composition further contains by mass% at least one element selected from Cr: 1.00 % or less and Mo: 1.000 % or less.
3. The Ni-containing steel plate according to Claim 1 or 2, wherein the chemical composition further contains by mass% at least one element selected from Cu: 1.00 % or less, V: 0.100 % or less, Nb: 0.100 % or less, Ti: 0.100 % or less, and B: 0.0030 % or less.
4. The Ni-containing steel plate according to any one of Claims 1 to 3, wherein the chemical composition further contains by mass% at least one element selected from Ca: 0.0050 % or less and REM: 0.0050 % or less.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/004399

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C22C38/08(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)

C22C38/00-38/60, 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	WO 2012/005330 A1 (Nippon Steel Corp.), 12 January 2012 (12.01.2012), claims & JP 4975888 B2 & US 2013/0098514 A1 & EP 2592166 A1 & CN 102985576 A & KR 10-2013-0014069 A	1-4
A	JP 6-184630 A (Nippon Steel Corp.), 05 July 1994 (05.07.1994), claims (Family: none)	1-4
P, A	JP 2013-14811 A (Nippon Steel & Sumitomo Metal Corp.), 24 January 2013 (24.01.2013), claims (Family: none)	1-4

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

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"&" document member of the same patent family

Date of the actual completion of the international search
09 October, 2013 (09.10.13)Date of mailing of the international search report
22 October, 2013 (22.10.13)Name and mailing address of the ISA/
Japanese Patent Office

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REFERENCES CITED IN THE DESCRIPTION

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- **SUZUKI SHIGEHARU ; NAKANO YOSHIFUMI.** *Steel and Iron*, 1982, vol. 69 (5), S492 [0006]
- Handbook of Metal. Maruzen, 801 [0003]
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