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(54) **THICK STEEL PLATE FOR TANK GIVING WELD HEAT AFFECTED ZONE WITH EXCELLENT TOUGHNESS**

(57) A thick steel plate for tanks which contains given components and satisfies the relationship (Ti content [Ti])×(N content [N])≥0.000085 and in which the nonmetallic particles having a size of 1 μm or larger in terms of equivalent circular diameter have a specific average composition and the Ti-containing nitrides satisfy specific average number densities.

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Description

Technical Field

[0001] The present invention relates to a thick steel plate for a tank, excellent in toughness of the weld heat affected zone (Heat Affected Zone; hereinafter, sometimes simply referred to as HAZ).

Background Art

[0002] From the viewpoint of step saving, component saving, low component configuration, etc., manufacturers are encouraged to apply a thermo-mechanical control process (hereinafter, sometimes simply referred to as TMCP) utilizing a rolling-accelerated cooling system to a thick steel plate for tanks used in the fields of an energy storage facility, a chemical plant, a power generation facility, a nuclear reactor pressure vessel, etc. For example, as contrasted with the heat treatment-type ASTM (The American Society for Testing and Materials) SA-537 steel manufactured through a heat treatment such as annealing, quenching and tempering, TMCP-type ASTM SA-841 manufactured by omitting the heat treatment above has been recently standardized.

[0003] On the other hand, in the manufacture of a large structure such as tank, welding for joining thick steel plates, so-called base plates, constituting a majority of the structure is essential. During welding, the base plate near the welding part is exposed to a large quantity of heat to form a site called HAZ. In the HAZ part, the base plate microstructure formed by the thermomechanical treatment is canceled by heat input and coarsened, making it difficult to ensure the toughness in the HAZ part. In particular, for example, when a low component configuration, etc. is required as described above due to a restriction of, e.g., having to comply with standards, or when addition of an in-steel solid solution element having a dramatic effect on the improvement of toughness even with a slight amount is limited, if large heat-input welding is attempted to be applied to the base plate, coarsening of the HAZ microstructure is likely to occur, and it becomes more difficult to ensure the HAZ toughness.

[0004] Accordingly, various techniques utilizing a nonmetallic particle such as oxide have been proposed so as to enhance the HAZ toughness even when there is such a restriction in the component, etc.

[0005] For example, Patent Document 1 discloses a technique where in an oxide having a particle size of 0.2 to 5.0 μm and exerting an effect as an intragranular ferrite transformation nucleus, the proportions of Ti, Mg and Al constituting the oxide are specified so as to achieve excellent HAZ toughness particularly when the heat input is 200 kJ/cm or more, e.g., even under an ultra-large heat-input of about 1,500 kJ/cm. In Examples of Patent Document 1, the toughness at 0°C under heat inputs of 200 kJ/cm and 920 kJ/cm is evaluated.

[0006] Patent Document 2 discloses a technique where based on the finding that an Mn sulfide containing from 1 to 49 at% of Ca and having a particle size of 0.1 to 10 μm significantly promotes generation of intragranular ferrite transformation, the number density of the Mn sulfide is specified to enhance the HAZ toughness in ultra-large heat-input welding. In Examples of Patent Document 2, the toughness at 0°C under a heat input of 20 kJ/cm is evaluated.

[0007] Patent Document 3 discloses the finding that a finely dispersed particle produced by combining an oxide, etc. of Mn and formed among dendrite secondary arms refined by the addition of REM contributes to preventing an austenite grain from coarsening even in the HAZ part of ultra-large heat-input welding of 300 kJ/cm or more and the HAZ toughness is enhanced. In Examples of Patent Document 3, the toughness at 40°C under a heat input of 300 to 1,200 kJ/cm is evaluated.

[0008] Patent Document 4 discloses a technique where the average composition, particle size and dispersion degree of an Al-Mn oxide as an austenite pinning particle in HAZ are controlled and the toughness of large heat-input HAZ part in excess of 200 kJ/cm is thereby increased. In Examples of Patent Document 4, the toughness at 0°C under a heat input of 200 kJ/cm is evaluated.

[0009] On the other hand, as a technique capable of enhancing the average value and minimum value of HAZ toughness even when large heat-input welding is performed, Patent Document 5 discloses a technique of controlling the composition of an oxide to an REM-Zr-based composite oxide containing REM and Zr. Patent Document 5 is a technique utilizing an REM-Zr-based composite oxide and in this point, differs from Patent Documents 1 to 4 utilizing an oxide other than that. In Patent Documents 1 to 4, Zr is not contained in the steel or REM and Zr are not contained in the steel, and thus, the composite oxide above is therefore not formed. Specifically, Patent Document 5 discloses a technique where production of intragranular ferrite is ensured by appropriately controlling the composition of an REM-Zr-based composite oxide and where production of coarse Ti nitride that has been conventionally crystallized from an oxide as a starting point in molten steel is suppressed and production of coarse grain boundary ferrite is suppressed by adding a predetermined amount of B. In Examples of Patent Document 5, the HAZ toughness at -40°C when welded with a heat input of 50 kJ/mm or 60 kJ/mm is evaluated.

Citation List

Patent Document

[0010]

Patent Document 1: JP-A-H11-279684
Patent Document 2: JP-A-2003-321728
Patent Document 3: JP-A-2003-286540
Patent Document 4: JP-A-2012-052224
Patent Document 5: JP-A-2013-127108

Summary of Invention

Technical Problem

[0011] All of the techniques described in Patent Documents 1 to 5 relate to techniques for enhancing the HAZ toughness in the t/4 part at temperatures of down to -40°C when performing large heat-input welding where the heat input amount is approximately from several tens to hundred and tens of kJ/mm. However, the thick steel plate for tanks is required to have good HAZ toughness also when the heat input amount is lower than the above value(s), for example, when small heat-input welding of approximately from 5 to 25 kJ/mm is performed. In this joint, it is known that when large heat-input welding is performed, the prior austenite grain size is coarsened, whereas when small heat-input welding is performed, the steel is generally hardened by a microalloy (e.g., B) and the prior austenite grain size is not so much coarsened. Accordingly, the techniques described in Patent Documents 1 to 5 for improving the HAZ toughness in large heat-input welding cannot be directly used as a technique for improving the HAZ toughness in small heat-input welding.

[0012] In addition, considering the application to the uses above, it is required to have excellent cryogenic HAZ toughness when an impact test is performed at -51°C. However, in Patent Documents above, the HAZ toughness is evaluated only by performing an impact test at 0°C (Patent Documents 1, 2 and 4) or -40°C (Patent Documents 3 and 5). Since the effect of a coarse inclusion such as nonmetallic particle on HAZ toughness is likely to emerge at a very low temperature of -51°C, the technique for improving HAZ toughness under large heat-input welding as in Patent Documents described above is required to be further improved.

[0013] In addition, Patent Document 5 is a technique of adding B as an essential component, where the N amount and the Ti amount must be controlled between the deoxidation/desulfurization process and casting process so as to control the B amount. Furthermore, the cleanliness of the steel needs to be maintained by setting the addition amount of Al to be relatively low. As a result, a large load is imposed on the steelmaking step such as deoxidation/desulfurization, or the tolerance for the steelmaking control conditions is low. Thus, there is room for improvement toward mass production.

[0014] The present invention has been made by taking into account these circumstances, and an object thereof is to provide a thick steel plate for a tank, capable of being manufactured under a condition with a relatively low load on the steelmaking step, such as deoxidation, desulfurization and nitrogen control, when, for example, small heat-input welding of approximately from 5 to 25 kJ/mm is performed, and having excellent HAZ toughness at a very low temperature such as -51°C.

Solution to Problem

[0015] In the thick steel plate for a tank, which is excellent in toughness of a weld heat affected zone and is capable of solving the above problem(s),

(1) the thick steel plate has a composition comprising, in mass%:

C: from 0.02 to 0.15%;
Si: from 0.05 to 0.5%;
Mn: from 0.6 to 2.0%;
P: more than 0% and 0.030% or less;
S: more than 0% and 0.025% or less;
Al: from 0.02 to 0.07%;
Nb: 0.005% or more and less than 0.050%;
Ti: from 0.003 to 0.03%;
N: from 0.0020 to 0.010%;

O: more than 0% and 0.0040% or less;
REM: from 0.0002 to 0.050%;
Zr: from 0.0003 to 0.020%; and
Ca: from 0.0003 to 0.0060%;
with the remainder being iron and inevitable impurities, and
$[Ti] \times [N] \geq 0.000085$ is satisfied, wherein [Ti] is the Ti content and [N] is the N content, and

(2) when a thickness of the steel plate is t, the following requirements (2-1) and (2-2) are satisfied at t/2:

(2-1) an average composition of nonmetallic particles having an equivalent-circle diameter of 1 μm or more satisfies, in mass%:

$20\% \leq Al_2O_3 \leq 40\%$;
$5\% \leq TiO_2 \leq 20\%$;
5% ≤ oxide of REM ≤ 45%;
$5\% \leq ZrO_2 \leq 60\%$; and
$5\% \leq CaO \leq 40\%$, and

(2-2) an average number density of Ti-containing nitrides satisfies:

0.8 pieces or less per 1 mm^2 for those having a major axis length of 2 μm or more; and
1.0×10^5 pieces or more per 1 mm^2 for those having an equivalent-circle diameter of 20 nm or more and 500 nm or less.

[0016] In a preferred embodiment, the steel plate further comprises V: more than 0% and 0.1 % or less.
[0017] In a preferred embodiment, the steel plate further comprises at least one element selected from the group consisting of Cu: more than 0% and 0.50% or less; Ni: more than 0% and 0.85% or less; Cr: more than 0% and 0.30% or less; and Mo: more than 0% and 0.5% or less.

Advantageous Effects of Invention

[0018] According to the present invention, when small heat-input welding of approximately from 5 to 25 kJ/mm is performed, a thick steel plate for a tank, excellent in HAZ toughness at a very low temperature, for example, at -51 °C, can be provided.
[0019] Moreover, according to the present invention, a high-strength thick steel plate being excellent in the cryogenic HAZ toughness as described above and having a tensile strength of 485 MPa or more can be efficiently obtained without a load on the steelmaking step such as deoxidation, desulfurization and nitrogen control and therefore, the productivity, etc. are also very excellent.

Description of Embodiments

[0020] The present inventors have made many studies to provide a thick steel plate for tanks, ensuring excellent HAZ toughness even when small heat-input welding is performed. More specifically, from the viewpoint of enhancing the HAZ toughness by reducing coarse TiN that becomes an origin of fracture, attention was focused on an REM-Zr-based composite oxide, similarly to the case of Patent Document 5. Here, however, in order to attain the above-described object, the technique of Patent Document 5 cannot be directly applied to the present invention. As described above, Patent Document 5 relates to a technique for enhancing the HAZ toughness in large heat-input welding (for example, 60 kJ/mm), and the prior austenite grain size is likely to be coarsened there. In Patent Document 5, for example, B is added so as to suppress production of coarse grain boundary ferrite and improve the HAZ toughness. In contrast, the present invention relates to a technique for enhancing the HAZ toughness in small heat-input welding where the heat input amount is small (for example, 20 kJ/mm) as compared with Patent Document 5, and the prior austenite grain size is less coarsened than in the case of Patent Document 5. Accordingly, the present invention is based on the premise that B as an indispensable element (an element for suppressing production of coarse grain boundary ferrite and improving HAZ toughness) in Patent Document 5 is not added.
[0021] More specifically, the present inventors have made studies to provide a technique for enhancing the HAZ toughness in small heat-input welding, where the number density of coarse TiN can be reduced, similarly to the case of Patent Document 5, by utilizing an REM-Zr-based composite oxide and the number density of fine TiN can be increased without addition of B, unlike the case of Patent Document 5. Above all, in the present invention, the evaluation of HAZ

toughness is performed at a lower temperature of -51°C than the case of Patent Document above, and in this case, an adverse effect of a coarse inclusion such as Ti-containing nitrogen on the HAZ toughness is likely to emerge. As a result, it has been found that when control is performed as in the following (a) to (c), the desired object can be attained, and the present invention has been accomplished based on this finding.

(a) As for the components in a steel, it is effective particularly to contain both Al and Nb in predetermined amounts without adding B and to control the Ti-N balance represented by the product of the Ti content, i.e. [Ti], and the N content, i.e. [N], to not less than the specific value, whereby the production of fine Ti-containing nitride useful for the enhancement of HAZ toughness can be increased while maintaining high base plate strength even without placing load on the steelmaking step.
(b) As for the average composition of the REM-Zr-based composite oxides, it is effective particularly to appropriately control the average composition of the oxides above having an equivalent-circle diameter of 1 μm or more, whereby the melting point of the oxides lowers and in turn, the number of formation sites of coarse Ti-containing nitrides decreases, making it possible to reduce the production of coarse Ti-containing nitride.
(c) As for the average number density of the Ti-containing nitrides, it is effective to control and reduce the average number density of the coarse Ti-containing nitrides having a major axis length of 2 μm or more and to control and increase the number average density of the fine Ti-containing nitrides having an equivalent-circle diameter of 20 nm or more and 500 nm or less, whereby good cryogenic HAZ toughness can be ensured.

[0022] In the present invention, both the composition of REM-Zr-based composite oxide and the number density of Ti-containing nitrides are a value in the central part (t/2 part) of the thickness t of the steel plate. In general, coarse TiN, etc. are readily formed in the central part of a steel plate and therefore, in many related arts including the above-described Patent Documents, the oxide composition, number density of Ti-containing nitrides, and the like are evaluated in the t/4 part of the steel plate. The present invention is very useful in the point of not containing B and in that the oxide composition and the number density of Ti-containing nitrides in the central part of steel plate, where these have been difficult to control, can be controlled.
[0023] In the description of the present invention, the "excellent cryogenic HAZ toughness" means that when a Charpy impact test is performed by the method described in Examples later and the absorption energy at -51 °C is measured, the minimum value is 48 J or more. In the following, this is sometimes simply referred as excellent HAZ toughness.
[0024] In the description of the present invention, the thick steel plate means a steel plate in which the thickness is roughly 6 mm or more and is preferably 150 mm or less.
[0025] In the description of the present invention, the "Ti-containing nitrides having a major axis length of 2 μm or more" are sometimes simply referred to as "coarse Ti-containing nitrides", and the "Ti-containing nitrides having an equivalent-circle diameter of 20 nm or more and 500 nm or less" are sometimes simply referred to as "fine Ti-containing nitrides".
[0026] The constituent features of the present invention are described in detail below.

(1) Components in steel

[0027] The thick steel plate for tanks in the present invention contains C: from 0.02 to 0.15%, Si: from 0.05 to 0.5%, Mn: from 0.6 to 2.0%, P: more than 0% and 0.030% or less, S: more than 0% and 0.025% or less, Al: from 0.02 to 0.07%, Nb: 0.005% or more and less than 0.050%, Ti: from 0.003 to 0.03%, N: from 0.0020 to 0.010%, O: more than 0% and 0.0040% or less, REM: from 0.0002 to 0.050%, Zr: from 0.0003 to 0.020%, and Ca: from 0.0003 to 0.0060%, with the remainder being iron and inevitable impurities, and $[Ti]\times[N] \geq 0.000085$ is satisfied, wherein [Ti] is the Ti content and [N] is the N content.

C: from 0.02 to 0.15%

[0028] C is an indispensable element for ensuring the strength by enhancing the hardenability, and for this purpose, as the lower limit of the C amount, it is set to be 0.02% or more. The amount is preferably 0.03% or more, more preferably 0.05% or more. However, if the C amount is excessive, martensite (including island martensite) is readily produced, and the HAZ toughness deteriorates. Accordingly, as the upper limit of the C amount, it is set to be 0.15% or less. The amount is preferably 0.12% or less, more preferably 0.10% or less.

Si: from 0.05 to 0.5%

[0029] Si is an element contributing to reduction of the load in the steelmaking (deoxidation, desulfurization, nitrogen control) step and being useful for increasing the number density of the fine Ti-containing nitrides. In order to effectively bring out these effects, as the lower limit of the Si amount, it is set to be 0.05% or more. The amount is preferably 0.08% or more, more preferably 0.15% or more. However, if the Si amount is excessive, island martensite is readily formed, and the HAZ toughness deteriorates. Accordingly, as the upper limit of the Si amount, it is set to be 0.5% or less. The Si amount is preferably 0.45% or less, more preferably 0.35% or less.

Mn: from 0.6 to 2.0%

[0030] Mn is an element effective to ensure the strength by enhancing the hardenability, and as the lower limit of the Mn amount, it is therefore set to be 0.6% or more. The Mn amount is preferably 0.8% or more, more preferably 1.0% or more. However, if the Mn amount is too large, the steel becomes hard, and the HAZ toughness deteriorates. Accordingly, as the upper limit of the Mn amount, it is set to be 2.0% or less. The amount is preferably 1.8% or less, more preferably 1.6% or less.

P: more than 0% and 0.030% or less

[0031] P is an element inevitably contained in the steel. If the upper limit of the P amount exceeds 0.030%, the HAZ toughness is significantly deteriorated. In addition, in the case of applying the steel to usage such as nuclear reactor pressure vessel, there is a concern about embrittlement due to neutron irradiation. Accordingly, as the upper limit of the P amount, it is set to be 0.030% or less. The amount is preferably 0.020% or less, more preferably 0.010% or less. From the viewpoint of ensuring the HAZ toughness, the P amount is preferably smaller, but it is industrially difficult to control the amount to 0%.

S: more than 0% and 0.025% or less

[0032] As with P, S is an element inevitably contained in the steel, and if the upper limit of the S amount is too large, the HAZ toughness deteriorates. In addition, in the case of applying the steel to usage such as nuclear reactor pressure vessel, there is a concern about embrittlement due to neutron irradiation. Accordingly, as the upper limit of the S amount, it is set to be 0.025% or less. The amount is preferably 0.020% or less, more preferably 0.015% or less, still more preferably 0.010% or less. From the viewpoint of ensuring the HAZ toughness, the S amount is preferably smaller, but it is industrially difficult to control the amount to less than 0.0001%, and the lower limit of the S amount is therefore about 0.0001%.

Al: from 0.02 to 0.07%

[0033] Al is an element, when added in an appropriate amount, contributing to reduction of the load in the steelmaking step (deoxidation, desulfurization, nitrogen control). In addition, Al is an element contributing to lowering the melting point of a nonmetallic particle that works out to a nucleation site of coarse Ti-containing nitride, thereby suppressing the formation of coarse Ti-containing nitride and ensuring HAZ toughness. Furthermore, Al is an element effective to complete the deoxidation step → desulfurization step in the steelmaking step within a predetermined time. In order to effectively bring out these effects, as the lower limit of the Al amount, it is set to be 0.02% or more. The amount is preferably 0.023% or more, more preferably 0.025% or more. On the other hand, when manufacturing the steel plate of the present invention, as described later, it is recommended to add Al before Zr, but if the Al amount is too large, a desired oxide composition cannot be realized, and coarse Ti-containing nitride is therefore readily formed, and as a result, the HAZ toughness is deteriorated. Accordingly, as the upper limit of the Al amount, it is set to be 0.07% or less. The Al amount is preferably 0.06% or less, more preferably 0.05% or less.

Nb: 0.005% or more and less than 0.050%

[0034] Nb is an element effective to enhance the base plate strength without deteriorating the weldability when manufacturing the base plate by applying a heat treatment-omitted type TMCP. In order to effectively bring out such an effect, as the lower limit of the Nb amount, it is set to be 0.005% or more. The Nb amount is preferably 0.010% or more, more preferably 0.020% or more. However, if the Nb amount is 0.050% or more, the HAZ toughness deteriorates. Accordingly, in the present invention, as the upper limit of the Nb amount, it is set to be less than 0.050%. The Nb amount is preferably 0.040% or less, more preferably 0.030% or less.

Ti: from 0.003 to 0.03%

[0035] Ti is an element essential to ensure the number density of the fine Ti-containing nitrides and obtain excellent

HAZ toughness. In order to effectively bring out these effects, as the lower limit of the Ti amount, it is set to be 0.003% or more. The amount is preferably 0.005% or more, more preferably 0.010% or more. On the other hand, if the Ti amount excessive, although the number density of the fine Ti-containing nitrides may be ensured, a lot of coarse Ti-containing nitrides that lower the minimum value of HAZ toughness are formed. Accordingly, as the upper limit of the Ti amount, it is set to be 0.03% or less. The amount is preferably 0.025% or less, more preferably 0.020% or less.

N: from 0.0020 to 0.010%

[0036] N is an element essential to ensure the number density of the fine Ti-containing nitrides and obtain excellent HAZ toughness. In order to effectively bring out these effects, as the lower limit of the N amount, it is set to be 0.0020% or more. The amount is preferably 0.003% or more, more preferably 0.0040% or more. However, if the N amount is large, the HAZ toughness rather deteriorates probably due to solute N. Accordingly, as the upper limit of the N amount, it is set to be 0.010% or less. The amount is preferably 0.0095% or less, more preferably 0.0085% or less.

O (oxygen): more than 0% and 0.0040% or less

[0037] The amount of O is preferably small from the viewpoint of enhancing cleanliness. In addition, if a large amount of O is contained, the HAZ toughness deteriorates. Considering these, as the upper limit of the O amount, it is set to be 0.0040% or less. The amount is preferably 0.0035% or less, more preferably 0.0030% or less. Although the O amount is preferably small, it is industrially difficult to control the amount to 0%.

REM (rare earth element): from 0.0002 to 0.050%

[0038] REM is an element contributing to lowering the melting point of a nonmetallic particle that becomes a nucleation site of coarse Ti-containing nitride, thereby suppressing the formation of coarse Ti-containing nitride, and consequently enhancing the HAZ toughness. In order to effectively bring out these effects, as the lower limit of the REM amount, it is set to be 0.0002% or more. The REM amount is preferably 0.0005% or more, more preferably 0.0010% or more. On the other hand, even if a large amount of REM is incorporated, the effect is saturated. Accordingly, the upper limit of the REM amount is set to be 0.050%. From the viewpoint of preventing clogging of an immersion nozzle during casting and thereby enhancing the productivity, as the upper limit of the REM amount, it is preferably 0.03% or less, more preferably 0.010% or less, still more preferably 0.0050% or less.

[0039] In the description of the present invention, REM means lanthanoid elements (15 elements from La to Lu), Sc (scandium), and Y (yttrium).

Zr: from 0.0003 to 0.020%

[0040] Zr is an element contributing to lowering the melting point of a nonmetallic particle that becomes a nucleation site of coarse Ti-containing nitride, thereby suppressing the formation of coarse Ti-containing nitride, and consequently enhancing the HAZ toughness. In order to effectively bring out these effects, as the lower limit of the Zr amount, it is set to be 0.0003% or more. The Zr amount is preferably 0.0005% or more, more preferably 0.0010% or more, still more preferably 0.0015% or more. On the other hand, if Zr is excessively added, solute Zr in the molten steel is increased and crystallized to surround oxide•sulfide during casting, and the HAZ toughness is thereby deteriorated. Accordingly, as the upper limit of the Zr amount, it is set to be 0.020% or less. The Zr amount is preferably 0.010% or less, more preferably 0.0070% or less, still more preferably 0.0050% or less.

Ca: from 0.0003 to 0.0060%

[0041] Ca is an element, when added in an appropriate amount, contributing to lowering the melting point of a non-metallic particle that becomes a nucleation site of coarse Ti-containing nitride, thereby suppressing the formation of coarse Ti-containing nitride, and consequently enhancing the HAZ toughness. In order to effectively bring out these effects, as the lower limit of the Ca amount, it is set to be 0.0003% or more. The amount is preferably 0.0005% or more, more preferably 0.0010% or more. On the other hand, if the Ca amount exceeds 0.0060%, a large amount of coarse Ca-based inclusions are formed, and these are aggregated to adversely affect the HAZ toughness. Accordingly, the upper limit of the Ca amount is set to be 0.0060%. The Ca amount is preferably 0.0050% or less, more preferably 0.0040% or less.

$[Ti]x[N] \geq 0.000085$ for Ti content, i.e. [Ti], and N content, i.e. [N]

[0042] The Ti-N balance represented by the formula above is related to the driving force for forming Ti-containing nitride and is determined, as a parameter effective to ensure the number density of the fine Ti-containing nitrides, by the present inventors through a number of fundamental experiments. If the Ti-N balance is less than 0.000085, the number density of the fine Ti-containing nitrides contributing to enhancement of the HAZ toughness is not obtained. The Ti-N balance is preferably large and is preferably 0.000090 or more, more preferably 0.000095 or more. The upper limit is not particularly limited from the viewpoint of enhancing the HAZ toughness but is determined in relation to the upper limit of each of the Ti content and N content above.
[0043] In the steel plate of the present invention, the above-described components are basic components, and the remainder is iron and inevitable impurities.
[0044] In the present invention, from the viewpoint of, for example, enhancing other properties, it is preferable to further contain the following selected components.

V: more than 0% and 0.1 % or less

[0045] V is an element effective to enhance the strength. In order to effectively bring out such an effect, as the lower limit of the V amount, it is preferably set to be 0.003% or more. The amount is more preferably 0.010% or more. On the other hand, if the V amount exceeds 0.1 %, the weldability deteriorates. Accordingly, as the upper limit of the V amount, it is preferably set to be 0.1% or less, and the amount is more preferably 0.08% or less.
[0046] At least one element selected from the group consisting of Cu: more than 0% and 0.50% or less, Ni: more than 0% and 0.85% or less, Cr: more than 0% and 0.30% or less, and Mo: more than 0% and 0.5% or less
[0047] Cu, Ni, Cr and Mo are elements contributing mainly to enhancement of the base plate strength. In the present invention, one of these elements may be used alone, or two or more thereof may be used in combination.
[0048] Specifically, the elements above are preferably controlled as follows.
[0049] Cu is an element effective to increase the strength by enhancing the hardenability. In order to effectively bring out these effects, as the lower limit of the Cu amount, it is preferably set to be 0.01% or more. The amount is more preferably 0.05% or more, still more preferably 0.10% or more. However, even if this element is added excessively, the effects above are saturated, and the cost rises. Accordingly, as the upper limit of the Cu amount, it is preferably set to be 0.50% or less.
[0050] Ni is an element effective to enhance the base plate strength and the HAZ toughness. In order to effectively bring out these effects, as the lower limit of the Ni amount, it is preferably set to be 0.01% or more. The amount is more preferably 0.05% or more, still more preferably 0.10% or more. However, even if this element is added excessively, the effects above are saturated, and the cost rises. Accordingly, as the upper limit of the Ni amount, it is preferably set to be 0.85% or less.
[0051] Cr is an element effective to enhance the strength. In order to effectively bring out such an effect, as the lower limit of the Cr amount, it is preferably set to be 0.01% or more. The amount is more preferably 0.05% or more, still more preferably 0.10% or more. However, even if this element is added excessively, the effect above is saturated, and the cost rises. Accordingly, as the upper limit of the Cr amount, it is preferably set to be 0.30% or less.
[0052] Mo is an element effective to enhance the base plate strength. In order to effectively bring out such an effect, as the lower limit of the Mo amount, it is preferably set to be 0.01% or more. The amount is more preferably 0.05% or more, still more preferably 0.10% or more. However, even if this element is added excessively, the effect above is saturated, and the cost rises. Accordingly, as the upper limit of the Mo amount, it is preferably set to be 0.5% or less.
[0053] It is preferred that the steel plate of the present invention does not positively contain Mg and B and the upper limit of the content thereof is reduced to about an inevitable impurity level.
[0054] More specifically, as the upper limit of the Mg amount, it is preferably set to be 0.0005% or less. Because, Mg has high affinity for O (oxygen), and the adding order or adding method thereof is very difficult to be controlled for obtaining a nonmetallic particle having a low-melting-point composition contributing to the reduction of coarse Ti-containing nitride.
[0055] As described above, in the present invention, B is not contained. Specifically, as the upper limit of the B amount, it is preferably set to be 0.0005% or less. In general, B is considered to be an element segregating in the prior γ grain boundary during thermal cycle of welding to retard ferrite transformation and suppress formation of coarse grain boundary ferrite, thereby contributing to enhancement of the HAZ toughness. However, such an effect of the addition of B is exerted in a region where the heat input amount is larger than that in the present invention and the prior γ grain size is larger than that in the present invention (roughly on the order of 30 to 110 kJ/mm). In the present invention, the heat input amount is as small as approximately from 5 to 25 kJ/mm, and the prior γ grain size is relatively fine as well. Accordingly, the hardenability is reduced, and the solute B concentration per unit area of the grain boundary decreases, and as a result, a ferrite microstructure is thoroughly developed. In such a region, the addition of B makes a small contribution to

the HAZ toughness-increasing effect, but conversely, the addition of B may make the rolling conditions difficult, and it is therefore preferable not to positively add this element.

(2) Average composition of nonmetallic particles having an equivalent-circle diameter of 1 μm or more

[0056] In the thick steel plate for tanks of the present invention, the average composition of nonmetallic particles having an equivalent-circle diameter of 1 μm or more satisfies, in mass%, 20%≤Al_2O_3≤40%, 5%≤TiO_2≤20%, 5%≤oxide of REM≤45%, 5%≤ZrO_2≤60%, and 5%≤CaO≤40%. A nonmetallic particle such as oxide formed in the molten steel is in general more likely to become a formation site of Ti-containing nitride in the solidification process than the molten steel in the periphery, and as a result, coarse Ti-containing nitride of μm order is formed to reduce the HAZ toughness. On other hand, when the average composition of nonmetallic particles is appropriately controlled as above, configurations or physical properties less likely to become a formation site of Ti-containing nitride can be obtained, and reduction in the HAZ toughness can be prevented. Although the reason therefor is not clarified in detail, it is presumed that the melting point of nonmetallic particles controlled to have the above-described average composition lowers and the formation site of Ti-containing nitride in the solidification is thereby reduced.
[0057] The reason why the average composition of the above-described nonmetallic particles is set to the range above is as explained above, and out of this range, the number density of coarse Ti-containing nitrides cannot be reduced to the specific level or less.
[0058] The method for calculating the average composition of the nonmetallic particles above is described in detail in the section of Examples later.
[0059] In the present invention, the reason for limiting the size of the target nonmetallic particle to an equivalent circle diameter of 1 μm or more is that a nonmetallic particle with a size on this level becomes a principal formation site of coarse Ti-containing nitride causing reduction in the HAZ toughness. The equivalent-circle diameter as used herein means a diameter when the nonmetallic particle such as Al_2O_3 dispersed in the steel is converted to a circle having the same area.
[0060] In addition, the "nonmetallic particle" as used in the present invention means a particle usually present in a hot-rolled plate used for the thick steel plate of the present invention and is not limited to an oxide (including both a single oxide and a composite oxide) but encompasses particles of nitride, sulfide, etc. More specifically, the average composition above is not an average composition of oxide dispersed in the steel but means an average composition covering all nonmetallic particles of nitride, sulfide, etc. in addition to the oxide. In the present invention, it is important that out of nonmetallic particles, the average composition of the above-described specific oxides, i.e., Al_2O_3, TiO_2, oxide of REM, ZrO_2 and CaO, satisfies the range above, and as long as the range above is satisfied, the average composition of other oxides is not particularly limited. Similarly, the average composition of sulfide, etc. except for those oxides is not particularly limited as well. This is because these particles have no great effect on the HAZ toughness.

(3) Average number density of Ti-containing nitrides

[0061] Furthermore, the thick steel plate for tanks of the present invention satisfies the requirement that the density of the coarse Ti-containing nitrides having a major axis length of 2 μm or more is 0.8 pieces or less per 1 mm^2 and the density of the fine Ti-containing nitrides having an equivalent-circle diameter of 20 nm or more and 500 nm or less is 1.0×10^5 pieces or more per 1 mm^2. The major axis length as used herein means the length of a long side when the Ti-containing nitride is regarded as a rectangle. Because, the Ti-containing nitrides in the cross-section observed are generally present in the form of a rectangle. The equivalent-circle diameter means a diameter when the Ti-containing nitride is converted to a circle having the same area.
[0062] First, the number density of coarse Ti-containing nitrides is set to be 0.8 pieces or less per 1 mm^2, whereby the minimum value of HAZ toughness at -51°C can be ensured at the specific level or more. This is a finding arose from fundamental experiments conducted by the present inventors, and it has been found that in a region of a very low temperature (-51°C) as the evaluation temperature of HAZ toughness in the present invention, the coarse Ti-containing nitrides having the size above, when present at not less than the specific density near a notch position for an impact test, adversely affects the HAZ toughness to reduce the minimum value of HAZ toughness. Accordingly, in order to ensure that the minimum value of HAZ toughness is not less than the specific level, the number density of coarse Ti-containing nitrides is set to be 0.8 pieces or less per 1 mm^2. The number density of coarse Ti-containing nitrides is preferably as smaller as possible and is preferably 0.7 pieces or less, more preferably 0.5 pieces or less, most preferably 0, per 1 mm^2.
[0063] The number density of the fine Ti-containing nitrides is set to be 1.0×10^5 pieces or more per 1 mm^2. In addition to control of the number density of coarse Ti-containing nitrides, the number density of the fine Ti-containing nitrides is further controlled, whereby for the first time, the minimum value of HAZ toughness at -51°C can be ensured at a predetermined level or more. This is a finding arose from fundamental experiments conducted by the present inventors. More

specifically, it has been found that even in a portion located near the Fusion Line and exposed to a very high temperature when heat input corresponding to 20 kJ/mm is applied, the fine Ti-containing nitrides having the size above are not completely dissolved but remains undissolved at least in part and pins the coarsening of prior γ grain size. In order to effectively bring out these effects and ensure that the minimum value of cryogenic HAZ toughness is not less than the specific level, the number density of the fine Ti-containing nitrides is controlled as above. The number density of the fine Ti-containing nitrides is preferably as larger as possible and is preferably 1.5×10^5 pieces or more, more preferably 2.0×10^5 pieces or more, per 1 mm^2. The upper limit thereof is not particularly limited in relation to the above-described action but is substantially considered to be roughly about 1.0×10^7 pieces or less per 1 mm^2.

[0064] In the present invention, the reason why the sizes of fine Ti-containing nitride and coarse Ti-containing nitride are set as above is because it has been found from experiments that those having sizes in the ranges above are particularly effective in ensuring the maximum value of HAZ toughness.

[0065] The Ti-containing nitride as used in the present invention is intended to encompass all compounds as long as they are a nitride containing Ti. Typical examples thereof include TiN, but it is of course not limited thereto. For example, it may be a compound containing C, such as carbonitride of Ti, or may be a compound containing a nitride-forming element other than Ti, such as nitride of TiNb.

[0066] In the foregoing pages, the thick steel plate for tanks of the present invention is described in detail.

[0067] The method for manufacturing the thick steel plate for tanks is described below. The present invention is characterized particularly in that the components in the steel are appropriately controlled and the average composition of nonmetallic particles and the number density of Ti-containing nitrides are appropriately controlled, and the preferable method in the steelmaking step and the subsequent rolling step are as follows.

[Steelmaking step]

[0068] In the present invention, during melting, the dissolved oxygen amount in the molten steel is controlled to the range of, in mass%, from 0.002 to 0.01% by deoxidation using Mn, Si and Al and thereafter, respective elements are added in the order of Ti $\rightarrow$ (REM, Zr) $\rightarrow$ Ca.

[0069] First, deoxidation is performed using Mn, Si and Al. These elements are an element contributing to load reduction in the steelmaking step of deoxidation $\rightarrow$ desulfurization $\rightarrow$ nitrogen control, more specifically, an element facilitating controlling the concentration of each trace element (oxygen, sulfur, nitrogen, and Ti in the molten steel) during casting to the target control range. Out of these elements, if each content of Si and Al in particular falls below the predetermined range, the control tolerance at the control point of the steelmaking step is narrowed, and it becomes difficult for each concentration of oxygen amount, sulfur amount, nitrogen amount and Ti amount in the molten steel during casting to be controlled to the target control range. Here, the target control range is specifically 40 ppm or less for oxygen, 25 ppm or less for sulfur, target value$\pm$20 ppm or less for nitrogen, and target value$\pm$30 ppm or less for Ti. For example, when the target value of Ti is set to be 0.015%, Si and Al are controlled to be within the ranges specified in the present invention (i.e., Si: from 0.05 to 0.5%, and Al: from 0.02 to 0.07%), whereby Ti can be controlled to fall within the range of target value (0.015%)$\pm$30 ppm (= 0.003%) or less.

[0070] Next, the dissolved oxygen amount in the molten steel before adding Ti, REM, Zr and Ca is controlled to the range of 0.002 to 0.01%. If the dissolved oxygen amount is less than 0.002%, a required amount of the average composition of an oxide-based inclusion having an appropriate composition cannot be ensured. Consequently, coarse TiN may be crystallized or become an origin of occurrence of intragranular ferrite transformation (Inter Granular Bainite, IGB). On the other hand, if the dissolved oxygen amount exceeds 0.01%, the HAZ toughness deteriorates. As the lower limit of the dissolved oxygen amount, it is preferably 0.0025% or more, more preferably 0.003% or more. As the upper limit of the dissolved oxygen amount, it is preferably 0.009% or less, more preferably 0.008% or less.

[0071] Subsequently, respective elements are added in the order of Al $\rightarrow$ Ti $\rightarrow$ (REM, Zr) $\rightarrow$ Ca. If respective elements are added in the order other than the adding order above, a required number of oxide-based inclusions having an appropriate composition cannot be ensured. In particular, since Ca has very strong deoxidizing power, if Ca is added in advance of Ti or Al, oxygen to be bonded to Ti or Al is entirely removed, and the desired average composition of TiO_2 or Al_2O_3 cannot be ensured. The (REM, Zr) means that the adding order of REM and Zr is not particularly limited. That is, as long as the addition thereof is conducted after the addition of Ti and before the addition of Ca, it may be either in the order of REM $\rightarrow$ Zr or in the order of Zr $\rightarrow$ REM. Alternatively, REM and Zr may be added simultaneously.

[0072] The total time from Ti addition to Ca addition is preferably controlled to roughly the range of 3 to 20 minutes. If the total time falls below 3 minutes, the reaction becomes excessive, and the Ca concentration in the inclusion rises too high. On the other hand, if the total time exceeds 20 minutes, the inclusion is coarsened to adversely affect the toughness.

[0073] After adding respective elements as above, the molten steel is solidified. The solidification method is not particularly limited, but in particular, the cooling time in the temperature range of 1,500 to 1,450°C during casting is preferably controlled to within 300 seconds. If the cooling time in the temperature range above exceeds 300 seconds, the crystallized TiN is coarsened to adversely affect the toughness and in addition, the productivity decreases.

[0074] Thereafter, a steel plate is manufactured by normal TMCP. As the TMCP conditions, for example, the following method is preferably used.

[0075] Heating condition before rolling: for example, from 950 to 1,200°C (preferably from 1,050 to 1,150°C), finish rolling temperature: for example, from 680 to 700°C.

[0076] Rolling reduction in two-phase region: for example, 30% or more.

[0077] Average cooling rate in the temperature region after finishing rolling temperature to 530°C: 2°C/sec or more.

[0078] This condition is set because if the average cooling rate in the temperature region above is less than 2°C/sec, the strength is insufficient. The average cooling rate is preferably 3°C/sec or more. Here, the upper limit thereof is not particularly limited, but considering the productivity, etc. in the actual operation level, the average cooling rate is roughly 30°C/sec or less.

EXAMPLES

[0079] The present invention is described more specifically by referring to Examples, but the present invention is not limited by the following examples and can be carried out by adding changes within the range conformable to the gist described above and below, and all of these changes are encompassed by the technical scope of the present invention.

[0080] First, the steel having the composition shown in Table 1 was melted in a vacuum melting furnace, and 240 ton of slab was obtained using the obtained molten steel. More specifically, during melting, the dissolved oxygen amount in the molten steel was controlled to the range of, in mass%, from 0.002 to 0.01 % by deoxidation using Mn, Si and Al. Thereafter, respective elements were added in the order of Ti $\rightarrow$ (REM, Zr) $\rightarrow$ Ca while controlling the time from Ti addition to Ca addition to become from 3 to 20 minutes, and the cooling time in the temperature range of 1,500 to 1,450°C during casting was set to be within 300 seconds.

[0081] In this Example, REM was added in the form of misch metal containing, in mass%, about 50% of Ce and about 25% of La. In the Table, "-" means that the corresponding element was not added.

[0082] In the steelmaking step, the oxygen concentration, sulfur concentration, nitrogen concentration and Ti concentration in the molten steel were measured. In this Example, those where all concentrations could be controlled to fall within the target control range were judged as "pass", and those where the concentration of at least one element deviated from the target control range were judged as "fail".

[0083] Next, the slab obtained above was hot-rolled under the following conditions to obtain a hot-rolled plate having a thickness of 80 mm. The thus-obtained steel plate was designated as "TMCP" in the column of Base plate Production Method of Table 2.

Heating condition before rolling: 1,100°C

Rolling reduction in two-phase region: 30%

Average cooling rate from finish rolling temperature to 530°C: from 2 to 8°C/sec

[0084] Here, the "as-air cooled" in the column of Base plate Production Method of Table 2 indicates that the slab was cooled at a lower rate (0.6°C/sec) than the above-described average cooling rate.

[0085] Using each hot-rolled plate obtained by the method above, the following items were measured.

(Measurement of average composition of nonmetallic particles having an equivalent-circle diameter of 1 μm or more)

[0086] In the thickness-direction cross-section of the hot-rolled plate, nonmetallic particles were observed using EPMA-8705 manufactured by Shimadzu Corporation around the thickness central part (t/2). In detail, the cross-section was observed at an observation magnification of 400 times and an observation visual field of about 50 mm^2 (7 mm in sheet thickness direction and 7 mm in sheet width direction by arranging the thickness central part to become the center of the observation visual field), and the component composition in the central part of inclusion was quantitatively determined by characteristic X-ray wavelength dispersion spectroscopy for inclusions having an equivalent-circle diameter of 1 μm or more. The analysis target elements were Al, Mn, Si, Mg, Ca, Ti, Zr, S, REM (La, Ce, Nd, Dy, Y), and Nb. The relationship between the X-ray intensity of each element and the element concentration was previously determined as the calibration curve by using a known substance, and from the X-ray intensity obtained from the inclusion and the calibration curve above, the element concentration of the inclusion was quantitatively determined. The same operation was performed on a total of three cross-sections, and the average value thereof was defined as the average composition of nonmetallic particles having an equivalent-circle diameter of 1 μm or more. Out of the obtained results of quantitative determination, an inclusion having an oxygen content of 5% or more was taken as an oxide, and the concentrations converted to mass as a single oxide were averaged and defined as the average composition of oxides. The average composition of all oxides is shown in the Table below. Here, when a metal element is denoted by M, the oxide of REM is present in the form of M_2O_3, M_3O_5 or MO_2 in the steel material, but the composition was measured by converting all oxides to M_2O_3. In the case where a plurality of elements was observed from one inclusion, the composition of oxides was calculated by converting each element to its single oxide from the ratio of X-ray intensities indicating the presence of those elements.

(Measurement of number average density of fine Ti-containing nitrides having major axis of 20 to 500 nm)

[0087] A specimen was cut out from the position at a depth of t/2 (t: plate thickness) from the surface of the hot-rolled plate, such that the axial center of the specimen passes through the position of t/2. Thereafter, a Transmission Electron Microscope (TEM) replica specimen was prepared from a cross-section parallel to the rolling direction and the plate thickness direction, and its cross-section was observed using TEM. The observation conditions were magnification: 150,000 times and observation visual field: 0.66 μm $\times$ 0.78 μm, and three or more visual fields were observed. A particle containing Ti and N was distinguished by an energy dispersive X-ray detector (Energy Dispersive X-ray, EDX), and the particle was defined as Ti-containing nitride. Furthermore, by image analysis, the area of the Ti-containing nitride in the observation visual field was observed and converted to an equivalent-circle diameter, and the number of Ti-containing nitride particles of 500 nm or less was counted and converted to the number density per 1 mm^2. However, particles having an equivalent-circle diameter of less than 20 nm were excluded because of insufficient reliability of EDX. The number density per 1 mm^2 was measured similarly in all observation visual fields, and the average thereof was determined.

(Measurement of number average density of coarse Ti-containing nitrides having major axis of 2 μm or more)

[0088] A specimen was cut out from the position at a depth of t/2 (t: plate thickness) from the surface of the hot-rolled plate, such that the axial center of the specimen passes through the position of t/2. Thereafter, a cross-section parallel to the rolling direction and the plate thickness direction was photographed using an optical microscope at a magnification of 200 times in 20 visual fields, and the number of coarse Ti-containing nitrides was counted and converted to the number density per 1 mm^2, whereby the number density was determined. The area of the measured image was 0.148 mm^2 per visual field and 2.96 mm^2 per sample. The Ti-containing nitride was identified based on the shape and color, and an inclusion having an angular shape and a bright orange color was regarded as Ti-containing nitride. The major axis of the Ti-containing nitride was measured using an analysis software. Here, coarse Ti-containing nitride is often crystallized from an oxide as a starting point, but if crystallized, the oxide in the inside was excluded from the measurement target of the major axis.

(Measurement of Tensile Strength TS of Base plate)

[0089] A JIS Z2241 No. 4 specimen was sampled in parallel to the C-direction from the position at a depth of t/4 from the surface of the hot-rolled plate and subjected to a tensile test by the method described in JIS Z2241 to measure the tensile strength TS and the yield strength YS. Since the tensile test is little affected by the plate thickness direction and the value in the t/4 value is considered to have substantially the same meaning as the value in the t/2 part, in this Example, the tensile test was performed in the t/4 part. In this Example, those with TS of 485 MPa or more were judged to have excellent base plate strength (pass), and those with TS of less than 485 MPa were judged to have poor base plate strength (fail). Here, those where the base plate strength falls below the acceptance criterion of 485 MPa were not measured for the following HAZ toughness (in the Table, denoted by "not measured").

(Evaluation of Cryogenic HAZ Toughness)

[0090] A welded joint specimen having a plate thickness of 40 mm was sampled by reducing the hot-rolled plate (thickness: 80 mm) from both surfaces and then subjected to electro-gas arc welding under the conditions of a groove angle of 25°, a groove width (root gap) of 6 mm, and a heat input amount of 25 kJ/mm to obtain a welded joint. In evaluating the HAZ toughness in the welded joint, a region near the Fusion Line (also called a weld line or a weld fusion zone; in the Table, denoted by FL), which was exposed particularly to a very high temperature, was measured. Details are as follows.

[0091] Three Charpy specimens (10t $\times$ 10L $\times$ 55W, unit: mm, a V-notch specimen of JIS Z2242) each was sampled from the t/2 position of the specimen above, such that the bottom end of the notch is positioned at the fusion line and runs in the C-direction. Thereafter, a Charpy impact test was performed at -51°C by the method described in JIS Z2242 to determine the absorption energy (vE_{-51}), and the minimum value thereof was determined. Those where the minimum value of vE_{-51} was 48 J or more were judged to have excellent HAZ toughness (pass), and those where the minimum value of vE_{-51} was less than 48 J were judged to have poor HAZ toughness (fail).

[0092] These results are shown together in Table 2.

[Table 1A]

No.	Components in Steel (unit: mass%, remainder: iron and inevitable impurities)																		[Ti]*[N]
	C	Si	Mn	P	S	Al	Nb	Ti	N	O	REM	Zr	Ca	V	Cu	Ni	Cr	Mo	
1	0.08	0.20	1.52	0.007	0.0014	0.035	0.012	0.020	0.0062	0.0022	0.0027	0.0016	0.0010			0.19			0.000124
2	0.13	0.21	1.62	0.010	0.0014	0.030	0.019	0.024	0.0061	0.0018	0.0023	0.0009	0.0014						0.000147
3	0.03	0.17	1.51	0.005	0.0016	0.037	0.025	0.023	0.0070	0.0027	0.0013	0.0009	0.0011				0.28	0.2	0.000164
4	0.09	0.48	1.59	0.006	0.0014	0.034	0.022	0.025	0.0058	0.0018	0.0020	0.0009	0.0011		0.3				0.000143
5	0.12	0.08	1.59	0.006	0.0019	0.034	0.025	0.016	0.0077	0.0023	0.0014	0.0013	0.0017						0.000124
6	0.11	0.17	1.92	0.009	0.0017	0.032	0.019	0.016	0.0065	0.0027	0.0021	0.0019	0.0015						0.000106
7	0.10	0.20	0.73	0.008	0.0011	0.031	0.024	0.023	0.0077	0.0022	0.0028	0.0014	0.0016						0.000174
8	0.07	0.23	1.60	0.025	0.0012	0.036	0.019	0.016	0.0069	0.0017	0.0026	0.0017	0.0017						0.000113
9	0.08	0.22	1.55	0.007	0.0022	0.032	0.024	0.022	0.0058	0.0013	0.0013	0.0017	0.0016						0.000125
10	0.07	0.17	1.51	0.009	0.0010	0.020	0.020	0.021	0.0066	0.0027	0.0018	0.0010	0.0011						0.000141
11	0.10	0.19	1.41	0.005	0.0016	0.055	0.020	0.022	0.0071	0.0017	0.0013	0.0020	0.0017						0.000158
12	0.10	0.21	1.56	0.008	0.0016	0.036	0.034	0.020	0.0055	0.0014	0.0021	0.0008	0.0015						0.000111
13	0.08	0.16	1.36	0.008	0.0013	0.029	0.009	0.020	0.0057	0.0026	0.0028	0.0015	0.0013						0.000114
14	0.10	0.16	1.49	0.009	0.0012	0.028	0.022	0.029	0.0030	0.0025	0.0012	0.0016	0.0016						0.000087
15	0.09	0.23	1.52	0.009	0.0015	0.034	0.026	0.011	0.0091	0.0028	0.0015	0.0008	0.0016						0.000100
16	0.08	0.16	1.40	0.010	0.0009	0.035	0.022	0.019	0.0076	0.0038	0.0025	0.0017	0.0010						0.000146
17	0.09	0.18	1.55	0.010	0.0019	0.040	0.021	0.019	0.0076	0.0017	0.0124	0.0016	0.0015						0.000146
18	0.09	0.21	1.47	0.007	0.0019	0.034	0.016	0.021	0.0065	0.0022	0.0008	0.0013	0.0009						0.000137
19	0.10	0.17	1.53	0.005	0.0012	0.039	0.018	0.025	0.0054	0.0029	0.0014	0.0118	0.0008						0.000133
20	0.11	0.19	1.62	0.006	0.0017	0.037	0.016	0.018	0.0061	0.0015	0.0018	0.0005	0.0013						0.000108
21	0.11	0.23	1.40	0.005	0.0010	0.039	0.022	0.025	0.0057	0.0028	0.0019	0.0018	0.0005						0.000143
22	0.11	0.22	1.58	0.005	0.0009	0.030	0.025	0.024	0.0066	0.0020	0.0022	0.0012	0.0038						0.000155
23	0.11	0.21	1.45	0.005	0.0015	0.035	0.022	0.020	0.0072	0.0019	0.0020	0.0019	0.0015	0.06					0.000144
24	0.10	0.18	1.52	0.005	0.0011	0.027	0.026	0.016	0.0060	0.0027	0.0015	0.0009	0.0011		0.45				0.000097

(continued)

No.	Components in Steel (unit: mass%, remainder: iron and inevitable impurities)																		[Ti]*[N]
	C	Si	Mn	P	S	Al	Nb	Ti	N	O	REM	Zr	Ca	V	Cu	Ni	Cr	Mo	
25	0.07	0.21	1.46	0.006	0.0018	0.024	0.021	0.022	0.0069	0.0025	0.0013	0.0012	0.0009			0.72			0.000152
26	0.10	0.19	1.62	0.005	0.0010	0.038	0.024	0.023	0.0067	0.0026	0.0015	0.0017	0.0017				0.25		0.000155
27	0.09	0.19	1.35	0.008	0.0016	0.034	0.020	0.025	0.0069	0.0013	0.0018	0.0016	0.0016					0.37	0.000169

[Table 1B]

No.	Components in Steel (unit: mass%, remainder: iron and inevitable impurities)																		[Ti]*[N]
	C	Si	Mn	P	S	Al	Nb	Ti	N	O	REM	Zr	Ca	V	Cu	Ni	Cr	Mo	
28	0.25	0.17	1.58	0.010	0.0010	0.032	0.015	0.023	0.0052	0.0022	0.0019	0.0019	0.0017						0.000118
29	0.01	0.17	1.40	0.006	0.0014	0.038	0.018	0.018	0.0073	0.0026	0.0017	0.0012	0.0013						0.000135
30	0.09	0.60	1.46	0.010	0.0012	0.024	0.020	0.021	0.0071	0.0016	0.0015	0.0011	0.0015						0.000145
31	0.12	0.02	1.48	0.008	0.0011	0.029	0.025	0.020	0.0062	0.0017	0.0016	0.0012	0.0010						0.000124
32	0.09	0.23	2.20	0.010	0.0017	0.039	0.017	0.015	0.0075	0.0021	0.0015	0.0011	0.0011						0.000114
33	0.10	0.20	0.50	0.009	0.0010	0.029	0.023	0.022	0.0062	0.0019	0.0024	0.0018	0.0009						0.000138
34	0.09	0.20	1.56	0.040	0.0018	0.025	0.021	0.018	0.0067	0.0024	0.0014	0.0015	0.0008						0.000122
35	0.10	0.22	1.52	0.008	0.030	0.028	0.020	0.021	0.0075	0.0016	0.0017	0.0014	0.0010						0.000159
36	0.11	0.16	1.41	0.008	0.0012	0.010	0.023	0.015	0.0063	0.0024	0.0018	0.0013	0.0016						0.000096
37	0.08	0.19	1.41	0.004	0.0014	0.085	0.020	0.017	0.0065	0.0014	0.0020	0.0020	0.0014						0.000107
38	0.07	0.17	1.58	0.004	0.0019	0.035	-	0.017	0.0075	0.0015	0.0019	0.0012	0.0010						0.000127
39	0.08	0.18	1.41	0.004	0.0012	0.030	0.058	0.021	0.0059	0.0029	0.0028	0.0015	0.0008						0.000122
40	0.09	0.16	1.38	0.008	0.0015	0.031	0.017	0.002	0.0064	0.0017	0.0026	0.0010	0.0013						0.000013
41	0.08	0.20	1.54	0.005	0.0019	0.034	0.021	0.040	0.0053	0.0028	0.0026	0.0014	0.0015						0.000214
42	0.12	0.15	1.57	0.008	0.0014	0.024	0.026	0.017	0.0015	0.0020	0.0012	0.0017	0.0010						0.000026
43	0.09	0.20	1.52	0.009	0.0017	0.037	0.017	0.020	0.0120	0.0028	0.0027	0.0016	0.0013						0.000246
44	0.09	0.21	1.42	0.008	0.0016	0.026	0.016	0.018	0.0075	0.0050	0.0025	0.0012	0.0016						0.000136
45	0.10	0.24	1.56	0.009	0.0015	0.034	0.017	0.022	0.0074	0.0018	0.0525	0.0012	0.0016						0.000164
46	0.10	0.17	1.45	0.007	0.0013	0.024	0.015	0.017	0.0066	0.0014	-	0.0016	0.0008						0.000111
47	0.09	0.22	1.45	0.007	0.0017	0.029	0.026	0.021	0.0071	0.0022	0.0018	0.0258	0.0014						0.000148
48	0.07	0.18	1.41	0.009	0.0011	0.038	0.026	0.017	0.0069	0.0025	0.0014	-	0.0010						0.000118
49	0.08	0.23	1.47	0.010	0.0018	0.026	0.025	0.016	0.0070	0.0023	0.0020	0.0013	0.0088						0.000110
50	0.07	0.24	1.58	0.008	0.0009	0.024	0.026	0.021	0.0055	0.0025	0.0025	0.0015	-						0.000113
51	0.07	0.18	1.35	0.005	0.0013	0.029	0.018	0.016	0.0066	0.0020	0.0025	0.0017	0.0016						0.000105

[Table 2A]

No.	Steelmaking Step		Average Composition of Nonmetallic Particle (mass%)					Number Density of TiN (pieces/mm^2)		Base plate Strength	HAZ Toughness (minimum value)
	Control of Concentrations of Oxygen, Sulfur, Nitrogen and Ti in Molten Steel During Casting to Target Control Range	Base plate Production Method	Al_2O_3	TiO_2	Oxide of REM	ZrO_2	CaO	Number Density of Coarse TiN	Number Density of Fine TiN	TS (MPa)	vE_{-51}(J) FL Notch
1	Pass	TMCP	30%	7%	18%	11%	10%	0.0	1.7E+05	507	63
2	Pass	TMCP	25%	9%	16%	6%	14%	0.1	8.4E+05	516	114
3	Pass	TMCP	28%	8%	8%	5%	10%	0.5	1.6E+06	533	106
4	Pass	TMCP	26%	9%	13%	6%	10%	0.3	6.1E+05	507	82
5	Pass	TMCP	31%	6%	11%	9%	19%	0.0	1.8E+05	511	83
6	Pass	TMCP	31%	7%	17%	14%	16%	0.0	2.1E+05	522	89
7	Pass	TMCP	27%	9%	18%	10%	16%	0.5	2.0E+06	486	56
8	Pass	TMCP	30%	6%	18%	12%	16%	0.0	2.1E+05	490	63
9	Pass	TMCP	26%	8%	9%	11%	17%	0.2	6.0E+05	491	54
10	Pass	TMCP	22%	10%	16%	9%	14%	0.3	9.0E+05	486	62
11	Pass	TMCP	32%	6%	6%	10%	13%	0.7	2.2E+06	496	52
12	Pass	TMCP	30%	7%	15%	6%	14%	0.0	2.2E+05	500	57
13	Pass	TMCP	28%	8%	20%	11%	15%	0.0	2.6E+05	488	61
14	Pass	TMCP	23%	11%	8%	11%	16%	0.0	1.8E+05	496	52
15	Pass	TMCP	34%	5%	12%	6%	20%	0.0	2.9E+05	495	54
16	Pass	TMCP	29%	7%	16%	11%	10%	0.3	9.4E+05	489	52
17	Pass	TMCP	26%	6%	44%	9%	12%	0.3	7.5E+05	495	61
18	Pass	TMCP	29%	8%	6%	9%	9%	0.2	9.7E+05	494	62
19	Pass	TMCP	25%	7%	7%	52%	6%	0.2	6.7E+05	500	52
20	Pass	TMCP	32%	7%	12%	5%	13%	0.0	1.3E+05	508	55

(continued)

No.	Steelmaking Step		Average Composition of Nonmetallic Particle (mass%)					Number Density of TiN (pieces/mm^2)		Base plate Strength	HAZ Toughness (minimum value)
	Control of Concentrations of Oxygen, Sulfur, Nitrogen and Ti in Molten Steel During Casting to Target Control Range	Base plate Production Method	Al_2O_3	TiO_2	Oxide of REM	ZrO_2	CaO	Number Density of Coarse TiN	Number Density of Fine TiN	TS (MPa)	vE_{-51}(J) FL Notch
21	Pass	TMCP	28%	8%	11%	10%	5%	0.3	7.2E+05	497	61
22	Pass	TMCP	26%	9%	15%	8%	36%	0.6	1.5E+06	507	110
23	Pass	TMCP	28%	7%	14%	12%	15%	0.2	9.3E+05	509	107
24	Pass	TMCP	28%	8%	13%	8%	14%	0.0	2.5E+05	510	53
25	Pass	TMCP	25%	10%	10%	10%	11%	0.5	2.4E+06	502	72
26	Pass	TMCP	28%	7%	9%	10%	15%	0.5	1.7E+06	547	109
27	Pass	TMCP	26%	8%	11%	11%	15%	0.4	2.0E+06	564	109

[Table 2B]

No.	Steelmaking Step		Average Composition of Nonmetallic Particle (mass%)					Number Density of TiN (pieces/mm^2)		Base plate Strength	HAZ Toughness (minimum value)
	Control of Concentrations of Oxygen, Sulfur, Nitrogen and Ti in Molten Steel During Casting to Target Control Range	Base plate Production Method	Al_2O_3	TiO_2	Oxide of REM	ZrO_2	CaO	Number Density of Coarse TiN	Number Density of Fine TiN	TS (MPa)	vE_{-51}(J) FL Notch
28	Pass	TMCP	28%	9%	13%	13%	16%	0.0	3.4E+05	551	21
29	Pass	TMCP	33%	7%	11%	8%	13%	0.3	1.0E+06	442	not measured
30	Pass	TMCP	24%	10%	12%	9%	19%	0.3	5.8E+05	491	20
31	Fail	TMCP	29%	9%	12%	9%	11%	0.0	2.8E+05	504	8
32	Pass	TMCP	35%	6%	10%	8%	11%	0.0	2.8E+05	523	14
33	Pass	TMCP	25%	9%	17%	13%	10%	0.3	9.4E+05	454	not measured
34	Pass	TMCP	26%	9%	12%	12%	11%	0.0	2.0E+05	496	12
35	Pass	TMCP	27%	9%	12%	11%	10%	0.6	2.0E+06	499	9
36	Fail	TMCP	17%	12%	28%	21%	8%	0.1	3.3E+05	499	5
37	Pass	TMCP	51%	5%	8%	8%	8%	6.6	3.4E+05	486	11
38	Pass	TMCP	31%	6%	14%	9%	10%	0.1	5.0E+05	491	6
39	Pass	TMCP	26%	8%	20%	11%	9%	0.0	2.9E+05	453	not measured
40	Pass	TMCP	39%	1%	26%	11%	11%	5.4	1.6E+06	489	5
41	Pass	TMCP	21%	12%	12%	7%	20%	7.9	1.8E+06	493	15
42	Pass	TMCP	26%	9%	11%	15%	12%	0.0	2.3E+05	510	7
43	Pass	TMCP	30%	7%	18%	11%	13%	0.5	2.3E+06	497	13
44	Pass	TMCP	26%	8%	20%	10%	19%	2.4	9.2E+05	493	12
45	Pass	TMCP	15%	4%	62%	4%	8%	3.1	2.5E+06	500	4
46	Pass	TMCP	28%	8%	0%	15%	15%	2.1	3.3E+05	497	13
47	Pass	TMCP	12%	5%	7%	63%	10%	3.5	7.5E+05	494	5

(continued)

No.	Steelmaking Step		Average Composition of Nonmetallic Particle (mass%)					Number Density of TiN (pieces/mm^2)		Base plate Strength	HAZ Toughness (minimum value)
	Control of Concentrations of Oxygen, Sulfur, Nitrogen and Ti in Molten Steel During Casting to Target Control Range	Base plate Production Method	Al_2O_3	TiO_2	Oxide of REM	ZrO_2	CaO	Number Density of Coarse TiN	Number Density of Fine TiN	TS (MPa)	vE_{-51}(J) FL Notch
48	Pass	TMCP	34%	7%	9%	0%	11%	1.8	3.1E+05	486	14
49	Pass	TMCP	24%	6%	15%	9%	9%	4.9	1.5E+05	491	4
50	Pass	TMCP	24%	9%	20%	12%	12%	1.9	1.6E+05	489	13
51	Pass	as-air cooled	29%	7%	20%	14%	14%	0.0	2.7E+05	448	not measured

[0093] From the results in the Tables above, the following discussion can be made.

[0094] In Nos. 1 to 27 that are the cases satisfying the requirements of the present invention, where all of the components in the steel, the average composition of nonmetallic particles, and the number density of Ti-containing nitrides were appropriately controlled, the base plate strength was excellent and the HAZ toughness (vE_{-51}) at -51 °C when the heat input amount is set to 25 kJ/mm was good.

[0095] On the other hand, in the following cases failing in satisfying any of the requirements of the present invention, the below-described defect arises.

[0096] In No. 28 that is the case where the C amount exceeds the upper limit, the HAZ toughness was reduced.

[0097] In No. 29 that is the case where the C amount is below the lower limit, the base plate strength was reduced. Accordingly, the HAZ toughness was not measured.

[0098] In No. 30 that is the case where the Si amount exceeds the upper limit, the HAZ toughness was reduced.

[0099] In No. 31 that is the case where the Si amount is below the lower limit, at least one of the oxygen concentration, the sulfur concentration, the nitrogen concentration and the Ti concentration in the molten steel deviated from the target control range, and the HAZ toughness was reduced.

[0100] In No. 32 that is the case where the Mn amount exceeds the upper limit, the HAZ toughness was reduced.

[0101] In No. 33 that is the case where the Mn amount is below the lower limit, the base plate strength was reduced. Accordingly, the HAZ toughness was not measured.

[0102] In No. 34 that is the case where the P amount exceeds the upper limit, the HAZ toughness was reduced.

[0103] In No. 35 that is the case where the S amount exceeds the upper limit, the HAZ toughness was reduced.

[0104] In No. 36 that is the case where the Al amount is below the lower limit, at least one of the oxygen concentration, the sulfur concentration, the nitrogen concentration and the Ti concentration in the molten steel deviated from the target control range, and the HAZ toughness was reduced.

[0105] In No. 37 that is the case where the Al amount exceeds the upper limit, the average composition of the nonmetallic particle Al_2O_3 was increased, and the number density of coarse TiN was also increased, and as a result, the HAZ toughness was reduced.

[0106] In No. 38 that is the case where Nb was not added, the HAZ toughness was reduced.

[0107] In No. 39 that is the case where the Nb amount exceeds the upper limit, the base plate strength was reduced. Accordingly, the HAZ toughness was not measured.

[0108] In No. 40 that is the case where the Ti amount is below the lower limit, the average composition of the nonmetallic particle TiO_2 was decreased, and the number density of coarse TiN was increased, and as a result, the HAZ toughness was reduced.

[0109] In No. 41 that is the case where the Ti amount exceeds the upper limit, the number density of coarse TiN was increased, and the HAZ toughness was reduced.

[0110] In both of Nos. 42 and 43 that are the cases where the N amount is outside the lower and upper limits, the HAZ toughness was reduced.

[0111] In No. 44 that is the case where the O amount exceeds the upper limit, the number density of coarse TiN was increased, and the HAZ toughness was reduced.

[0112] In No. 45 that is the case where the REM amount exceeds the upper limit, all of the average compositions of respective oxides of nonmetallic particles failed to satisfy the requirements of the present invention, and since the number density of coarse TiN was increased, the HAZ toughness was reduced.

[0113] In No. 46 that is the case where REM was not added, REM oxide was not produced in the nonmetallic particle and since the number density of coarse TiN was increased, the HAZ toughness was reduced.

[0114] In No. 47 that is the case where the Zr amount exceeds the upper limit, the average composition of nonmetallic particle Al_2O_3 was small, leading to increase in the average composition of ZrO_2, and since the number density of coarse TiN was increased, the HAZ toughness was reduced.

[0115] In No. 48 that is the case where Zr was not added, ZrO_2 was not produced in the nonmetallic particle, and since the number density of coarse TiN was increased, the HAZ toughness was reduced.

[0116] In No. 49 that is the case where the Ca amount exceeds the upper limit, the number density of coarse TiN was increased, and the HAZ toughness was reduced.

[0117] In No. 50 that is the case where Ca was not added, the number density of coarse TiN was increased, and the HAZ toughness was reduced.

[0118] In No. 51 where the components in the steel satisfy the requirements of the present invention but the steel plate was manufactured "as-air cooled", the base plate strength was reduced. Accordingly, the HAZ toughness was not measured.

[0119] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope of the invention.

[0120] This application is based on Japanese Patent Application No. 2014-212542 filed on October 17, 2014, the contents of which are incorporated herein by way of reference.

Industrial Applicability

[0121] The rolled steel material of the present invention is useful for tanks to be used in the fields of an energy storage facility, a chemical plant, a power generation facility, a nuclear reactor pressure vessel, etc.

Claims

1. A thick steel plate for a tank, excellent in toughness of a weld heat affected zone, wherein

    (1) the thick steel plate has a composition comprising, in mass%:

    C: from 0.02 to 0.15%;
    Si: from 0.05 to 0.5%;
    Mn: from 0.6 to 2.0%;
    P: more than 0% and 0.030% or less;
    S: more than 0% and 0.025% or less;
    Al: from 0.02 to 0.07%;
    Nb: 0.005% or more and less than 0.050%;
    Ti: from 0.003 to 0.03%;
    N: from 0.0020 to 0.010%;
    O: more than 0% and 0.0040% or less;
    REM: from 0.0002 to 0.050%;
    Zr: from 0.0003 to 0.020%; and
    Ca: from 0.0003 to 0.0060%;
    with the remainder being iron and inevitable impurities, and
    $[Ti]\times[N] \geq 0.000085$ is satisfied, wherein [Ti] is the Ti content and [N] is the N content, and

    (2) when a thickness of the steel plate is t, the following requirements (2-1) and (2-2) are satisfied at t/2:

    (2-1) an average composition of nonmetallic particles having an equivalent-circle diameter of 1 μm or more satisfies, in mass%:

    $20\% \leq Al_2O_3 \leq 40\%$;
    $5\% \leq TiO_2 \leq 20\%$;
    $5\% \leq$ oxide of REM $\leq 45\%$;
    $5\% \leq ZrO_2 \leq 60\%$; and
    $5\% \leq CaO \leq 40\%$, and

    (2-2) an average number density of Ti-containing nitrides satisfies:

    0.8 pieces or less per 1 mm^2 for those having a major axis length of 2 μm or more; and
    1.0×10^5 pieces or more per 1 mm^2 for those having an equivalent-circle diameter of 20 nm or more and 500 nm or less.

2. The thick steel plate for a tank according to claim 1, further comprising at least one of the following (a) and (b):

    (a) in mass%, V: more than 0% and 0.1 % or less; and
    (b) in mass%, at least one element selected from the group consisting of Cu: more than 0% and 0.50% or less; Ni: more than 0% and 0.85% or less; Cr: more than 0% and 0.30% or less; and Mo: more than 0% and 0.5% or less.

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2015/078205

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/14*(2006.01)i, *C22C38/58*(2006.01)i, *C21C7/04* (2006.01)n, *C21D8/02*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C22C38/14, C22C38/58, C21C7/04, 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	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

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 2014-185364 A (Kobe Steel, Ltd.), 02 October 2014 (02.10.2014), claims; paragraphs [0051] to [0059]; tables 2 to 7 & WO 2014/148447 A1	1-2
A	JP 2012-162797 A (Kobe Steel, Ltd.), 30 August 2012 (30.08.2012), claims; paragraphs [0103] to [0135]; tables 3 to 6 & EP 2666880 A1 paragraphs [0103] to [0135]; tables 3 to 6; claims & WO 2012/099119 A1 & CN 103328672 A & KR 10-2013-0105713 A	1-2

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

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Date of the actual completion of the international search	Date of mailing of the international search report
08 December 2015 (08.12.15)	15 December 2015 (15.12.15)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/078205

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 2011-219797 A (Kobe Steel, Ltd.), 04 November 2011 (04.11.2011), claims; paragraphs [0026] to [0034]; tables 1 to 2 (Family: none)	1-2

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

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- JP H11279684 A **[0010]**
- JP 2003321728 A **[0010]**
- JP 2003286540 A **[0010]**
- JP 2012052224 A **[0010]**
- JP 2013127108 A **[0010]**
- JP 2014212542 A **[0120]**