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(54) STEEL MATERIAL HAVING EXCELLENT TOUGHNESS IN WELD-HEAT-AFFECTED ZONE

(57) Provided is a steel having excellent toughness in a heat affected zone (HAZ) even upon high heat input welding with a heat input of 60 kJ/mm or higher. (a) The steel includes an oxide containing Zr, at least one rare-earth element, and Ca. (b) Of all inclusions in the steel, inclusions with an equivalent circle diameter of 0.1 to 2 μm are present in a number density of 120 or greater per square millimeter of an observation field area, and oxides with an equivalent circle diameter greater than 3 μm are present in a number density of 5.0 or less per square millimeter of an observation field area. (c) The inclusions in the steel have chemical compositions meeting a condition specified by Formula (1):

$$(\mathrm{Insol.Ti} - 3.4 \times \mathrm{Insol.N})/\mathrm{Insol.Al} = 1.0 \text{ to } 8 \quad (1)$$

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Description

Technical Field

[0001] The present invention generally relates to steels for use typically in bridges, multi-storied buildings, and ships. Specifically, the present invention relates to a steel excellent in toughness in a zone affected by weld heat upon welding. Such zone affected by weld heat is hereinafter also referred to as a "heat affected zone" or "HAZ".

Background Art

[0002] Steels for use typically in bridges, multi-storied buildings, and ships require properties at higher and higher levels and, among the properties, particularly require satisfactory toughness. These steels are joined by welding frequently. Disadvantageously, a heat affected zone (HAZ) of the resulting weld joint is particularly affected by the heat and readily suffers from toughness deterioration. The toughness deterioration occurs more significantly with an increasing heat input upon welding. This is probably because, with an increased heat input upon welding, the HAZ is cooled at a lower cooling rate, has inferior hardenability, and suffers from the formation of coarse martensite-austenite constituents. To prevent this, the heat input upon welding may be minimized so as to provide better HAZ toughness. However, in contrast, demands are made to employ a high heat input welding process with a weld heat input of 50 kJ/mm or more so as to provide better welding performance efficiency. Such high heat input welding is exemplified by electro-gas welding, electro-slag welding, and submerged arc welding.

[0003] Under these circumstances, the present applicant has proposed steels that less suffer from HAZ toughness deterioration upon a high heat input welding process in Patent Literature 1 to 3. The steels characteristically contain ZrO_2 and at least one of a rare-earth element oxide and CaO as oxides acting as nuclei for intragranular ferrite transformation. The oxides exist in a liquefied state in a molten steel and are finely dispersed in the resulting steel. In addition, the oxides are thermally stable, resist solid-solution and disappearance even upon exposure to a high temperature on the order of 1400°C for a long time, and thereby significantly contribute to better HAZ toughness.

[0004] In addition, the present applicant has made intensive investigations to improve the technique disclosed in Patent Literature 1 and to provide a steel that does not suffer from deterioration in HAZ toughness even upon welding with a higher heat input, where the technique uses the oxides acting as nuclei for intragranular ferrite transformation. As a result, the present applicant has proposed a technique as disclosed in Patent Literature 4.

[0005] Patent literature 4 discloses that the sizes and number (number density) of total oxides (not limited to oxides acting as nuclei for intragranular ferrite transformation, but also including total oxides) in the steel are greatly involved in improvement of HAZ toughness; and that, among the oxides, coarse oxides each having an equivalent circle diameter of greater than 5.0 μm should be reduced to a number density of 5 or less so as to provide a steel having excellent HAZ toughness even upon high heat input welding with a heat input of about 50 kJ/mm.

Citation List

Patent literature

[0006]

Patent literature 1: Japanese Unexamined Patent Application Publication (JP-A) No. 2007-100213
Patent Literature 2: JP-A No. 2007-247004
Patent literature 3: JP-A No. 2007-247005
Patent Literature 4: JP-A No. 2009-197267

Summary of Invention

Technical Problem

[0007] The technique disclosed in Patent Literature 4 significantly reduces the number density of coarse oxides and succeeds in providing better HAZ toughness even upon welding with a higher heat input as compared with the HAZ toughness evaluation method disclosed in an experimental example of Patent Literature 1. Specifically, in the technique disclosed in Patent literature 1, a heat cycle was applied to a sample, and an absorbed energy (vE_{-40}) at -40°C was measured as an index for toughness. The heat cycle was applied by holding the sample at a heating temperature of 1400°C for 5 seconds and cooling the sample for a cooling time of 300 seconds in a temperature range from 800°C down to 500°C. Specifically, the heat cycle was performed as heat input at a temperature of 1400°C for 5 seconds and

as cooling for a cooling time Tc of 300 seconds. In contrast, according to the technique disclosed in Patent Literature 4, a heat cycle was applied, and an absorbed energy was measured by the procedure as above, where the heat cycle was performed for a longer holding time at 1400°C of 30 seconds. Specifically, the heat cycle was performed as heat input at a temperature of 1400°C for 30 seconds and as cooling for a cooling time Tc of 300 seconds. It was verified that the steel had satisfactory HAZ toughness even in this case. However, with an increasing weld heat input in recent years, demands have been made to give better HAZ toughness upon welding with a still higher heat input.

[0008] The present invention has been made while focusing attention on these circumstances. An object of the present invention is to provide a steel that has excellent HAZ toughness even upon high heat input welding with a heat input of 60 kJ/mm or more. Solution to Problem

[0009] The present invention has achieved the object and provides a steel having excellent toughness in a heat affected zone. The steel contains C in a content of 0.02% to 0.15% (in mass percent, hereinafter the same for chemical compositions), Si in a content of 0.5% or less, Mn in a content of 2.5% or less, P in a content of 0.03% or less, S in a content of 0.02% or less, Al in a content of 0.050% or less, Ti in a content of 0.005% to 0.10%, at least one rare-earth element (REM) in a content of 0.0003% to 0.015%, Ca in a content of 0.0003% to 0.010%, Zr in a content of 0.0010% to 0.050%, N in a content of 0.010% or less, and O in a content of 0.0005% to 0.010%, with the remainder including iron and inevitable impurities. The steel meets conditions (a), (b), and (c) as follows. (a) The steel includes an oxide containing Zr, at least one rare-earth element, and Ca. (b) Of total inclusions contained in the steel, inclusions each having an equivalent circle diameter of 0.1 to 2 μm are present in a number density of 120 or more per square millimeter of an observation view field area, and oxides each having an equivalent circle diameter of greater than 3 μm are present in a number density of 5.0 or less per square millimeter of an observation view field area. (c) Inclusions each having an equivalent circle diameter of 0.1 to 2 μm in the steel have a chemical composition meeting a condition specified by Formula (1):

$$(\mathrm{Insol.Ti}-3.4\times\mathrm{Insol.N})/\mathrm{Insol.Al}=1.0\ \text{to}\ 8 \qquad (1)$$

[0010] The number density of inclusions as specified in the condition (b) is a value determined by observation with an electron probe x-ray microanalyzer (EPMA).

[0011] Assume that Ti, N, or Al is an element X. In this case, "Insol.X" in Formula (1) is determined in the following manner. The steel is electrolytically extracted An electrolytic solution after electrolytic extraction is filtrated respectively through two filters, i.e., one having an opening of 0.1 μm and one having an opening of 2.0 μm. The amounts of element Ti or Al in the extraction residues on the filters are quantitatively measured by inductively coupled plasma emission spectrometry (ICPES), whereas the amounts of nitrogen (N) in the extraction residues are quantitatively measured by indophenol blue absorptiometry. The amount of the element X is calculated by subtracting $\mathrm{Insol.X_{2.0}}$ from $\mathrm{Insol.X_{0.1}}$, where $\mathrm{Insol.X_{2.0}}$ represents the amount of the element X in the extraction residue remaining on the filter having an opening of 2.0 μm; and $\mathrm{Insol.X_{0.1}}$ represents the amount of the element X in the extraction residue remaining on the filter having an opening of 0.1 μm.

[0012] The steel may further contain one or more elements typically selected from groups [1], [2], and [3] as follows:

[1] at least one element selected from the group consisting of Cu in a content of 2% or less, Ni in a content of 3.5% or less, Cr in a content of 3% or less, and Mo in a content of 1% or less;
[2] at least one of Nb in a content of 0.25% or less and V in a content of 0.1% or less; and
[3] boron (B) in a content of 0.005% or less.

Advantageous Effects of Invention

[0013] The steel according to the present invention includes oxides (oxides containing Zr, at least one rare-earth element (REM), and Ca) acting as nuclei for intragranular α transformation. As used herein the term "alpha (α)" refers to ferrite or a mixed microstructure of ferrite and bainite. In addition, the steel has appropriately controlled sizes and number densities (specifically, particle size distribution) of inclusions and oxides present in the steel. Accordingly, the steel provided according to the present invention has excellent HAZ toughness upon high heat input welding with a heat input of 60 kJ/mm or more. Specifically, the steel according to the present invention includes fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm in an amount at a predetermined level or more, where such fine inclusions are useful to provide better HAZ toughness. In addition, the steel has a significantly reduced number density of coarse oxides each having an equivalent circle diameter of greater than 3 μm, where such coarse oxides adversely affect the improvement of HAZ toughness. Thus, the steel has excellent HAZ toughness. In addition, the steel according to the present invention has an appropriately controlled compositional ratio between titanium oxide and aluminum oxide in the

fine inclusions and can have better HAZ toughness even upon welding with a higher heat input as compared with the HAZ toughness evaluation method disclosed in the examples (experimental examples) of Patent Literature 4.

Description of Embodiments

[0014] After the proposal of the technique disclosed in Patent Literature 4, the inventors have still made intensive investigations so as to provide a steel having excellent HAZ toughness upon high heat input welding with a still higher heat input. Specifically, the inventors have aimed to provide a steel having excellent HAZ toughness even upon a heat cycle with a still higher heat input as compared with the technique in Patent Literature 4. The heat cycle is performed by "holding the steel at a heating temperature of 1400°C for 60 seconds and cooling the steel for a cooling time of 450 seconds in a temperature range of from 800°C down to 500°C". In other words, the heat cycle is performed with a heat input of 1400°C for 60 seconds and with cooling for a cooling time Tc of 450 seconds. The inventors have found that, for this purpose, it is insufficient to reduce oxides each having an equivalent circle diameter of greater than 5.0 μm to a number density of 5 or less as in the technique disclosed in Patent Literature 4, but it is very important to reduce the number density of oxides each having an equivalent circle diameter of greater than 3 μm, where the oxides of this size have received attention by none of conventional technologies including the technique in Patent Literature 4. The inventors have also found that it is important to control the compositional ratio between titanium oxide and aluminum oxide contained in fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm. The present invention has been made based on these findings. The term "equivalent circle diameter" is hereinafter also simply referred to as "particle size".

[0015] The present invention specifies conditions (A), (B), and (C) as follows. (A) The number density of fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm is increased (to 120 or more per square millimeter), where the fine inclusions are useful for better HAZ toughness. (B) The number density of oxides each having an equivalent circle diameter of greater than 3 μm is reduced (to 5.0 or less per square millimeter), where the oxides adversely effect the improvement of HAZ toughness. (C) The compositional ratio between titanium oxide and aluminum oxide contained in the fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm is adapted to fall within a predetermined range. Specifically, values calculated after electrolytic extraction meet the condition specified by Formula (1). Thus, the steel according to the present invention can have better HAZ toughness even upon welding with a still higher heat input as compared with the technique disclosed in Patent Literature 4.

[0016] Specifically, the present invention specifies, as features, not only the condition (A), but also the conditions (B) and (C), in relation to the technique disclosed in Patent Literature 4. The inventors have found that appropriate control of the compositional ratio between titanium oxide and aluminum oxide in the fine inclusions as specified by the condition (C) allows the inclusions to have lower melting points; and that the inclusions having such lower melting points become a liquid phase upon a high heat input welding to facilitate the formation of inclusions acting as nuclei for intragranular α transformation and to allow the steel to have better HAZ toughness.

[0017] It is difficult to accurately measure the compositional ratio between titanium oxide and aluminum oxide in the fine inclusions by EPMA, as described below. In the present invention, therefore, the compositional ratio is measured by electrolytic extraction, ICP emission spectrometry, and indophenol blue absorptiometry in combination. Accordingly, the condition (C) specifies the compositional ratio between titanium oxide and aluminum oxide contained in an extraction residue that passes through a filter having an opening of 2.0 μm, but does not pass through and remains on a filter having an opening of 0.1 μm. The present invention therefore specifies, as features, the number density of inclusions each having an equivalent circle diameter of 0.1 to 2 μm (the condition (A)) and the compositional ratio between titanium oxide and aluminum oxide contained in the inclusions (the condition (C)).

[0018] The technique disclosed in Patent Literature 4 controls the number density of oxides each having an equivalent circle diameter of greater than 5.0 μm. In contrast, the present invention controls the number density of oxides each having an equivalent circle diameter of greater than 3 μm to allow the steel to have still better HAZ toughness. After intensive investigations, the inventors have found that control of the compositional ratio between titanium oxide and aluminum oxide in the fine inclusions eliminates the need of especially focusing attention on, and controlling, oxides each having an equivalent circle diameter of greater than 3 μm to 5 μm as in the technique disclosed in Patent Literature 4, but merely requires control of the number density of oxides each having an equivalent circle diameter of greater than 3 μm, so as to have satisfactory HAZ toughness.

[0019] Herein, oxides acting as nuclei for intragranular α transformation (namely, oxides containing Zr, at least one rare-earth element (REM), and Ca) may be preferably distinguished from all oxides contained in the steel. To this end and for the sake of description convenience, the former is also specifically referred to as "Zr-REM-Ca oxides", whereas the latter is specifically referred to as "total oxides" in the description. As used herein the term "oxide" refers to not only a single oxide including an oxide alone, but also a multicomponent oxide including such an oxide and another inclusion. Such inclusions other than oxides are exemplified by sulfides, nitrides, carbides, and composite compounds of them.

[0020] The essential elements (Zr, REM, and Ca) constituting the Zr-REM-Ca oxides are also specifically referred to as "intragranular α transformation nucleation elements".

[0021] The steel according to the present invention includes not only the oxides, but also non-oxides such as sulfides, nitrides, carbides, and composite compounds of them. As used herein the term "total inclusions" generically refers to such oxides, sulfides, nitrides, carbides, and composite compounds of them present in the steel. Also as used herein, the term "fine inclusions" refers to, of total inclusions in the steel, inclusions each having an equivalent circle diameter of 0.1 to 2 μm.

[0022] Also as used herein, the term "fine oxides" refers to, of total oxides in the steel, oxides each having an equivalent circle diameter of 0.1 to 2 μm; whereas the term "coarse oxides" refers to, of total oxides in the steel, oxides each having an equivalent circle diameter of greater than 3 μm, so as to distinguish the two types of oxides. In this connection, the technique disclosed in Patent Literature 4 defines "oxides each having an equivalent circle diameter of greater than 5 μm" as "coarse oxides". In contrast, oxides each having an equivalent circle diameter of greater than 3 μm are herein defined as "coarse oxides".

[0023] As used herein the term "steel having excellent HAZ toughness upon high heat input welding" refers to a steel having an absorbed energy at -40°C (vE_{-40}) of 100 J or more after subjected to a heat cycle (thermal hysteresis). In the heat cycle, the steel is held at 1400°C for 60 seconds and cooled for a cooling time of 450 seconds in a temperature range of from 800°C down to 500°C. The thermal hysteresis corresponds to a thermal hysteresis of the steel when the steel is subjected to high heat input welding with a heat input of 60 kJ/mm or more. The thermal hysteresis is also specifically referred to as a "high heat input thermal hysteresis". The heat input by the heat cycle is higher as compared with the heat input (about 50 kJ/mm) applied by the heat cycle described in Patent Literature 4. In this meaning, the "high heat input welding" in the present invention provides a heat input at higher level as compared with the "high heat input welding" described in Patent Literature 4. The higher the absorbed energy vE_{-40} is, the better. The absorbed energy vE_{-40} is preferably 130 J or more.

[0024] The conditions (a), (b), and (c) specified in the present invention will be described in detail below.

(a) Zr-REM-Ca oxides

[0025] Initially, the Zr-REM-Ca oxides acting as origins (nuclei) for intragranular α transformation will be illustrated The term "Zr-REM-Ca oxide" refers to one including all of zirconium oxide, a rare-earth element oxide, and calcium oxide.

[0026] Part of the Zr-REM-Ca oxides may be present as a single oxide containing one of the intragranular α transformation nucleation elements alone, or may be present as a multicomponent oxide containing two or more of the intragranular α transformation nucleation elements. The single oxide is exemplified by ZrO_2 for Zr; CaO for Ca; and M_2O_3 M_3O_5, and MO_2 for a rare-earth element, where "M' represents the rare-earth element. These oxides may be present as an aggregate with each other or as composite precipitates in which other compounds such as sulfides and/or nitrides are precipitated in the oxides.

[0027] The Zr-REM-Ca oxides essentially contain a titanium oxide and an aluminum oxide. Such fine Zr-REM-Ca oxides each having an equivalent circle diameter of 0.1 to 2 μm, as containing a titanium oxide and an aluminum oxide, accelerate the intragranular α transformation and allow the steel to have still better HAZ toughness. The compositional ratio between titanium oxide and aluminum oxide contained in the fine Zr-REM-Ca oxides will be described in detail below.

[0028] Part of the titanium oxide may be present as a single oxide (e.g., Ti_2O_3, Ti_3O_5, and TiO_2). Likewise, part of the aluminum oxide may be present as a single oxide (e.g., Al_2O_3).

(b) Particle Size Distribution of Total Inclusions

[0029] Next, the number density and size of total inclusions, which feature the present invention, will be illustrated In the steel according to the present invention, when observed by EPMA:

(i) fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm are present in a number density of 120 or more per square millimeter of an observation view field area; and
(ii) coarse oxides each having an equivalent circle diameter of greater than 3 μm are present in a number density of 5.0 or less per square millimeter of an observation view field area.

[0030] In the steel according to the present invention, the number density of oxides each having an equivalent circle diameter of greater than 3 μm is controlled. The present invention does not require separate control of oxides each having an equivalent circle diameter of greater than 3 μm as distinguished from oxides each having an equivalent circle diameter of greater than 5 μm as specified in Patent Literature 4. This is because the steel according to the present invention has an appropriately controlled compositional ratio between titanium oxide and aluminum oxide in the fine inclusions.

[0031] The steel according to the present invention is adapted to have a number density of the coarse oxides of 5.0 or less per square millimeter of an observation view field area, where the coarse oxides each have an equivalent circle

diameter of greater than 3 μm, as specified in the condition (ii). The smaller the number density is, the better. The number density is preferably 3 or less, more preferably 1 or less, and most preferably approximately zero (0), per square millimeter.

[0032] The number density of the coarse oxides each having an equivalent circle diameter of greater than 3 μm may be determined by observing a cross section of the steel typically by EPMA, quantitatively analyzing chemical compositions of inclusions observed in an observation view field, defining inclusions having an oxygen content of 5 percent by mass or more as oxides, and determining equivalent circle diameters of the oxides typically by observation with a transmission electron micrroscope (TEM).

[0033] On the other hand, the steel according to the present invention has a number density of the fine inclusions of 120 or more per square millimeter of an observation view field area, where the fine inclusions each have an equivalent circle diameter of 0.1 to 2 μm, as specified in the condition (i). The formation of the fine particles in an amount at a predetermined level or more contributes to an increased amount of oxides acting as nuclei for intragranular α transformation and allows the steel to have better HAZ toughness. The number density of the fine inclusions is preferably 200 or more, more preferably 500 or more, and furthermore preferably 1000 or more, per square millimeter.

[0034] The number density of the fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm may be determined typically by observing a cross section of the steel by a TEM. In the steel according to the present invention, inclusions each having an equivalent circle diameter of less than 0.1 μm little contribute to better HAZ toughness due to inclusion dispersion and are not included in the number of the inclusions.

[0035] As used herein the term "equivalent circle diameter" refers to a diameter of an assumed circle having an equivalent area to the size (area) of an inclusion particle or an oxide particle observed under a TEM.

(c) Compositional Ratio between Titanium Oxide and Aluminum Oxide in Fine Inclusions

[0036] The steel according to the present invention contains fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm so that the compositional ratio between titanium oxide and aluminum oxide in the fine particles falls within a predetermined range, where the fine inclusions contribute to better HAZ toughness. This significantly features the steel. Specifically, assume that titanium oxide and aluminum oxide in fine Zr-REM-Ca oxides acting as nuclei for intragranular α transformation is controlled within a predetermined range. This allows part of the Zr-REM-Ca oxides to be a liquid phase in a HAZ upon high heat input welding. The liquid-phase substance crystallizes as a crystal structure that effectively acts as a nucleus for intragranular α transformation during a downstream cooling process. This reduces the interfacial energy between intragranular α and matrix austenite (γ), further reduces the interfacial energy between the intragranular α and the Zr-REM-Ca oxides, and still more accelerates the intragranular α transformation. This in turn allows the steel to have better HAZ toughness.

[0037] The compositional ratio between titanium oxide and aluminum oxide in the fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm may be measured by electrolytic extraction, ICP emission spectrometry, and indophenol blue absorptiometry in combination. Specifically, the steel according to the present invention meets the condition specified by Formula (1):

$$(\mathrm{Insol.Ti}-3.4\times\mathrm{Insol.N})/\mathrm{Insol.Al}=1.0\ \text{to}\ 8 \qquad (1)$$

[0038] The Insol.Ti, Insol.N, and Insol.Al respectively present contents of Ti, N, and Al present in the form of compounds in the steel. The contents are calculated by a procedure as follows. Specifically, the steel is electrolytically extracted, an electrolytic solution after the extraction is filtrated using two filters, i.e., one having an opening of 0.1 μm and one having an opening of 2.0 μm, and extraction residues remaining on the filters are separately collected. Next, the amounts of Ti, N, and Al in the extraction residues are quantitatively determined by ICP emission spectrometry for the amounts of Ti and Al elements, and by indophenol blue absorptiometry for the amount of nitrogen (N) element. Hereinafter these elements are generically referred to as an element X. The amount of element X in the extraction residue remaining on the filter having an opening of 0.1 μm is defined as "Insol.$X_{0.1}$", whereas the amount of element X in the extraction residue remaining on the filter having an opening of 2.0 μm is defined as "Insol.$X_{2.0}$". The Insol.X is calculated by subtracting Insol.$X_{2.0}$ from Insol.$X_{0.1}$ according to the formula:

$$\mathrm{Insol.X}=\mathrm{Insol.X_{0.1}}-\mathrm{Insol.X_{2.0}}$$

[0039] Specifically, Insol.Ti, Insol.N, and Insol.Al in Formula (1) respectively represent the amounts of Ti, N, and Al in inclusions that pass through the filter having an opening of 2.0 μm, but do not pass through the filter having an opening

of 0.1 μm. The Insol.Ti, Insol.N, and Insol.Al as measured in the above manner are herein respectively assumed to be the amounts of Ti, N, and Al in the fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm.

[0040] It is important in the present invention to specify the relationship among the amounts of Ti, N, and Al in fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm in the steel. This is because such fine inclusions effectively contribute to better HAZ toughness; but inclusions each having an equivalent circle diameter of greater than 2 μm (particularly having an equivalent circle diameter of greater than 3 μm) may invite brittle fracture to cause the steel to have inferior HAZ toughness contrarily.

[0041] The term "Insol.Ti-3.4×Insol.N" refers to the amount ofTi present as a titanium oxide in the electrolytic extraction residue.

[0042] Specifically, the "Insol.Ti" refers to the amount of compound-form titanium present in the form of a compound in the steel. Such compound-form titanium is present as a compound that is exemplified by titanium oxides (e.g., TiO_2), titanium nitride (TiN), and a composite compound of them (e.g., an oxynitride). The compound-form titanium present in the form of a compound further includes carbides. However, there exists little titanium carbide having such a particle size of greater than 0.1 μm as to remain on the filter having an opening of 0.1 μm. For this reason, Insol.Ti does not approximately include the amount of titanium derived from titanium carbide.

[0043] The term "Insol.N" refers to the amount of compound-form nitrogen that is present as a compound in the steel Nitrogen herein is present as a nitride. The nitride is exemplified by TiN, ZrN, BN, and AlN. However, the term "Insol.N" approximately refers to the amount of nitrogen constituting TiN. This is because ZrN, BN, and AlN hardly grow up to such a size as to remain on the filter having an opening of 0.1 μm. Thus, the term Insol.N does not approximately include the amount of nitrogen derived from ZrN, BN, and AlN.

[0044] Titanium has an atomic weight of 47.88, and nitrogen has an atomic weight of 14.01. The ratio of the titanium atomic weight to the nitrogen atomic weight is approximately 3.4. Accordingly, the amount of titanium forming TiN can be determined by multiplying Insol.N by 3.4 (3.4×Insol.N). Next, the amount of titanium present as a titanium oxide in the steel can be calculated by subtracting the amount of titanium forming TiN (3.4×Insol.N) from Insol.Ti.

[0045] The term "Insol.Al" refers to the amount of aluminum present as a compound in the steel and approximately refers to the amount of aluminum constituting aluminum oxides (aluminum compounds typified by Al_2O_3). Aluminum (Al) may be possibly present not only as an oxide, but also as a nitride or another compound However, aluminum nitride hardly grows up to such a size as to remain on the filter having an opening of 0.1 μm, as described above. Accordingly, the Insol.Al does not approximately include the amount of aluminum derived from aluminum nitride (AlN).

[0046] The left-hand value of Formula (1) represents the compositional ratio (in mass) between titanium oxide and aluminum oxide contained in the extraction residue passing the filter having an opening of 2.0 μm, but not passing the filter having an opening of 0.1 μm. Specifically, the extraction residue corresponds to inclusions each having an equivalent circle diameter of 0.1 to 2 μm. The left-hand value of Formula (1) represents the chemical composition of inclusions that are effective for better HAZ toughness.

[0047] The significance of specifying the condition as Formula (1) has been demonstrated by examples described below. Specifically, Samples Nos. 32 and 33 given in Tables 1 and 2 below were steels having approximately the same chemical compositions with each other. Sample No. 32 had a left-hand value of Formula (1) being controlled within the range of 1.0 to 8 and had satisfactory HAZ toughness. In contrast, Sample No. 33 had a left-hand value of Formula (1) of less than 1.0 and failed to have better HAZ toughness.

[0048] Comparison among Samples Nos. 4,16, and 29 given in Tables 1 and 2 can provide a similar consideration. Specifically, these samples were steels having the approximately same chemical compositions. Among them, Samples Nos. 4 and 16 each had a left-hand value of Formula (1) controlled within the range of 1.0 to 8 and had satisfactory HAZ toughness. In contrast, Sample No. 29 had a left-hand value of Formula (1) of less than 1.0 and failed to have better HAZ toughness.

[0049] The electrolytic solution can be a solution capable of dissolving the steel matrix by electrolysis. The electrolytic solution usable herein is exemplified by a solution containing 10% of acetylacetone and 1% of tetramethylammonium chloride in methanol.

[0050] The electrolysis conditions may be such conditions as to dissolve the steel matrix. Typically, the current density is preferably from 100 to 200 A/m^2.

[0051] In the present invention, inclusions in the steel are recovered by electrolytic extraction, the recovered inclusions are separated using filters having different openings, and the chemical compositions of fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm are measured by ICP emission spectrometry and indophenol blue absorptiometry, as described above. This procedure enables accurate determination of the amount of titanium constituting titanium oxides in the fine inclusions. Specifically, the chemical compositions of inclusions in a steel have been conventionally generally analyzed by identifying inclusions by EPMA and quantitatively analyzing the chemical compositions of the inclusions. However, the analysis of chemical compositions of fine inclusions each having an equivalent circle diameter of about 0.1 to about 2 μm by EPMA fails to accurately quantitatively determine the amount of titanium typically constituting titanium oxides while distinguishing the amount from the amount of titanium constituting titanium nitride. This is because

inclusions effective for better HAZ toughness are fine and each have an equivalent circle diameter of 0.1 to 2 μm, and the titanium oxides and titanium nitride seldom exist separately, but generally exist as composite compounds in the steel. Accordingly, the analysis by EPMA fails to accurately quantitatively determine the amount of titanium constituting titanium oxides alone, which titanium oxides constitute a composite compound with titanium nitride. In contrast, in the present invention, chemical compositions of such inclusions are measured by electrolytic extraction, ICP emission spectrometry, and indophenol blue absorptiometry in combination. This enables precise quantitative determination of the compositional ratio between titanium oxide and aluminum oxide in the fine inclusions.

[0052] If the left-hand value of Formula (1) is less than 1.0, aluminum oxides may be present in excess to titanium oxides, and the inclusions may less allow intragranular α transformation to occur. This may cause the steel to have inferior HAZ toughness. To prevent this, the left-hand value of Formula (1) is controlled to 1.0 or more, preferably 1.5 or more, and more preferably 2.0 or more.

[0053] However, if the left-hand value of Formula (1) is greater than 8, titanium oxides may be present in excess to aluminum oxides. This causes oxides to have higher melting points and to hardly be a liquid phase in a HAZ upon welding. The resulting steel may fail to have better HAZ toughness. To prevent this, the left-hand value of Formula (1) is controlled to 8 or less, preferably 7.5 or less, and more preferably 7.0 or less.

(d) Preferred embodiments

[0054] Total oxides in the steel according to the present invention preferably have an average chemical composition including 5% to 50% of ZrO_2, 5% to 50% of a rare-earth element oxide (M_2O_3, where M represents the rare-earth element), and 50% or less of CaO. The average chemical composition is determined by measuring chemical compositions of total oxides in the steel, and converting the chemical compositions into masses of single oxides (100% in a total). Oxides, when having a chemical composition within the range, effectively act as nuclei for intragranular ferrite transformation. If the individual oxides are present in contents lower than the lower limits, oxides acting as nuclei for intragranular ferrite formation upon welding are present in an insufficient amount and may often fail to satisfactorily effectively contribute to better HAZ toughness. In contrast, if the individual oxides are present in contents greater than the upper limits, fine oxides effectively acting as nuclei for intragranular ferrite formation may be present in a lower number density due to oxide coarsening and may hardly contribute to effectively better HAZ toughness.

[0055] The content of ZrO_2 is more preferably 8% or more, and furthermore preferably 10% or more; and is more preferably 45% or less, and furthermore preferably 40% or less in terms of upper limit.

[0056] The content of the rare-earth element oxide is more preferably 10% or more, and furthermore preferably 13% or more; and is more preferably 45% or less, and furthermore preferably 40% or less in terms of upper limit. The rare-earth element oxide may be present in the forms typically of M_2O_3 M_3O_5, and MO_2 in the steel, where M represents a rare-earth element. The content of the rare-earth element oxide refers to the content of all such rare-earth element oxides as being converted into M_2O_3.

[0057] CaO effectively acts as a nucleus for intragranular ferrite transformation, but, if contained in excess, may cause the total oxides to less effectively invite or accelerate intragranular ferrite transformation contrarily. In addition, CaO, if contained in excess, may cause dissolved loss of nozzles used in casting. To prevent this, the content of CaO is preferably 50% or less, more preferably 45% or less, and furthermore preferably 40% or less, and particularly preferably 30% or less in terms of upper limit. To exhibit the activities effectively, CaO is contained in a content of preferably 3% or more, more preferably 5% or more, and furthermore preferably 10% or more.

[0058] The remainder of the total oxides is not limited in chemical composition and may include oxides of oxide-forming elements contained in the steel according to the present invention. Such oxides are exemplified by SiO_2, Al_2O_3, and MnO.

[0059] The chemical compositions of the total oxides in the steel may be measured by observing the steel surface typically by EPMA, and quantitatively analyzing oxides observed in an observation view field Measurement conditions will be described in experimental examples below.

[0060] Next, chemical compositions of the steel (base metal) according to the present invention will be illustrated. The steel according to the present invention contains, as basic chemical compositions, C in a content of 0.02% to 0.15%, Si in a content of 0.5% or less, Mn in a content of 2.5% or less, P in a content of 0.03% or less, S in a content of 0.02% or less, Al in a content of 0.050% or less, Ti in a content of 0.005% to 0.10%, at least one rare-earth element (REM) in a content of 0.0003% to 0.015%, Ca in a content of 0.0003% to 0.010%, Zr in a content of 0.0010% to 0.050%, and N in a content of 0.010% or less. The ranges are specified for reasons as follows.

[0061] Carbon (C) element is essential to ensure the strength of the steel (base metal) and should be present in a content of 0.02% or more. The carbon content is preferably 0.04% or more, and more preferably 0.05% or more. However, carbon, if present in a content greater than 0.15%, may cause the formation of martensite-austenite constituent (MA) in a large amount in a HAZ upon welding, thereby not only cause HAZ toughness deterioration, but also adversely affect weldability. To prevent this, the carbon content is controlled to 0.15% or less, preferably 0.10% or less, and more preferably 0.08% or less.

[0062] Silicon (Si) element has a deoxidation action and contributes to better strength of the steel (base metal) by solute strengthening. To exhibit the activities effectively, Si is preferably contained in a content of 0.01% or more, more preferably 0.02% or more, furthermore preferably 0.05% or more, and particularly preferably 0.10% or more. However, Si, if present in a content of greater than 0.5%, may cause the steel to have inferior weldability and/or toughness. To prevent this, the Si content is controlled to 0.5% or less, preferably 0.45% or less, and more preferably 0.40% or less.

[0063] Particularly for still better HAZ toughness, it is recommended that the Si content is controlled to 0.30% or less, preferably 0.05% or less, and more preferably 0.01% or less. However, with a decreasing Si content, the steel strength may be decreased although the HAZ toughness may be improved.

[0064] Manganese (Mn) element contributes to higher strength of the steel (base metal). To exhibit the activities effectively, Mn is preferably present in a content of 0.4% or more, more preferably 0.50% or more, furthermore preferably 0.7% or more, and particularly preferably 0.8% or more. However, Mn, if present in a content greater than 2.5%, may cause the steel (base metal) to have inferior weldability. To prevent this, the Mn content is controlled to 2.5% or less, preferably 2.3% or less, and more preferably 2.0% or less.

[0065] Phosphorus (P) element is susceptible to segregation and is segregated particularly at grain boundaries in the steel to cause the steel to have inferior HAZ toughness. To prevent this, the phosphorus content is controlled to 0.03% or less, preferably 0.020% or less, and more preferably 0.015% or less. In general, phosphorus is inevitably contained in a content of about 0.001%.

[0066] Sulfur (S) element is combined with Mn to form a sulfide (MnS), thereby impairs the toughness and thickness-direction ductility of the base metal, and is harmful. In addition, sulfur, if combined with a rare-earth element such as La or Ce to form a rare-earth element sulfide (e.g., LaS or CeS), may inhibit the formation of the rare-earth element oxide and cause the steel to have inferior HAZ toughness. To prevent these, the sulfur content is controlled to 0.02% or less, preferably 0.015% or less, more preferably 0.010% or less, and furthermore preferably 0.006% or less. In general, sulfur is inevitably contained in a content of about 0.0005%.

[0067] Aluminum (Al) element acts as a deoxidizer. However, Al, if present in excess, may reduce oxides, thereby form coarse aluminum oxides, and cause the steel to have inferior HAZ toughness. To prevent this, the Al content is controlled to 0.050% or less, preferably 0.04% or less, more preferably 0.03% or less, furthermore preferably 0.025% or less, and particularly preferably 0.010% or less. In general, Al is inevitably contained in a content of about 0.0005%.

[0068] Titanium (Ti) element forms nitrides (e.g., TiN) and titanium-containing oxides in the steel and thereby contributes to better HAZ toughness. To exhibit the activities, Ti may be present in a content of 0.005% or more, preferably 0.007% or more, and more preferably 0.010% or more. However, Ti, if present in excess, may cause the base metal itself to be hardened by titanium solute strengthening to lead to degradation in HAZ toughness. To prevent this, the Ti content is controlled to 0.10% or less, preferably 0.07% or less, and more preferably 0.06% or less.

[0069] The at least one rare-earth element (REM) and Ca element are necessary to respectively form oxides of them. The presence of these oxides allows the total oxides to disperse finely. The finely dispersed oxides act as nuclei for intragranular α transformation and contribute to better HAZ toughness.

[0070] The rare-earth element should be present in a content of 0.0003% or more, preferably 0.001% or more, and more preferably 0.0020% or more. However, the rare-earth element, if present in excess, may cause the formation of coarse oxides in excess to cause the steel to have inferior HAZ toughness. In addition, the rare-earth element, if present in excess, may form solute rare-earth element, and the solute rare-earth element may be segregated to impair the base metal toughness. To prevent these, the rare-earth element content is controlled to 0.015% or less, preferably 0.010% or less, and more preferably 0.007% or less.

[0071] As used herein the term "rare-earth element" or "REM" refers to and includes lanthanoid elements, as well as Sc (scandium) and Y (yttrium). The lanthanoid elements include fifteen elements from La to Lu in the periodic table. Among these elements, the steel preferably contains at least one element selected from the group consisting of La, Ce, and Y, and more preferably contains at least one of La and Ce.

[0072] Calcium (Ca) should be present in a content of 0.0003% or more, preferably 0.0005% or more, more preferably 0.0008% or more, and furthermore preferably 0.001% or more. However, Ca, if present in excess, may form CaO in excess to form inclusions containing CaO in a high content. This may cause the inclusions to less effectively act as nuclei for intragranular transformation and cause the steel to have inferior HAZ toughness contrarily. To prevent this, the Ca content is controlled to 0.010% or less, preferably 0.009% or less, and more preferably 0.008% or less.

[0073] Zirconium (Zr) element forms Zr-containing multicomponent oxides and contributes to better HAZ toughness. To exhibit the activities effectively, Zr is contained in a content of 0.0010% or more, preferably 0.002% or more, and more preferably 0.0023% or more. However, Zr, if present in excess, may form a large amount of ZrO_2 and thereby cause the inclusions to less effectively act as nuclei for intragranular transformation. In addition, such excessive Zr may form fine nitride (ZrN) and carbide (ZrC) causing precipitation strengthening and cause the base metal itself to have inferior toughness. To prevent these, the Zr content is controlled to 0.050% or less, preferably 0.04% or less, more preferably 0.03% or less, and furthermore preferably 0.01% or less.

[0074] Nitrogen (N) element precipitates as nitrides (e.g., ZrN and TiN). The nitrides exhibit a pinning effect, thereby

prevent austenite grains from coarsening, and accelerate ferrite transformation, where the austenite grains are formed in a HAZ upon welding. Thus, nitrogen contributes to better HAZ toughness. To exhibit the activities effectively, nitrogen is preferably contained in a content of 0.003% or more, more preferably 0.004% or more, and furthermore preferably 0.005% or more. With an increasing content thereof, nitrogen forms nitrides in a larger amount to accelerate refinement of the austenite grains and more effectively contributes to better HAZ toughness. However, nitrogen, if present in a content greater than 0.010%, may be present as solute nitrogen in a larger amount to impair the toughness of the base metal itself and to impair HAZ toughness. To prevent this, the nitrogen content is controlled to 0.010% or less, preferably 0.009% or less, and more preferably 0.008% or less.

[0075] The steel according to the present invention contains the above-mentioned elements as essential elements, as well as oxygen (O) in a content of 0.0005% to 0.010%. As used herein the "oxygen (O) content" (from 0.0005% to 0.010%) refers to a total oxygen content and refers to the total content of oxide-forming oxygen (O) and free, solute oxygen (O) dissolved in the steel.

[0076] The remainder of the steel includes iron and inevitable impurities (e.g., Mg, As, and Se).

[0077] The steel according to the present invention may effectively further contain one or more other elements selected typically from the groups [1] to [3] as follows:

[1] at least one element selected from the group consisting of Cu in a content of 2% or less, Ni in a content of 3.5% or less, Cr in a content of 3% or less, and Mo in a content of 1% or less;
[2] at least one of Nb in a content of 0.25% or less and V in a content of 0.1% or less; and
[3] B in a content of 0.005% or less.

[0078] The ranges are specified for reasons as follows.

[1] At least one element selected from the group consisting of Cu, Ni, Cr, and Mo

[0079] Copper (Cu), nickel (Ni), chromium (Cr), and molybdenum (Mo) elements all contribute to higher strength of the steel. Each of these elements may be added alone or in combination.

[0080] Cu, if present in a content greater than 2%, may excessively increase the base metal strength to contrarily reduce the base metal toughness and may thereby impair the HAZ toughness. To prevent this, the Cu content is preferably controlled to 2% or less, more preferably 1.8% or less, and furthermore preferably 1.5% or less. To effectively exhibit the activities by addition, Cu may be present in a content of preferably 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.2% or more.

[0081] Ni, if present in a content greater than 3.5%, may excessively increase the base metal strength to contrarily reduce the base metal toughness and may thereby impair the HAZ toughness. To prevent this, the Ni content is preferably controlled to 3.5% or less, more preferably 3.0% or less, and furthermore preferably 2.5% or less. To effectively exhibit the activities by addition, Ni may be present in a content of preferably 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.2% or more.

[0082] Cr, if present in a content greater than 3%, may excessively increase the base metal strength to contrarily reduce the base metal toughness and may thereby impair the HAZ toughness. To prevent this, the Cr content is preferably controlled to 3% or less, more preferably 2% or less, and furthermore preferably 1% or less. To effectively exhibit the activities by addition, Cr is preferably contained in a content of 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.15% or more.

[0083] Mo, if present in a content greater than 1%, may excessively increase the base metal strength to contrarily reduce the base metal toughness and may thereby impair the HAZ toughness. To prevent this, the Mo content is preferably controlled to 1% or less, more preferably 0.9% or less, and furthermore preferably 0.80% or less. To effectively exhibit the activities by addition, Mo may be present in a content of preferably 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.15% or more.

[2] At least one of Nb and V

[0084] Niobium (Nb) and vanadium (V) elements each precipitate as carbonitrides. The carbonitrides exhibit a pinning effect and thereby prevent austenite grains from coarsening during welding. Thus, these elements effectively contribute to better HAZ toughness. Each of Nb and V may be added alone or in combination.

[0085] However, Nb, if present in a content greater than 0.25%, may cause the precipitated carbonitrides to coarsen and may contrarily impair the HAZ toughness. To prevent this, the Nb content is preferably controlled to 0.25% or less, more preferably 0.2% or less, and furthermore preferably 0.15% or less. To effectively exhibit the activities by addition, Nb may be present in a content of preferably 0.002% or more, more preferably 0.01% or more, and furthermore preferably 0.02% or more.

[0086] Vanadium (V), if contained in a content greater than 0.1%, may cause the precipitated carbonitrides to coarsen and may contrarily impair the HAZ toughness, as with Nb. To prevent this, the vanadium content is preferably controlled to 0.1% or less, more preferably 0.09% or less, and furthermore preferably 0.08% or less. To effectively exhibit the activities by addition, vanadium may be present in a content of preferably 0.002% or more, more preferably 0.005% or more, and furthermore preferably 0.01% or more.

[3] Boron (B)

[0087] Boron (B) element suppresses the formation of grain-boundary ferrite grains to allow the steel to have better HAZ toughness. However, boron, if present in a content greater than 0.005%, may precipitate as BN (boron nitride) at austenite grain boundaries to contrarily invite deterioration in toughness. To prevent this, the boron content is preferably controlled to 0.005% or less, and more preferably 0.0040% or less. To effectively exhibit the activities by addition, boron may be present in a content of preferably 0.0010% or more, and more preferably 0.0015% or more.

[0088] The steel according to the present invention can surely have an absorbed energy at -40°C (vE_{-40}) of 100 J or more (preferably, 130 J or more), even when a thermal hysteresis is applied to the steel, where the thermal hysteresis is applied by holding the steel at 1450°C for 60 seconds and then cooling the steel for a cooling time of 450 seconds in a temperature range of from 800°C down to 500°C. The steel according to the present invention is therefore usable as materials for structures such as bridges, multi-storied buildings, and ships and is protected from toughness deterioration in a heat affected zone upon not only low to moderate heat input welding, but also high heat input welding with a heat input of 60 kJ/mm or more. The steel according to the present invention may be applied to a steel plate (thick steel sheet) having a thickness of about 3.0 mm or more.

[0089] Next, a preferred method for producing the steel according to the present invention will be illustrated The steel according to the present invention may be produced by deoxidizing a molten steel and adding Ti and Al successively in this order (Ti→Al). The successive addition of Ti and Al in this order to the deoxidized, molten steel allows appropriate control of the compositional ratio between titanium oxide and aluminum oxide in fine inclusions each having an equivalent circle diameter of about 0.1 to about 2 μm and enables production of a steel meeting the condition specified by Formula (1). Specifically, titanium oxides have smaller interfacial energy with the molten steel as compared with aluminum oxides and Zr-REM-Ca oxides. Titanium, when added to the molten steel before the addition of Al, Zr, REM, and Ca, can form fine titanium oxides and, as a result, allows fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm to be formed in a predetermined amount, where the fine inclusions contribute to better HAZ toughness. The addition of Al after the addition of Ti enables the formation of a multicomponent oxide containing both Ti and Al. This may reduce the activity as titanium oxides to less than 1. Zr, REM, and Ca, when added after the formation of the multicomponent oxide, form Zr-REM-Ca oxides, where Zr, rare-earth element, and Ca elements act as deoxidizers stronger as compared with Ti and Al. In this process, the reduction of the titanium oxides and aluminum oxides is suppressed, and the Zr-REM-Ca oxides can thereby contain the titanium oxides and aluminum oxides in predetermined amounts. The successive addition of Ti and Al in this order as above allows oxides acting as nuclei for intragranular α transformation to be formed in larger amounts as compared with the case where Ti, Al, Zr, REM, and Ca are added in the same amounts, but Ti and Al are added in another order.

[0090] In contrast, successive addition of Al and Ti in this order (Al→Ti) fails to adapt the chemical compositions of inclusions to meet the condition specified by Formula (1). Ti has lower deoxidizing power as compared with Al. Accordingly, Ti, if added to the molten steel after the addition of Al, fails to reduce a previously-formed aluminum oxide, thereby forms titanium oxides in a smaller amount, and fails to allow the Zr-REM-Ca oxides to contain a predetermined amount of titanium oxides. The formed titanium oxides herein are present as single oxides and have an activity as the titanium oxide of approximately 1. When Zr, REM, and Ca having higher deoxidizing power as compared with Ti are added in this state, the titanium oxides are reduced and are present in a smaller amount. This causes the Zr-REM-Ca oxides to fail to contain predetermined amounts of titanium oxides. To prevent this, it is recommended not to use Al for deoxidation of the molten steel in the production of the steel according to the present invention. Deoxidation with Al, if performed, may cause aluminum oxides to remain in the molten steel. This may impede the formation of Zr-REM-Ca oxides containing predetermined amounts of titanium oxides.

[0091] The molten steel may be deoxidized by a known method. Typically, in an embodiment, contents of elements other than Al, Ti, REM, Ca, and Zr are adjusted to give a molten steel, the molten steel is deoxidized using at least one element selected from the group consisting of C, Si, and Mn, and successively combined with Ti and Al in this order.

[0092] The addition of Al, REM, Ca, and Zr after the addition of Ti may be performed typically by:

(1) successively adding Ti and Al in this order, and thereafter adding REM, Ca, and Zr in any order;
(2) successively adding Ti and Al in this order, and thereafter adding REM, Ca, and Zr simultaneously; or
(3) adding Ti, and thereafter adding Al, REM, Ca, and Zr simultaneously.

[0093] The rare-earth element, Ca, Zr, and Ti to be added to the molten steel may each be in any form not critical. For example, pure La, pure Ce, and/or pure Y may be added as the rare-earth element. Likewise, Ca, Zr, and Ti may be added respectively as pure Ca, pure Zr, and pure Ti; or may be added as an Fe-Si-La alloy, Fe-Si-Ce alloy, Fe-Si-Ca alloy, Fe-Si-La-Ce alloy, Fe-Ca alloy, Fe-Zr alloy, Fe-Ti alloy, and/or Ni-Ca alloy. A misch metal may also be added to the molten steel. The "misch metal" is a mixture of rare-earth elements and specifically contains Ce in a content of about 40% to about 50% and La in a content of about 20% to about 40%. The misch metal often contains Ca as an impurity. The misch metal, when containing Ca, should be added in such an amount that the total content of Ca including Ca in the misch metal falls within the range specified in the present invention.

[0094] The resulting molten steel obtained after compositional adjustment may be subjected to continuous casting according to a common procedure to give a slab, then subjected to a process such as hot rolling according to a common procedure, and yields the steel according to the present invention.

[0095] The present application claims priority to Japanese Patent Application No. 2012-138047, filed June 19, 2012, the entire contents of which are incorporated herein by reference.

Examples

[0096] 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 invention; that various changes and modifications can naturally be made therein without deviating from the spirit and scope of the invention as described herein; and all such changes and modifications should be considered to be within the scope of the invention.

[0097] Ingots of test steels having chemical compositions given in Table 1 (with the remainder being iron and inevitable impurities) were prepared using a vacuum melting furnace (capacity 150 kg). Upon the ingot making of the test steels, elements other than Al, Ti, REM, Ca, and Zr were adjusted in contents, and deoxidation was performed using at least one element selected from the group consisting of C, Si, and Mn so as to adjust the amount of dissolved oxygen in the molten steels. To the molten steels after adjustment of dissolve oxygen amount, Al and Ti were added, and subsequently REM, Ca, and Zr were added The order of the additions of Al and Ti is given in Table 1. The test steels given in Table 1 were produced by the same method, except for performing addition of Ti and Al in different orders. Ti, Zr, REM, and Ca were respectively added in the forms of Fe-Ti alloy, Fe-Zr alloy, a misch metal containing about 25% of La and about 50% of Ce, and Ni-Ca alloy. Of the test steels given in Table 1, test steels meeting conditions specified in the present invention were verified to have a total oxygen content (oxygen content) in the range of 0.0005% to 0.010%.

[0098] After the addition of the elements, the molten steels were cast into 150-kg ingots and cooled. The resulting ingots were heated, hot-rolled, and yielded steel plates each having a thickness of 30 to 80 mm. The hot rolling was performed at a heating temperature of 1100°C and a finishing mill delivery temperature of 880°C.

[0099] The resulting steel plates were subjected to measurements of the chemical compositions of total oxides, and the number densities of inclusions and oxides according to procedures as follows. Specifically, a sample was cut out from a transverse section of each steel plate at a position one-fourth the thickness (t) of the steel plate. The surface of the cut sample was observed using an EPMA JXA-8500F (device name) supplied by JOEL DATUM (now JOEL Ltd, DATUM Solution Business Operation), and chemical compositions of inclusions each having an equivalent circle diameter of 0.1 μm or more were quantitatively analyzed The observation was performed at an acceleration voltage of 20 kV, a sample current of 0.01 μA, in an observation view field area of 1 to 5 cm^2, with a number of inclusions to be analyzed of 100 or more. The chemical compositions at the center part of each inclusion were quantitatively analyzed by wavelength dispersive spectrometry of characteristic X-rays. Elements to be analyzed were Si, Mn, S, Al, Ti, La, Ce, Ca, Zr, and oxygen (O). The relationship between X-ray intensity and content of each element was previously determined as a calibration curve. The content of the element in an inclusion to be analyzed was quantitatively determined from the calibration curve and the X-ray intensity obtained from the inclusion.

[0100] Of the analyzed inclusions, those having an oxygen content of 5% or more were defined as oxides based on the quantitative determination results. When two or more elements were observed in one inclusion, the chemical composition of the oxide (inclusion) was calculated by converting the ratio of X-ray intensities indicating the presence of the elements into masses in terms of single oxides of individual elements. The converted masses of single oxides were averaged and defined as an average composition of oxides herein. Of oxides, the average compositions of the rare-earth element oxide, ZrO_2, and CaO are given in Table 2. Such rare-earth element oxide may be present in the form of M_2O_5, M_3O_5, and MO_2 in the steel, where M represents a rare-earth element. The composition of the rare-earth element oxide was calculated while converting all the oxides into M_2O_3. The term "others" in Table 2 refers to oxides (e.g., Al_2O_3, MnO, and SiO_2) other than rare-earth element oxides, ZrO_2, and CaO.

[0101] Next, the inclusions after quantitative determination were observed under a TEM at a 30000-fold observation magnification to measure equivalent circle diameters of the inclusions. Of the inclusions, those each having an equivalent circle diameter (particle size) of 0.1 to 2 μm were counted to give a number. The number of the inclusions was converted

into a value per square millimeter of the observation view field area and was given as a number density in Table 2.

[0102] Of the analyzed inclusions, inclusions having an oxygen content of 5 percent by mass or more were defined as oxides based on the quantitative determination results. The oxides were observed under a TEM at a 30000-fold observation magnification to measure equivalent circle diameters of the oxides. Of the oxides, oxides each having an equivalent circle diameter (particle size) of greater than 3 μm was counted to give a number. The number of the oxides was converted into a value per square millimeter of the observation view field area and was given in Table 2.

[0103] Next, a sample having a size of 10 mm by 20 mm by 20 mm was cut out from a transverse section of each of the steel plates at a position one-fourth the thickness (t) of the steel plate and electrolytically extracted. The electrolytic solution after the electrolytic extraction was filtrated separately through two filters, i.e., one having an opening of 0.1 μm and one having an opening of 2.0 μm, and extraction residues remaining on the filters were collected The electrolytic solution used herein was a solution containing 10% of acetylacetone and 1% of tetramethylammonium chloride in methanol. The electrolytic extraction was performed at a current density of 100 to 200 A/m^2.

[0104] The collected extraction residues were subjected to quantitative determination to measure the amounts of Ti and Al by ICP emission spectrometry and the amount of nitrogen by indophenol blue absorptiometry using the UV-VIS spectrophotometer UVmini-1240 (supplied by Shimadzu Corporation). Based on these, the left hand value of Formula (1) was calculated according to the above-mentioned procedure. The calculation results are given in Table 2.

[0105] Next, a welding simulation test simulating a high heat input welding was performed as follows so as to evaluate toughness of a HAZ affected by heat upon welding. Specifically, a sample was cut out from each steel plate at a position one-fourth the thickness (t) of the steel plate and subjected to the welding simulation test, in which a heat cycle was applied to the sample by heating the sample to 1400°C, holding the sample at that temperature for 60 seconds, and then cooling the sample. The cooling rate was adjusted so that a cooling time in the temperature range of from 800°C down to 500°C be 450 seconds.

[0106] From the sample after the application of the heat cycle, three V-notched Charpy test specimens were sampled along the rolling direction, and the specimens were subjected to an impact test according to Japanese Industrial Standard (JIS) Z2242 to evaluate impact properties of the sample after cooling. The impact test was performed so as to measure an absorbed energy at -40°C (vE_{-40}) of each specimen and to average the values of the three specimens. A sample having an average vE_{-40} of 100 J or more was accepted herein as having satisfactory HAZ toughness. The measurement results are given in Table 2.

[0107] Tables 1 and 2 indicate as follows. Samples Nos. 1 to 18, and 32 were samples meeting the conditions specified in the present invention. In these samples, large amounts of fine inclusions each having an equivalent circle diameter of 0.1 to 2 μm were formed so as to prevent the formation of oxides each having an equivalent circle diameter of greater than 3 μm; and the fine inclusions had appropriately controlled chemical compositions. The steels as the samples thereby had satisfactory HAZ toughness.

[0108] In contrast, Samples Nos. 19 to 31, and 33 were samples not meeting at least one of the conditions specified in the present invention. Among them, the steel as Sample No. 19 contained Al in an excessively high content, included large amounts of coarse oxides each having an equivalent circle diameter greater than 3 μm, and had inferior HAZ toughness. The steel as Sample No. 20 contained nitrogen in an excessively high content and thereby contained solute nitrogen in an excessively high content. The steel had inferior HAZ toughness probably for this reason.

[0109] The steel as Sample No. 21 contained Ti in an excessively high content, underwent solute strengthening of the base metal due to titanium solid-solution, and, as a result, had inferior HAZ toughness. The steel as Sample No. 22 contained Ti in an excessively low content and had inferior HAZ toughness. The steel as Sample No. 23 contained Zr in an excessively high content and thereby contained ZrO_2 in a high content. This caused Zr-REM-Ca oxides to less effectively act as nuclei for intragranular α transformation and to fail to give a fine microstructure. The steel had inferior HAZ toughness probably for these reasons. The steel as Sample No. 24 contained Zr in an excessively low content, thereby contained ZrO_2 in a low content, and contained a small amount of Zr-REM-Ca oxides acting as nuclei for intragranular α transformation. The steel had inferior HAZ toughness probably for these reasons.

[0110] The steel as Sample No. 25 contained rare-earth elements in a high content, thereby contained rare-earth element oxides in a high content. In addition, the rare-earth element oxides coarsened to form an excessive amount of coarse oxides each having an equivalent circle diameter greater than 3 μm and probably failed to effectively contribute to better HAZ toughness. The steel as Sample No. 26 contained rare-earth elements in an excessively low content, thereby contained rare-earth element oxides in a low content, and contained a small amount of Zr-REM-Ca oxides acting as nuclei for intragranular α transformation. The steel had inferior HAZ toughness probably for these reasons. The steel as Sample No. 27 contained Ca in an excessively high content and thereby contained CaO in a high content. This probably caused Zr-REM-Ca oxides to less effectively act as nuclei for intragranular α transformation and to fail to give a fine microstructure. The steel had inferior HAZ toughness probably for these reasons. The steel as Sample No. 28 contained Ca in an excessively low content, thereby probably failed to form CaO, and contained a small amount of Zr-REM-Ca oxides acting as nuclei for intragranular α transformation. The steel had inferior HAZ toughness probably for these reasons.

[0111] Samples Nos. 29, 30, and 33 were samples whose ingot making was performed by adding Ti and Al in an order not meeting the recommended condition in the present invention. These samples thereby failed to meet the condition specified in the present invention by Formula (1). The steels as these samples had inferior HAZ toughness. The steel as Sample No. 31 contained Ti, N, and Al in contents in poor balance and contained inclusions with chemical compositions not meeting the condition specified by Formula (1) and exceeding the range specified in the present invention. The inclusions probably had higher melting points, did not become a liquid phase upon high heat input welding, and hardly contributed to the formation of inclusions acting as nuclei for intragranular α transformation. The steel failed to have better HAZ toughness probably for these reasons.

[Table 1-1]

No.	Order of additions of Ti and Al	Chemical composition (in mass percent)																			
		C	Si	Mn	P	S	Al	Ti	REM			Ca	Zr	N	Cu	N	Cr	Mo	Nb	V	B
									La	Ce	Total										
1	Ti→Al	0.15	0.01	1.45	0.008	0.0025	0.010	0.015	0.0009	0.0015	0.0024	0.0015	0.0018	0.0060	-	-	-	-	0.05	-	-
2	Ti→Al	0.02	0.12	122	0.006	0.0032	0.007	0.022	0.0005	0.0010	0.0015	0.0022	0.0025	0.0043	-	-	-	-	0.04	0.06	0.0026
3	Ti→Al	0.07	0.47	1.56	0.003	0.0018	0.009	0.031	0.0011	0.0023	0.0034	0.0036	0.0030	0.0085	0.53	-	-	0.25	-	-	-
4	Ti→Al	0.06	0.03	244	0.007	0.0022	0.003	0.020	0.0010	0.0025	0.0035	0.0024	0.0034	0.0062	-	3.35	-	-	-	-	-
5	Ti→Al	0.08	0.02	225	0.027	0.0033	0.011	0.027	0.0017	0.0033	0.0050	0.0018	0.0027	0.0058	-	124	-	-	-	-	0.0050
6	Ti→Al	0.04	0.06	1.70	0.010	0.0187	0.012	0.026	0.0013	0.0031	0.0044	0.0020	0.0042	0.0063	0.33	0.33	-	-	-	-	-
7	Ti→Al	0.09	0.01	127	0.007	0.0025	0.047	0.021	0.0008	0.0018	0.0026	0.0033	0.0032	0.0061	1.10	-	025	-	-	-	-
8	Ti→Al	0.06	0.04	1.54	0.009	0.0029	0.009	0.023	0.0012	0.0020	0.0032	0.0013	0.0033	0.0096	-	-	-	0.82	-	-	-
9	Ti→Al	0.05	0.07	1.48	0.005	0.0030	0.007	0.098	0.0007	0.0019	0.0026	0.0015	0.0035	0.0070	1.88	-	-	-	0.03	-	0.0018
10	Ti→Al	0.07	0.06	1.37	0.007	0.0025	0.004	0.005	0.0020	0.0045	0.0065	0.0027	0.0028	0.0055	-	-	-	-	-	0.08	0.0033
11	Ti→Al	0.06	0.03	1.62	0.015	0.0105	0.008	0.018	0.0013	0.0036	0.0049	0.0021	0.0470	0.0051	-	219	0.15	0.33	-	-	-
12	Ti→Al	0.06	0.02	0.49	0.006	0.0035	0.006	0.014	0.0009	0.0013	0.0022	0.0023	0.0012	0.0053	-	-	-	-	0.18	-	-
13	Ti→Al	0.08	0.05	1.44	0.007	0.0029	0.008	0.016	0.0043	0.0098	0.0141	0.0019	0.0027	0.0063	-	0.63	0.62	-	-	0.02	-
14	Ti→Al	0.04	0.36	1.53	0.010	0.0027	0.007	0.022	0.0001	0.0002	0.0003	0.0020	0.0032	0.0062	0.58	-	-	-	-	-	0.0019
15	Ti→Al	0.10	0.03	1.51	0.008	0.0032	0.010	0.018	0.0007	0.0018	0.0025	0.0098	0.0022	0.0060	-	-	-	-	0.11	0.03	0.0023
16	Ti→Al	0.06	0.02	1.78	0.007	0.0003	0.008	0.021	0.0008	0.0022	0.0030	0.0003	0.0031	0.0059	-	-	-	-	-	-	-
17	Ti→Al	0.07	0.04	1.39	0.008	0.0025	0.003	0.068	0.0009	0.0024	0.0033	0.0033	0.0029	0.0085	-	0.38	-	0.13	-	0.05	0.0041
18	Ti→Al	0.06	0.04	1.56	0.006	0.0026	0.025	0.013	0.0012	0.0026	0.0038	0.0024	0.0028	0.0044	0.43	-	-	-	0.03	-	-
19	Ti→Al	0.06	0.06	1.55	0.007	0.0028	0.053	0.024	0.0016	0.0032	0.0048	0.0015	0.0032	0.0063	-	-	-	-	-	0.05	0.0011
20	Ti→Al	0.07	0.04	1.43	0.006	0.0030	0.007	0.029	0.0008	0.0014	0.0022	0.0015	0.0033	0.0110	-	-	-	-	-	-	-
21	Ti→Al	0.06	0.05	1.72	0.007	0.0019	0.006	0.105	0.0017	0.0036	0.0053	0.0030	0.0042	0.0064	-	0.72	-	0.20	-	0.03	-
22	Ti→Al	0.05	0.04	12.9	0.015	0.0023	0.008	0.004	0.0008	0.0025	0.0033	0.0021	0.0018	0.0055	-	1.30	-	-	-	-	-
23	Ti→Al	0.06	0.06	233	0.007	0.0033	0.010	0.025	0.0013	0.0037	0.0050	0.0015	0.0550	0.0072	0.40	-	0.32	-	-	-	-

(continued)

No.	Order of additions of Ti and Al	Chemical composition (in mass percent)																			
		C	Si	Mn	P	S	Al	Ti	REM			Ca	Zr	N	Cu	N	Cr	Mo	Nb	V	B
									La	Ce	Total										
24	Ti→Al	0.07	0.03	212	0.008	0.0034	0.014	0.024	0.0007	0.0019	0.0026	0.0027	0.0008	0.0050	-	-	-	-	0.05	-	-
25	Ti→Al	0.06	0.12	1.75	0,009	0.0029	0.011	0.016	0.0048	0.0110	0.0158	0.0021	0.0026	0.0058	-	-	-	-	-	-	0.0032
26	Ti→Al	0.08	0.05	1.63	0.007	0.0025	0.007	0.022	-	0.0002	0.0002	0.0016	0.0034	0.0046	-	-	0.15	-	-	-	-
27	Ti→Al	0.04	0.06	124	0.008	0.0026	0.006	0.024	0.0005	0.0011	0.0016	0.0110	0.0038	0.0069	0.39	-	-	0.18	-	-	-
28	Ti→Al	0.06	0.05	1.45	0.008	0.0030	0.009	0.016	0.0012	0.0031	0.0043	<0.0003	0.0029	0.0055	-	0.68	-	-	-	-	0.0018

[Table 1-2]

No.	Order of additions of Ti and Al	Chemical composition (in mass percent)																		
		C	Si	Mn	P	S	Al	Ti	REM			Ca	Zr	N	Cu	Ni	Cr	Mo	Nb	V	B
									La	Ce	Total										
29	Al→Ti	0.06	0.04	210	0.007	0.0040	0.005	0.023	0.0013	0.0036	0.0049	0.0022	0.0043	0.0053	-	-	-	-	0.04	-	-
30	Al→Ti	0.07	0.04	1.67	0.009	0.0032	0.015	0.017	0.0009	0.0017	0.0026	0.0034	0.0033	0.0051	-	-	0.30	-	-	-	-
31	Ti→Al	0.06	0.05	1.33	0.007	0.0028	0.003	0.085	0.0008	0.0023	0.0031	0.0027	0.0025	0.0047	-	-	-	-	-	-	-
32	Ti→Al	0.06	0.04	1.42	0.007	0.0025	0.009	0.021	0.0010	0.0024	0.0034	0.0013	0.0027	0.0063	-	-	-	-	-	-	-
33	Al→Ti	0.07	0.07	1.51	0.006	0,0032	0.011	0.019	0.0009	0.0016	0.0025	0.0019	0.0022	0.0058	-	-	-	-	-	-	-

[Table 2]

No.	Composition of total oxides (in mass percent)				Number density per square millimeter		Insol.Ti	Insol.N	Insol.Al	Lefthand value of Formula (1)	vE_{40} (J)
	Rare-earth element oxide	ZrO_2	CaO	Others	0.1 to 2 μm	greater than 3 μm					
1	13.8	17.4	9.3	59.5	1103	0.60	0.0033	0.0004	0.0010	1.9	145
2	112	21.0	14.9	52.9	1320	3.84	0.0050	0.0003	0.0007	5.7	153
3	17.7	16.4	21.8	44.1	754	1.42	0.0075	0.0011	0.0009	4.2	162
4	20.1	14.8	16.4	48.8	821	3.73	0.0048	0.0008	0.0004	52	158
5	24.4	18.6	15.4	41.7	1022	4.14	0.0046	0.0006	0.0008	32	155
6	23.4	11.0	14.6	51.0	456	425	0.0043	0.0007	0.0007	2.7	143
7	11.3	15.3	13.8	59.6	923	3.14	0.0046	0.0007	0.0021	1.1	115
8	14.5	18.4	7.0	60.0	1056	2.33	0.0080	0.0014	0.0006	5.4	154
9	12.3	19.7	6.7	61.3	838	1.77	0.0093	0.0013	0.0007	7.0	112
10	30.7	20.4	14.2	34.8	1022	4.02	0.0020	0.0004	0.0003	2.1	126
11	21.4	47.4	9.9	21.3	415	4.91	0.0042	0.0007	0.0009	2.0	131
12	10.8	14.8	12.9	61.5	1078	1.86	0.0036	0.0008	0.0007	1.3	125
13	49.4	182	10.9	21.5	133	4.69	0.0042	0.0009	0.0006	1.9	134
14	11.7	11.7	122	64.4	1008	0.94	0.0051	0.0009	0.0007	2.9	127
15	12.6	123	46.4	28.7	698	4.22	0.0044	0.0007	0.0008	2.5	143
16	15.8	13.5	5.5	652	1135	225	0.0053	0.0010	0.0009	2.1	140
17	15.9	13.0	20.5	50.6	796	4.65	0.0098	0.0015	0.0006	7.8	126
18	22.7	17.9	12.0	47.4	832	4.75	0.0030	0.0002	0.0022	1.1	111
19	14.8	9.7	10.5	65.0	1259	7.82	0.0043	0.0006	0.0021	1.1	73
20	11.7	18.5	12.5	57.4	1069	1.25	0.0058	0.0015	0.0006	1.2	82
21	18.4	20.9	15.4	45.3	1020	6.16	0.0088	0.0009	0.0008	7.2	79
22	20.4	9.6	11.8	58.3	1156	1.61	0.0018	0.0003	0.0005	1.6	68
23	25.0	55.8	9.3	9.9	81	12.49	0.0047	0.0011	0.0009	1.1	63
24	18.6	4.1	18.3	58.9	1215	2.31	0.0051	0.0008	0.0010	2.4	71

(continued)

No.	Composition of total oxides (in mass percent)				Number density per square millimeter		Insol.Ti	Insol.N	Insol.Al	Lefthand value of Formula (1)	vE_{40} (J)
	Rare-earth element oxide	ZrO_2	CaO	Others	0.1 to 2 μm	greater than 3 μm					
25	50.6	14.0	14.2	21.2	512	1200	0.0041	0.0008	0.0008	1.7	62
26	3.9	16.3	8.5	71.3	1403	4.46	0.0047	0.0005	0.0007	4.3	65
27	11.3	17.2	51.9	19.7	412	12.57	0.0049	0.0010	0.0006	2.5	59
28	21.3	19.5	-	59.1	1115	2.25	0.0039	0.0007	0.0009	1.7	83
29	26.6	10.3	11.0	52.1	1042	8.10	0.0035	0.0010	0.0004	0.3	73
30	17.1	20.3	20.4	422	912	9.44	0.0037	0.0009	0.0012	0.5	81
31	15.1	17.7	15.1	52.1	1083	1.87	0.0085	0.0010	0.0006	8.5	72
32	18.2	17.7	82	55.9	1212	3.76	0.0044	0.0006	0.0006	3.9	155
33	13.1	13.5	11.3	62.1	1008	7.30	0.0028	0.0006	0.0010	0.8	81

Claims

1. A steel excellent in heat affected zone toughness, the steel comprising:

C in a content of 0.02% to 0.15% (in mass percent, hereinafter the same for chemical compositions);
Si in a content of 0.5% or less;
Mn in a content of 2.5% or less;
P in a content of 0.03% or less;
S in a content of 0.02% or less;
Al in a content of 0.050% or less;
Ti in a content of 0.005% to 0.10%;
at least one rare-earth element (REM) in a content of 0.0003% to 0.015%;
Ca in a content of 0.0003% to 0.010%;
Zr in a content of 0.0010% to 0.050%;
N in a content of 0.010% or less; and
O in a content of 0.0005% to 0.010%,
with the remainder consisting of iron and inevitable impurities;

(a) the steel comprising an oxide comprising Zr, at least one rare-earth element, and Ca;
(b) of total inclusions contained in the steel:

inclusions with an equivalent circle diameter of 0.1 to 2 μm being present in a number density of 120 or more per square millimeter of an observation view field area; and
oxides with an equivalent circle diameter of greater than 3 μm being present in a number density of 5.0 or less per square millimeter of an observation view field area; and

(c) inclusions with an equivalent circle diameter of 0.1 to 2 μm in the steel having a chemical composition meeting a condition specified by Formula (1):

$$(Insol.Ti-3.4\times Insol.N)/Insol.Al=1.0 \text{ to } 8 \qquad (1)$$

2. The steel according to claim 1,
further comprising at least one element selected from the group consisting of:

Cu in a content of 2% or less;
Ni in a content of 3.5% or less;
Cr in a content of 3% or less; and
Mo in a content of 1% or less.

3. The steel according to one of claims 1 and 2,
further comprising at least one of

Nb in a content of 0.25% or less; and
V in a content of 0.1% or less.

4. The steel according to one of claims 1 and 2, further comprising
B in a content of 0.005% or less.

5. The steel according to claim 3,
further comprising
B in a content of 0.005% or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/065142

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21C7/04*(2006.01)i, *C21C7/06*(2006.01)i, *C22C38/14*(2006.01)i, *C22C38/58*(2006.01)i

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, C21C7/04, C21C7/06, C22C38/14, C22C38/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013
Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2011-127220 A (Kobe Steel, Ltd.), 30 June 2011 (30.06.2011), claims; paragraph [0057] & CN 102061428 A & KR 10-2011-0055428 A	1-5
Y	JP 2002-121641 A (Nippon Steel Corp.), 26 April 2002 (26.04.2002), paragraphs [0002], [0025], [0026] (Family: none)	1-5
Y	JP 2007-302949 A (Nippon Steel Corp.), 22 November 2007 (22.11.2007), paragraphs [0029], [0030] (Family: none)	1-5

☒ 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
09 August, 2013 (09.08.13)	20 August, 2013 (20.08.13)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/065142

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2005-040816 A (Nippon Steel Corp.), 17 February 2005 (17.02.2005), paragraph [0061] & US 2005/0016980 A1 & US 2011/0250471 A1 & EP 1500457 A1	1-5

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REFERENCES CITED IN THE DESCRIPTION

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