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(54) **STEEL PRODUCT USABLE AT LOW TEMPERATURE AND METHOD FOR PRODUCTION THEREOF**

BEI NIEDRIGER TEMPERATUR VERWENDBARES STAHLPRODUKT UND HERSTELLUNGSVERFAHREN DAFÜR

PRODUIT DE TYPE ACIER UTILISABLE À BASSE TEMPÉRATURE ET PROCÉDÉ POUR LA PRODUCTION DE CELUI-CI

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Description

TECHNICAL FIELD

[0001] The present invention relates to a Ni-containing steel product usable at low temperatures and a method for producing the same. More specifically, the present invention relates to a Ni-containing steel suitable for structural material for low temperature storage tanks such as for LNG (Liquefied Natural Gas), and a method for producing the same.

BACKGROUND ART

[0002] Excellent fracture toughness is required for a steel which is usable at low temperature storage tanks for low temperature substances such as LNG, in view of safety. A representative example of the steel to meet such demand is a 9% Ni steel.

[0003] Conventionally, 9% Ni steels have experienced various improvements, including reduction in impurities such as P and S, reduction in C, and the use of a three-step heat treatment process, namely, "quenching (Q), lamellartizing (L) and tempering (T)." Also an attempt has been made with the addition of Mo as an effective alloying element in order to improve the strength and toughness of the Ni-containing steel. The purpose of the above QLT treatment and the addition of Mo are to increase the amount of retained austenite, which plays an important role in improvement in toughness. The state of the art as disclosed in patent documents can be summarized as follows.

[0004] Patent Document 1 discloses a 9% Ni steel, which contains 0.04 to 0.5% Mo and has a thickness of 40 mm or more, being produced by a three-step heat treatment process (QLT) or a direct quenching-lamellartizing (DQ-LT).

[0005] Patent Document 2 discloses a method for producing a 9% Ni steel having a thickness of 40 mm or more, by using a quenching-tempering treatment process (Q-T) or a direct quenching-tempering treatment process (DQ-T).

[0006] Recently the prices of steel products have been rapidly increasing for many reasons including the rising prices of alloying elements. The prices of the 9% Ni steels may particularly rise since they need a large amount of expensive alloying elements such as Ni. In order to curtail the steel cost, there is a need for development of a cost-reducing, low-Ni steel that has an equivalent or superior property, for example excellent toughness, to that of the 9% Ni steel. The state of the art in the low-Ni type steel usable at a low temperature includes the following.

[0007] Patent Document 3 discloses a steel usable at a low temperature containing 4.0 to 7.5% Ni and having an Ms of 370°C or lower. The above Patent Document 2 discloses a steel containing 7.5 to 10% Ni and a method for producing the same by using the DQ-LT process. Moreover, Patent Document 4 discloses a steel containing 5.5 to 10% Ni and a method for producing the same by using a continuous casting process.

[0008] In Patent Documents 5 and 6, steels containing 1.5 to 9.5% Ni and 0.02 to 0.08% Mo are disclosed.

[0009] JP 58-100624 discloses a steel containing <=0.10% C, 0.01-1.0% Si, 0.5-1.8% Mn, 1.1- 8.0% Ni, 0.001-0.20% Al, <=0.010% N, each <=0.013% P and S, 0.003-0.05% Nb, and if necessary, containing <=0.08%>=1 kind among B, Ti, Zr, V, Ta, Ca, rare earth elements, <=1.8%>=1 kind among Cu, Cr, Mo, W and the balance Fe is cast. Such ingot is roughly rolled according to need, and the slab is heated to 800- 1,180 deg.C. Thereafter, the slab is subjected to finish rolling at <=70% cumulative draft in the temp. region of two phases of austenite+ferrite or bainite. The slab is then quickly cooled and tempered. Thus, the Ni steel having high performance for stopping of brittle cracking and having excellent toughness is obtained.

[Patent Document 1] Japanese Laid-open Patent Publication No. 04-371520.
[Patent Document 2] Japanese Laid-open Patent Publication No. 06-184630.
[Patent Document 3] Japanese Laid-open Patent Publication No. 06-136483.
[Patent Document 4] Japanese Laid-open Patent Publication No. 07-90504.
[Patent Document 5] Japanese Laid-open Patent Publication No. 09-302445.
[Patent Document 6] Japanese Laid-open Patent Publication No. 2002-129280.

[0010] However, Patent Document 1 gives no detailed conditions for rolling and provides no steel having equivalent properties to those of the steel of the present invention, described later, when the Ni content is more than 6% to less than 8%.

[0011] Patent Document 2 describes a steel containing 7.52 % Ni as a comparative example. Because of an unsuitable chemical composition and producing method, the amount of retained austenite is 1.5%, which is not enough to realize the equivalent properties to those of the 9% Ni steel, thus being referred to as a comparative example.

[0012] Patent Document 3 discloses a method in order to improve toughness in the weld heat affected zone (HAZ). However, it fails to disclose a chemical composition design and a producing method for obtaining base material properties comparable to those of the 9% Ni steel. Moreover, the base material properties themselves are nowhere disclosed in the said document.

[0013] The above Patent Document 2 describes rolling reductions of 20 to 90% at 700 to 900°C, which is, however, not a rolling reduction per pass. The toughness of the steel thus produced falls short of 250 J at -196°C.

[0014] Patent Document 4 describes components capable of continuous casting. However the said patent document fails to disclose a method for producing a base material and its properties. Further, the minimum content of Ni disclosed concretely in the said document is 9.08%, and thus no means are disclosed in order to obtain base material properties equivalent to those of the 9% Ni steel with a low Ni content.

[0015] Both Patent Documents 5 and 6 disclose the DQ-LT process that discontinues water cooling at 400°C or lower. However, no conditions for the heating temperature and rolling are disclosed. Further, both of the documents disclose no properties for a Ni content of around 7%. Instead, inventive examples of the documents show that as a base material property, the 9% Ni steel has a vTs of lower than -196°C, whereas the vTs of 5.0% Ni steel is -160°C and that of 1.5% Ni steel is -125°C. Thus, the decrease in Ni content has a direct adverse influence on toughness.

[0016] As mentioned above, all the said patent documents do not concretely disclose a steel having an equivalent property to that of the 9% Ni steel with a Ni content lower than the 9% Ni steel, and a method for producing the said low-Ni steel.

DISCLOSURE OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0017] The objective of the present invention is to provide a steel product having equivalent properties to those of the 9% Ni steel with a Ni content lower than the 9% Ni steel, and also to provide a method for producing the same.

[0018] The present inventors, in an attempt to accomplish the above objective, conducted an extensive study on the above-described prior arts. As a result, the inventors have found that the prior arts are insufficient in the refinement of the microstructure and also insufficient in securing the amount of retained austenite. That is to say, there is a need for the means to make the base material microstructure itself fine while at the same time stabilizing austenite with a Ni content lower than the 9% Ni steel.

[0019] The following are newly found means to stabilize austenite with a Ni content lower than the 9% Ni steel, in addition to the conventionally known addition of a minute amount of Mo.

[0020] The first means is to introduce a lattice defect in the untransformed austenite in order to lower the Mf, in which the martensite transformation finishes. The transformation from austenite to martensite is a shearing type transformation, which involves dislocation migration, and the lattice defect in the austenite serves as an obstruction to dislocation migration. This procedure impedes the finishing of the shearing type transformation from austenite to martensite, thereby lowering the Mf. Lowering the Mf increases the amount of the retained austenite at room temperature.

[0021] The second means is related to refinement of the untransformed austenite phase. In the shearing type transformation from untransformed austenite to martensite, the minimum unit (lath) of instantaneously formed martensite is approximately 0.5 to 1 μm in the thickness direction. This transformation in reality involves an increase in volume. This leads to the finding that if the size of the untransformed austenite phase is equal to or smaller than the minimum unit of the instantaneously formed martensite, the volume-increasing martensite transformation is significantly inhibited and consequently the said untransformed austenite phase exists more stable than would be expected from the actual amount of the chemical composition.

[0022] The retained austenite in a steel of low Ni content thus obtained is not only comparable in the amount to that was obtained in the conventional quenched-tempered material obtained from the 9% Ni steel, but also is characterized in the following respect. As opposed to the retained austenite in the conventional quenched-tempered material obtained from the 9% Ni steel, which is an acicular structure in a two-dimensional view and a thin plate in a three-dimensional view and exhibits a large aspect ratio, the austenite in the low Ni steel is an extremely fine granular structure in a two-dimensional view, even though the overall amount of the austenite is substantially the same as that of the austenite in the 9% Ni steel. For this reason, the retained austenite can be secured stably even with a low Ni content.

[0023] In order to introduce a lattice defect (dislocation) to the untransformed austenite, and at the same time making the untransformed austenite phase fine, the conditions for heating, rolling and cooling are important. A high rolling reduction at a low temperature is known to introduce a large amount of lattice defects (dislocations) and to make the resulting microstructure fine. For the microstructure refinement, the addition of Nb as a trace element is particularly effective. This is based on the fact that the finely precipitated Nb(C,N) impedes the dislocation migration and consequently the lattice defect (dislocation) density in the austenite increases.

[0024] The present invention has been made on the basis of the above findings. The gists of the present invention are steel products and methods for producing the said steel products described in the following.

[0025]

(1) A steel product usable at a low temperature, characterized by consisting of,

by mass percent, C: 0.01 to 0.1%, Si: 0.005 to 0.6%, Mn: 0.3 to 2%, Ni: more than 6% to less than 8%, sol.Al: 0.005 to 0.05%, N: 0.0005 to 0.005%, optionally one or more selected from among Mo: 0.1% or less, Cu: 2.0% or less, Cr: 0.8% or less, V: 0.08% or less, Nb: 0.08% or less, Ti: 0.03% or less, B: 0.0030% or less, Ca: 0.0050% or less and Mg: 0.0050% or less and the balance: Fe and impurities, with the proviso that the following formula (1) is satisfied; it contains austenite of 1.7% or more in area ratio and cementite, and the said austenite has an aspect ratio of 3.5 or less in average and an average circle-equivalent grain diameter of 1.0 μm or less, and the said cementite has an aspect ratio of 5.0 or less in average and an average circle-equivalent diameter of 0.6 μm or less:

$$20C + 2.4Mn + Ni + 0.5Cu + 0.5Mo \geq 10 \quad \cdots\cdots \quad (1),$$

wherein each element symbol in the formula (1) represents the content (by mass %) of the element concerned.

(2) A method for producing a steel product usable at a low temperature, which comprises the following steps:

heating a steel slab, which has the chemical composition specified in the (1) above, to a temperature region of 850 to 1050°C;
rolling the said steel slab in a temperature region of 700 to 830°C at a rolling reduction of 5% or more per pass and a cumulative rolling reduction of 25% or more;
finishing the rolling within a temperature region of 700 to 800°C;
immediately after the said roll finishing, performing an accelerated cooling on the resulting product to a temperature region of 200°C or lower, at a cooling rate of 10°C/s or higher from the starting temperature of the said accelerated cooling to at least 600°C, and at a cooling rate of 5°C/s or higher from 600°C to 200°C; and
after the said accelerated cooling, tempering the resulting product at a temperature of 650°C or lower.

(3) The method for producing a steel product usable at a low temperature according to the (2) above, which further contains the following lamellartizing treatment between the accelerated cooling after the rolling and tempering at 650°C or lower;
heating the resulting product in a temperature region of 600 to 800°C and then cooling the same to a temperature region of 200°C or lower, at a cooling rate of 5°C/s or higher.

BEST MODE FOR CARRYING OUT THE INVENTION

[0026] The above-specified chemical compositions, microstructures and production conditions of the steel product of the present invention will next be described in detail. In the following description, the symbol "%" for the content of each component of the steel product represents "% by mass".

C: 0.01 to 0.1%

[0027] C is an effective element for lowering the Mf and stabilizing the retained austenite. However, C hardens the martensite matrix itself and thus causes a deterioration of toughness, overwhelming its improvement realized by an increase in the amount of the austenite. Therefore, C is contained to an amount necessary to secure strength or somewhat more than that amount, but it is vital to avoid an excessive C content that might cause a deterioration of toughness. If the content of C is less than 0.01%, the strength is insufficient. On the other hand, if the content of C exceeds 0.1%, the toughness is deteriorated. Accordingly, the content of C is set to 0.01 to 0.1%. A more preferable C content range is 0.03 to 0.07%.

Si: 0.005 to 0.6%

[0028] Si is effective as a deoxidizing element. Also Si is effective as an element to inhibit the precipitation of cementite and improve the stability of the austenite in tempering. However, an excessive content of Si causes a deterioration of toughness. Therefore, the content of Si is set to 0.005 to 0.6%. A more preferable Si content range is 0.03 to 0.5% and further more preferable content range of Si is 0.1 to 0.3%.

Mn: 0.3 to 2%

[0029] Mn is effective for lowering the Mf and stabilizing the austenite, and the more the Mn content is, the more austenite can be obtained. However, if the content of Mn is excessive, the toughness of martensite matrix is deteriorated. Therefore, the content of Mn is set to 0.3 to 2%. A more preferable lower limit of Mn content is 0.5% and further an even more preferable lower limit of Mn content is 0.7%. A more preferable upper limit of Mn content is 1.5% and further an even more preferable upper limit of Mn content is 1.0%.

Ni: more than 6% to less than 8%

[0030] In the present invention, Ni is the most important element in order to enhance the strength of the steel and to contribute to the stability of the austenite. A more Ni content level is preferable, since the more the Ni content is, the higher strength can be obtained and moreover the lower Mf, which increases the amount of the retained austenite, can be gained. However, a large amount of Ni causes an increase in cost, and therefore the content of Ni is set to less than 8%. A more preferable upper limit of Ni content is 7.5%. On the other hand, it is necessary to contain more than 6% Ni in order to obtain a steel product of equivalent properties to that of the 9% Ni steel, which is one of the objectives of the present invention. A more preferable lower limit of Ni content is 6.5%.

sol.Al: 0.005 to 0.05%

[0031] Like Si, Al is effective as a deoxidizing element and as an element in order to inhibit precipitation of cementite and improve the stability of the austenite in tempering. Further, Al forms AlN with N, and the said AlN has an effect on refinement of the austenite grains during heating. Therefore, the content of 0.005% or more of Al as sol.Al is needed. However, an excessive content of Al causes a deterioration of toughness. Accordingly, the content of Al as sol.Al is set to 0.005 to 0.05%. A more preferable content range of sol.Al is 0.02 to 0.04%.

N: 0.0005 to 0.005%

[0032] N is an element to contribute to the stability of the austenite and therefore it is preferably contained. Further, N forms AlN with Al, and the said AlN has an effect on refinement of the austenite grains during heating. In order to obtain the said effects, the content of 0.005% or more of N is needed. On the other hand, the content of N must be set to 0.005% or less, since an excessive content of N causes a deterioration of the martensite matrix. A more preferable content range of N is 0.002 to 0.004%.

[0033] One of the steel products of the present invention is a steel product, which contains the above-described components and the balance of Fe and impurities. Another steel product of the present invention is a steel product containing, in addition to the above-described components, one or more selected from among Mo, Cu, Cr, V, Nb, Ti, B, Ca and Mg. These components will be described below.

Mo: 0.1% or less

[0034] In the low temperature region, Mo is an austenite stabilizing element and effective for increasing the amount of the austenite. In order to obtain this effect, it is preferable to contain 0.01% or more of Mo. On the other hand, the content of Mo must be set to 0.1% or less, since if the content of Mo exceeds 0.1% it causes a deterioration of toughness of the martensite matrix. A more preferable lower limit of Mo content is 0.02%. A more preferable upper limit of Mo content is 0.06% and further more preferable upper limit of Mo content is 0.05%.

Cu: 2.0% or less

[0035] The dissolved Cu in the matrix is effective to stabilize the austenite. Therefore, in order to obtain the said effect, it is preferable to contain 0.05% or more of Cu. Although Cu is effective for enhancing strength, it deteriorates toughness, because the dissolved Cu precipitates in the form of ε-Cu by tempering treatment. Accordingly, the upper limit of Cu content is set to 2.0%.

Cr: 0.8% or less

[0036] Cr is an element effective for enhancing strength. In order to obtain this effect, it is preferable to contain 0.05% or more of Cr. However, if the content of Cr exceeds 0.8%, toughness is deteriorated. Therefore, the upper limit of Cr content is set to 0.8%.

V: 0.08% or less

[0037] V is an element effective for enhancing steel strength, that is, it forms precipitates on tempering treatment and strengthens the steel. In order to obtain this effect, the content of V is preferably set to 0.005% or more. However, if the content of V exceeds 0.08%, the said precipitates become excessive and they deteriorate toughness. Therefore, the content of V is set to 0.08% or less.

Nb: 0.08% or less

[0038] Nb enlarges the non-recrystallization temperature region in rolling and thus is effective for the refinement of microstructures after rolling and enhancement of toughness. In order to obtain these effects, it is preferable to contain 0.005% or more of Nb. However, if the content of Nb exceeds 0.08%, toughness is deteriorated. Accordingly, the upper limit of Nb content is set to 0.08%.

Ti: 0.03% or less

[0039] Ti is an element effective for preventing cracks of slab. In order to obtain this effect, it is preferable to contain 0.005% or more of Ti. However, if the Ti content exceeds 0.03%, toughness is deteriorated. Therefore, the upper limit of Ti content is set to 0.03%.

B: 0.0030% or less

[0040] B is an element effective for enhancing strength. In order to obtain this effect, it is preferable to contain 0.0002% or more of B. However, if the B content exceeds 0.0030%, toughness is deteriorated. Accordingly, the upper limit of B content is set to 0.0030%.

Ca: 0.0050% or less

[0041] Ca is an element effective for improving toughness. In order to obtain this effect, it is preferable to contain 0.0002% or more of Ca. However, if the Ca content exceeds 0.0050%, toughness is deteriorated. Therefore, the upper limit of Ca content is set to 0.0050%.

Mg: 0.0050% or less

[0042] Mg is an element effective for improving toughness. In order to obtain this effect, the content of Mg is preferably set to 0.0005% or more. However, if the Mg content exceeds 0.0050%, toughness is deteriorated. Therefore, the upper limit of Mg content is set to 0.0050%.

$20C + 2.4Mn + Ni \geq 10$ or $20C + 2.4Mn + Ni + 0.5Cu + 0.5Mo \geq 10$

[0043] In order to obtain an equivalent toughness to that of the 9% Ni steel by using a steel product having a lower Ni content, it is important to secure an amount of the retained austenite. It is also important to add chemical components which can stabilize the austenite, although the amount of the retained austenite which can be obtained varies depending on the conditions of heating, rolling, and heat treatment. In order to stabilize the austenite, the value of "20C + 2.4Mn + Ni" or "20C + 2.4Mn + Ni + 0.5Cu + 0.5Mo" must be 10 or more. A more preferable lower and the upper limit of the said value are 10.5 and 12, respectively.

Amount of austenite:

[0044] A certain amount of the austenite in the steel product serves as important means to improve toughness with a low Ni content. In order to obtain a low Ni steel with equivalent toughness to that of the 9% Ni steel, it must contain austenite of 1.7% or more in area ratio. A more preferable lower limit of the amount of the austenite is 2.0% and further more preferable its lower limit is 3.0%. The upper limit of the amount of the austenite is not specified, since the more the austenite there is, the more effectively the toughness is improved. However, an amount that exceeds 40% causes a lack of strength. Therefore, it is preferable to set the upper limit of the amount of the austenite at 40%.

Configuration of austenite:

[0045] In order to stabilize the austenite while keeping a low Ni content, it is necessary that the untransformed austenite phase is fine. This requires the austenite to be fine granular structure, with an aspect ratio of 3.5 or less in average and an average circle-equivalent grain diameter of 1.0 μm or less. A preferable aspect ratio is 2.5 or less. The above circle-equivalent grain diameter refers to the diameter of a circle of an equivalent area to the projected area of the austenite. For the circle-equivalent grain diameter, a microstructure which is observed as a result of cutting off the steel product along a plane parallel to the rolling direction (vertical direction to the thickness) is measured. The projected area of the austenite can be measured with an image analyzing apparatus.

Configuration of cementite:

[0046] Cementite precipitates from the martensite matrix and is also formed by a decomposition of the untransformed austenite. The above precipitation of cementite decreases strength and deteriorates toughness. Therefore, it is necessary to keep the size of cementite at 0.6 μm or less in the average circle-equivalent diameter. The average circle-equivalent diameter of cementite is the same as described above. That is, regarding the circle-equivalent diameter of cementite, the measurement is made for cementite instead of austenite grain.

[0047] Next, a method for producing the above-described steel product will be described.

(1) Heating of steel slab

[0048] In order to improve the toughness of a steel product, it is important to refine the prior-austenite grains, that is, the austenite grains in the steel slab prior to rolling. The refinement of the austenite grains also contributes to increasing the amount of the retained austenite. Therefore, the heating temperature of the steel slab prior to rolling is set at 850 to 1050°C. Heating at lower than 850°C causes a lack of strength, on the other hand, heating at higher than 1050°C deteriorates toughness. It is preferable to set the said heating temperature at 900 to 1000°C.

(2) Rolling

[0049] In order to refine the microstructure and increase the amount of austenite, sufficient rolling needs to be carried out in the non-recrystallization temperature region of austenite. That is to say, the rolling, which has a rolling reduction of 5% or more per pass and a cumulative rolling reduction of 25% or more, in a temperature region of 700 to 830°C is necessary for introducing a lattice defect (dislocation) in austenite in the non-recrystallization temperature region thereof and thereby inhibiting the untransformed austenite from transforming to martensite. The said rolling must be finished within a temperature region of 700 to 800°C. If the finishing temperature is lower than 700°C, the anisotropy of the steel product becomes noticeable. If the finishing temperature exceeds 800°C, toughness is deteriorated.

(3) Cooling

[0050] After the above roll finishing, it is necessary to perform an accelerated cooling on the resulting product to a temperature region of 200°C or lower. In the accelerated cooling, a cooling rate of 10°C/s or higher from the starting temperature of the said accelerated cooling to at least 600°C is required. The purpose of this is to maximize the amount of the lattice defects (dislocations) which are introduced in finish rolling. Also in order to obtain a martensite phase, a cooling rate of 5°C/s or higher from the said starting temperature of the accelerating cooling to 200°C is required. If the said accelerated cooling is finished at a temperature higher than 200°C, martensite cannot be sufficiently obtained which results in deterioration of strength. The time from the above-mentioned roll finishing to the starting of the above accelerated cooling is as short as possible. A preferable period of time from the above roll finishing to the starting of the above accelerated cooling is 30 seconds or less.

(4) Tempering

[0051] After the said accelerating cooling, the resulting product must be tempered at a temperature of 650°C or lower. The martensite, which was formed by the cooling treatment, that is, quenching, can be tempered by this treatment. By the said tempering treatment, it is possible to adjust strength and at the same time to improve toughness. If the tempering treatment is carried out at a temperature higher than 650°C, strength is deteriorated.

(5) Heating in two phase region (Lamellartizing)

[0052] In order to further increase the amount of the retained austenite, it is preferable to perform heating in the two phase region of ferrite and austenite before tempering treatment. The lamellartizing is necessary to heat the resulting product in a temperature region of 600 to 800°C and then to cool the same to a temperature region of 200°C or lower, at a cooling rate of 5°C/s or higher. A more preferable heating temperature region of the said lamellartizing is 680 to 750°C.

EXAMPLES

[0053] Sample materials having chemical compositions shown in Table 1 were melted to prepare steel plates of 20 mm thick. On the rolling process each rolling reduction per pass was 5% or more. The producing conditions of them are shown in Table 2. From a portion of one-fourth thickness (1/4 t portion) of each of the obtained steel plates, tensile strength test specimens and Charpy test specimens were cut off. The amount of austenite was measured by an X-ray diffraction method. For the size and the configuration of austenite and cementite, a transmission electron microscope was used to observe 20 views of each of the austenite and the cementite at a magnification of 40000 times in order to obtain the average aspect ratio of each. The average circle-equivalent grain diameter of austenite and the average circle-equivalent diameter of cementite were obtained with an image processing apparatus. The results of these measurements are shown in Table 3.

[0054] [Table 1]

[0055] [Table 2]

[0056] [Table 3]

[0057] The "inventive examples" shown in Table 3 are those having the chemical composition specified in the present invention and produced by the method according to the present invention. The inventive examples also satisfy the above-described formulas (1) and (2), and the inventive conditions for the area ratio and configuration of austenite and moreover the configuration of cementite. Each of the inventive examples has a YS of 585 MPa or more, a TS of 690 to 825 MPa, and a Charpy impact energy of 250 J or more at -196°C.

[0058] Toughness is particularly improved to have an absorbed energy of 290 J or more in the cases (testing numbers T2, T4, T6, T7, T8, T10, T13 and T15) where the examples, which contain austenite of 1.7% or more in area ratio, satisfy both of the two microstructural requirements: (1) the austenite has an aspect ratio of 3.5 or less in average and an average circle-equivalent grain diameter of 1.0 μm or less, and (2) cementite has an aspect ratio of 5.0 or less in average and an average circle-equivalent diameter of 0.6 μm or less.

[0059] To the contrary, the comparative examples, where any one of the conditions such as chemical composition is outside the inventive ranges, have low impact energy, resulting in insufficient low temperature toughness.

[0060] As for the mechanical properties of the 9% Ni steel of the same thickness produced by the conventional method (quenching-tempering), YS is 610 MPa, TS is 720 MPa and the Charpy absorbed energy at -196°C is 280 J. This indicates that the steel of the present invention, in spite of its lower Ni content, has equivalent properties to those of the 9% Ni steel.

INDUSTRIAL APPLICABILITY

[0061] The present invention provides a steel product that has equivalent or superior mechanical properties to those of the steel containing 9% Ni even though it has a low Ni content of more than 6% to less than 8%. The steel product has excellent low temperature toughness as well as low cost, and therefore it is suitable for structural material for storage tanks for low temperature substances such as LNG.

Table 1

Classification	Steel No.	Chemical composition (mass %, The balance: Fe and impurities)														
		C	Si	Mn	Cu	Ni	Cr	Mo	V	Nb	Ti	B	Al	N	Ca	Mg	Value of formula (1) or (2)
Inventive ex.	1	0.04	0.22	1.11	-	7.1	-	-	-	-	-	-	0.031	0.0035	-	-	10.6
	2	0.03	0.23	1.26	-	6.9	-	0.05	-	-	-	-	0.029	0.0034	-	-	10.5
	3	0.06	0.26	0.93	-	7.2	-	-	-	-	-	-	0.035	0.0046	-	-	10.6
	4	0.05	0.12	1.24	-	7.1	-	-	-	-	-	-	0.034	0.0034	-	-	11.1
	5	0.06	0.05	1.31	-	7.8	-	0.02	-	-	-	-	0.007	0.0029	-	-	12.2
	6	0.04	0.24	1.08	0.89	7.5	-	0.08	-	-	-	-	0.026	0.0008	-	-	11.4
	7	0.06	0.23	0.82	-	6.9	-	-	0.03	-	-	-	0.031	0.0047	-	-	10.1
	8	0.07	0.27	1.11	-	6.2	-	0.05	-	-	-	-	0.034	0.0031	-	-	10.3
	9	0.02	0.56	1.84	1.22	6.2	-	-	-	-	-	-	0.047	0.0028	-	-	11.6
	10	0.10	0.07	0.46	-	7.2	-	-	-	-	-	-	0.031	0.0034	-	-	10.3
	11	0.06	0.24	1.26	-	6.9	-	0.06	0.01	-	-	-	0.021	0.0035	-	-	11.2
	12	0.05	0.12	1.25	-	7.2	0.1	-	-	-	-	-	0.031	0.0031	-	-	11.3
	13	0.04	0.21	1.31	-	7.8	-	-	-	0.016	0.009	-	0.026	0.0029	-	-	11.7
	14	0.03	0.2	1.42	-	6.1	-	-	-	-	-	0.0012	0.002	0.0041	-	0.0024	10.1
	15	0.05	0.19	1.02	-	6.9	-	-	-	-	-	-	0.005	0.0023	0.0022	-	10.3
Comparative ex.	16	0.12 *	0.12	1.31	-	7.1	-	-	-	-	-	-	0.033	0.0031	-	-	12.6
	17	0.06	0.72 *	1.46	-	7.0	-	-	-	-	-	-	0.034	0.0032	-	-	11.7
	18	0.05	0.24	2.60 *	-	7.0	-	0.05	-	-	-	-	0.024	0.0044	-	-	14.3
	19	0.04	0.23	1.31	-	5.3*	-	0.05	-	-	-	-	0.033	0.0036	-	-	9.3*
	20	0.06	0.22	1.23	-	7.2	-	0.05	-	-	-	-	0.065*	0.0038	-	-	11.4
	21	0.07	0.24	1.15	-	6.8	-	0.05	-	-	-	-	0.031	0.0067*	-	-	11.0
	22	0.07	0.22	1.23	-	6.9	-	0.12*	-	-	-	-	0.007	0.0024	-	-	11.3
	23	0.06	0.21	1.19	-	6.8	-	-	0.09*	-	-	-	0.032	0.0033	-	-	10.9

Note: A mark * denotes out of the chemical composition spesified in the invention.

Table 2

Classification	Producing condition	Heating temperature of steel slab (°C)	Cumulative rolling reduction (%)	Roll finishing temperature (°C)	Finishing temperrature of accelerated cooling (°C)	Cooling rate (°C/s)		Reheating temperature (°C)	Tempering temperature (°C)
						over 200°C	over 600°C		
Inventive ex.	A	1050	42	760	170	17	26	-	580
	B	950	33	720	150	13	22	-	560
	C	1050	42	780	170	16	24	760	540
	D	900	25	700	170	12	21	740	520
	E	1000	33	740	150	16	25	-	540
Comparative ex.	F	*1150	33	760	170	16	26	-	560
	G	1050	*19	740	150	17	27	-	580
	H	1000	33	*820	170	12	25	760	540
	I	950	25	740	*420	16	27	-	*670
	J	950	33	720	170	*3	*7	-	580

Note: A mark * denotes out of the condition specified in the invention.

Table 3

Classification	Testing No.	Steel No.	Producing condition	Austenite			Cementite		Mechanical properties		
				Area ratio (%)	Aspect ratio	Circle-equivalent grain diameter (μ	Aspect ratio	Circle-equivalent diameter (μm)	YS(MPa)	TS(MPa)	vE-196 (J)
Inventive ex.	T1	1	B	2.3	*3.7	*1.2	2.6	0.07	627	718	279
	T2	2	D	4.3	1.1	0.13	2.1	0.05	604	700	291
	T3	3	A	2.3	2.7	0.74	*7.2	1.50	654	754	269
	T4	4	D	6.8	1.1	0.13	2.1	0.05	631	753	292
	T5	5	B	3.9	*4.2	*1.3	2.6	0.07	686	807	256
	T6	6	C	8.3	2.7	0.74	3.3	0.11	618	746	295
	T7	7	B	1.8	1.7	0.30	2.6	0.07	664	764	298
	T8	8	B	2.0	1.7	0.30	2.6	0.07	659	759	298
	T9	9	D	12.3	1.1	0.13	*6.4	0.08	594	721	278
	T10	10	E	2.0	2.6	0.67	3.2	0.10	698	811	299
	T11	11	D	7.1	1.1	0.13	*5.4	0.09	651	782	262
	T12	12	E	4.2	*4.6	*1.32	2.7	0.08	694	810	253
	T13	13	D	8.6	2.9	0.62	2.9	0.06	645	766	298
	T14	14	C	2.9	*5.1	*1.22	2.1	0.07	682	812	266
	T15	15	D	4.6	3.1	0.60	2.6	0.08	621	741	296
Comparative ex.	T16	1	F	2.3	*5.2	*2.70	*6.9	*0.81	627	718	*65
	T17	4	G	*1.2	*6.0	*3.63	*6.4	*0.88	658	753	*76
	T18	6	H	*1.4	2.6	0.67	3.2	0.10	653	746	*104
	T19	9	I	*1.3	2.3	0.52	3.0	0.09	*569	*670	*136
	T20	11	J	*1.0	1.7	0.30	2.6	0.07	682	782	*89
	T21	16	D	2.7	2.7	0.74	3.3	0.11	702	820	*92
	T22	17	C	3.2	2.7	0.74	3.3	0.11	678	792	*89
	T23	18	B	2.8	1.7	0.30	2.6	0.07	700	818	*99
	T24	19	D	*0.3	1.1	0.13	2.1	0.05	633	712	*112
	T25	20	A	2.3	2.7	0.74	3.3	0.11	674	780	*96
	T26	21	E	2.4	2.6	0.67	3.2	0.10	676	783	*90
	T27	22	C	4.6	2.7	0.74	3.3	0.11	676	798	*89
	T28	23	A	2.8	2.7	0.74	3.3	0.11	725	852	*138

Note: A mark * denotes short of the target value of the present invention.

Claims

1. A steel product usable at a low temperature, **characterized by** consisting of, by mass percent, C: 0.01 to 0.1%, Si: 0.005 to 0.6%, Mn: 0.3 to 2%, Ni: more than 6% to less than 8%, sol.Al: 0.005 to 0.05%, N: 0.0005 to 0.005%, optionally one or more selected from among Mo: 0.1% or less, Cu: 2.0% or less, Cr: 0.8% or less, V: 0.08% or less, Nb: 0.08% or less, Ti: 0.03% or less, B: 0.0030% or less, Ca: 0.0050% or less and Mg: 0.0050% or less and the balance: Fe and impurities, with the proviso that the following formula (1) is satisfied; it contains austenite of 1.7% or more in area ratio and cementite, and the said austenite has an aspect ratio of 3.5 or less in average and an average circle-equivalent grain diameter of 1.0 μm or less, and the said cementite has an aspect ratio of 5.0 or less in average and an average circle-equivalent diameter of 0.6 μm or less:

$$20C + 2.4Mn + Ni + 0.5Cu + 0.5Mo \geq 10 \cdots\cdots (1),$$

wherein each element symbol in the formula (1) represents the content (by mass %) of the element concerned.

2. A method for producing a steel product usable at a low temperature, which comprises the following steps:

   heating a steel slab, which has the chemical composition specified in claim 1, to a temperature region of 850 to 1050°C;
   rolling the said steel slab in a temperature region of 700 to 830°C at a rolling reduction of 5% or more per pass and a cumulative rolling reduction of 25% or more;
   finishing the rolling within a temperature region of 700 to 800°C;
   immediately after the said roll finishing, performing an accelerated cooling on the resulting product to a temperature region of 200°C or lower, at a cooling rate of 10°C/s or higher from the starting temperature of the said accelerated cooling to at least 600°C, and at a cooling rate of 5°C/s or higher from 600°C to 200°C; and
   after the said accelerated cooling, tempering the resulting product at a temperature of 650°C or lower.

3. The method for producing a steel product usable at a low temperature according to claim 2, which further contains the following lamellartizing treatment between the accelerated cooling after the rolling and the tempering at 650°C or lower;
   heating the resulting product in a temperature region of 600 to 800°C and then cooling the same to a temperature region of 200°C or lower, at a cooling rate of 5°C/s or higher.

Patentansprüche

1. Bei niedriger Temperatur verwendbares Stahlprodukt, **dadurch gekennzeichnet, dass** es, in Masseprozent, aus folgendem besteht

   C. 0,01 bis 0,1 %, Si: 0,005 bis 0,6 %, Mn: 0,3 bis 2 %, Ni: mehr als 6 % bis weniger als 8 %; Al fest: 0,005 bis 0,05 %, Ni: 0,0005 bis 0,005 %, gegebenenfalls einem oder mehreren, ausgewählt aus Mo: 0,1 % oder weniger, Cu: 2,0 % oder weniger, Cr: 0,8 % oder weniger, V: 0,08 % oder weniger, Nb: 0,08 % oder weniger, Ti: 0,03 % oder weniger, B: 0,0030 % oder weniger, Ca: 0,0050 % oder weniger und Mg: 0,0050 % oder weniger, Rest: Fe und Verunreinigungen, mit der Maßgabe, dass die folgende Formel (1) erfüllt ist; es Austenit von 1,7 % oder mehr in einem Flächenverhältnis und Zementit enthält, und der Austenit ein Aspektverhältnis von 3,5 oder weniger im Durchschnitt und einen durchschnittlichen kreisäquivalenten Korndurchmesser von 1,0 μm oder weniger aufweist, und der Zementit ein Aspektverhältnis von 5,0 oder weniger im Durchschnitt und einen durchschnittlichen kreisäquivalenten Korndurchmesser von 0,6 μm oder weniger aufweist:

$$20C + 2{,}4Mn + Ni + 0{,}5Cu + 0{,}5Mo \geq 10 \quad (1)$$

   wobei jedes Elementsymbol in der Formel (1) den Gehalt (Masse-%) des jeweiligen betroffenen Elements darstellt.

2. Verfahren zur Herstellung eines bei niedriger Temperatur verwendbaren Stahlprodukts, welches die folgenden Schritte umfasst:

Erhitzen einer Stahlplatte, die die in Anspruch 1 spezifizierte chemische Zusammensetzung aufweist, auf einen Temperaturbereich von 850 bis 1050 °C;
Walzen der Stahlplatte in einem Temperaturbereich von 700 bis 830 °C bei einer Walzreduktion von 5 % oder mehr pro Durchgang und einer kumulativen Walzreduktion von 25 % oder mehr;
Beenden des Walzens in einem Temperaturbereich von 700 bis 800 °C;
unmittelbar nach dem Beenden des Walzens Durchführen eines beschleunigten Abkühlens mit dem resultierenden Produkt auf einen Temperaturbereich von 200 °C oder weniger mit einer Abkühlgeschwindigkeit 10 °C/s oder höher ab der Starttemperatur des beschleunigten Abkühlens auf mindestens 600 °C und bei einer Abkühlgeschwindigkeit von 5 °C/s oder höher von 600 °C auf 200 °C; und
nach dem beschleunigten Abkühlen, Tempern des resultierenden Produkts bei einer Temperatur von 650 °C oder weniger.

3. Verfahren zur Herstellung eines bei niedriger Temperatur verwendbaren Stahlprodukts nach Anspruch 2, das weiterhin die folgende Lamellenbildungsbehandlung zwischen dem beschleunigten Abkühlen nach dem Walzen und dem Tempern bei 650 °C oder weniger enthält,
Erhitzen des resultierenden Produkts in einem Temperaturbereich von 600 bis 800 °C und dann Abkühlen desselben auf einen Temperaturbereich von 200 °C oder weniger, mit einer Abkühlgeschwindigkeit von 5 °C/s oder höher.

Revendications

1. Produit en acier utilisable à une faible température, **caractérisé en ce qu'**il est constitué de,
en pourcent en masse, C : de 0,01 à 0,1 %, Si : de 0,005 à 0,6 %, Mn : de 0,3 à 2 %, Ni : plus de 6 % à moins de 8 %, sol.Al : de 0,005 à 0,05 %, N : de 0,0005 à 0,005 %, éventuellement un ou plusieurs choisis parmi Mo : 0,1 % ou inférieur, Cu : 2,0 % ou inférieur, Cr : 0,8 % ou inférieur, V : 0,08 % ou inférieur, Nb : 0,08 % ou inférieur, Ti : 0,03 % ou inférieur, B : 0,0030 % ou inférieur, Ca : 0,0050 % ou inférieur et Mg : 0,0050 % ou inférieur et du reste : Fe et des impuretés, à condition que la formule (1) suivante est satisfaite ; il contient de l'austénite dans un rapport de surface de 1,7 % ou supérieur et de la cémentite, et ladite austénite présente un rapport d'allongement de 3,5 ou inférieur en moyenne et un diamètre de grain équivalent-cercle moyen de 1,0 μm ou inférieur, et ladite cémentite présente un rapport d'allongement de 5,0 ou inférieur en moyenne et un diamètre équivalent-cercle moyen de 0,6 μm ou inférieur :

$$20C + 2.4Mn + Ni + 0.5Cu + 0.5Mo \geq 10 \cdots\cdots (1),$$

où chaque symbole d'élément dans la formule (1) représente la teneur (en % en masse) de l'élément concerné.

2. Procédé de production d'un produit en acier utilisable à une faible température, lequel comprend les étapes suivantes :

le chauffage d'une plaque d'acier, laquelle présente la composition chimique spécifiée dans la revendication 1, dans une région de température de 850 à 1 050°C ;
le laminage de ladite plaque en acier dans une région de température de 700 à 830°C à une réduction de laminage de 5 % ou supérieure par masse et une réduction de laminage cumulée de 25 % ou supérieure ;
la finition du laminage dans une région de température de 700 à 800°C ;
immédiatement après ladite finition de laminage, la réalisation d'un refroidissement accéléré sur le produit résultant dans une région de température de 200°C ou inférieure, à une vitesse de refroidissement de 10°C/s ou supérieure à partir de la température de départ dudit refroidissement accéléré jusqu'à au moins 600°C, et à une vitesse de refroidissement de 5°C/s ou supérieure de 600°C à 200°C ; et
après ledit refroidissement accéléré, le maintien à température du produit résultant à une température de 650°C ou inférieure.

3. Procédé de production d'un produit en acier utilisable à une faible température selon la revendication 2, lequel contient de plus le traitement de lamellisation suivant entre le refroidissement accéléré après le laminage et le

maintien à température à 650°C ou inférieure ;
le chauffage du produit résultant dans une région de température de 600 à 800°C et le refroidissement subséquent de celui-ci dans une région de température de 200°C ou inférieure, à une vitesse de refroidissement de 5°C/s ou supérieure.

REFERENCES CITED IN THE DESCRIPTION

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