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(54) **THICK STEEL SHEET HAVING EXCELLENT WELDING HEAT-AFFECTED ZONE TOUGHNESS**

DICKES STAHLBLECH MIT HERVORRAGENDER ZÄHIGKEIT DER WÄRMEEINFLUSSZONE

FEUILLE D'ACIER ÉPAISSE AYANT UNE EXCELLENTE TÉNACITÉ DANS LA ZONE AFFECTÉE THERMIQUEMENT PAR LE SOUDAGE

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Description

Technical Field

5 **[0001]** The present invention generally relates to steel plates (thick steel plates) to be applied to welded structures such as bridges, high-rise buildings, ships (marine vessels), and line pipes. More specifically, the present invention relates to a steel plate having excellent toughness in a heat affected zone after high heat input welding. The heat affected zone is hereinafter also simply referred to as HAZ.

10 Background Art

[0002] Welded structures such as bridges, high-rise buildings, ships, and line pipes have recently had larger and larger sizes. These welded structures have been increasingly made from steel plates having a thickness of 50 mm or more. This requires welding of such steel plates having a thickness of 50 mm or more. Under these circumstances, demands
15 have been made to provide high heat input welding for better welding working efficiency.

[0003] The HAZ upon high heat input welding, however, is held in the high-temperature austenite (γ) region for a long time upon heating and then gradually cooled. This often causes the coarsening of the microstructure typically by growth of austenite grains upon heating and formation of coarse ferrite (α) grains during the cooling process. This in turn causes the HAZ to have lower toughness upon high heat input welding. To prevent this, demands have been made to develop
20 a technique for maintaining the toughness of HAZ stably at high level upon high heat input welding. The toughness of HAZ is hereinafter also referred to as "HAZ toughness".

[0004] Proposed techniques to ensure the HAZ toughness at certain level include techniques relating to austenite grain growth pinning by inclusion particles, and to microstructure refinement by intragranular ferrite formation occurring at such inclusion particles. The inclusions are exemplified by oxides, nitrides, and sulfides. Such proposed techniques
25 include techniques described in Patent Literature (PTL) and PTL 2. Specifically, PTL 1 and PTL 2 disclose that fine titanium nitride particles, when dispersed and precipitated as austenite grain growth pinning particles in a steel, inhibit the coarsening of austenite grains formed in the HAZ upon high heat input welding and inhibit the HAZ toughness from deteriorating. The titanium nitride particles readily disappear with a higher welding heat input, and there is a need for a special scheme in order to obtain stable HAZ toughness.

[0005] The present inventors have also proposed a technique of precisely controlling the size and number (number density) of fine titanium nitride particles so as to improve HAZ toughness upon high heat input welding in PTL 3. However, the assumed heat input in this technique is at most 55 kJ/mm, and there is a need for further improvements so as to support further higher welding heat input.

[0006] PTL 4 to 7 have proposed techniques of utilizing oxide inclusions as austenite grain growth pinning particles, where the oxide inclusions are stable at high temperatures. The oxide inclusions, however, are few in number as compared with titanium-containing nitrides and fail to provide a sufficient pinning effect. The techniques therefore fail to support high heat input welding sufficiently, and there is a need for still further improvements.

[0007] Specifically, PTL 4 describes that the presence of oxides containing rare-earth elements (REM) and/or Zr gives good HAZ properties. However, the assumed heat input in the technique remains still low, and the technique is not
40 considered to always provide good HAZ properties upon high heat input welding. PTL 5 describes a technique of using oxides containing REM and/or Zr as with PTL 4. In this technique, the HAZ toughness is evaluated as Charpy absorbed energy (Charpy impact energy). It is considered, however, that not only the average, but also the minimum of this parameter should be maintained or secured at high level from the viewpoint of material reliability.

[0008] PTL 6 describes a technique of using both oxide inclusions and titanium-containing inclusions as austenite grain growth pinning particles to give high HAZ toughness. In the technique in PTL 6, the HAZ toughness is evaluated by a thermal cycle test that simulates high heat input welding. The test is performed at a highest heating temperature of 1400°C at which part of titanium-containing nitrides remains. In actual, however, the highest heating temperature in the HAZ partially becomes as high as greater than 1450°C, and this still further promotes the disappearance of titanium-containing nitrides. Accordingly, a high heat input welding test is desirably actually performed so as to accurately evaluate
50 the HAZ toughness upon high heat input. The present inventors have proposed a technique using the austenite grain growth pinning effect of fine oxide inclusions in PTL 7. This technique also utilizes the inhibition of reprecipitation of fine manganese sulfide particles and requires complicated control of determining amounts of alloy elements to be added based on the dissolved oxygen amount and dissolved sulfur amount.

[0009] Independently, exemplary techniques relating to the microstructure refinement due to intragranular ferrite formation occurring at inclusion particles are as follows. PTL 8 describes a technique of utilizing MnS (manganese sulfide) and complex oxides containing Ti and REM. The present inventors have proposed a technique of controlling the form of inclusions to promote the intragranular ferrite formation in PTL 9. These techniques have been made on the assumption that inclusions having a low interfacial energy between intragranular ferrite and the inclusions are effective in intragranular

ferrite formation. However, the techniques have not yet reached sufficient HAZ toughness upon high heat input. This is because the intragranular ferrite formation is largely affected also by the interfacial energy between intragranular ferrite and austenite, and is not sufficiently obtained merely by decreasing the interfacial energy between intragranular ferrite and inclusions.

[0010] The present inventors have developed a technique to provide high HAZ toughness using intragranular ferrite formation occurring at oxi-sulfides and have proposed in PTL 10. However, in return for the high HAZ toughness, there is a need for dispersing relatively large-sized oxi-sulfide particles having a size of 2 μm or more. Thus, this technique has also not yet reached sufficient HAZ toughness upon high heat input. Specifically, the technique described in PTL 8 employs a small heat input as assumed; whereas the techniques described in PTL 9 and PTL 10 provide, in Charpy absorbed energy, a high average, but a minimum that is susceptible to improvements under present circumstances.

[0011] In addition, the present inventors have proposed techniques of dispersing oxides having a controlled micro-structure to give high HAZ toughness in PTL 11 and PTL 12. These techniques actually provide steel plates having excellent heat affected zone toughness, but are still susceptible to improvements upon production.

[0012] The technique described in PTL 11 controls the amount of Ca to be added based on the amount of dissolved oxygen before the addition of Ca so as to provide predetermined oxide particle form. This technique, however, should be performed so that the time from the Ti addition to the Ca addition falls within the range of 3 to 20 minutes and may increase the operator's burden. The technique described in PTL 12 requires holding of the work for a time of 40 minutes to 90 minutes in a period of time from the Ca addition to casting (pouring) and is still susceptible to improvements in productivity. PTL 13 discloses a thick steel plate having excellent heat affected zone toughness. PTL 13 is silent about the size and distribution of the titanium nitride particles.

Citation List

Patent Literature

[0013]

PTL1: Japanese Unexamined Patent Application Publication (JP-A) No. 2001-98340

PTL2: JP-A No. 2004-218010

PTL 3: JP-A No. 2010-95781

PTL 4: JP-A No. 2001-20031

PTL 5: JP-A No. 2007-247005

PTL6: JP-A No. 2008-223062

PTL 7: JP-A No. 2009-179844

PTL8: JP-A No. Hei7(1995)-252586

PTL9: JP-A No. 2008-223081

PTL 10: JP-A No. 2009-138255

PTL 11: JP-A No. 2010-168644

PTL 12: JP-A No. 2011-219797

PTL 13: JP-A No.2010-168644

Summary of Invention

Technical Problem

[0014] The present invention has been made under the circumstances of the conventional techniques and has an object to provide a steel plate that can have not only a higher average, but also a higher minimum charpy impact value in HAZ toughness even upon high heat input welding, has excellent heat affected zone toughness, and exhibits excellent productivity.

Solution to Problem

[0015] The present invention provides, according to a first embodiment, a steel plate having excellent heat affected zone toughness, the steel plate having a thickness of 50 mm or more. The steel plate contains, in mass percent, C in a content of 0.03% to 0.12%, Si in a content of 0.10% to 0.25%, Mn in a content of 1.0% to 2.0%, P in a content of 0.03% or less (excluding 0%), S in a content of 0.015% or less (excluding 0%), Al in a content of 0.004% to 0.05%, Ti in a content of 0.010% to 0.050%, at least one rare-earth element (REM) in a content of 0.0003% to 0.02%, Zr in a content of 0.0003% to 0.02%, Ca in a content of 0.0005% to 0.010%, N in a content of 0.002% to 0.010%; and optionally at least

one element selected from the group consisting of Ni in a content of 0.05% to 1.50%; Cu in a content of 0.05% to 1.50%; Cr in a content of 0.05% to 1.50%; Mo in a content of 0.05% to 1.50%; Nb in a content of 0.002% to 0.10%; V in a content of 0.002% to 0.10%; and B in a content of 0.0005% to 0.0050%, with the remained being iron and inevitable impurities. The steel plate includes oxide particles that contain constituent elements excluding oxygen in contents, in mass percent, meeting conditions as follows: $2\% < \text{Ti} < 40\%$, $5\% < \text{Al} < 30\%$, $5\% < \text{Ca} < 40\%$, $5\% < \text{REM} < 50\%$, $2\% < \text{Zr} < 30\%$, and $1.0 \leq \text{REM}/\text{Zr}$. Of the oxide particles, oxide particles having an equivalent circle diameter of less than $2\text{ }\mu\text{m}$ are present in a number density of 300 or more per square millimeter, and oxide particles having an equivalent circle diameter of $2\text{ }\mu\text{m}$ or more are present in a number density of 100 or less per square millimeter. The steel plate includes titanium nitride particles. Of the titanium nitride particles, titanium nitride particles having an equivalent circle diameter of $1\text{ }\mu\text{m}$ or more are present in a number density of 7 or less per square millimeter, and titanium nitride particles having an equivalent circle diameter of 20 nm or more are present in a number density of 1.0×10^6 or more per square millimeter. The steel plate has d_f and d_a meeting a condition specified by the relational expression:

$$|d_a - d_f|/d_a \leq 0.35,$$

in which the d_f is defined so that the titanium nitride particles having an equivalent circle diameter of 20 nm or more are classified into ranges of equivalent circle diameter of from 20 nm up to 500 nm every 5 nm in an increasing order, in which particles in each of the ranges have an equivalent circle diameter of $(d_i - 5)$ to less than d_i , where d_i is 25, 30, 35, ..., 500, and the d_i in a range having a largest number of titanium nitride particles present in the range is defined as the d_f . The d_a represents an average equivalent circle diameter of the titanium nitride particles having an equivalent circle diameter of 20 nm to less than 500 nm.

[0016] As used above and hereinafter the term "equivalent circle diameter" refers to the diameter of an assumed circle having an equivalent area to the size (area) of an oxide particle or a titanium nitride particle in question. The equivalent circle diameter may be determined by observation under a transmission electron microscope (TEM) or a scanning electron microscope (SEM).

[0017] According to a second embodiment, the steel plate having excellent heat affected zone toughness may include specific oxides in a number density of 300 or more per square millimeter, where the specific oxides include constituent elements excluding oxygen in contents, in mass percent, meeting conditions as follows: $2\% < \text{Ti} < 40\%$, $5\% < \text{Al} < 30\%$, $5\% < \text{Ca} < 40\%$, $5\% < \text{REM} < 50\%$, $2\% < \text{Zr} < 30\%$, and $1.5 \leq \text{REM}/\text{Zr}$.

Advantageous Effects of Invention

[0018] The present invention provides a steel plate that can have a higher average and a higher minimum in HAZ toughness not only upon low to moderate heat input welding, but also even upon high heat input welding, has such excellent heat affected zone toughness, and still exhibits excellent productivity.

Description of Embodiments

[0019] The present inventors have made searches for ways to allow a steel plate to have better HAZ toughness upon high heat input under production conditions with relatively high productivity. As a result, the present inventors have found as follows. Assume that intragranular ferrite formation occurring at oxides is ensured, coarse titanium nitride particles acting as an inhibitory factor to HAZ toughness are inhibited to be formed, and titanium nitride particles are dispersed in an appropriately controlled form. This allows a steel plate to have productivity and HAZ toughness upon high heat input both at satisfactory levels. Specifically, the present inventors have findings as follows. Assume that the oxides are controlled appropriately in their chemical compositions. This ensures intragranular ferrite formation. Further assume that the titanium nitride particles are appropriately controlled in size and number to inhibit coarsening of prior austenite grains. This enables the refinement of grain-boundary ferrite grains that are formed at prior austenite grain boundaries. Thus, a steel plate having excellent HAZ toughness upon high heat input is provided.

[0020] More specifically, the present inventors have verified as follows. Assume that, of the oxides, those having an equivalent circle diameter of less than $2\text{ }\mu\text{m}$ are dispersed in a number density of 300 or more per square millimeter, but those having an equivalent circle diameter of $2\text{ }\mu\text{m}$ or more are controlled to be dispersed in a number density of 100 or less per square millimeter. This provides excellent HAZ toughness.

[0021] The present invention has been made based on the above-mentioned findings. The individual elements and conditions are specified for reasons as follows.

[0022] In the steel plate, oxide particles meeting the conditions of constituent elements excluding oxygen in contents, in mass percent: $2\% < \text{Ti} < 40\%$, $5\% < \text{Al} < 30\%$, $5\% < \text{Ca} < 40\%$, $5\% < \text{REM} < 50\%$, $2\% < \text{Zr} < 30\%$, and $1.0 \leq \text{REM}/\text{Zr}$,

and having an equivalent circle diameter of less than 2 μm are present in a number density of 300 or more per square millimeter.

[0023] The majority of oxide particles are controlled to have an equivalent circle diameter of less than 2 μm . Such fine oxide particles promote intragranular ferrite formation to improve the HAZ toughness. In contrast, oxide particles having an equivalent circle diameter of 2 μm or more may lower the barrier energy upon formation of coarse titanium nitride particles to increase the amount of formed coarse titanium nitride particles. Oxide particles, if having a chemical composition, in mass percent, not meeting the conditions of $2\% < \text{Ti} < 40\%$, $5\% < \text{Al} < 30\%$, $5\% < \text{Ca} < 40\%$, $5\% < \text{REM} < 50\%$, $2\% < \text{Zr} < 30\%$, and $1.0 \leq \text{REM}/\text{Zr}$, may fail to contribute to sufficient intragranular ferrite formation. In a preferred embodiment, the ratio (in mass percent) of REM to Zr in the oxide particles may be controlled to 1.5 or more. This further reduces the amount of coarsely formed titanium nitride particles in the surface of the oxide particles in molten steel to achieve still further excellent HAZ toughness.

[0024] In the steel plate, oxide particles having an equivalent circle diameter of 2 μm or more are present in a number density of 100 or less per square millimeter.

[0025] Of the oxide particles meeting the chemical composition as above, those having an equivalent circle diameter of 2 μm or more cause deterioration in HAZ toughness and are preferably minimized. From this viewpoint, the number density of oxide particles having an equivalent circle diameter of 2 μm or more is controlled to 100 or less per square millimeter in the present invention.

[0026] According to an embodiment of the present invention, the form of titanium nitride (particles) is specified in detail. The titanium nitride inhibits austenite grain coarsening upon HAZ high-temperature heating, reduces the sizes of grain-boundary ferrite grains formed during cooling, and thereby contributes to better HAZ toughness. To sufficiently inhibit austenite grain coarsening, a large number of titanium nitride particles should naturally be dispersed. In addition to this, the present inventors have found that the titanium nitride particles are dissolved at a lower dissolution rate upon HAZ high-temperature heating with more uniformized sizes of the particles; and that appropriate control of the size and number of the titanium nitride particles can effectively inhibit austenite grain coarsening even upon high heat input welding. Specifically, the steel plate, when meeting two conditions as follows, can exhibit satisfactory HAZ toughness upon high heat input.

[0027] In the first condition, titanium nitride particles having an equivalent circle diameter of 1 μm or more are controlled to be present in a number density of 7 or less per square millimeter.

[0028] The titanium nitride particles having an equivalent circle diameter of 1 μm or more, if present in a number density of greater than 7 per square millimeter, may cause the steel plate to have inferior HAZ toughness. Such titanium nitride particles have a rectangular parallelepiped shape, still have remarkably high hardness as compared with the steel, and cause stress concentration to significantly impair the HAZ toughness. Accordingly, the coarse titanium nitride particles should be more strictly controlled as compared with coarse oxide particles.

[0029] In the second condition, titanium nitride particles having an equivalent circle diameter of 20 nm or more are present in a number density of 1.0×10^6 or more per square millimeter.

[0030] The titanium nitride particles having an equivalent circle diameter of 20 nm or more, if present in a number density of less than 1.0×10^6 per square millimeter, may fail to sufficiently act as titanium nitride particles necessary in inhibition of austenite grain coarsening. Ultrafine titanium nitride particles having an equivalent circle diameter of less than 20 nm disappear in a short time in high-temperature heating upon high heat input welding, thereby little contribute to the inhibition of austenite grain coarsening, and do not require special control.

$$|da - df|/da \leq 0.35$$

[0031] Titanium nitride particles are energetically unstable with a decreasing size thereof. Specifically, titanium nitride particles more readily disappear upon HAZ high-temperature heating with a smaller (decreasing) size as compared to the average size of all titanium nitride particles. For this reason, particles that contribute to austenite grain coarsening inhibition are substantially present in an increasing number with an increasing number of titanium nitride particles having a larger size than the average size, or having a size smaller than, but relatively near to, the average size.

[0032] The present inventors have found herein as follows. When a size-number histogram of titanium nitride particles is plotted, the size and number of the particles are preferably controlled so that the difference between the average size and a size in which the largest number of titanium nitride particles is recorded becomes small. This increases the number of the substantially contributive titanium nitride particles and achieves highly effective inhibition of austenite grain coarsening.

[0033] More specifically, the control may be performed that the difference between values df and da becomes small. The df is defined as follows. The titanium nitride particles having an equivalent circle diameter of 20 nm or more are classified into ranges of equivalent circle diameter from 20 nm up to 500 nm every 5 nm in an increasing order, in which

particles in each of the ranges have an equivalent circle diameter of $(d_i - 5)$ to less than d_i , where d_i is 25, 30, 35,...500, and the d_i in a range having a largest number of titanium nitride particles present in the range is defined as the d_f . The d_a represents the average equivalent circle diameter of the titanium nitride particles having an equivalent circle diameter of 20 nm to less than 500 nm. This control increases the number of substantially contributive titanium nitride particles and achieves highly effective inhibition of austenite grain coarsening.

[0034] The average equivalent circle diameter of titanium nitride particles was calculated in the following manner. Specifically, a sample was subjected to transmission electron microscopic (TEM) observation under conditions mentioned below in experimental examples. The areas of individual titanium nitride particles in the observation view field were measured by image analysis, from which equivalent circle diameters of the individual titanium nitride particles were calculated. Of the particles, titanium nitride particles having an equivalent circle diameter of 20 nm to less than 500 nm were selected, and the arithmetic mean of the equivalent circle diameters of the selected particles was determined.

[0035] Specifically, if the value specified by the formula: $|d_a - d_f|/d_a$ is greater than 0.35, titanium nitride particles, even if present in a large number, may fail to sufficiently inhibit austenite grain coarsening and fail to provide satisfactory HAZ toughness upon high heat input.

Production Method

[0036] The steel plate according to the present invention meets the above-mentioned conditions. Specifically, the steel plate contains oxide particles including constituent elements excluding oxygen in contents, in mass percent, meeting conditions: $2\% < \text{Ti} < 40\%$, $5\% < \text{Al} < 30\%$, $5\% < \text{Ca} < 40\%$, $5\% < \text{REM} < 50\%$, $2\% < \text{Zr} < 30\%$, and $1.0 \leq \text{REM}/\text{Zr}$. Of the oxide particles, oxide particles having an equivalent circle diameter of less than $2 \mu\text{m}$ are present in a number density of 300 or more per square millimeter; and oxide particles having an equivalent circle diameter of $2 \mu\text{m}$ or more are present in a number density of 100 or less per square millimeter. Of titanium nitride particles contained in the steel plate, titanium nitride particles having an equivalent circle diameter of $1 \mu\text{m}$ or more are present in a number density of 7 or less per square millimeter, and titanium nitride particles having an equivalent circle diameter of 20 nm or more are present in a number density of 1.0×10^6 or more per square millimeter. In addition, the steel plate meets the conditions as specified by the relational expression of $|d_a - d_f|/d_a \leq 0.35$. The steel plate is preferably produced under production conditions as follows.

[0037] The preferred production conditions are as follows. In ingot-making, the dissolved oxygen content in the molten steel is controlled to the range of 0.002% to 0.01% (in mass percent) by deoxidation typically using Mn and Si. Thereafter Al, Ti, (REM, Zr), and Ca are added in the specified order in such a controlled manner that a time t_1 from the REM or Zr addition to the Ca addition be 5 minutes or longer. In addition, a cooling time t_2 in the temperature range of 1500°C to 1450°C upon casting may be set within 300 seconds, and a cooling time t_3 in the temperature range of 1300°C to 1200°C upon casting may be set within 680 seconds. In a preferred embodiment, the mass ratio $[\text{REM}]/[\text{Zr}]$ of the REM content [REM] to the Zr content [Zr] may be controlled to 1.8 or more, and the time t_1 may be controlled to 10 minutes or longer. This may provide more an appropriate oxide particle form and reduce the amount of coarsely formed titanium nitride particles in the surface of the oxide particles to give still better HAZ toughness. Next, why the production conditions are specified will be described in detail below. As used herein the term "(REM, Zr)" refers to that REM and Zr may be added simultaneously or non-simultaneously in any order.

[0038] Initially, the dissolved oxygen content in the molten steel is controlled to the range of 0.002% to 0.01% by deoxidation typically using Mn and Si.

[0039] The dissolved oxygen, if present in a content less than 0.002%, may fail to provide a necessary amount of oxide particles having such an appropriate chemical composition as to induce intragranular ferrite formation. The dissolved oxygen, if present in a content greater than 0.01%, may cause the formation of a larger amount of coarse oxide particles having an equivalent circle diameter of $2 \mu\text{m}$ or more to cause the steel plate to have inferior HAZ toughness.

[0040] Secondary, the time t_1 from the addition of REM or Zr to the addition of Ca is controlled to 5 minutes or longer.

[0041] The oxides specified in the present invention effectively promote intragranular ferrite formation and hardly function as nucleation sites for coarse titanium nitride particles. In particular to allow the REM/Zr ratio (in mass percent) in the oxides to be 1.0 or more, an oxide formation reaction of REM or Zr preferably proceeds sufficiently before the addition of Ca that acts as a strong deoxidizing element. Specifically, the time t_1 from the addition of REM or Zr to the addition of Ca is preferably controlled to 5 minutes or longer. This can give oxide particles that are present in a predetermined number density and meet the condition: $\text{REM}/\text{Zr} \geq 1.0$. If the time t_1 from the addition of REM or Zr to the addition of Ca is shorter than 5 minutes, oxide particles meeting the condition: $\text{REM}/\text{Zr} \geq 1.0$ may be formed insufficiently. In a preferred embodiment, the mass ratio $[\text{REM}]/[\text{Zr}]$ of the REM content [REM] to the Zr content [Zr] is controlled to 1.8 or more, and the time t_1 is controlled to 10 minutes or longer. This can give oxide particles that are present in a predetermined number density and meet the condition: $\text{REM}/\text{Zr} \geq 1.5$.

[0042] The elements Al, Ti, (REM, Zr), and Ca are added in the specified order in ingot making. This is because these elements, if added in a order other than the specified order, may fail to ensure a sufficient number of oxide particles

having such an appropriate chemical composition as to act as nucleation sites of intragranular ferrite. In particular, Ca is a strong deoxidizing element and has extremely strong deoxidation power and, if added prior to Ti and Al, may significantly reduce the amount of oxygen to be combined with Ti and Al.

[0043] The cooling time t_2 in the temperature range of 1500°C to 1450°C upon casting is controlled within 300 seconds.

[0044] If the cooling time t_2 in the temperature range of 1500°C to 1450°C upon casting is longer than 300 seconds, coarse oxide particles may be increased, or coarse titanium nitride particles may be formed due to component segregation upon solidification, to cause the steel plate to have inferior HAZ toughness.

[0045] The cooling time t_3 in the temperature range of 1300°C to 1200°C upon casting is controlled within 680 seconds.

[0046] If the cooling time t_3 in the temperature range of 1300°C to 1200°C upon casting is longer than 680 seconds, the relational expression of $|d_a - d_f|/d_a \leq 0.35$ may not be satisfied. This is probably because as follows.

[0047] Titanium nitride particles formed upon casting are classified into A, B, and C as follows. The titanium nitride particles A are those formed in the molten steel. The titanium nitride particles B are those formed in a solidification segregation portion of the solidified steel. The titanium nitride particles are those formed in a non-solidification-segregation portion of the solidified steel. The titanium nitride particles A, B, and C are formed in the specified order and have sizes (particle diameters) in decreasing order ($A > B > C$). In contrast, the titanium nitride particles A, B, and C are present in increasing order of number ($A < B < C$). Most of titanium nitride particles having sizes corresponding to the d_f are the titanium nitride particles C. The titanium nitride particles A are present in a smaller number as compared with the titanium nitride particles B and C and little affect the average equivalent circle diameter d_a of titanium nitride particles. It is therefore considered that, to control the value specified by $|d_a - d_f|/d_a$ within a predetermined range, the formation of the titanium nitride particles B and C is preferably controlled. Assume that the cooling time t_3 in the temperature range of 1300°C to 1200°C upon casting is longer than 680 seconds. In this case, the titanium nitride particles B grow prior to the formation of the titanium nitride particles C and may cause the specific titanium nitride particles to have a larger average equivalent circle diameter d_a , to probably cause the value specified by $|d_a - d_f|/d_a$ to be greater than 0.35.

Chemical Compositions

[0048] Next, the chemical compositions of the steel plate according to the present invention will be described. Assume that the steel plate according to the present invention includes individual chemical compositions (elements) in contents out of appropriate ranges. In this case, the base metal (steel plate) may fail to have properties and the HAZ at good levels even when the steel plate includes oxide particles in the appropriate dispersion state as described above. Accordingly, the steel plate according to the present invention includes chemical compositions in contents within ranges as described below. The contents of elements constituting oxides, such as Al, Ca, and Ti, among the chemical compositions, are contents as including part of the elements constituting the oxides. The contents (%) of the chemical compositions are all in mass percent.

C of 0.03% to 0.12%

[0049] Carbon (C) element is essential for ensuring the strength of the steel plate. Carbon, if present in a content less than 0.03%, may fail to provide a necessary strength. In contrast, carbon, if present in an excessively high content, may cause the formation of a large amount of hard martensite-austenite constituent (MA) to cause the base metal to have inferior toughness. To prevent this, the carbon content may be controlled to 0.12% or less. Of the carbon content, the lower limit is preferably 0.04%, and the upper limit is preferably 0.10%.

Si of 0.10% to 0.25%

[0050] Silicon (Si) element allows titanium (Ti) to have higher activity and may be added as appropriate to provide the predetermined titanium nitride particle form. Si, if added in an amount of less than 0.10%, may fail to allow the titanium nitride particles having an equivalent circle diameter of 20 nm or more to be present in a number density of 1.0×10^6 per square millimeter or more. Si, if added in an amount of greater than 0.25%, may readily cause the formation of coarse titanium nitride particles and the formation of a hard MA phase, to fail to provide a predetermined HAZ toughness. Of the Si content, the lower limit is preferably 0.12% and more preferably 0.14%, and the upper limit is preferably 0.22% and more preferably 0.20%.

Mn of 1.0% to 2.0%

[0051] Manganese (Mn) element is useful in ensuring the strength of the steel plate. To allow the element to exhibit such effects effectively, Mn is preferably present in a content of 1.0% or more. However, Mn, if present in an excessively high content of greater than 2.0%, may cause the HAZ to have an excessively high strength and to have inferior toughness.

To prevent this, the Mn content is preferably 2.0% or less. Of the Mn content, the lower limit is preferably 1.4%, and the upper limit is preferably 1.8%.

P of 0.03% or less (excluding 0%)

[0052] Phosphorus (P) element is an impurity element that readily causes grain boundary fracture and adversely affects the toughness. To prevent this, the phosphorus content is preferably minimized. From the viewpoint of ensuring the HAZ toughness, the phosphorus content is controlled to 0.03% or less, and preferably 0.02% or less. However, it is difficult to industrially control the phosphorus content in the steel to 0%.

S of 0.015% or less (excluding 0%)

[0053] Sulfur (S) element forms manganese sulfide at the prior austenite grain boundary in the HAZ and causes the steel plate to have inferior HAZ toughness. To prevent this, the sulfur content is preferably minimized. From the viewpoint of ensuring the HAZ toughness, the sulfur content is controlled to 0.015% or less, and preferably 0.010% or less. However, it is difficult to industrially control the sulfur content in the steel to 0%.

Al of 0.004% to 0.05%

[0054] Aluminum (Al) element forms oxides that act as nucleation sites for intragranular ferrite. Al, if present in a content of less than 0.004%, may fail to provide the predetermined oxide form and fail to sufficiently promote intragranular transformation to cause the steel plate to have inferior HAZ toughness. In contrast, Al, if present in an excessively high content, may cause the formation of coarse oxide particles to cause the steel plate to have inferior HAZ toughness. To prevent this, the Al content may be controlled to 0.05% or less. Of the Al content, the lower limit is preferably 0.007%, and the upper limit is preferably 0.04%.

Ti of 0.010% to 0.050%

[0055] Titanium (Ti) element forms titanium nitride and, when added prior to REM, Zr, and Ca, enables fine dispersion of oxides that effectively promote intragranular ferrite formation. To provide the predetermined titanium nitride and oxide forms, Ti may be contained in a content of 0.010% or more. However, Ti, if present in an excessively high content, may cause the formation of a larger amount of coarse titanium nitride particles to cause the steel plate to have inferior HAZ toughness. To prevent this, the Ti content may be controlled to 0.050% or less. Of the Ti content, the lower limit is preferably 0.012%, and the upper limit is preferably 0.035% and more preferably 0.025%.

REM of 0.0003% to 0.02% and Zr of 0.0003% to 0.02%

[0056] Rare-earth elements (REM) and zirconium (Zr) element, when added after the addition of Ti but before the addition of Ca, form oxides that are effective in intragranular ferrite formation. These oxides, when compositively precipitated with titanium nitride, more suitably act as intragranular ferrite formation sites. The elements exhibit these effects increasingly with increasing contents. To allow the elements to exhibit the effects effectively, REM and Zr may be present each in a content of 0.0003% or more. However, these elements, if present in an excessively high content, may cause the oxides to be coarsened to cause the steel plate to have inferior HAZ toughness. To prevent this, the contents of REM and Zr may be each controlled to 0.02% or less. Of the contents of these elements, the lower limit is more preferably 0.0005%, and the upper limit is more preferably 0.015%.

Ca of 0.0005% to 0.010%

[0057] Calcium (Ca) element, when added 5 minutes or longer after the addition of REM and Zr (in any order), forms oxides that are effective in intragranular ferrite formation and inhibit the formation of coarse titanium nitride particles. To allow the element to exhibit such effects effectively, Ca may be contained in a content of 0.0005% or more. However, Ca, if present in an excessively high content, may form coarse oxide particles to cause the steel plate to have inferior HAZ toughness. To prevent this, the Ca content may be controlled to 0.010% or less. Of the Ca content, the lower limit is preferably 0.0008%, and the upper limit is preferably 0.008%.

N of 0.002% to 0.010%

[0058] Nitrogen (N) element, when forming fine titanium nitride particles, is useful in ensuring the HAZ toughness.

Nitrogen, if present in a content of 0.002% or more, may provide the desired titanium nitride particles. However, nitrogen, if present in an excessively high content, may promote the formation of coarse titanium nitride particles. To prevent this, the nitrogen content may be controlled to 0.010% or less. Of the nitrogen content, the lower limit is preferably 0.003%, and the upper limit is preferably 0.008%.

[0059] The above-mentioned elements are essential elements specified in the present invention, with the remainder being iron and inevitable impurities. As inevitable impurities, Sn, As, Pb, and other elements may be contained, where the elements are brought into the steel under circumstances of raw materials, facility materials, and production facilities. It is also effective to actively add any of elements as follows. This may allow the steel plate to have further better property or properties depending on the type of the chemical composition (element) to be added.

[0060] In a preferred embodiment, at least one element selected from the group consisting of Ni of 0.05% to 1.50%, Cu of 0.05% to 1.50%, Cr of 0.05% to 1.50%, and Mo of 0.05% to 1.50% may be added.

[0061] Nickel (Ni), copper (Cu), Chromium (Cr), and molybdenum (Mo) elements are each effective in allowing the steel plate to have a higher strength. These elements exhibit increasing effects with increasing contents. To allow the elements to exhibit such effects effectively, the elements are preferably contained each in a content of 0.05% or more. However, the elements, if present in an excessively high content, may cause the steel plate to have an excessively high strength and to have inferior HAZ toughness. To prevent this, the contents of the elements are each preferably controlled to 1.50% or less. Of each of the contents of the elements, the lower limit is more preferably 0.10%, and the upper limit is more preferably 1.20%.

[0062] In a preferred embodiment, at least one of Nb of 0.002% to 0.10% and V of 0.002% to 0.10% may be added.

[0063] Niobium (Nb) and vanadium (V) elements precipitate as carbonitrides, inhibit the coarsening of austenite grains, and are effective in allowing the base metal to have good toughness. These elements exhibit increasing effects with increasing contents. To allow the elements to exhibit such effects effectively, the elements are preferably contained each in a content of 0.002% or more. However, the elements, if contained in excessively high contents, may cause the coarsening of the HAZ microstructure to cause the steel plate to have inferior HAZ toughness. To prevent this, the contents of the elements are each preferably controlled to 0.10% or less. Of each of the contents of the elements, the lower limit is more preferably 0.005%, and the upper limit is more preferably 0.08%.

[0064] In a preferred embodiment, B of 0.0005% to 0.0050% may be added

[0065] Boron (B) element inhibits the formation of coarse grain boundary ferrite and effectively allows the steel plate to have better HAZ toughness. The element exhibits an increasing effect as above with an increasing content thereof. To allow the element to exhibit such effects effectively, the element is preferably contained in a content of 0.0005% or more. The boron content is more preferably 0.0010% or more, and furthermore preferably 0.0015% or more. However, boron, if present in an excessively high content, may promote the formation of a coarse bainite packet at prior austenite grain boundaries to cause the steel plate to have inferior HAZ toughness contrarily. Of the boron content, the upper limit is preferably 0.0045%, more preferably 0.0040%, and furthermore preferably 0.0035%.

[0066] As is described in the description of chemical compositions, it is effective for the steel plate to contain at least one element selected from the group consisting of Ni, Cu, Cr, and Mo. In this case, the contents (in mass percent) of these elements preferably meet the condition: $[Ni] + [Cu] + [Cr] + [Mo] < 2.5\%$, where [Ni], [Cu], [Cr], and [Mo] are contents (in mass percent) respectively of Ni, Cu, Cr, and Mo.

[0067] Coarse titanium nitride particles are formed in a liquid phase in a solidification stage of the molten steel, where Ti and N are enriched in the liquid phase due to solidification segregation. The elements, when present in a total content ($[Ni] + [Cu] + [Cr] + [Mo]$) of greater than 2.5%, may cause the solidification temperature to be lowered. This may cause the liquid phase to remain even cooled down to a low temperature. At such low temperatures, the driving force for the formation of coarse titanium nitride particles becomes large to cause the formation of a larger amount of the coarse titanium nitride particles.

$$|da-df|/da \leq 0.35$$

[0068] The value specified by $|da-df|/da$ is a parameter that relates to the number of titanium nitride particles contributing to austenite grain coarsening inhibition upon HAZ high-temperature heating. If the value is greater than 0.35, the austenite grains are not sufficiently inhibited from coarsening and fail to provide predetermined HAZ toughness. The upper limit of the value is preferably 0.30 and more preferably 0.25.

[0069] The present invention relates to steel plates. In general, the term "steel plate" refers to a steel sheet having a thickness of 3.0 mm or more as defined in Japanese Industrial Standards (JIS). In contrast, the steel plate according to the present invention has been invented as targeting the welding of steel plates having a thickness of 50 mm or more. In this connection, the target steel sheets herein may be considered to be steel sheets (steel plates) having a thickness of 50 mm or more.

Examples

[0070] The present invention will be illustrated in further detail with reference to several examples (experimental examples) below. It should be noted, however, that the examples are by no means intended to limit the scope of the present invention; that various changes and modifications can naturally be made therein without deviating from the spirit and scope of the present invention as described herein; and all such changes and modifications should be considered to be within the scope of the present invention.

[0071] In examples (experimental examples) in the present invention, steel plates were produced in the following manner. Initially, molten steels having chemical compositions given in Tables 1 and 2 were prepared using a vacuum induction furnace (VIF: 150 kg). The molten steels were cast to give slabs (150 mm by 250 mm in section). The slabs were subjected to hot rolling and yielded hot-rolled plates having a thickness of 80 mm. The hot rolling was performed under conditions as follows. Prior to rolling, heating was performed at 1100°C for 3 hours. Then the hot rolling was performed at a finish rolling temperature of 780°C or higher, an average cooling rate down to 450°C of 6°C/s, and a cooling stop temperature of 450°C.

[0072] Upon production of the hot-rolled plates (steel plates), conditions as follows were controlled, as indicated in Tables 3 and 4. The controlled conditions are the dissolved oxygen content [O_f] (in mass percent) in the molten steel before the addition of Al (Ti); the order of the additions of Al, Ti, REM, Zr, and Ca; the time t₁ from the addition of REM or Zr to the addition of Ca; the mass ratio [REM]/[Zr] of the REM content [REM] to the Zr content [Zr], where this ratio is indicated as "REM/Zr" in the tables; the cooling time t₂ in the temperature range of 1500°C to 1450°C upon casting; and the cooling time t₃ in the temperature range of 1300°C to 1200°C upon casting.

[0073] REM as in Tables 1 and 2 was added in the form of a misch metal containing, in mass percent, about 50% of Ce and about 25% of La. The symbol "-" in Tables 1 and 2 refers to that an element in question was not added.

[0074] In Tables 3 and 4, the order of the additions of Al, Ti, REM, Zr, and Ca is indicated as "○" when the elements were added in the specified order of Al, Ti, (REM, Zr), and Ca; and is indicated as "×" when the elements were added in any order excluding the specified order.

[Table 1]

No.	C	Si	Mn	P	S	Al	Ti	REM	Zr	Ca	N	Ni	Cu	Cr	Mo	Nb	V	B
1	0.05	0.19	1.56	0.006	0.002	0.010	0.018	0.0020	0.0018	0.0018	0.0062	-	-	-	-	-	-	-
2	0.04	0.16	1.51	0.009	0.002	0.012	0.017	0.0022	0.0019	0.0021	0.0072	-	-	-	-	-	-	-
3	0.08	0.15	1.72	0.007	0.003	0.008	0.015	0.0023	0.0010	0.0017	0.0048	-	-	-	-	-	-	-
4	0.06	0.19	1.46	0.007	0.002	0.025	0.020	0.0019	0.0022	0.0016	0.0042	-	-	-	-	-	-	-
5	0.07	0.16	1.58	0.010	0.002	0.007	0.019	0.0018	0.0017	0.0012	0.0056	0.25	-	-	-	-	-	-
6	0.10	0.15	1.51	0.007	0.002	0.008	0.020	0.0021	0.0018	0.0009	0.0055	-	0.35	-	-	-	-	-
7	0.05	0.21	1.13	0.026	0.001	0.011	0.021	0.0020	0.0016	0.0015	0.0069	-	-	0.62	-	-	-	-
8	0.11	0.16	1.46	0.006	0.001	0.007	0.017	0.0022	0.0018	0.0038	0.0075	-	-	-	0.19	-	-	-
9	0.08	0.17	1.62	0.018	0.002	0.007	0.023	0.0018	0.0014	0.0032	0.0038	0.45	-	0.25	-	-	-	-
10	0.04	0.22	1.69	0.005	0.002	0.008	0.016	0.0017	0.0018	0.0020	0.0046	-	-	-	-	0.016	-	-
11	0.05	0.14	1.50	0.006	0.002	0.031	0.011	0.0007	0.0006	0.0016	0.0049	-	-	-	-	-	0.028	-
12	0.09	0.16	1.77	0.008	0.001	0.009	0.013	0.0015	0.0011	0.0023	0.0046	-	-	-	-	-	-	0.0019
13	0.08	0.18	1.70	0.007	0.003	0.010	0.015	0.0030	0.0013	0.0069	0.0055	0.23	-	0.68	-	-	-	-
14	0.05	0.17	1.63	0.004	0.013	0.012	0.026	0.0024	0.0023	0.0018	0.0047	1.07	0.86	1.24	-	-	-	-
15	0.09	0.15	1.51	0.008	0.002	0.016	0.020	0.0026	0.0024	0.0023	0.0042	0.99	0.25	0.71	0.38	-	-	-
16	0.05	0.15	1.53	0.007	0.002	0.014	0.020	0.0068	0.0019	0.0039	0.0059	1.25	0.10	-	-	0.012	-	-
17	0.08	0.12	1.49	0.009	0.002	0.008	0.022	0.0038	0.0025	0.0009	0.0079	0.55	0.35	-	0.24	-	-	0.0014
18	0.04	0.15	1.56	0.004	0.002	0.015	0.020	0.0019	0.0010	0.0017	0.0042	1.15	0.45	0.68	0.34	-	-	-
19	0.03	0.16	1.92	0.007	0.005	0.017	0.017	0.0024	0.0018	0.0027	0.0063	-	-	-	-	-	-	-
20	0.10	0.17	1.88	0.007	0.002	0.008	0.033	0.0015	0.0012	0.0016	0.0049	-	-	0.07	-	0.088	-	-
21	0.06	0.19	1.46	0.004	0.008	0.010	0.027	0.0042	0.0009	0.0017	0.0085	0.25	0.16	-	1.25	-	-	-
22	0.10	0.12	1.50	0.011	0.003	0.005	0.012	0.0030	0.0020	0.0014	0.0062	-	-	0.39	0.06	-	0.035	0.0007
23	0.05	0.11	1.52	0.009	0.001	0.014	0.036	0.0022	0.0010	0.0015	0.0074	-	-	-	-	0.063	-	-
24	0.04	0.24	1.59	0.008	0.001	0.023	0.014	0.0031	0.0020	0.0019	0.0063	-	0.15	-	-	-	0.088	-
25	0.06	0.14	1.60	0.009	0.002	0.044	0.016	0.0004	0.0011	0.0016	0.0051	0.38	0.22	-	-	0.009	-	0.0029

(continued)

No.	C	Si	Mn	P	S	Al	Ti	REM	Zr	Ca	N	Ni	Cu	Cr	Mo	Nb	V	B
26	0.05	0.17	1.53	0.008	0.001	0.030	0.047	0.0036	0.0018	0.0017	0.0048	-	-	-	-	-	0.063	-
27	0.09	0.12	1.57	0.007	0.001	0.028	0.017	0.0008	0.0008	0.0023	0.0070	0.56	0.81	-	-	-	-	0.0042
28	0.05	0.14	1.58	0.007	0.001	0.010	0.016	0.0016	0.0021	0.0031	0.0048	0.41	0.26	-	-	0.009	-	0.0025
29	0.06	0.21	1.58	0.007	0.009	0.020	0.016	0.0032	0.0024	0.0016	0.0042	-	-	-	0.79	-	-	-
30	0.05	0.18	1.72	0.017	0.001	0.016	0.019	0.0155	0.0153	0.0024	0.0059	0.46	0.23	0.89	-	-	-	0.0021
31	0.04	0.17	1.41	0.006	0.002	0.011	0.030	0.0013	0.0004	0.0019	0.0062	-	-	-	-	0.016	0.025	-
32	0.10	0.15	1.63	0.007	0.002	0.007	0.026	0.0028	0.0015	0.0008	0.0026	0.07	0.07	-	-	-	-	0.0033
33	0.06	0.20	1.62	0.006	0.003	0.013	0.019	0.0033	0.0029	0.0007	0.0061	-	-	-	-	0.004	0.004	-
34	0.09	0.14	1.49	0.007	0.002	0.012	0.020	0.0020	0.0012	0.0084	0.0050	-	-	-	-	-	0.009	0.0025
35	0.05	0.13	1.72	0.007	0.001	0.011	0.025	0.0024	0.0013	0.0022	0.0041	0.72	1.25	0.26	-	-	-	-

[Table 2]

No.	C	Si	Mn	P	S	Al	Ti	REM	Zr	Ca	N	Ni	Cu	Cr	Mo	Nb	V	B
36	0.09	0.15	1.46	0.006	0.002	0.008	0.016	0.0018	0.0020	0.0020	0.0051	-	-	-	-	-	-	-
37	0.08	0.14	1.53	0.007	0.001	0.008	0.015	0.0024	0.0021	0.0019	0.0039	-	-	-	-	-	-	-
38	0.07	0.13	1.75	0.008	0.002	0.009	0.013	0.0013	0.0011	0.0020	0.0066	-	-	-	-	-	-	-
39	0.08	0.21	1.42	0.009	0.002	0.012	0.019	0.0017	0.0015	0.0021	0.0057	-	-	-	-	-	-	-
40	0.05	0.19	1.63	0.006	0.001	0.018	0.017	0.0029	0.0025	0.0015	0.0071	-	-	-	-	-	-	-
41	0.04	0.17	1.60	0.007	0.003	0.016	0.016	0.0018	0.0020	0.0013	0.0079	-	-	-	-	-	-	-
42	0.04	0.09	1.71	0.006	0.002	0.020	0.023	0.0015	0.0013	0.0010	0.0070	-	-	-	-	-	-	-
43	0.07	0.26	1.73	0.007	0.001	0.016	0.021	0.0013	0.0013	0.0012	0.0066	-	-	-	-	-	-	-
44	0.09	0.21	1.56	0.032	0.002	0.009	0.018	0.0016	0.0020	0.0018	0.0105	-	-	-	-	-	-	-
45	0.05	0.17	1.55	0.009	0.002	0.003	0.020	0.0019	0.0021	0.0017	0.0069	-	-	-	-	-	-	-
46	0.06	0.19	1.48	0.006	0.007	0.051	0.051	0.0015	0.0017	0.0015	0.0058	-	-	1.58	-	-	-	-
47	0.07	0.16	1.52	0.005	0.009	0.026	0.009	0.0012	0.0019	0.0016	0.0047	0.51	1.52	-	-	-	-	-
48	0.05	0.15	1.62	0.004	0.003	0.008	0.015	0.0002	0.0018	0.0019	0.0070	1.54	-	-	-	-	-	-
49	0.04	0.18	1.64	0.007	0.016	0.009	0.032	0.0211	0.0017	0.0020	0.0060	-	-	-	1.57	-	-	-
50	0.06	0.17	1.58	0.007	0.002	0.010	0.034	0.0018	0.0001	0.0021	0.0040	-	-	-	-	0.105	-	-
51	0.04	0.19	2.03	0.009	0.001	0.007	0.026	0.0021	0.0206	0.0010	0.0040	-	-	0.25	-	-	-	-
52	0.13	0.14	1.75	0.006	0.001	0.015	0.018	0.0020	0.0020	0.0004	0.0046	-	-	-	-	-	-	-
53	0.05	0.13	1.42	0.007	0.001	0.017	0.017	0.0027	0.0017	0.0024	0.0018	-	-	-	-	-	-	-
54	0.05	0.17	1.59	0.007	0.006	0.019	0.016	0.0020	0.0019	0.0105	0.0046	-	-	-	-	-	0.106	-
55	0.05	0.18	1.46	0.007	0.005	0.028	0.023	0.0045	0.0011	0.0037	0.0071	-	-	-	-	-	-	0.0053

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[Table 3]

No.	[Of] mass percent	Order of addition	t1(min)	REM/Zr	t2(s)	t3(s)
1	0.0030	○	7	1.6	271	530
2	0.0041	○	5	1.8	255	530
3	0.0035	○	15	3.0	263	530
4	0.0036	○	12	1.5	256	530
5	0.0048	○	7	1.4	259	480
6	0.0042	○	12	1.7	271	660
7	0.0030	○	10	1.9	268	530
8	0.0026	○	25	1.8	292	530
9	0.0051	○	10	2.0	245	500
10	0.0051	○	15	1.6	268	530
11	0.0063	○	5	1.5	281	500
12	0.0038	○	20	2.0	277	530
13	0.0052	○	35	2.8	270	530
14	0.0026	○	12	1.3	245	480
15	0.0035	○	20	2.0	213	530
16	0.0077	○	7	6.7	239	530
17	0.0039	○	5	2.0	188	600
18	0.0031	○	12	3.0	251	530
19	0.0022	○	5	2.4	246	530
20	0.0022	○	25	2.7	191	530
21	0.0027	○	18	12.0	210	500
22	0.0043	○	7	2.0	253	660
23	0.0086	○	20	2.5	225	600
24	0.0053	○	12	2.8	270	530
25	0.0040	○	65	1.0	268	530
26	0.0027	○	55	4.8	259	530
27	0.0030	○	12	2.5	260	500
28	0.0027	○	7	1.6	245	500
29	0.0039	○	20	2.0	211	530
30	0.0091	○	25	1.9	278	530
31	0.0025	○	7	5.0	288	500
32	0.0053	○	12	3.0	206	530
33	0.0038	○	60	2.0	225	500
34	0.0031	○	40	3.0	271	530
35	0.0066	○	35	3.7	284	530

[Table 4]

No.	[Of] mass percent	Order of addition	t1(min)	REM/Zr	t2(s)	t3(s)
36	0.0059	○	3	1.6	270	530
37	0.0041	×	15	1.7	271	530
38	0.0107	○	7	1.2	231	530
39	0.0018	○	12	1.9	286	500
40	0.0033	○	45	1.7	275	720
41	0.0032	○	50	1.2	310	480
42	0.0030	○	5	2.0	270	530
43	0.0024	○	7	1.9	288	530
44	0.0041	○	20	1.4	265	600
45	0.0051	○	18	1.2	276	530
46	0.0023	○	5	1.8	261	530
47	0.0046	○	12	1.0	250	530
48	0.0033	○	20	0.3	292	660
49	0.0028	○	15	20.0	261	500
50	0.0034	○	5	15.0	259	530
51	0.0025	○	20	0.2	280	500
52	0.0039	○	25	1.5	274	530
53	0.0039	○	12	2.2	288	530
54	0.0042	○	25	1.5	249	600
55	0.0042	○	12	7.3	240	530

[0075] The hot-rolled plates (steel plates) produced under the conditions as above were each subjected to measurements of number densities N1, NA, N2, N3, and N4, the value $|da-df|/da$, and HAZ toughness by measurement methods below. The number density N1 refers to the number density of oxide particles having an equivalent circle diameter of less than 2 μm , containing Ti, Al, Ca, REM, and Zr in contents within the predetermined ranges, and having a ratio $[\text{REM}]/[\text{Zr}]$ of equal to or greater than 1.0. The number density NA refers to the number density of oxide particles having an equivalent circle diameter of less than 2 μm , containing Ti, Al, Ca, REM, and Zr in contents within the predetermined ranges, and having a ratio $[\text{REM}]/[\text{Zr}]$ of equal to or greater than 1.5. The number density N2 refers to the number density of oxide particles having an equivalent circle diameter of 2 μm or more. The number density N3 refers to the number density of titanium nitride particles having an equivalent circle diameter of 1 μm or more. The number density N4 refers to the number density of titanium nitride particles having an equivalent circle diameter of 20 nm or more. The measurement results are indicated in Tables 5 and 6.

Number Density Measurement of Oxide Particles Having Equivalent Circle Diameter of Less Than 2 μm

[0076] Test specimens were cut out from the steel plates in a position at a depth of one-fourth the thickness from the surface so that the axis of the test specimen passed through the position at a depth of one-fourth the thickness. The test specimens were observed in a cross section in parallel with the rolling direction and thickness direction using the field emission scanning electron microscope SUPRA35 (trade name) supplied by Carl Zeiss AG. The field emission scanning electron microscope is hereinafter also simply referred to as FE-SEM. The observation was performed at 5000-fold magnification in an observation area of 0.048 mm^2 . The areas of individual oxide particles in the observation view field were measured by image analysis, and based on which the equivalent circle diameters of the oxide particles were calculated. Whether the oxide particles had chemical compositions meeting the conditions was determined using an energy dispersive X-ray spectrometer (EDX). The chemical composition measurement using the EDX was performed at an acceleration voltage of 15 kV for a measurement time of 100 seconds. The numbers (N1, NA) of oxide particles having an equivalent circle diameter of less than 2 μm were determined each as a number density per square millimeter.

However, oxide particles having an equivalent circle diameter of $0.2\text{ }\mu\text{m}$ or less did not have sufficient reliability in EDX analysis and were excluded from the analysis.

Number Density Measurement of Oxide Particles Having Equivalent Circle Diameter of $2\text{ }\mu\text{m}$ or More

[0077] Test specimens were cut out from the steel plates in a position at a depth of one-fourth the thickness from the surface so that the axis of the test specimen passed through the position at a depth of one-fourth the thickness. The test specimens were observed in a cross section in parallel with the rolling direction and thickness direction using the FE-SEM. The observation was performed at 1000-fold magnification in an observation view field of 0.06 mm^2 at 20 points. The areas of individual oxide particles in the observation view field were measured by image analysis, and based on which the equivalent circle diameters of the oxide particles were calculated. Whether the oxide particles had chemical compositions meeting the conditions was determined using an energy dispersive X-ray spectrometer (EDX). The chemical composition measurement using the EDX was performed at an acceleration voltage of 15 kV for a measurement time of 100 seconds. The number (N2) of oxide particles having an equivalent circle diameter of $2\text{ }\mu\text{m}$ or more was determined as a number density per square millimeter.

Number Density Measurement of Titanium Nitride Particles Having Equivalent Circle Diameter of $1\text{ }\mu\text{m}$ or More

[0078] Test specimens were cut out from the steel plates in a position at a depth of one-fourth the thickness from the surface so that the axis of the test specimen passed through the position at a depth of one-fourth the thickness. The test specimens were observed in a cross section in parallel with the rolling direction and thickness direction, and images of 20 view fields in the cross section were taken using an optical microscope at 200-fold magnification. The number of coarse titanium nitride particles was counted and converted into a number density (N3) per square millimeter. The measured images have an area of 0.148 mm^2 per view field and an area of 2.96 mm^2 per test specimen. Titanium nitride particles were identified based on shape and color. Vivid orange, angular inclusions were considered as titanium nitride particles. The equivalent circle diameters of the titanium nitride particles were calculated using an analysis software. A coarse titanium nitride particle often forms with an oxide as a nucleation site. In this case, the oxide in the titanium nitride was excluded from the object for the measurement of equivalent circle diameter.

Number Density Measurement of Titanium Nitride Particles Having Equivalent Circle Diameter of 20 nm or More, and Calculation of $|da-df|/da$

[0079] Specimens were cut out from the steel plates in a position at a depth of one-fourth the thickness. The cross sections of the specimens in parallel with the rolling direction and thickness direction were treated to give replica TEM test specimens. The replica TEM test specimens were observed with a transmission electron microscope (TEM) at 15000-fold magnification in 4 view fields each having an area of $6.84\text{ }\mu\text{m}$ by $8.05\text{ }\mu\text{m}$, based on which particles containing Ti and N were identified using an energy dispersive X-ray fluorescence spectrometer (EDX) and treated as titanium-containing nitrides. The areas of titanium-containing nitrides in the view fields were measured by image analysis and converted into equivalent circle diameters. The number of titanium-containing nitride particles having an equivalent circle diameter of 20 nm or more was determined and converted into a value per square millimeter to give the number density (N4). Based on the resulting data, df and da were determined as follows. The titanium nitride particles having an equivalent circle diameter of 20 nm or more were classified into ranges of equivalent circle diameter from 20 nm up to 500 nm every 5 nm in an increasing order, in which particles in each of the ranges had an equivalent circle diameter of (d_i-5) to less than d_i , where d_i is 25, 30, 35,...500, and the d_i in a range having a largest number of titanium nitride particles present in the range was defined as the df. The da was defined as the average equivalent circle diameter of titanium nitride particles having an equivalent circle diameter of 20 nm to less than 500 nm. Thus, the value $|da-df|/da$ was calculated.

HAZ Toughness Evaluation

[0080] Specimens for weld joint was sampled from the steel plates, processed to have a V groove, and subjected to electrogas arc welding with a heat input of 50 kJ/mm . Each three Charpy impact test specimens (V-notched test specimens prescribed in JIS Z 2242) were sampled from the specimens, where the test specimens had notches in a heat affected zone (HAZ) adjacent to the weld line (bond) in a position at a depth of one-fourth the thickness from the surface of the steel plate. The Charpy impact test specimens were subjected to Charpy impact tests at -40°C to measure absorbed energy (vE_{-40}). Of the measured absorbed energy, the average and minimum were determined. A specimen having an average vE_{-40} of greater than 180 J and a minimum vE_{-40} of greater than 120 J was evaluated as having excellent HAZ toughness.

[0081] Independently, three test specimens were prepared and subjected to Charpy impact tests under the conditions

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as mentioned above, except for performing electrogas arc welding with a heat input of 60 kJ/mm to measure absorbed energy (vE_{-40}) of the three specimens, and the average of which was determined Based on the measured data, a specimen having an average vE_{-40} of greater than 120 J was evaluated as having excellent HAZ toughness; and a specimen having an average vE_{-40} of greater than 150 J was evaluated as having particularly excellent HAZ toughness.

[Table 5]

No.	N1 (per mm ²)	NA (per mm ²)	N2 (per mm ²)	N3 (per mm ²)	N4 (x10 ⁶ per mm ²)	da- df /da	HAZ toughness vE_{-40} (J)		
							50kJ/mm		60kJ/mm
							Average	Minimum	Average
1	313	208	12	4.1	1.3	0.10	187	153	131
2	375	271	18	3.4	1.5	0.11	194	176	135
3	500	354	13	1.0	1.7	0.12	235	207	160
4	417	271	19	3.4	1.2	0.10	208	171	145
5	333	208	22	4.4	1.3	0.07	185	129	129
6	396	292	20	3.0	1.3	0.34	190	141	128
7	479	313	15	1.7	2.2	0.16	208	186	154
8	458	333	16	2.0	2.1	0.23	188	156	151
9	542	375	26	0.7	1.6	0.08	237	221	165
10	438	292	25	3.4	1.2	0.12	190	146	132
11	354	188	33	4.7	1.0	0.12	184	128	122
12	500	354	15	1.4	1.5	0.10	228	200	153
13	563	396	27	1.7	1.6	0.11	235	215	162
14	396	229	8	6.4	1.2	0.09	182	135	123
15	500	333	32	1.0	1.5	0.08	225	218	156
16	396	271	63	3.4	1.5	0.12	198	166	132
17	375	292	15	3.0	1.4	0.07	208	200	148
18	521	375	8	5.7	1.1	0.12	187	172	152
19	313	271	7	3.4	1.5	0.13	190	172	136
20	521	313	6	17	1.9	0.08	194	144	151
21	667	500	13	4.4	1.5	0.11	182	125	153
22	333	250	10	3.4	1.4	0.32	191	166	143
23	625	417	83	4.4	1.1	0.23	205	190	158
24	563	396	32	4.7	1.3	0.10	210	190	152
25	375	250	93	4.1	1.4	0.12	182	125	123
26	542	396	63	4.7	2.6	0.10	213	176	159
27	479	333	15	0.7	2.0	0.13	214	199	152
28	333	208	11	4.4	1.3	0.09	196	166	130
29	521	333	10	1.0	1.7	0.10	231	206	159
30	792	417	97	1.4	1.9	0.11	201	125	151
31	354	271	15	3.0	1.5	0.18	215	186	142
32	521	375	17	0.3	1.4	0.16	203	171	155
33	375	333	18	2.7	1.8	0.12	229	207	159

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(continued)

No.	N1 (per mm ²)	NA (per mm ²)	N2 (per mm ²)	N3 (per mm ²)	N4 (x10 ⁶ per mm ²)	da- df /da	HAZ toughness vE-40 (J)		
							50kJ/mm		60kJ/mm
							Average	Minimum	Average
34	521	375	87	1.4	1.8	0.10	208	133	152
35	583	438	43	2.4	1.6	0.18	210	181	156

[Table 6]

No.	N1 (per mm ²)	NA (per mm ²)	N2 (per mm ²)	N3 (per mm ²)	N4 (x10 ⁶ per mm ²)	da- df /da	HAZ toughness vE-40 (J)		
							50kJ/mm		60kJ/mm
							Average	Minimum	Average
36	292	208	28	4.1	1.4	0.15	177	140	115
37	271	188	15	4.4	1.3	0.14	176	139	103
38	354	208	111	4.7	1.3	0.13	184	105	128
39	292	208	7	3.4	1.5	0.10	176	151	115
40	417	292	18	3.7	1.1	0.36	175	145	113
41	375	250	103	7.1	0.8	0.22	166	103	91
42	375	250	17	0.7	0.9	0.15	175	161	134
43	396	250	13	7.4	1.1	0.21	170	115	126
44	396	292	19	7.1	2.1	0.17	128	61	88
45	292	208	23	5.1	1.1	0.12	170	116	115
46	333	208	127	7.8	0.8	0.12	106	38	67
47	250	208	44	3.4	0.9	0.15	165	110	93
48	271	125	12	4.4	1.3	0.30	160	113	82
49	729	604	117	2.4	2.3	0.10	131	64	90
50	292	167	13	3.4	1.5	0.13	158	125	97
51	313	167	123	3.0	1.5	0.28	125	51	65
52	271	229	13	7.1	1.4	0.11	151	82	101
53	479	333	20	0.0	0.9	0.31	177	165	124
54	438	292	117	3.7	1.3	0.12	145	88	98
55	625	563	29	1.4	2.3	0.12	170	134	115

[0082] The data demonstrate that the steel plates of Nos. 1 to 35 are examples meeting conditions specified in the present invention and were appropriately controlled typically in chemical compositions and the dispersion of oxide particles and titanium nitride particles. These steel plates had excellent HAZ toughness (average and minimum) with a heat input of 50 kJ/mm and excellent HAZ toughness (average) with a heat input of 60 kJ/mm. Specifically, the steel plates of Nos. 1 to 35 can be considered as steel plates having excellent heat affected zone toughness.

[0083] Of the steel plates, those meeting the conditions specified in the second embodiment had an average vE₄₀ of greater than 150 J and were evaluated as steel plates having particularly excellent heat affected zone toughness.

[0084] In contrast, the steel plates of Nos. 36 to 55 are comparative examples not meeting at least one of the conditions specified in the present invention. The data demonstrate that these steel plates failed to meet the criterion in either one of the HAZ toughness (average and minimum) with a heat input of 50 kJ/mm and the HAZ toughness (average) with a heat input of 60 kJ/mm.

[0085] While the present invention has been described in detail with reference to specific embodiments, it is apparent to those skilled in the art that various changes and modifications can be made therein without deviating from the spirit and scope of the present invention.

[0086] The present application is based on Japanese Patent Application No. 2012-205840 filed September 19, 2012.

Industrial Applicability

[0087] The steel plate according to the present invention has excellent toughness in a heat affected zone after high heat input and is useful in welded structures such as bridges, high-rise buildings, ships, and line pipes.

Claims

1. A steel plate having excellent heat affected zone toughness, the steel plate having a thickness of 50 mm or more and consisting of:

in mass percent,

C in a content of 0.03% to 0.12%;

Si in a content of 0.10% to 0.25%;

Mn in a content of 1.0% to 2.0%;

P in a content of 0.03% or less, excluding 0%;

S in a content of 0.015% or less, excluding 0%;

Al in a content of 0.004% to 0.05%;

Ti in a content of 0.010% to 0.050%;

at least one rare-earth element (REM) in a content of 0.0003% to 0.02%;

Zr in a content of 0.0003% to 0.02%;

Ca in a content of 0.0005% to 0.010%;

N in a content of 0.002% to 0.010%; and optionally at least one element selected from the group consisting of

Ni in a content of 0.05% to 1.50%;

Cu in a content of 0.05% to 1.50%;

Cr in a content of 0.05% to 1.50%;

Mo in a content of 0.05% to 1.50%;

Nb in a content of 0.002% to 0.10%;

V in a content of 0.002% to 0.10%; and

B in a content of 0.0005% to 0.0050%,

with the remainder consisting of iron and inevitable impurities,

the steel plate comprising oxide particles, the oxide particles comprising constituent elements excluding oxygen in contents, in mass percent, meeting conditions as follows:

$$2\% < \text{Ti} < 40\%;$$

$$5\% < \text{Al} < 30\%;$$

$$5\% < \text{Ca} < 40\%;$$

$$5\% < \text{REM} < 50\%;$$

$$2\% < \text{Zr} < 30\%;$$

and

$$1.0 \leq \text{REM}/\text{Zr},$$

of the oxide particles,

oxide particles with an equivalent circle diameter of less than 2 μm being present in a number density of 300 or more per square millimeter; and
oxide particles with an equivalent circle diameter of 2 μm or more being present in a number density of 100 or less per square millimeter,

the steel plate comprising titanium nitride particles, of titanium nitride particles contained in the steel plate,

titanium nitride particles with an equivalent circle diameter of 1 μm or more being present in a number density of 7 or less per square millimeter; and
titanium nitride particles with an equivalent circle diameter of 20 nm or more being present in a number density of 1.0×10^6 or more per square millimeter,

the steel plate having d_a and d_f meeting a condition specified by the relational expression:

$$|d_a - d_f|/d_a \leq 0.35,$$

wherein the d_f is defined so that the titanium nitride particles having an equivalent circle diameter of 20 nm or more are classified into ranges of equivalent circle diameter of from 20 nm up to 500 nm every 5 nm in an increasing order, in which particles in each of the ranges have an equivalent circle diameter of $(d_i - 5)$ to less than d_i , where d_i is 25, 30, 35,...500, and the d_i in a range having a largest number of titanium nitride particles present in the range is defined as the d_f , and
wherein the d_a represents an average equivalent circle diameter of the titanium nitride particles having an equivalent circle diameter of 20 nm to less than 500 nm.

2. The steel plate having excellent heat affected zone toughness according to claim 1,
wherein the steel plate comprises oxide particles having an equivalent circle diameter of less than 2 μm and comprising constituent elements excluding oxygen in contents, in mass percent, meeting conditions as follows:

$$2\% < \text{Ti} < 40\%;$$

$$5\% < \text{Al} < 30\%;$$

$$5\% < \text{Ca} < 40\%;$$

$$5\% < \text{REM} < 50\%;$$

$$2\% < \text{Zr} < 30\%;$$

and

$$1.5 \leq \text{REM}/\text{Zr},$$

the oxide particles being present in a number density of 300 or more per square millimeter.

Patentansprüche

1. Stahlblech mit hervorragender Robustheit eines wärmebetroffenen Bereichs, das Stahlblech aufweisend eine Dicke von 50 mm oder mehr und bestehend aus
- in Massenprozent
- C in einem Gehalt von 0.03% bis 0.12%;
- Si in einem Gehalt von 0.10% bis 0.25%;
- Mn in einem Gehalt von 1.0% bis 2.0%;
- P in einem Gehalt von 0.03% oder weniger, ausschließend 0%;
- S in einem Gehalt von 0.015% oder weniger, ausschließend 0%;
- Al in einem Gehalt von 0.004% bis 0.05%;
- Ti in einem Gehalt von 0.010% bis 0.050%;
- mindestens ein Seltenerdelement (REM) in einem Gehalt von 0.0003% bis 0.02%;
- Zr in einem Gehalt von 0.0003% bis 0.02%;
- Ca in einem Gehalt von 0.0005% bis 0.010%;
- N in einem Gehalt von 0.002% bis 0.010%; und
- gegebenenfalls mindestens ein Element, ausgewählt aus der Gruppe, bestehend aus Ni in einem Gehalt von 0.05% bis 1.50%;
- Cu in einem Gehalt von 0.05% bis 1.50%;
- Cr in einem Gehalt von 0.05% bis 1.50%;
- Mo in einem Gehalt von 0.05% bis 1.50%;
- Nb in einem Gehalt von 0.002% bis 0.10%;
- V in einem Gehalt von 0.002% bis 0.10%; und
- B in einem Gehalt von 0.0005% bis 0.0050%,
- wobei der Rest aus Eisen und unvermeidlichen Verunreinigungen besteht,
- das Stahlblech Oxidteilchen umfasst, wobei die Oxidteilchen Bestandteile, ausschließend Sauerstoff, in Gehalten in Massenprozent umfassen, welche die nachstehenden Bedingungen erfüllen:

$$2\% < \text{Ti} < 40\%;$$

$$5\% < \text{Al} < 30\%;$$

$$5\% < \text{Ca} < 40\%;$$

$$5\% < \text{REM} < 50\%;$$

$$2\% < \text{Zr} < 30\%;$$

und

$$1.0 \leq \text{REM/Zr},$$

der Oxidteilchen,

wobei Oxidteilchen mit einem Äquivalenzkreisdurchmesser von weniger als 2 μm in einer Anzahldichte von 300 oder mehr pro Quadratmillimeter vorhanden sind; und

wobei Oxidteilchen mit einem Äquivalenzkreisdurchmesser von 2 μm oder mehr in einer Anzahldichte von 100 oder weniger pro Quadratmillimeter vorhanden sind,

wobei das Stahlblech Titanitridteilchen umfasst, wobei von den Titanitridteilchen, enthalten in dem Stahlblech,

Titannitridteilchen mit einem Äquivalenzkreisdurchmesser von 1 µm oder mehr in einer Anzahldichte von 7 oder weniger pro Quadratmillimeter vorhanden sind; und
 Titannitridteilchen mit einem Äquivalenzkreisdurchmesser von 20 nm oder mehr in einer Anzahldichte von 1.0×10^6 oder mehr pro Quadratmillimeter vorhanden sind,

das Stahlblech da und df aufweist, welche einer Bedingung, bestimmt durch den Vergleichsausdruck:

$$|da-df|/da \leq 0.35$$

genügen,

wobei df definiert ist, so dass die Titannitridteilchen, die einen Äquivalenzkreisdurchmesser von 20 nm oder mehr aufweisen, in Bereichen von Äquivalenzkreisdurchmesser von 20 nm bis 500 nm alle 5 nm in aufsteigender Ordnung definiert werden, in welcher Teilchen in jedem der Bereiche einen Äquivalenzkreisdurchmesser von (di-5) bis weniger als di aufweisen, wobei di 25, 30, 35,...500 ist und das di in einem Bereich, der eine größte Anzahl an anwesenden Titannitridteilchen in dem Bereich aufweist, als das df definiert ist, und
 wobei das da einen durchschnittlichen Äquivalenzkreisdurchmesser der Titannitridteilchen mit einem Äquivalenzkreisdurchmesser von 20 nm bis weniger als 500 nm darstellt

2. Stahlblech mit hervorragender Robustheit eines wärmebetroffenen Bereichs nach Anspruch 1, wobei das Stahlblech Oxidteilchen umfasst, die einen Äquivalenzkreisdurchmesser von weniger als 2 µm aufweisen und Bestandteile, ausschließend Sauerstoff, in Gehalten in Massenprozent umfassen, welche die nachstehenden Bedingungen erfüllen:

$$2\% < Ti < 40\%;$$

$$5\% < Al < 30\%;$$

$$5\% < Ca < 40\%;$$

$$5\% < REM < 50\%;$$

$$2\% < Zr < 30\%;$$

und

$$1.5 \leq REM/Zr,$$

wobei die Oxidteilchen in einer Anzahldichte von 300 oder mehr pro Quadratmillimeter vorhanden sind.

Revendications

1. Feuille d'acier ayant une excellente ténacité dans une zone affectée thermiquement, la feuille d'acier ayant une épaisseur de 50 mm ou plus et étant constituée de
 en pourcentage en masse,
 C en une teneur allant de 0,03 % à 0,12 % ;
 Si en une teneur allant de 0,10 % à 0,25 % ;
 Mn en une teneur allant de 1,0 % à 2,0 % ;
 P en une teneur de 0,03 % ou moins, excluant 0 % ;
 S en une teneur de 0,015 % ou moins, excluant 0 % ;

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Al en une teneur allant de 0,004 % à 0,05 % ;
Ti en une teneur allant de 0,010 % à 0,050 % ;
au moins un élément de terres rares (REM) en une teneur allant de 0,0003 % à 0,02 % ;
Zr en une teneur allant de 0,0003 % à 0,02 % ;
Ca en une teneur allant de 0,0005 % à 0,010 % ;
N en une teneur allant de 0,002 % à 0,010 % ; et
éventuellement au moins un élément sélectionné parmi le groupe constitué de
Ni en une teneur allant de 0,05 % à 1,50 % ;
Cu en une teneur allant de 0,05 % à 1,50 % ;
Cr en une teneur allant de 0,05 % à 1,50 % ;
Mo en une teneur allant de 0,05 % à 1,50 % ;
Nb en une teneur allant de 0,002 % à 0,10 % ;
V en une teneur allant de 0,002 % à 0,10 % ; et
B en une teneur allant de 0,0005 % à 0,0050 %, le reste étant constitué de fer et d'impuretés inévitables,
la feuille d'acier comprenant des particules d'oxyde, les particules d'oxyde comprenant des éléments constitutifs sans tenir compte de l'oxygène présent, en pourcentage en masse, respectant les conditions suivantes :

$$2 \% < \text{Ti} < 40 \% ;$$

$$5 \% < \text{Al} < 30 \% ;$$

$$5 \% < \text{Ca} < 40 \% ;$$

$$5 \% < \text{REM} < 50 \% ;$$

$$2 \% < \text{Zr} < 30 \% ;$$

et

$$1,0 \leq \text{REM/Zr},$$

des particules d'oxyde,
des particules d'oxyde avec un diamètre de cercle équivalent inférieur à 2 μm étant présentes en une densité en nombre de 300 ou plus par millimètre carré ; et
des particules d'oxyde avec un diamètre de cercle équivalent de 2 μm ou plus étant présentes en une densité en nombre de 100 ou moins par millimètre carré,
la feuille d'acier comprenant des particules de nitrure de titane, de particules de nitrure de titane contenues dans la feuille d'acier,
des particules de nitrure de titane avec un diamètre de cercle équivalent de 1 μm ou plus étant présentes en une densité en nombre de 7 ou moins par millimètre carré ; et
des particules de nitrure de titane avec un diamètre de cercle équivalent de 20 nm ou plus étant présentes en une densité en nombre de $1,0 \times 10^6$ ou plus par millimètre carré,
la feuille d'acier ayant d_a et d_f respectant une condition spécifiée par l'expression relationnelle :

$$|d_a - d_f| / d_a \leq 0,35$$

dans laquelle le d_f est défini de sorte que les particules de nitrure de titane ayant un diamètre de cercle équivalent de 20 nm ou plus soient classées dans des plages de diamètres de cercle équivalent allant de 20 nm jusqu'à 500 nm tous les 5 nm dans un ordre croissant, dans lequel des particules dans chacune des plages ont un diamètre de

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cercle équivalent de $(d_i - 5)$ à moins de d_i , où d_i est égal à 25, 30, 35, ... 500, et le d_i dans une plage ayant un nombre maximal de particules de nitrure de titane présentes dans la plage est défini en tant que le d_f , et dans laquelle le d_a représente un diamètre de cercle équivalent moyen des particules de nitrure de titane ayant un diamètre de cercle équivalent de 20 nm à moins de 500 nm.

2. Feuille d'acier ayant une excellente ténacité dans une zone affectée thermiquement selon la revendication 1, dans laquelle la feuille d'acier comprend des particules d'oxyde ayant un diamètre de cercle équivalent inférieur à 2 μm et comprenant des éléments constitutifs sans tenir compte de l'oxygène présent, en pourcentage en masse, respectant les conditions suivantes :

$$2 \% < \text{Ti} < 40 \% ;$$

$$5 \% < \text{Al} < 30 \% ;$$

$$5 \% < \text{Ca} < 40 \% ;$$

$$5 \% < \text{REM} < 50 \% ;$$

$$2 \% < \text{Zr} < 30 \% ;$$

et

$$1,5 \leq \text{REM}/\text{Zr},$$

les particules d'oxyde étant présentes en une densité en nombre de 300 ou plus par millimètre carré.

REFERENCES CITED IN THE DESCRIPTION

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